The preparation, Analyses, And The Determination Of The Properties Of A Series Of Six Glasses Containing Bismuth, A New Type Of Glass.

An Acknowledgement.

I wish to take this opportunity to acknowledge my gratitude to Dr. Riegel for his interest in this work, and for the kind advice which he has given me during the preparation of this thesis.

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The Preparation, Analysis, And The Determination Of The Properties Of A Series Of Six Glasses Containing Bismuth, A New Type Of Glass.

I. Introduction.

Purpose of this study- The main purpose of this study was to ascertain if, melting together silica, soda, and bismuth oxide, would give a true glass, one which would remain amorphous at room temperature, or whether a segregation of the constituents would occur on cooling the molten glass. In the second place, we wished to know whether bismuth acts as a decolorizer in glass, as does arsenic, or as an intensifier, as does iron. If it acted as a decolorizer, glasses could be made containing considerable quantities of it, and possessing no undesirable color, while if it acted as an intensifier, glasses containing it would be practically worthless for anything excepting cheap ware, such as bottles. The presence of iron oxide in glass in any appreciable quantities (.5 - 1.0%) gives it a green color which renders it unfit for use in optical instruments. In the third place, we wished to note the effect of varying amounts of bismuth on the various properties of glass such as, density, refractive index, dispersion, durability, etc. An important question involved is this: Can one prepare a glass containing bismuth as its chief constituent, with desirable optical properties, having a small coefficient of expansion (not tending to crack easily), sufficient resistance to weathering, and above all, no tendency to devitrify? A purely scientific study of bismuth glasses of various compositions can reveal the answers to questions such as the above.

<u>Previous work with regard to silicates of bismuth</u>- Natural bismuth silicates are known to exist. C. M. Kersten[1] found cubic crystals of a reddish-brown mineral, sometimes yellow or black, at Schneeburg, Saxony, which he called eulytine. Analysis showed this to be bismuth orthosilicate, $Bi_4(SiO_4)_3$. A monoclinic variety was found at Johanngeorgenstadt, having the same composition. Eulytine has density 6.106 and hardness $5\frac{1}{4}$-6. A Frenzel found a ferruginous bismuth silicate in the same locality, which he called bismuthoferrite, its composition approximating, $Bi_2O_3 \cdot 2Fe_2O_3 \cdot 4\,SiO_2$., and having density 4.47.

Bismuth silicates have been synthesized by C. N. Otin[2]. Otin melted together Bi_2O_3 and SiO_2 in different proportions and examined the products thermally and microscopically, and determined their densities. As a result of his investigations he was drawn to the conclusion that silicates containing Bi_2O_3 and SiO_2 in the following proportions are true chemical compounds: $Bi_2O_3 \cdot 8SiO_2$; $Bi_2O_3 \cdot 3SiO_2$; $Bi_2O_3 \cdot SiO_2$; $3Bi_2O_3 \cdot 2SiO_2$; $2\,Bi_2O_3 \cdot SiO_2$; $3Bi_2O_3 \cdot SiO_2$; and $10\,Bi_2O_3 \cdot SiO_2$; while the following are mixtures: $Bi_2O_3 \cdot 10\,SiO_2$; $Bi_2O_3 \cdot 6\,SiO_2$;

1. Mellor-Treatise On Inorganic & Theoretical Chem. Vol.VI p.836.
2. Chem. Abstracts. 7, (1913), 3933.

$Bi_2O_3 \cdot 5\ SiO_2$; and $Bi_2O_3 \cdot 4\ SiO_2$. The color of the first seven silicates varied from a gray in the case of the first through amber-yellow, yellow-brown, to brown-green in the case of $3Bi_2O_3 \cdot SiO_2$. It is of interest to note that this last silicate exhibited double refraction, indicating a rhombic or similar crystal structure.

K. Fuwa[1] has investigated the coloring effect of small amounts of bismuth in both silicate and borosilicate glasses. His glasses had the compositions:

$$\left.\begin{array}{l} R'_2O \cdot R''O \cdot 3\ SiO_2 \\ R'_2O \cdot R''O \cdot 5\ B_2O_3 \cdot 3\ SiO_2 \end{array}\right\} \begin{array}{l} R' = Na \text{ or } K. \\ R'' = Ca, Mg, Zn, Pb \text{ or } Ba. \end{array}$$

Bismuth basic carbonate $(2\ (BiO)_2 \cdot CO_3 \cdot H_2O)$ imparted colors varying from grey to brown to the majority of glasses when present to the extent of 2.5 to 5%, but others were colorless. In general, borosilicate glasses showed the least color, while potash glasses containing boron were darkest. On reheating, the brown color was developed, the glasses in some instances becoming opaque. It was thought that the coloration in the case of the borosilicates was colloidal in character. Basic nitrate of bismuth produced colors less pronounced than those obtained with the basic carbonate; but on reheating the glasses, this difference disappeared.

It would appear according to Hovestadt[2] that glasses have been made containing bismuth in quantities up to 10%. However, these glasses already contained other basic elements besides the alkali metals. No data on these glasses have been published, as

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1. Chem. Abstracts 1925 p.2110.
2. Jena Glass, Its Scientific and Industrial Application p.9.

far as is known. The preparation and study of soda bismuth silicates therefore seems never to have been undertaken.

On glasses containing elements close to bismuth in the periodic table- It might be instructive to see what effect elements which lie close to bismuth in the periodic table have upon glass.

Thallous silicate has been prepared by Wyronboff[1] in the form of yellow tetragonal crystals of $Tl_6Si_2O_7 . H_2O$, which are transparent at ordinary temperatures, and up to 130°C, but which above 150° become opaque and lose water. Thallium glasses have been studied by Lamy[2] and Müller[3], but it is to be regretted that these undoubtedly interesting references were not available for consultation.

Arsenic, being an acid element, does not form a silicate, but has a marked effect on the properties of glasses. In the glass industry, white arsenic (As_2O_3) is added to lime glass batches to lessen the formation of seeds, and to produce a glass of better transparency[4]. The fact that arsenic acts as a decolorizer in glass melts has been known for a comparatively long time. Arsenic will remove the green color in glass due to the presence of iron; it will also remove the ill effects caused by an excess of selenium or manganese dioxide in glass[5]. K. Fuwa [6] has investigated the decolorizing action of arsenic on glasses containing small amounts of bismuth. He found that the addition of .5 - 1% of As_2O_3 pre-

1. Mellor-Treatise On Inorganic and Theoretical Chem. Vol.VI.p.826
2. Bull. Soc. Chimie (2), 5, 164, (1866).
3. Pub. Astrophysical Observatory of Potsdam 4,3,1885.
4. Gelstharp, Chem. Abstracts, 2, 1889, (1924)
5. Firth, Hodkin, Turner, and Parkin, Jour. Soc. Glass Tech. vol.X, no. 37 (1926) p.3.
6. Chem. Abstracts 3. (1925)

vented the formation of color, except after reheating. In this connection, Hodkin and Turner[1] have found that reheating in a reducing flame a glass containing arsenic causes discoloration, even .02 - .05% of As_2O_3 being sufficient. The effect seems to be independent of the presence of nitre or of manganese as a decolorizer. It was formerly thought that the arsenic in glass existed entirely as the pentoxide. However, work by Scholes[2] and Allen and Zies[3] has definitely disproved this belief. Scholes found that some arsenic remains in the trivalent form, and that the amount of arsenic determined by the carbonate fusion method was greater than that found in the residue left after treating the glass with hydrofluoric acid. Allen and Zies found that the amount of arsenic trioxide volatilized during the melting of the glass varied from 11 to 33% of that added to the batch. Recently the results of an extensive investigation on the function of arsenic in glass have become available[4]. Arsenic trioxide was added to soda lime glass in amounts varying from one to 250 parts per 1000 parts of sand. The glass had the batch composition:

Sand	1000 parts.
Soda ash	325 "
Limespar	228 "

The above investigators drew the following conclusions:

1. When As_2O_3 is added and the batch is melted in closed pots at 1400°C, nearly the whole of the arsenic is retained when the amount added does not exceed 10 parts per 1000 of sand, while 60%

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1. Chemical Abstracts 3, 3510, (1920)
2. Jour. Ind. Eng. Chemistry. 4, 1617, (1912)
3. Jour. Am. Cer. Society 1, 787-90 (1918)
4. Hodkin, Turner, Firth, Parkin, Jour. Soc. Glass Tech. Vol.X, no. 37, (1926) p.3.

or more is retained even when 250 parts per 1000 of sand are added.

2. Under the conditions of the experiment, with no oxidizers present in the batch, from 40 to 70% of the arsenic retained was present as As_2O_5.

3. No beneficial effect on the rate of melting has been found to be associated with the presence of As_2O_3 in the batch, and with larger amounts of oxide, a higher temperature is required than without it.

4. The presence of As_2O_3 in amounts greater than two parts per 1000 parts of sand is liable in soda lime silicated to produce on the surface of the glass a scum composed mostly of silica.

5. As_2O_3 when added to the batch in amounts below ten parts per 1000 of sand does not appear to exert any beneficial effects on the rate of refining of the glass.

6. The presence of As_2O_3 does quite definitely reduce the green tint due to iron in the glass.

7. As_2O_3 when present to the extent of 150-250 parts per 1000 parts of sand produces glasses of varying degrees of opacity.

Parkin and Turner[1] have studied the phenomenon of devitrification in arsenic-containing glasses. Their results are summed up in the following table:

As_2O_3 in batch.	Temperature of devitrification.	
(parts per 1000 of sand)	Incipient	Definite.
0	620°C.	640°C.
50	610	640
100	600	640
200	700	750
250	700	750

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[1] Jour. Soc. Glass Tech. Vol.X. No. 37 (1926) p.20.

Glasses containing under 100 parts of As_2O_3 per 1000 of sand showed only surface devitrification, while those containing over 100 parts of As_2O_3 changed completely to a porcelain-like mass on reheating.

Opinion seems divided on the question of the effect of antimony or its compounds in glass. As a result of his investigations, Springer[1] reached the conclusion that we must abandon the idea that antimony or its compounds have any effect on either the color, decolorization, or the clearing of glasses. K. Fuwa[2], likewise found that Sb_2O_3 produced no particular coloration in either silicate or borosilicate glasses. He found, however, in the case of high antimony glasses (30% Sb_2O_3), that reheating in a gas-fired kiln usually produced an iridescent effect, light grayish-black to black in color on their surface. The observations of Hodkin and Turner[3] bear out the latter statement. As little as .02 - .05% Sb_2O_3 in a glass is sufficient to produce discolorization when the glass is worked in a reducing flame. This result is not altered by the presence of oxidizers or decolorizers in the glass. A borosilicate glass containing antimony seems to be well suited for use in lamp chimneys due to its resistance to sudden temperature changes.[4] Such a glass is composed of:

Sb_2O_3	4- 10%
H_3BO_3	15- 25%
Alkali	1 - 4%
Silica	the remainder.

[1] Chem. Abstracts 2133, (1916)
[2] Chem. Abstracts 3583, (1923)
[3] Chem. Abstracts 3, 3510, (1920)
[4] Arion, Chem. Abstracts 1, 688, (1913)

Lead, in the form of the oxide, is a very important constituent of glasses, especially those suited for optical purposes. Glasses containing large quantities of lead are realiseable in practise. A glass containing about 80% of PbO has a refractive index of about 1.79. The following table gives the density and optical properties of the two heaviest lead glasses listed by Schott[1]:

Description	Density	N_D	Total dispersion	"v" value
Heaviest silicate flint	5.92	1.9044	.04174	21.7
Very heavy silicate flint	4.99	1.7782	.02941	26.5

Peddle[2] has investigated the properties of two series of soda-lead silicates, having the molar compositions 100 SiO_2, 20 Na_2O, xPbO, and 100 SiO_2, 40 Na_2O, xPbO where x is made to vary from 5, 10, 15, 20, 30 to 40 in the different batches. Peddle investigated the density, refractive index and dispersion, devitrification, solubility, and durability of the above glasses. He found that increase of PbO content increased the density, refractive index, total dispersion, durability and resistance to devitrification; decreasing the melting point and the solubility in reagents. Glasses of high lead content exerted a powerful corrosive action on the clay of the melting pot. All of the glasses were very brilliant. Peddle has carried out similar studies of potash-lead-silicates, and of soda-potash-lead silicates.[3] The potash lead silicates were much more soluble than the corresponding soda

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1. Hovestadt-"Jena Glass", p. 392.
2. Jour. Soc. Glass Tech. Vol. 4, No. 16, (1920) p. 288.
3. Ibid, Vol.IV, 310 (1926); Ibid, Vol.IV, 320, (1926).

glasses. In nearly every case, the densities of the potash glasses were lower than those of the corresponding soda glasses. However, the potash glasses possessed a higher refractive index and total dispersion, as well as a greater brilliance, than the soda lead glasses. As regards devitrification, no marked tendency was observed with any of the glasses, although a skin formed on the surface of the reheated glass, which grew worse as the potash content increased. The potash-soda-lead silicates were made in two series 100 SiO_2 . $10Na_2O$. $10K_2O$. xPbO, and 100 SiO_2 . $20Na_2O$, 20 K_2O, xPbO, where x varies from 5 to 40 as above. They possessed a color and brilliance intermediate between the corresponding glasses of the Na_2O and K_2O series. In regard to refractive index, dispersion, and solubility, the glasses lay midway between the soda and potash glasses, in a majority of cases. Glasses of the two series showed signs of devitrification when the amount of silica was greater than 61% (glasses 100 SiO_2 . $10Na_2O$. $10K_2O$. 5 PbO, and 100 SiO_2 . 10 K_2O . 10 PbO). As a result of his studies, Peddle concluded that glasses of the following composition would be suitable for use in optical instruments:

(1) Glasses in the vicinity of 100 SiO_2 . $20Na_2O$. 30PbO, and 100 SiO_2 . 20 Na_2O . 40 PbO

(2) Glass 100 SiO_2 . 20 K_2O . 40 PbO

(3) Glasses in the vicinity of 100 SiO_2 . $10Na_2O$. $10K_2O$. 30PbO, and 100 SiO_2 . $10Na_2O$. 10 K_2O . 40 PbO.

II. Raw Materials.

Where obtained- The raw materials used in the glasses studied were, bismuth oxide, soda ash, sodium nitrate, sand, and white arsenic. The bismuth oxide was furnished by The American Smelting and Refining Company, and was of a high degree of purity. The soda ash was a very pure Solvay product. The sodium nitrate used came from a carton labelled C.P. The silica was a pure sand, finely powdered. The white arsenic was of a commercial grade, analysing about 98% pure.

Purity of raw materials- All raw materials were analysed for moisture, and iron and alumina content. The silica and soda ash were also heated to redness and the loss of weight determined, this being the loss on ignition. The soda ash and white arsenic were tested for purity by standard volumetric methods. The results of the analysis are incorporated in the following table:

Analysis of Raw Materials.

Raw Material	Loss in Weight at 120°C.	Loss in Weight on ignition.	Purity (% of main constituent)	Iron and Alumina
Sand	.065%	0.26%	99.13%	0.61%
Soda ash	16.23 %	16.63%	70.25%	.013%
Nitre (C.P.)	.04 %			.000%
Bismuth oxide			99.67%	.001%
White arsenic	.05%		97.97%	.078%

The sand, after treatment with hydrofluoric acid, left an insoluble residue constituting .44% of the weight of the sample. On testing spectroscopically, this residue was found to contain sodium, showing that the residue was probably sodium fluosilicate. It might also be remarked that the soda ash was found to contain 1.71% of caustic soda.

Quantities of raw materials used in the batches- The glasses in the series studied had the general molecular formula $100SiO_2 \cdot 40Na_2O \cdot xBi_2O_3$, where x was 2.5, 5, 7.5, 10, 15, and 20 in the different glasses. It is seen that this series follows closely Peddle's first series of soda-lead-silicates. It would be interesting to compare the properties of bismuth glasses and lead glasses of practically identical percentage composition. The following table illustrates the scheme for building up the batches and the designation of the different melts.

Melt No.	Molecules of SiO_2	Molecules of Na_2O	Molecules of Bi_2O_3
3½B	100	40	2.5
4 B	100	40	5.0
4½B	100	40	7.5
5 B	100	40	10.0
6 B	100	40	15.0
7 B	100	40	20.0

The bismuth was introduced as the trioxide. Part of the sodium was introduced as the nitrate to guard against separation of metallic bismuth during the melting process. White arsenic was employed as a decolorizer in the melts, so that the optical properties of the glasses could be more easily investigated. Later, a series of melts will be carried out, without the use of arsenic, for the purpose of determining the true color of the bismuth glasses.

Preliminary melts were carried out using batches of about 100 grams. Chemical analyses for bismuth and sodium, and density and refractive index measurements were made on these glasses. Later, melts were made with batches of about 300 grams. These latter glasses were more homogeneous than those from the smaller batches, and could be used for the determination of constituents present in smaller amounts, such as arsenic, iron, and alumina, and for the measurement of dispersion values, and solubility. The following table gives the relative weights of raw materials taken for each batch:

Melt No.	Sand	Soda ash	Nitre	Bismuth oxide	Arsenic
3½B	40 g.	14 g.	22.8 g.	7.7 g.	.5 g.
4 B	40	14	22.8	15.4	.5
4½B	40	14	22.8	23.1	.5
5 B	40	14	22.8	30.8	.5
6 B	40	14	22.8	46.2	.5
7 B	40	14	22.8	61.6	.5

If we calculate the combined soda ash and nitre as sodium oxide, and take into account the purity of all the raw materials, we find that the batch compositions are as given in the following table:

Batch No.	SiO_2	Na_2O	Bi_2O_3	As_2O_3	H_2O	$Fe_2O_3+Al_2O_3$
3½B	61.23%	22.00%	11.85%	.76%	3.77%	.38%
4 B	54.75	19.67	21.19	.68	3.37	.34
4½B	49.50	17.79	28.74	.61	3.05	.31
5 B	45.17	16.23	34.97	.56	2.78	.28
6 B	38.45	13.82	44.65	.48	2.37	.24
7 B	33.47	12.03	51.82	.41	2.06	.21

The glasses would have the following composition, were there no volatilization of the batch (except water) nor pot attack:

Batch No.	SiO_2	Na_2O	Bi_2O_3	As_2O_3	Fe + Al oxides
3½B	63.62	22.86	12.31	.79	.40
4 B	56.65	20.36	21.93	.70	.35
4½B	51.05	18.35	29.64	.63	.32
5 B	46.46	16.70	35.97	.57	.29
6 B	39.38	14.15	45.73	.49	.24
7 B	34.16	12.28	52.91	.42	.21

The glass batches have the following molecular compositions:

3½B -- 100 SiO_2 . 28.55 Na_2O . 2.07 Bi_2O_3
4 B -- 100 SiO_2 . 41.30 Na_2O . 5.11 Bi_2O_3
4½B -- 100 SiO_2 . 34.90 Na_2O . 7.55 Bi_2O_3
5 B -- 100 SiO_2 . 35.00 Na_2O . 10 Bi_2O_3
6 B -- 100 SiO_2 . 34.9 Na_2O . 15.1 Bi_2O_3
7 B -- 100 SiO_2 . 34.8 Na_2O . 20.1 Bi_2O_3

III. Melting The Batch.

Small melts- For the small melts a small gas-fired furnace, capable of holding but one crucible at a time, was used. The general design of this furnace is shown in the accompanying sketch. The well mixed batch was placed in the crucible, and the whole heated in the furnace till no more gas was evolved, and the glass was in a state of quiet fusion. The fused glass was then poured out upon a bed of sand in the annealing furnace. A button of glass was thus obtained suitable for density determinations, and for chemical analysis, but not for the accurate determination of optical properties.

Large melts- Inasmuch as the smaller melts gave glasses which contained many striae, a series of larger melts were subsequently carried out. The amounts of all constituents were increased in the same ratio, 3 for the first three glasses, and 2.5 for the last three.

Glasses 3½B, 4B, 4½B- The furnace was of the same design as the smaller one used above, but had a capacity of three crucibles. Therefore melts 3½B, 4B and 4½B were carried out together. The batch compositions for these glasses are as follows:

Melt No.	Sand	Soda ash	Nitre	Bismuth	Arsenic.
3½B	120 g..	42 g.	68.4 g.	23.1 g.	1.50 g.
4 B	120	42	68.4	46.2	1.50
4½B	120	42	68.4	69.3	1.50

The three empty crucibles were set in the uncovered furnace and

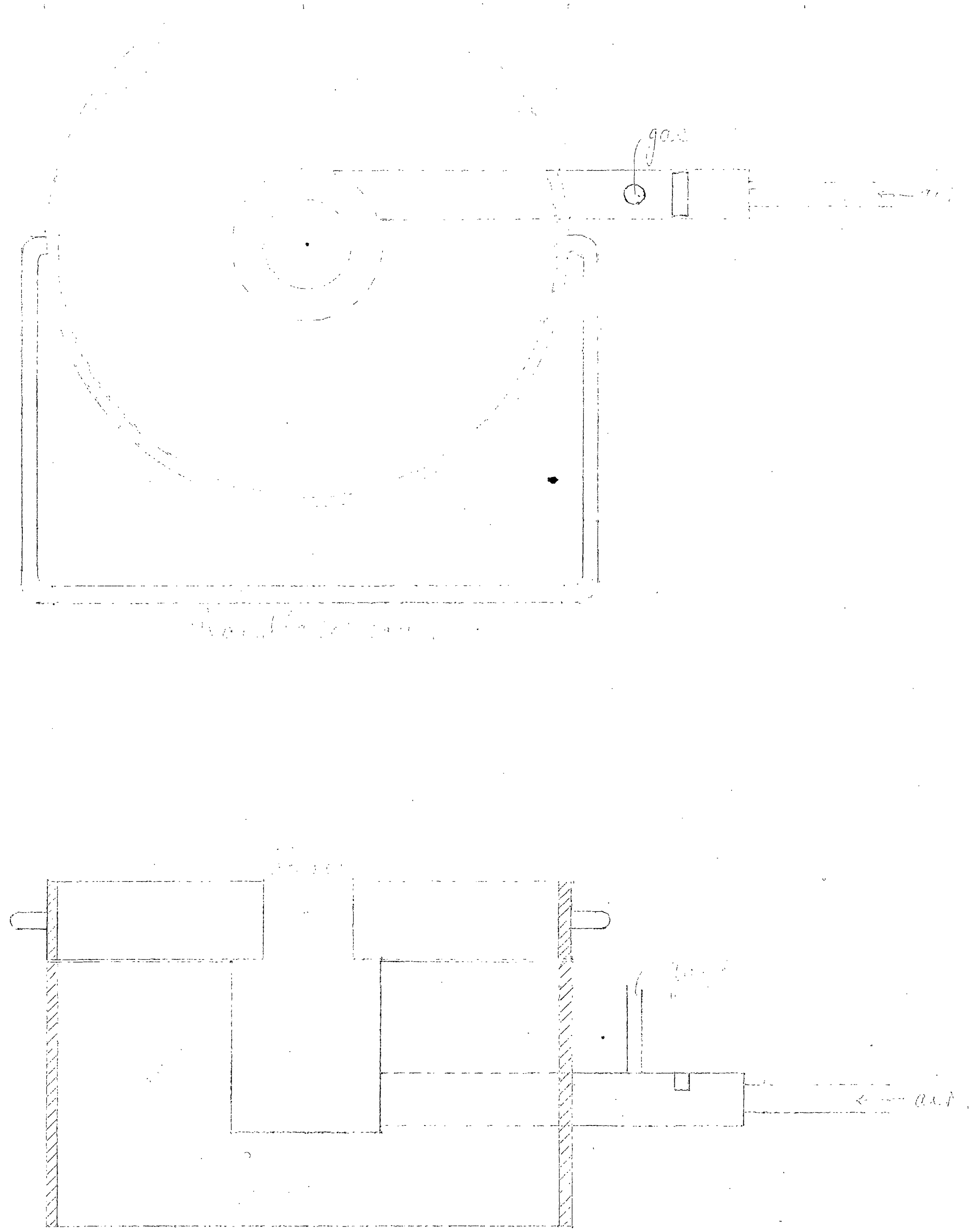


Fig. I. Furnace used for melting small volumes of [illegible].

Scale:- for small size, 1" = 4"; for large size, 1" = 8".

allowed to heat up for about two hours and one half. As the crucibles were a little too small to hold the whole batch, most of it was put in at first, allowed to melt down a little, and then the remainder added. The work was arranged so that as soon as this second addition had been made, most of the next batch could be added to the second crucible, and so on. The following table gives the schedule of melting:

Batch No.	First addition	Second addition	Removal of Crucibles	Time of Founding
3½B	2:55 P. M.	3:25 P. M.	5:25 P. M.	2h. 30m.
4 B	3:25	3:50	5:25	2h. 0m.
4½B	3:50	4:45 (cover put on)	5:25	1h. 35m.

Nothing striking was noticed during the process of founding these three glasses. Excessive effervescence did not take place, the batch melting quietly to a clear glass. Just before removing the crucibles from the furnace, each glass was thoroughly stirred with a porcelain tube to remove striae. The crucibles were then immediately set into clay pots and packed around with diatomaceous earth to retard radiation as much as possible and thus prevent excessive shattering of the glasses on cooling.

Glasses 5B, 6B, 7B- Melts 5B, 6B and 7B were next carried out. Due to low supplies of bismuth and nitre, slightly smaller batches were taken, and in the case of 7B, the soda ash content was increased in order to make up for the lack of nitre. These changes are made clear in the following table for the batch compositions of the above three glasses:

Melt No.	Sand	Soda ash	Nitre	Bismuth	Arsenic
5 B	100 g.	35 g.	57 g.	77 g.	1.25 g.
6 B	100	35	57	115.5	1.25
7 B	100	39.8	49.3	154	1.25

Due to the smallness of the batches, all could be added to the crucibles at one time. Aside from this, the procedure was about the same as in the case of the first three melts. The program for heating is given in the following table:

Batch No.	Addition of Batch.	Finished	Time of founding
5 B	2:15 P. M.	4:40 P. M.	2h. 25 min.
6 B	2:30 P. M.	4:40 P. M.	2 h.10 min.
7 B	2:50 P. M.	lost.	

The pot containing 7 B broke about one hour after the batch was placed in the furnace, so that this glass was a total loss.

Several interesting things were noticed in connection with the founding of these glasses. In the first place, glasses 5B and 6B exhibited violent frothing and even slight boiling over until all gas had escaped. They then settled into quiet fusion. Glass 7B had an extraordinary appearance when noticed about 20 minutes after the addition of the batch. The batch did not froth up but was in a state of violent boiling and bubbling, the surface of the glass resembling bubbling lava. The liquid was apparently quite mobile. Just before the estimated time at which the pot broke, 7B was losing bismuth oxide by volatilization. The bismuth oxide condensed on the cooler portions of the furnace lid in patches of a reddish brown color.

It was thought that stirring the glasses might do more harm than good in these smaller melts. Not only might striae be distributed throughout the mass to a greater extent, but also the stirrer might entrap air bubbles on its end - this not being hemispherical - and introduce them into the molten glass. Therefore, the pots were transferred, at the end of the founding time, to larger pots and packed around with diatomaceous earth.

IV. Annealing the Glasses.

Small melts- The annealing oven was of the gas-fired type used in the annealing of large pieces of flint and crown glass. As mentioned before, in the case of the smaller melts, the molten glass was poured in a round cake directly on the sand bed of the oven. The temperature of the oven was gradually lowered during four days, in order that the glass might cool without setting up strains.

Large melts- A slightly different procedure was followed in the case of the larger melts. Due to the comparatively rapid cooling, the glasses had all broken into smaller pieces. The pots were broken and the glasses separated and boxed. From each melt, two of the best and largest pieces were selected and ground roughly to the shape of prisms. These were then annealed by bringing them slowly nearly to the softening temperature, then allowing them to cool during four days. The prisms were reserved for density, and refractive index and dispersion measurements. Of each glass, 20-25 grams of the pieces were freed from adhering clay and ground up for chemical analysis and solubility tests.

V. Physical Aspect Of The Glasses.

Small melts- The annealed buttons were carefully examined for clearness, color, and for any evidences of incipient devitrification. The following table contains the results of the examination:

Glass No.	Physical Aspect.
3½B.	Colorless, quite clear, with but few small bubbles. Lack of surface luster suggests surface attack by atmosphere.
4 B.	Nearly colorless, quite clear, only very few bubbles. Surface a little dull.
4½B.	Very light green, slightly bubbly, clear body. Surface quite brilliant.
5 B.	Light yellowish-green. Rather bubbly, some bubbles of considerable size. Brilliant surface. Body not so clear as 4B.
6 B.	Little more yellow than 5B. Many bubbles present, some of considerable size. Body clear, surface very brilliant.
7 B.	Three trials were made before this melt was successful. First trial gave a very bubbly glass of yellowish green color. The glass was badly cracked due perhaps to poor annealing. Second trial gave a glass the surface of which became reduced on annealing. Very smoky in appearance, and badly cracked. Third trial was successful, giving a glass more yellow in color than any of the others, rather bubbly and but slightly cracked. The surface was a little tarnished.

Large melts- The unannealed pieces of glass from the larger melts were examined in the same manner as the buttons. The following table gives the results of the examination:

Glass No.	Physical Aspect.
$3\frac{1}{2}$B.	Nearly colorless. Contained bubbles, some of considerable size. Badly strained. Not uniformly clear; had a dull area from which radiated needle-like depressions. General surface quite brilliant.
4 B.	Slight greenish color. Contained several fair-sized bubbles and many very small ones. Badly strained. Presented same dull patch as did $3\frac{1}{2}$B, only spiral in shape; rest of glass clear. Surface of about same briliancy as $3\frac{1}{2}$B.
$4\frac{1}{2}$B.	Slight yellowish-green color. Quite free from bubbles. Considerably strained, grinding up with difficulty. Clear, in general, but with small dull patch. More brilliant than $3\frac{1}{2}$B or 4B.
5 B.	Light green but with more pronounced yellow cast than $4\frac{1}{2}$B. Very little strained, and quite free from bubbles. Uniformly clear, and very brilliant.
6 B.	Light green, more yellow than 5B. Almost entirely free from bubbles. Badly strained in certain places. Clear, and brilliant, more so than any of the other glass. Small dull patch, however, visible. Very difficult to grind to powder.

VI. Preparation Of The Glasses For Analysis.

Small melts- The annealed buttons of glass were first broken into several smaller pieces, the largest being saved for a density determination. These coarse pieces were still further broken up, by pounding in an agate mortar. Small portions (2-3 grams) were powdered to pass through a 200-mesh sieve. The combined portions of powder were then transferred to glass-stoppered bottles and dried about six hours at 100-120°C.

During the grinding, marked differences were noted in the behavior of the different glasses. There was a perceptible increase in brittleness or ease of grinding as the bismuth content increased. The glasses containing most SiO_2 and Na_2O were the hardest and most difficult to grind. The tendency to fly when crushed was very noticeable in the case of the lower bismuth glasses.

Large melts- Pieces of these glasses, free from adhering clay, were ground up in the same manner as above, but with more caution, so as to obtain as much glass as possible of 150-mesh size. Since uniformity of size of the particles of glass was desired for the solubility tests, the 150-mesh powder (meaning that all of the powder fell through a 150-mesh sieve) was thrown onto a 200-mesh sieve and whatever remained behind after long shaking was saved for the solubility tests. A glass powder was thus obtained, the size of whose particles lay between 150-and 200-mesh. From 20-25 grams of powder passing the 150-mesh sieve, about 7 grams of uniform grams were obtained.

Obviously, no gradual increase in ease of grinding could be detected in the case of these unannealed glasses.

VII. Chemicals And Reagents.

In all cases where the purity of chemicals or reagents was in doubt, the materials were purified, or a blank determination was made on a sample. Acids, such as hydrochloric, or sulfuric were used without purification, the C.P. product being employed.

Ammonium hydroxide- C.P. ammonia was used at first as it came in the bottle, but since it seemed probable that it might contain some silica as impurity, it was redistilled into water and then filtered. About 500 cc. were purified at a time.

Ammonium carbonate- U.S.P. ammonium carbonate was analysed for silica, by decomposing a 10g sample with hydrochloric acid evaporating to dryness, diluting and filtering off the silica which was then burned. The silica content being found to be .001% was negligible for the present work.

Caustic potash- C.P. potassium hydroxide was analysed for silica by neutralizing 100cc. of normal solution with hydrochloric acid adding 5cc. in excess, evaporating to dryness, and baking the residue. The residue was dissolved in dilute hydrochloric acid and the silica filtered off and washed with dilute hydrochloric acid. After burning to constant weight, the residue was treated with hydrofluoric acid and sulfuric acid, the silica driven off, and the residue weighed. The difference between the first and second weighings gives the weight of silica. The silica content of the caustic solution was found to be 3 milligrams per liter. The analysed solution was preserved in a paraffined 1-liter flask to guard against further contamination.

Ammoniacal zinc oxide- Silica was determined in this reagent as follows: 10cc. were treated with 15cc. concentrated hydrochloric acid, the solution evaporated to dryness, baked, diluted, and the silica filtered off and washed with dilute hydrochloric acid. The residue was burned in the usual manner and weighed. The silica content of the reagent was found to be 20 milligrams per liter, or .2 milligrams per 10cc.

Hydrofluoric acid- Commercial hydrofluoric acid was used during the first analyses, but was abandoned due to its extreme impurity. It contained about .0042g. iron and alumina per 18cc., and a substance which contaminated the bismuth basic carbonate precipitate, causing it to turn red on heating. The amount of impurity was found in one case to be .0151g. for a bismuth precipitate weighing .3888g. Inasmuch as the time required for determining the impurity in each bismuth precipitate was as great as that required for the first two precipitations, the impure acid was discarded and C. P. hydrofluoric acid used altogether.

VIII. Chemical Analysis Of Glasses.

Carbonate fusions- A standard method for the decomposition of silicates consists in fusing the finely powdered material with about 4 times its weight of a mixture of sodium and potassium carbonates. By this procedure, the silica combines with the carbonate forming an alkaline silicate and liberating CO_2. The cooled melt may be then taken up with acid, which liberates silicic acid as a gelatinous precipitate. This is dehydrated to form insoluble silica which is removed by filtration, the filtrate then containing the basic elements originally present in the silicate. Obviously the alkalis, sodium and potassium, cannot be determined by this method.

Following the procedure in Scott[1] 1 g. of finely powdered glass was weighed into a platinum crucible of 20cc. capacity, mixed with 4g. of fusion mixture (K_2CO_3 5 pts., Na_2CO_3 7 pts.) and ½g. of potassium chlorate and the whole fused, the crucible being kept covered until decrepitation had ceased. The mixture was kept hot until the whole mass was in a liquid state, and no further evolution of gas took place. The crucible was grasped with tongs, and gently rotated while cooling, in order that the contents might solidify in a thin skin on the walls of the crucible. After the mass had become solid, the crucible was set on a stone table and covered, as the contraction of the cooling contents caused considerable scattering of fine particles. The cold cake was taken up with 50-100cc. of hot water and transferred to a porcelain casserole. Then 10cc. of concentrated HCl were added and solid lumps of the fusion cake were crushed up so that all of the alkali silicate might be decomposed. During this digestion the casserole was covered by a watch glass as the effervescence caused considerable spattering of solution. The cover was then removed, the solution evaporated to dryness and heated about ½ hour at 110-120°C. The residue was taken up with dilute HCl and water, and the silica filtered off, washed several times with dilute HCl to remove bismuth, then with hot water till free from chlorides. The filtrate was evaporated to dryness, the residue heated ½ hour at 110-120°C, taken up with dilute HCl and water, and the second portion of silica filtered off and washed as was the first portion. The two precipitates were combined in a platinum crucible and ignited to constant weight. One or two drops of H_2SO_4

[1] Scott (1925 Edition, Vol. II, part on Miscellaneous Analyses)

and 10cc. of HF were added to the silica, the crucible heated on the hot plate to expel silicon tetrafluoride, then to dryness to expel excess H_2SO_4. The residue was heated in a blast flame and weighed. The difference between the first and second weights gave the weight of silica in the glass sample, and this multiplied by 100 gave the percent. of silica.

The filtrate contained the bismuth and iron and alumina as chlorides. The bismuth was separated as the oxychloride as follows: The solution was evaporated down to a volume of less than 100cc. and ammonia added till a slight permanent cloudiness was obtained. Hot water was added till the volume was 500-600cc., and dilute ammonia added till litmus was only faintly reddened. The oxychloride of bismuth was allowed to settle for several hours sometimes over night, the supernatant liquid decanted through a weighed Gooch crucible, and the precipitate transferred to the crucible and washed with 5 or 6 portions of hot water. Prolonged washing with water is undesirable, as the BiOCl is gradually changed back to the hydroxide. The Gooch crucible and precipitate was dried at 120°C and weighed. The bismuth was figured as Bi_2O_3.

In the filtrate, iron and alumina were precipitated by adding ammonia, and filtering off the hydroxides which were then washed and ignited to constant weight. As the precipitate had but a light reddish color, the iron was not separated.

This procedure was followed until it was found that the fusion mixture attacked the platinum crucible. A 20cc. crucible was spoiled after four or five fusions. However, the cause of the destruction of the crucible being not at once suspected, a 10cc.

crucible was substituted for the larger one which had been shipped away for repair. The small crucible was spoiled in about the same length of time, showing unquestionably that the bismuth glass fusions had a particularly caustic action on platinum.

A few words may be said concerning the results of those analyses which were performed prior to the destruction of the crucibles. The glasses used were not those in the series finally decided upon, but will serve as examples. The following short table shows the results of some analyses:

Glass #1B.

No.	Silica(theory)	Silica(found)	Bi_2O_3(theory)	Bi_2O_3(found)
1	40%	38.25%	50%	———
2	40%	38.19	50	49.77%
3	40%	38.16	50	50.59

The silica figures are uncorrected for the residue left on evaporation with hydrofluoric acid. In the case of analysis 3, this was found to weigh 4.8 milligrams, and to have the appearance of fused bismuth oxide. Another glass having a batch composition supposedly identical with that of the preceeding glass was analysed with the following results:

Sample 2B.

No.	Silica(theory)	Silica(found) (uncorrected)	Bi_2O_3(theory)	Bi_2O_3(found)
1	40%	36.45%	50	51.09
2	40	35.27	50	52.01

A third glass with different batch composition was analysed giving the following figures for bismuth and silica:

Sample 3B.

No.	Silica(theory)	Silica(found) (uncorrected)	Bi_2O_3(theory)	Bi_2O_3(found)
1	46.90%	47.84%	29.31%	28.07%
2	46.90	45.98%	29.31%	28.70%

It is keenly regretted that more analyses were not made by this method so that more definite conclusions could be drawn from the figures. In fact, technique had only begun to be developed on these earlier glass fusions, when the method had to be abandoned. Let us, however, see why the above method is undesirable, aside from the fact that fusions in platinum are dangerous. In the first place the silica retains even after washing with hydrochloric acid, a considerable amount of bismuth. One example has already been given. In the case of the second analysis on glass 3B, the residue left upon volatilization of the silica weighed 14.8 milligrams, and proved, on subsequent analysis to contain 6 milligrams of bismuth oxide, and a trace of iron. Mr. Sharp of Hamburg informs us that much the same results are obtained with antimony glasses, the silica being contaminated with antimony oxide. As a result of the comparatively high volatility of bismuth oxide at red heat, considerable loss might occur, during the heating to constant weight of the residue. In the second place, due to the variable contamination of the silica with bismuth, the figures obtained for the bismuth content of the glass are liable to vary considerably. A glance at the tables will show that they do vary, over one percent. in some cases. In the third place, we ask, if bismuth oxide is so volatile - and observations on batch fusions have shown that it is - must there not be a considerable loss during the carbonate fusion? It is regretted that some more fusions could not be made so that the bismuth figures so obtained could be compared with those obtained by decomposing the glass with hydrofluoric acid.

Carbonate fusions were performed in nickel and iron crucibles, but no analyses were made on the cold melts. The potassium chlorate vigorously oxidized the crucible, so that the silica was contaminated with metallic oxides. The metal of the crucible also reduced the bismuth oxide in the glass, and the liberated bismuth alloyed itself with the crucible. Therefore, the carbonate fusion method was abandoned entirely and the glass decomposed with hydrofluoric acid.

Decomposition of glass with hydrofluoric acid and determination of bismuth and sodium- By this method, all the constituents of the glasses may be determined, except silica and arsenic trioxide. When the method was first developed, only glass 4B, 5B and 6B of the small melts were available. Since then, 3½B, 4½B and 7B of the small melts have been prepared. Recently, the first five glasses from the large melts, 3½B, 4B, 4½B, 5B, 6B have become available. The method remains practically the same for them.

Of the finely powdered and well-dried glass definite portions (.5 or 1g.) were weighed into a 20cc. platinum crucible, and 1cc. of dilute sulfuric acid (1:1) added from a pipette. Two or 3 cc. of water, then 9cc. of C.P. 48% hydrofluoric acid (this was later changed to 5cc.) were added. The crucible was placed on a hot plate and most of the excess hydrofluoric acid driven off. It was then covered with a piece of platinum foil, and heated until excess H_2SO_4 had been expelled. After cooling, the residue was taken up with a warm solution of 10cc. of nitric acid in 10cc. of water, and transferred to a 600cc. beaker. The solution was diluted to about 400cc. with hot water, and ammonia added till a slight permanent cloudiness was obtained. An excess of ammonium carbonate was added, corresponding to 50cc. of 12% solution. The flocculent bismuth basic carbonate was allowed to settle on the hot plate, and the clear supernatant liquid decanted through a qualitative filter paper. The precipitate was transferred to the paper and well washed with hot water. About 150-200cc. of wash water were used. The filtrate was reserved for the determination of sodium. The precipitate was redissolved in 20cc. of dilute (1:1) nitric acid and again precipitated as basic carbonate. This second precipitation ensured the absence of basic sulfate from the bismuth precipitate. After filtering and washing the precipitate, it was dried on the paper in the oven. As much as possible of the precipitate was removed and transferred to a watch glass. To remove the remaining portions from the paper, two procedures were adopted. In the case of 4B, 5B, and 6B of the small melts, the paper was ignited and allowed to burn over a weighed porcelain crucible, so that the residue fell into the crucible. The bismuth oxide so produced was partly reduced to the metal. A few drops of nitric acid were added to change the metal to nitrate. After removing the excess HNO_3, the residue was converted on gentle ignition to the oxide. The other procedure was adopted in the case of glasses 3½B, 4½B and 7B of the small melts. The paper, after being freed from excess precipitate was replaced in the funnel, and the precipitate washed out with warm dilute nitric acid, the washings being caught in a porcelain crucible of 20-30cc. capacity. The washings were evaporated to dryness and the residue converted on heating to bismuth oxide. The rest of the precipitate from the watch glass was then transferred to the crucible and the whole gently heated to constant weight. Tests proved the precipitate to be free from sulfate.

Due to the time occupied in evaporating the acid washings, and in view of the fact that no more consistent results were obtained by this method than by the first method, it was abandoned and the first employed exclusively in the case of the glasses from the larger melts.

The bismuth oxide so obtained was contaminated with iron and alumina present in the glass. To obtain the correct weight of oxide, the precipitate was dissolved in hydrochloric acid and the bismuth separated as oxychloride, as described above. In some cases it was weighed. Iron and alumina remained in the filtrate and were precipitated as hydroxides with ammonia. They were filtered off, washed with hot water, and burned in a blast flame. The iron being very small in amount, was not separated from the alumina. The weight of the oxides, subtracted from the weight of impure bismuth oxide, gave the correct weight of bismuth oxide.

The filtrates from the bismuth basic carbonate contained all the sodium in the glass as sulfate. Spectroscopic tests made on the second filtrate revealed only a faint trace of sodium, so that at first this filtrate was discarded. The first filtrate was evaporated to dryness and as much ammonium nitrate as possible removed by strong heating on the hot plate. Part was volatilized, and part was decomposed into nitrous oxide and water. The dish was kept covered to prevent loss of material caused by the effervescence of the melted ammonium nitrate. The residue was taken up with hot water, and transferred to a $3\frac{1}{2}$" weighed porcelain dish. The solution was evaporated to dryness, the rest of the ammonium nitrate removed by gentle heating over a flame and the dish finally heated to just below redness until it lost no more weight.

The sodium sulfate so obtained was contaminated with silica, removed from the beaker used in the evaporation. It was taken up with hot water, the residue filtered off, washed free from sulfate and burned to constant weight. The weight of the residue, subtracted from the weight of impure sodium sulfate, gave the correct weight of sodium sulfate. The weight of Na_2O equivalent to this was obtained by multiplying the weight of sulfate by $\frac{62}{140.26}$.

The weight of iron and alumina from the bismuth oxide was at first taken as the iron and alumina content of the glass. Later, the variability of the results lead us to abandon the determination of these constituents in such small samples. In the case of the new melts, samples of several grams will be employed for the determination of iron, alumina, and arsenic pentoxide.

Results of Analyses - A few words of explanation should be given with reference to the following tables. The first contains the percentages of bismuth and sodium found in the glasses from the earlier smaller melts. Very good, consistent results were obtained in the case of glasses 4B, 5B, and 6B, when C.P. hydrofluoric acid was employed. However, in the case of glasses 3½B, 4½B, and 7B, variable results were obtained, until it was found that additional corrections were necessary in order to obtain the correct weight of bismuth oxide. Whereas, in the case of the first three glasses, the weighed Bi2^{O}3 dissolved in hydrochloric acid to give a clear solution, this was not true of the last three glasses. A considerable correction had to be applied for the silica removed from the beaker used in the precipitation of the bismuth basic carbonate. The weight of this silica usually lay between 2 and 5 milligrams, though in one case it was over 10 milligrams.

During the first analyses of the glass from the larger batches, extremely variable results were obtained. In some cases, the bismuth figures were low, and in some cases, very high. The very low figures were finally traced to incomplete preciptation of the bismuth. A new lot of ammonium carbonate was used for these glasses. It was found that, following the directions previously given, 35--40cc. of 15% solution did not give complète precipitation of bismuth. It was found necessary to use about 50cc of solution. As a result, the very low bismuth figures must be rejected. No explanation for the high bismuth figures occasionally obtained can be given.Consistent sodium figures were at first difficult to obtain, the observed figures being much lower than those calculated. Results which check very closely can hardly be expected, due to the large weight of the dish containing the sodium sulfate, and also to the correction for silica which had to be always applied.

Analyses For Bismuth And Sodium
- Small Melts -

Glass	Bi_2O_3 (calc)	Bi_2O_3 (obs)	Diff. (obs- calc)	Na_2O (calc)	Na_2O (obs)	Diff.
3½B	12.31%	12.91%		22.86%	—	
		12.47			—	
		12.74			~~24~~	
		—			24.51%	
		—			24.08	
Mean		12.72	+.41%		24.30	+1.44%
4'B	21.93%	20.62		20.36%	22.71	
		20.72			22.74	
Mean		20.67	-1.26%		22.73	+2.37%
4½B	29.64%	29.36		18.35%	21.15	
		29.78			—	
		29.39			—	
		29.55			—	
		29.50			20.51	
Mean		29.52	-.12%		20.83	+2.48%
5B	35.97%	34.27		16.70%	18.06	
		34.40			18.40	
Mean		34.34	-1.63%		18.23	+1.53%
6B	45.73%	45.67		14.15%	14.49	
		45.76			14.47	
		45.82			—	
Mean		45.75	+.02%		14.48	+.33%
7B	52.91%	52.82		12.28%	13.77	
		52.54			13.64	
		53.24			13.25	
Mean		52.87	-.04%		13.55	+1.27%

Analyses For Bismuth And Sodium
- Large Melts -

Glass	Bi_2O_3(cal)	Bi_2O_3(obs)	Diff. obs.-cal.	Na_2O(cal)	Na_2O(obs.)	Diff. obs-cal.
3½B	12.31%	12.48%		22.86%	—	
		11.95			23.78%	
		12.76			23.77%	
Mean		12.40	+.11%		23.78	+.92%
4B	21.93%	22.15		20.36%	21.75	
		21.85			22.00	
Mean		22.00	+.07%		21.87	+1.51%
4½B	29.64%	29.55		18.35%	—	
		29.98			19.57	
		29.68			18.89	
		29.42			~~19.09~~	
Mean		29.66	+.02%		19.18	+.83%
5B	35.97%	34.37		16.70%	15.14	
		34.65			14.83	
Mean		34.51	-1.46%		14.99	-1.71%
6B	45.73%	—		14.15%	14.30	
		44.66			—	
		45.29			14.17	
		44.80			—	
Mean		44.92	-.81%		14.24	+.09%

Conclusions from bismuth and sodium analyses- It is seen that, in the case of the small buttons, the difference between observed and theoretical Bi_2O_3 content is positive at first, takes a large drop into the negative region, rises nearly to zero, takes another drop and then again approaches very near to zero. The difference between abserved and calculated Na_2O content starts positive, reaches a maximum at 4½B, (corresponding to a maximum for Bi_2O_3 difference) then drops low and again rises. We must be very cautious in drawing conclusions from these facts, inasmuch as neither the silica nor arsenic content of these glasses have been determined. Much more work must be done along this line before definite conclusions can be reached regarding the character of the various bismuth soda silicates, whether they be true compounds in the chemical sense, or mixtures. More detailed information about Otin's methods (see page. 2) will be sought. The uselessness of drawing any conclusions at the present time will be clear when we compare the results of the analyses of the small buttons and of the larger melts.

VIIIa Determination of Silica And Arsenic Trioxide.

In view of the fact that the silica in bismuth glasses cannot be determined by the usual carbonate fusion method, the treatment of the glass with hydrofluoric acid, the silica is volatilized tetrafluoride, SiF_4. As this loss of silica is quantitative, it would serve as a basis for the estimation of silica, if all of the SiF_4 could be recovered.

Previous employment of the general principal.- So far as search of the literature can reveal, the volatitization ? method has never been employed for the determination of silica. Its general principle has, however, been long used for the determination of fluorine both in organic and in inorganic compounds. The hydrofluoric acid, liberated from the compound by H_2So_4 is caused to act upon an excess of silica. Knowing the amount of SiF_4 evolved, one can easily determine the fluorine content of the original sample. Much work has been done in the past, and several methods have been developed for absorbing the SiF_4 and determining its quantity. A brief account of some of the later of methods will be given, in the order of their development.

Fresenius(reviewed by Offermann, Zeit, Angew, Chem. 20,615 (1890) original in ibid 5, 190, 1866) was the first who really showed the worth of the volatitization method for the quantitative determination of fluorine, The fluoride sample weighing .5g., mixed with 10-15g of powered silica, was treated in a dry flask with 40-50 cc of strong H_2so_4. The Si F_4 generated was swept out with a stream of dry air. The gas was first passed through two U-tubes, the first of which contained fused calcium chloride, and the second containing in one arm fused calcium chloride and in the other anhydrous copper sulfate mixed with pumice. The absorption tubes were three in number and were accurately weighed before the experiment. The first contained in the bottom bend soda-lime, in one arm cotton moistened with water, and in the other cotton moistened with $CaCl_2$. The third contained pumice moistened with strong H_2SO_4. The reaction mixture was heated to 150-160°C. for several hours, cooled, the absorption tubes weighed and the increase in weight taken as the weight of SiF_4 Absorbed.

Penfield(American Chem.Jour.1,27,1879) has perfected a volumetric method for the determination of fluorine. He passed the SiF_4 into an alcoholic solution of potassium chloride.

The following reaction took place,

$$H_2SiF_6 + 2\,KCl = K_2\,Si\,F_6 + 2HCl.$$

The HCl liberated was titrated with standard ammonia, using cochineal as indication. Very good results were obtained by Penfield, as the following table will show,-

Analysis Of Fluorspar.

Fluorspar	F. (theory)	F. (found)	Difference
.2464 g	.1200 g	.1199 g	- .0001 g
.2039	.0993	.0989	- .0004
.2074	.1010	.1023	- .0013
.2147	.1046	.1064	- .0018
.9292	.4325	.4329	- .0004
.4673	.2277	.2283	- .0006
.9901	.4824	.4817	- .0007
1.0130	.4935	.4923	- .0012

Hoppe-Seyler (Tammann-Zeit. Anal. Chem. 24, 328, 1885; a review) developed a method for estimating fluorine inorganic compounds. The sample is well mixed with silica and treated in a flask with concentrated H_2So_4. The SiF_4 is absorbed in a solution of a barium salt, such as the bromide, iodide, or acetate. Barium fluosilicate is formed according to the equation, $3\,Si\,F_4 + 2\,Ba\,Br_2 + 2H_2O = 2\,Ba\,SiF_6 + 4\,HBr + SiO_2$. It is rendered insaluble by the addition of 80% by volume of alcohol, (39,060 parts of 50% alcohol dissolve 1 part of $Ba\,SiF_6$) The precipitate is filtered off, well washed with 50% alcohol and treated with hydrofluoric acid to dissolve out the silica, also formed during the absorption of the SiF_4. The barium fluosilicate is then treated with H_2SO_4 whereby barium is precipitated as the very insoluble sulfate, which is weighed. From this weight one may find the weight of fluorine in the original sample. A slightly different precedure is to heat the barium fluosilicate 1-2 hours on a steam bath with a solution of ammonium phosphate. The precipitate of barium phosphate is filtered off, treated with HCl again filtered and washed with Hcl. The filtrate contains the barium, which is precipitated as sulfate and weighed.

For the determination of fluorine in minerals, Tammann (Ibid, 24, 328, 1885) adopted the following procedure. The sample is mixed with powdered quartz, placed in the generating flask, and strong H_2So_4 added. A stream of dry air is used to sweep out the SiF_4. For cryolite, fluorspar, and similar minerals, 6-7 hours heating at 160-170° are necessary; for barium and potassium fluosilicates, 2-3 hours-are sufficient; The absorbing liquid is water, and it contains all of the fluorine from the sample. It is treated with barium acetate, the precipitate allowed to settle, and filtered. The barium fluosilicate is treated with hydrobromic acid, 75% alcohol added, and the precipitate filtered and washed with alcohol. The barium is then precipitated as $Ba\ So_4$ and weighed. Very low results were obtained as indicated in the following table,

Mineral(Cryolite)	F.(theory)	$BaSo_4$(found)	F(found).
.5916 g	.3204 g	.6172 g	.3017
.4754	.2575	.4631	.2264
.4749	.2572	.4880	.2372

Much better results were obtained by proceeding as followsBarium fluoride was analysed. The SiF_4 was absorbed in a solution of barium acetate containing hydrobromic acid. The barium fluosilicate was almost completely precipitated by the addition of much alcohol. It was filtered off and treated in the usual manner. Good results were obtained, as shown in the following table.

$Ba\ F_2$ taken	F(theory)	$BaSo_4$ weighed	F(found).
.7140 g	.1548 g	.3150 g	.1535g
.5968	.1293	.2638	.1289
.6934	.1503	.3127	.1528

A volumetric determination of fluorine was also worked out by Tammann. The absorption liquid is treated with caustic potash and allowed to stand. The precipitate is treated with hydrochloric acid, and KCl removed by washing with potassium acetate. Twelve volumes of 80% Alcohol are then added, then solution allowed to stand 2-3 hours, filtered, the precipitate washed with 60% alcohol, and titrated with standard caustic. The equations involved in this method are,

(1) $3\ SiF_4 + 2\ H_2O = 2\ H_2SiF_6 + SiO_2$, (absorption of SiF_4).

(2) $H_2SiF_6 + 2KOH = K_2SiF_6 + 2H_2O$ (precipitation with KOH).

(3) $K_2SiF_6 + 4KOH = 6KF + SiO_2 + 2H_2O$. (Titration with KOH).
S. Bein(Zeit Anal.Chem. 26, 733, 1887) estimates the fluorine content of a sampke by determining the quantity of SiO_2 formed in accordance with equation (1) above. His procedure is as follows. The size of sampke to be taken is regulated by its probable, fluorine content, about 1-1.2g for fluorspar, and a proportionably greater amount for minerals lower in fluorine. If fluorspar is used, the sample is mixed with 12-16 parts of silica and transferred to a well dried flask provided with a three-hole stopper. A glass tube through which well dried air may be passed is inserted in one hole of the stopper. Through the second hole passes a glass tube, widened at the end, and dipping into water in a test tube, This is the absorption tube, A dropping funnel is inserted in the third hole of the stopper. This contains about 100cc of concentrated sulfuric acid od specific gravity 1.85. To ensure complete dryness of every part of the apparatus, the flask is heated and the current of dry air is passed for a few minutes. The mixture of sample and silica is then transferred to the flask and the current of air started again being so regulated that about 2 bubbles per second pass the absorption tube. About 50cc of sulfuric acid are allowed to drop into the flask, which is then heated slowly in an oil bath to 170°C but no higher. After about 3 hours heating, during which time the flask is frequently agitated to assist the reaction, 25cc more of acid are added and the heating continued a few more minutes to ensure completion of the reaction. After allowing the separated silicic acid to settle a few minutes, it is filtered off, washed with weak acid, the precipitate heated to constant weight, and weighed as SiO_2. The weight of silica multiplied by 5.494 gives the weight of fluorine. Bein's results for fluorspar and sodium fluoride are given in the following table.-

Substance	F(theory)	F(found)
Ca F2	49.47%	49.06%
		49.29
Na F	45.24	45.02
		44.87

It is seen that the observed fluorine content is consistently lower than the theoretical value, due most likely to slight losses of SiF_4 because of traces of moisture still remaining in the apparatus.

Instead of decomposing the SiF_4, it may be absorbed by a solution of potassium fluoride, giving the potassium fluoslicate.
The amont of fluosilicate formed may be determined either gravimetrically or volumetrically. The former procedure was adopted by Coruot(Comptes Rendus 114,750,(1892). This investigator generated the SiF_4 in much the same manner as did Bein. For sweeping out the gas, either air or carbon dioxide dried in sulfuric acid towers may be used. The absorption contains a layer of mercury overwhich is poured 20cc of pure 10% potassium fluoride solution. The tube conducting the SiF_4 is widened at the end and opens 2-3 millimeters below the surface of the mercury. Thus the danger of clogging the tube is entirely eliminated.Caruot recommends a maximum temperature of 160°C for the generation of the $Si\ F_4$, and considers the reaction at an end when bubbles no longer appear at the surface of the reaction mixture in the flask, about $1\frac{1}{2}$ - 2 hours. The fluoride solution in the absorption bottle contains the gelatinous and barely visible potassium fluosilicate, which settles quite readily. The aqueous solution is decanted, and the mercury is washed with portions of water. The combined portions are treated with an equal volume of 90% alcohol and allowed to stand. The precipitate is washed by decautation with 50% alcohol there transferred to a tarred filter and washed free from fluoride. It is dried at 100°C and weighed as K_2SiF_6.The weight of K_2SiF_6 multiplied by .3794 gives

the weight of fluorine which came from the sample. The accuracy of this method abviously depend not only upon complete absorption of the SiF_4, without losses due to moisture in the apparatus, but also upon the complete, or nearly complete, insolubility of K_2SiF_6 in 50% alcohol. Though H. Rose(Mellor, A Treatise On Inorganic And Theoretical Chemistry Vol Vl P 949) atates that alcohol completely precipitates $K_2 SiF_6$ from aqueous solution, Adolph (Jour. Amer.Chem.Soc. 37,2500,(1915) throws doubt on this point. Also the jelly-like character of the fluosilicate (Mellor-Vol Vl P.947) does not tend to make its handling an easy matter.

The volumetric method developed by Offermann(Zeit angew, chem. 20,615,(1890) gives good results. Offermann carried out the volatitzation at 150-160° and collected the SiF_4 in a beaker of water, the bottom of which was covered with a layer of mercury. The SiF_4 was liberated below the level of the mercury so that the tube did not because clogged with silicic acid. The fluosilicicacid liberated was titrated with standard KOH, using cochineal as the indicator. 1cc of normal KOH is equivalent to .0190 g. of fluorine. Offermann's results for fluorspar are given in the following table,

Weight of sample	F.(found)	F.(theory)
.300 g	48.45%	48.72%
.400	48.45	"
.300	48.45	"
.300	48.45	"

Adolph(Jour.Amer. Chem. Soc. 37,2500, (1915). has conducted an extensive investigation of the conditions most favorable to the success of Offermann's method. As a result, he proposes the following improved procedure. The sample of fluoride, equivalent in fluorine content to .1-2 g. of fluorspar, is well mixed with three times its weight of iginted silica. The volatilization and absorption apparatus is shown in the figure. The dry mixture together with one grain of anhydrous $CuSO_4$ is placed in the

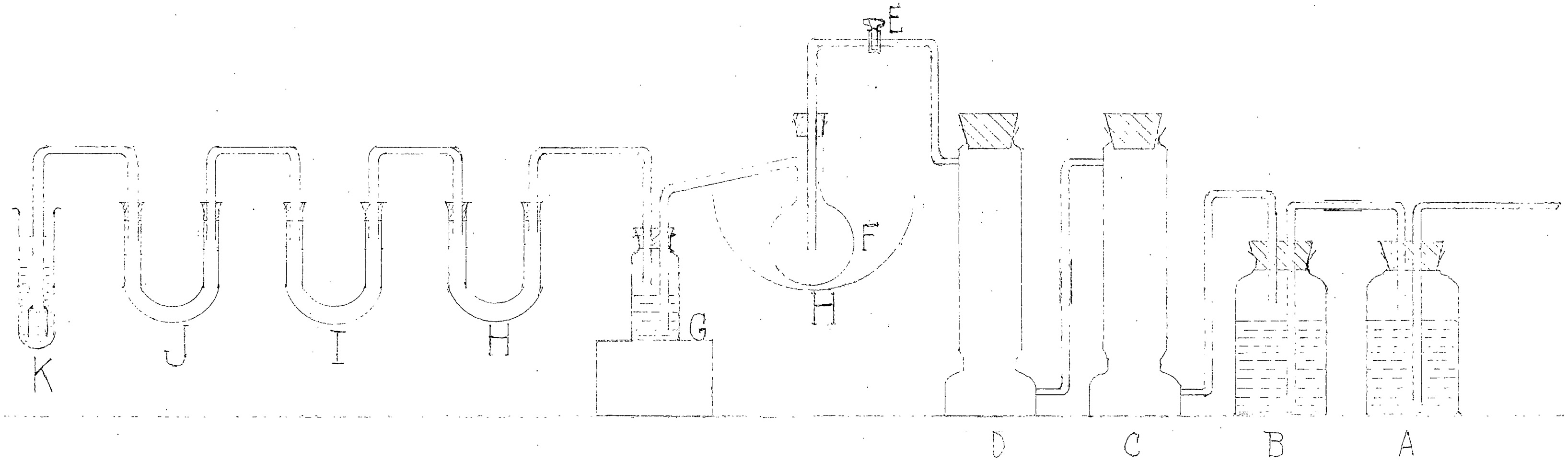


Fig. II; Adolphs apparatus for the determination of fluorine by volatilization method.

flask F, and 25cc of 98.6% H_2SO_4 added. The stopcock E is now closed while the flask is heated in the air bath H till after one half hour the temperature has reached 220°C. E is then opened and air dried in the drying towers A,B,C, and D is passed through at the rate of these bubbles per second. It is most important that the air be absolutely dry and free from carbon dioxide. Towers A and B contain strong $H_2 SO_4$ C contains soda lime, and D calcium chloride. Flask F is shaken occasionally to promote the reaction. The SiF_4 is passed through a drying flask G containing strong H_2SO_4, then through the U-tubes H,I, and J to condense any H_2SO_4 vapor. H. cobtains glass beads, and I and J are cooled in water. The SiF_4 is then passed into a test tube K containing about 50cc of water. The end of the incoming tube is widened to prevent clogging with the silica which at first sepabates. After 2-2½ hours the test tube is removed and its contents titrated with 0.1 N-KOH using phenolphthalein as indicator. 12 parts of KOH are equivalent to 3 parts of SiF_4, so that the weight of SiF_4 is found by multiplying the number of cc of KOH used by .0026025.

The success of this method depends on a number of factors. In the first place, Adolphe found that sulfuric acid considerably stronger or weaker than 98.6% gave results. Very low results were obtained using "concentrated" acid(96.9% H_2SO_4), only 40.4% fluorine in CaF_2 against 48.52% theory. On the other hand, very strong acid gave high results owing to the fact that SO_3 was evolved at the temperature of the experiment, and raised the acid content of the absorption liquid.

In the second place, temperature plays a very important part in the success of the experiment. The effect high and low temperatures on the amount of fluorine found in fluorspar is well shown in the following table.—

Effect Of Variation Of Temperature Of Experiment.

Temperature	F (found)	F(theory).
180° C	46.9 %	48.52
180	47.8	"
200	47.4	"
220	47.1	"
230	47.6	"
280	45.3	"
310	35.7	"
310	32.6	"

In the third place, the results were affected by the form of silica used. Feldspar and precipitated silica gave low results. Quartz gave the best results, though frequent agitation of the generating flask was necessary. The stronger the dehydrating agent present in the generating flask, the better were the results obtained.

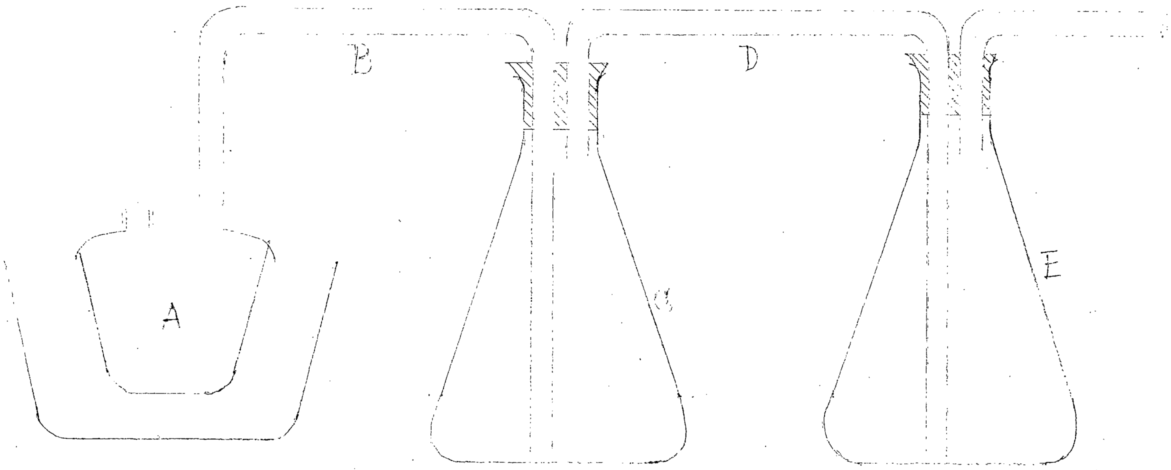


Fig III
Apparatus used in determination of silica by volatilization method.

Preliminary experiments on the volatitization method- preliminary studies were carried out to determine the experimental conditions under which the method would be most successful. The arrangement of the apparatus is shown in the sketch. The glass was decomposed in the platinum crucible A with hydrofluoric acid and sulfuric acid. To the top of A was fitted a platinum cover to which was attached a platinum tube B bent twice at night angles. The tube leads the SiF_4 into a small paraffined flask C containing dilute caustic potash. What SiF_4 escaped absorption in C was lead by a paraffined glass tube D into a second paraffined flask E, also containing dilute KOH. A tube from E led to a Bunsen pump, by means of which a current of air was drawn through the apparatus. An opening covered with a platinum cap was provided in the cover to A, ao that the hydrofluoric acid could be poured in while the suction was in action. The crucible was heated in a small sandbath by means of a Bunsen flame.

For a determination, about.5 -.75g of glass were used. It was weighed into the crucible.1cc of 1:1 H_2SO_4 added,and 2-3cc of water. The cover was then fitted, and the apparatus set up, the first absorption bttle containing 90cc of N-KOH, the second 50cc. Suction was started 3cc of 48% HF poured into the crucible through the opening in the lid, the small cover replaced and thr suction adjusted as that 4-5 bubbles per second passed the first absorption bottle. The temperature of the sand bath was raised gradually (during about two hours) to 200-220°, and kept there until no more H F passed over. The exact time at ehich the bulk of the SiF_4 was driven over could be as certained from the change in the appearance of the first absorption bottle. As the SiF_4 was absorbed, potassium fluosilicate was formed, which possessed a peculiar bluish iridescence in reflected light. By transmitted light, the color was bluish with a suggestion of violet, towards the-end of the heating, a white smoke would sometimes appear in the bottles. This might have been due to SO_3, formed by the decomposition of the H_2SO_4 in the crucible. After the apparatus had cooled, the flasks were removed, the connecting tubes washed out with hot water, and the two solutions analysed separately for their silica content, to determine how much SiF_4 had passed the first bottle.

Silica was separated from the fluorides present in the solution as follows. (Scott-Standard Methods of Chemical Analysis, 1920, Vol. 1 p. 179). The alkaline liquid was treated with 5-10 grams of solid ammonium carbonate boiled for 5 minutes and allowed to stand in the cold for two or three hours. By this procedure, the fluosilicate was completely decomposed, and flocculent SiO_2 was precipitated. This was filtered with gentle suction washed with cold ammonium carbonate solution and the silica burned to constant weight, volatilized with HF and H_2SO_4, and the residue weighed, the difference between the weights representing the pure SiO_2.

A considerable amount of silica remained in the filtrate, and was separated as follows. The solution was evaported nearly to dryness whereby some ammonium carbonate was removed. The residue was taken up with water, and neutralized with 2-N HCl, using Phenolphthalein as the indicator. The solution was boiled, restoring the color of the indicator. More HCl. was added, the solution again boiled, and the process repaeated until the pink color was destroyed by the addition of 1-2cc of HCl. about 5cc of ammoniacal zinc oxide were added to precepitate the $Si\ O_2$ as zinc silicate. The mixture was boiled until ammonia was completely expelled. The precipitate of zinc silicate and oxide was then filtered off, washed with hot water, and redissolved in about 10cc of stroing HCl. The solution was evaporated to dryness, baked carefully to dehydrate the silicic acid, and taken up with 10% HCl. The SiO_2 was filtered off, washed with 10% HCl, and the SiO_2 -

determined gravinvetrically. If it weighed more than 10 milligrams, the filtrate was again evported to dryness taken up with acid and a second portion of SiO_2 filtered off and weighed. Long baking of the residue is not necessary as the zinc chloride is itself a dehydrating agent fused. It should be remarked that when the suction was especially irregular, a third absorption bottle was included.

Results of the preliminary tests- at the time when this method was first tried only glasses 4B,5B and 6B of the small melts were available. Analyses were made on 4B and 5B, with the following results.

Glass 4B

Analysis No	Weight of sample	Silica found first bottle	second bottle	third bottle	total	$\%SiO_2$
1	1.0000g	two combined			.5749g	57.49 %
2	"	" "			.5623	56.23
3	.7500	" "			.4408	58.95
4	.7500	" "			.4114	54.95
5	.7500	together	.3828	.0101	.3929	52.39
6	1.000	together	.5505	.0102	.5607	56.07

Glass 5B

Analysis No	Weight of sample	first bottle	second bottle	third bottle	total	$\%SiO_2$
1	.7500g	Hand 2 together	.3620g	.0063	.3683g	49.11%
2	.7500	.3673	.0065		.3738	49.84

The extreme variability if these results was not explained, until I happened to examine carefully the far exterior of the platinum bend. It was found full of precipitated silicic acid. As a result the entire set of determinations had tobe rejected and the method abondoned. Work was not recommenced until the new melts were available for Analysis. Every precaution was then taken to guard against loss of silica, either in the tube, or by too rapid suction. Although the analyses by the improved method have been definitely started, the proposed procedure will be described.

Improved method for determination of silica- Among the improvements introduced may be mentioned the substitution of a second platinum tube with round bends in place of the paraffined glass tube leading from the first to the second bottle. To make certain that little or no silica was caught in the platinum tubes, these were heated to redness to drive out all moisture present and weighed. In order to eliminate as much moisture as possible from the generating crucible, anhydrous HF gas was generated in contact with the glass, by the action between calcium fluoride and strong sulfuric acid.

About .5g of powdered glass and 1.5g of C.P. CaF$_2$ were weighed into the platinum well mixed crucible well mixed and the cover fitted. Into each of the absorption bottles were poured 40cc of 2N-KOH. After the apparatus had been set up and moderate suction started 5cc of concentrated H$_2$SO$_4$ were poured into the crucible, and the sand bath heated slowly to about 100°C. Suction was maintained steady, so that 3-4 bubbles per second passed the first bottle. The temperature was raised cautiously to 100°C and then flame removed. Soon, the SiF$_4$ began to pass over into the absorption solution, as was evidenced by the formation a precipitate on the end of the tube. Almost pure SiF$_4$ passed over for a while during which time it was neccessary to see that the end of the tube did not become clogged. After excessive precipitation has ceased, the temperature was raised to 220-230° C. and maintained there for half an hour to ensure removal of all SiF$_4$. The crucible was then allowed to cool to room temperature, the suction being maintained constant. The flasks were removed ,the tubes washed out first with strong HCl then with hot water and the washings added to their respective flasks, The tubes were carefully heated to remove moisture, then to redness, cooled and reweighed to determine -

the amount of silica they still retained. This weight(0-5 milligrams) was added to the weight of silica found in the absorption solutions.

The silica in the two bottles was determined by the method outlined by Scott(loc.cit).

This new procedure is certain to give concordant results, since no silica can possibly elude either absorption in the bottles, or detection in the platinum tubes. Work will be prosecuted in this direction at the very first opportunity.

Determination of trivalent arsenic- No work has been done as yet with regard to the arsenic trifluoride which is absorbed together with the silicon tetrafluoride during the progress of the volatilization. Sufficientle large batches are not yet available, so that samples of five grams or more may be analysed for arsenic trioxide.

Allen and Zies (Jour.Am.Cer.Soc.1,739-86,1918) in their investigations on the condition of arsenic in glass, employed the volatitization method for the determination of trivalent arsenic. The glass was treated with HF and H_2SO_4 in a platinum still, and the AsF_3 absorbed in sodium hydroxide solution. The caustic solution was evaporated nearly to dryness and treated with a little hydrogen peroxide to convert the sodium arsenite to arsenate. Silica was then removed by treating the residue with HF and H_2SO_4. The salt was dissolved in water, filtered, and the arsenic determined by any of the standard methods, either volumetric or colorimetric.

This method will be tried when the next large melts are available.

IX. Determination Of Physical Properties.

1. Density- Preliminary determinations of the densities of the pieces of glass from the small melts were carried out by the immersion method. A piece of the glass weighing 8-10 grams was first weighed in air, then in water at 20°C., and the loss in weight determined, this giving, by Archimedes principle the weight of the displaced water. By the use of tables, this weight was changed to volume in cubic centimeters. Dividing this into the weight of the glass gave the density of the glass referred to water at 4°C. (denoted by $d\frac{20^\circ}{4^\circ}$).

Due to the presence of bubbles - some of them of considerable size - in the glass, it was thought that the figures for the densities would be in error. Consequently, the following method was tried. Small pieces of the glass were examined carefully for the absence of nearly all bubbles, and weighed. A picnometer bottle of about 25cc. capacity was weighed full of water at 20°C. The picnometer was then emptied, the pieces of glass put in, the picnometer again filled with water at 20°C., and weighed. Great care was taken to have the level of the water in the side arm the same in the two cases. The density of the glass was then calculated by means of the following formula:

$$D = \frac{Wg \times d}{Wg + W_1 - W_2}$$

where, D = density of the glass.
d = density of water at 20°C.
Wg = weight of glass pieces
W_1 = weight of full picnometer bottle without glass.
W_2 = weight of full picnometer bottle containing glass pieces.

Weights W_1 and W_2 were corrected for buoyancy of air.

In spite of all possible precautions, concordant results could not be obtained. This is illustrated in the following table:

Trial.	Glass No. 4B.		Glass No. 5B.	
	Density by immersion.	Density by picnometer	Density by immersion.	Density by picnometer
1	2.941	2.760	3.333	3.339
2	2.941	2.9456	3.333	3.375
3	2.941	2.9413	3.333	3.335

We see that, barring trial 1 on 4B, as possibly due to error of weighing, the density figures are subject to a variation of several figures in the third decimal place. The experimental error in determinations of density should not exceed one in the third decimal place. The uncertainty in the above figures is due wholly to errors in weighing the picnometer bottle when full of water. Unless the temperature is absolutely uniform throughout the body of water, a considerable error is introduced, as much as four or five milligrams. Errors in weighing due to the large mass of the bottle and water are negligible, it being found possible to move the pointer of the balance by changing the weight by .0002 gram. The evaporation of the water in the picnometer introduced a sensible error, even when the hole in the cap for the side arm was closed with paraffin. In one trial it amounted to .0004 gram per minute. As two or three minutes were required for a careful weighing, it will be seen that an uncertainty of a milligram or more is introduced. Take, for example, the following data:

W_g = 1.8195 g.
W_1 = 55.3175 g. (corrected)
W_2 = 56.5988 g. (corrected)
d = .99823g. per cc.

$$\text{whence,} \quad D = \frac{1.8195 \times .99823}{.5382} - 3.3748 \text{ g. per cc.}$$

suppose, due to the uncertainties mentioned above, that a second trial gave W_2 = 56.5948 g. (corrected). Substituting this above we find $D = 3.33\overset{498}{\underline{48}}$ g. per cc. It is thus clear how small an error in W_2 is required to make a very large error in D.

It was therefore thought best to try to improve the immersion method. By suitable precautions, nearly every source of error could be eliminated except that due to the presence of bubbles in the glass. The temperature of the water in which the glass was suspended was maintained within 0.2°C either side of 20°C. Any error due to the volume of the wire immersed in the water was eliminated by weighing the suspended wire alone, submerged to the same extent as when the glass was attached to it. No correction was made for the downward pull exerted by surface tension on the wire. The glass was weighed in air lying directly on the scale pan, this weight being certainly accurate to within ±.0001 grams. The weight of the glass in water could be determined with a maximum error of ±.0004 grams. The larger the piece of glass; the less effect does this last uncertainty have upon the final result. In the following table are given the densities determined by the improved immersion method. Due to the bubbles in the glass, these figures are not accurate beyond the third decimal place.

Glass No.	Density $\frac{20^\circ}{4^\circ}$	Weight of glass in air.
3½B	2.725	13.3287 g.
4 B	2.941	3.1915
4½B	3.171	17.4075
5 B	3.333	16.2230
6 B	3.732	8.2930
7 B	4.110	8.8575

The densities of the glasses from the larger melts were determined in exactly the same manner. As was mentioned in an earlier section, the density determinationswere made on the prisms ground for the refractive index and dispersion measurements. Inasmuch as these later glasses were much freer from bubbles than the earlier pieces, we may be sure of the densities in the following table to within ± 3 in the fourth decimal place.

Glass No.	Density $\frac{20^\circ}{4^\circ}$	Weight in air.
3½B	Due to the fact that these glasses were also found to be imperfect, the density values for the smaller melts were used for the curves.(See refractive index).	
4 B		
4½B		
5 B		
6 B		
7 B		

Conclusions from density determinations- It is seen from the first table that the density of bismuth glasses increases with the bismuth content, a fact which one would expect. In curve 1 values are plotted against percentage of Bi_2O_3 present. No curve be plotted showing the relation between density and moles of Bi_2O_3 present, since it has been found that the composition of the glass no longer correspond exactly to the series $100SiO_2 \cdot 40Na_2O \cdot XBi_2O_3$. The following conclusions may be drawn from the curve plotted,

1. Density increases with increase of Bi_2O_3 content.
2. The rate of increase of density increases with increasing Bi_2O_3 content.

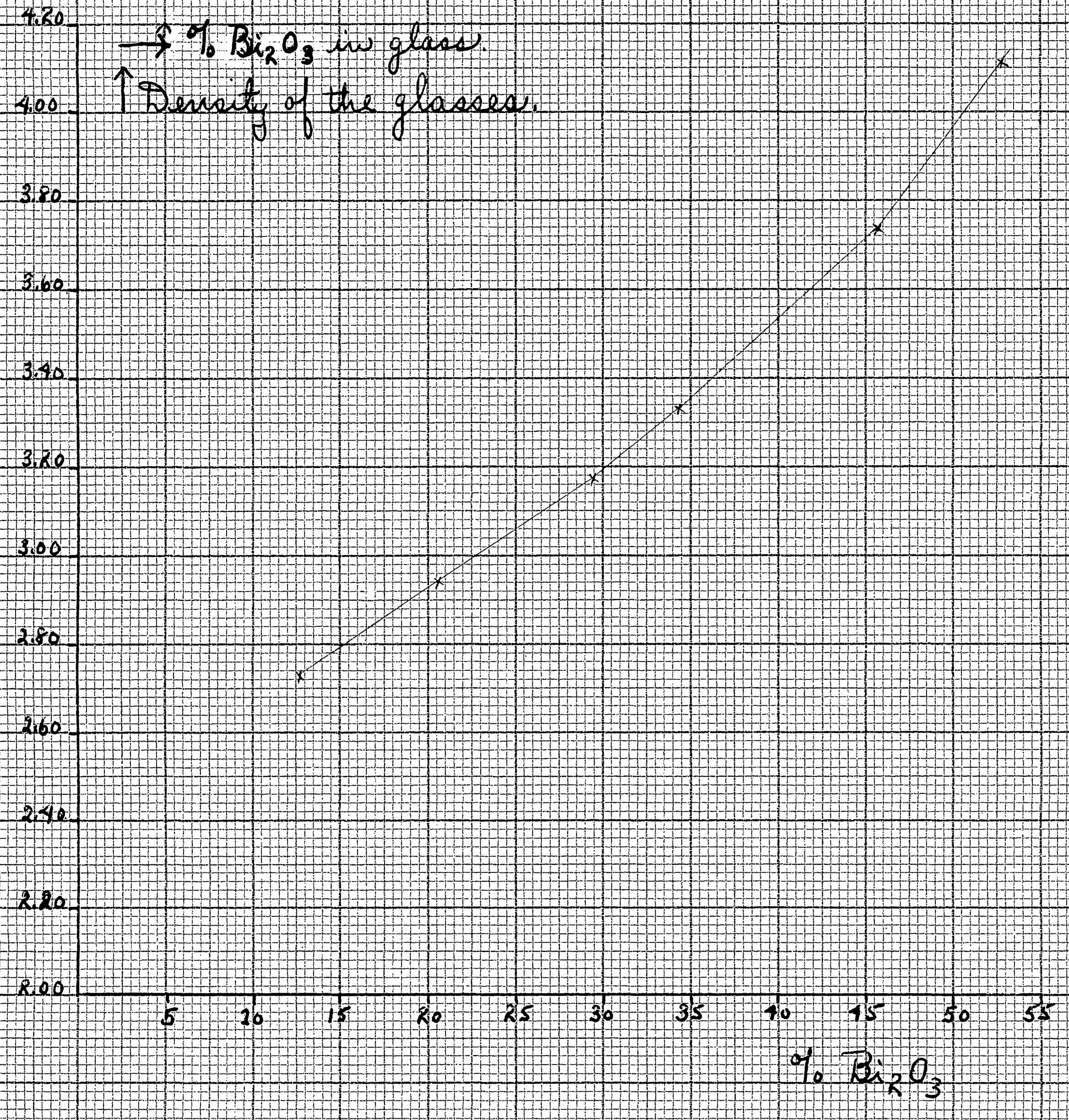
A comparison of the densitied of soda-bismuth and soda-lead silicates leads to the interesting conclusion that not only are the bismuth glasses heavier than the corresponding lead glasses, but that the difference increases in general, as we ascend the series. The facts are well shown in the following table,

Density of Bismuth Glasses	Density of Corresponding Lead glasses(Peddle)	Difference
2.725	2.710	.015
2.941	2.912	.029
3.171	3.112	.059
3.333	3.282	.051
3.732	3.543	.189
4.110	3.756	.354

As yet, no explanation can be offered for the drop in the difference for the fourth glasses in the table.

We are now in a position to determine approximately the specific density of Bi_2O_3, that is, the density of the oxide as it is present in the glass. For this purpose it will be sufficient to use only the bismuth, sodium, and silica figures, the latter being -

Curve I; density of the bismuth glasses plotted against Bismuth present.



calculated by subtracting from 100% the sum of Bi_2O_3 -Na_2O. This should not introduce an error of more than1-1.5% in the result.

The Winkelmann-Schott formula was used,

$$\frac{100}{D} = \frac{p_1}{d_1} + \frac{p_2}{d_2} + \frac{p_3}{d_3} + \ldots \text{etc.}$$

where,

D- observed density of glass.

p- % of oxides present

d- specific densities of the respective oxides.

The specific densities of the respective oxides.have been carefully determined by W. L. Baillie[1] (Chem.Abstracts 1921, p.3374). He has found the value 2.24 for SiO_2 and 3.20 for Na_2O. In the following table are given the bismuth and sodium figures found by analysis, the silica found by difference, the density of the glasses, and the calculated values for the specific density of Bi_2O_3,

Glass No.	Bi_2O_3%	Na_2O%	SiO_2%	Density	d for Bi_2O_3.
3½B	12.6972	24.30	62.98	2.725	12.23
4B	20.67	22.73	56.60	2.941	13.02
4½B	29.52	20.83 ~~21.30~~	50.35 ~~49.18~~	33171	10.15 ~~9.90~~
5 B	34.34	18.23	47.43	3.333	10.98
6 B	45.75	14.48	39.77	3.732	12.75
7 B	52.87	13.55	33.58	4.110	10.35

The density of Bi_2O_3 in the free state is 8.98. In spite of the extreme discordance of the above values for d, we may safely conclude that the specific density of Bi_2O_3 is considerably greater than its density in the free state.

X. Refractive Index And Dispersion.

Preliminary experiments on pieces from small melts. In the case of these glasses, the principle of total reflection as embodied in the Abbé and Pulfrich refractometers, was employed. Pieces of each glass were first ground with one face flat. A second flat face was ground at approximately a right angle to the first, and the two faces well polished, so that the line of intersection of the faces was as sharp and straight as possible. For contact liquid, α-bromonaphthaline was used for glasses 3½B, 4B, 4½B, 5B and methylene iodide for glasses 6B and 7B. Determinations of refractive index were made on the first five glasses, on the Abbé refractometer. The position of the glass piece was changed from place to place on the prism of the instrument, the scale being read each time. By averaging these readings, a figure was obtained which was certain, within one or two units in the third decimal place. Two pieces of glass 3½B were prepared and ground. The first gave an index of refraction abnormally low, about 1.500, while the second, which gave a much sharper edge on which to set in the refractometer, had a higher index. We felt justified in not considering further the first piece, inasmuch as we later found that absolutely no edge at all could be detected on the Pulfrich refractometer, in the case of this piece. The second piece gave an edge easy to set on. In the following table are given the values of the mean refractive index for white light for each setting, the simple mean of these settings, and the weighted mean, the latter giving the most probable value of the refractive index, the fourth decimal being omitted as uncertain.

Setting	$3\frac{1}{2}$B	4B	$4\frac{1}{2}$B	5B	6B
1.	1.5365	1.5648	1.5984	1.6200	1.6698
2	1.5370	1.5653	1.5985	1.6215	1.6699
3	1.5375	1.5655	1.5989	1.6217	1.6705
4	1.5365		1.5989		1.6704
5	1.5375				1.6704
Simple mean	1.5370	1.5652	1.5987	1.6211	1.6702
Weighted mean	1.538	1.565	1.599	1.621	1.670

All of these glasses gave fairly sharp edges in the instrument, except 4B. This glass was so small that it covered only a small portion of the total area of the prism. Hence, it gave a very diffuse edge, difficult to locate and set upon.

The same pieces were tested on the Pulfrich refractometer, using a strong sodium flame as the source of light. The refractive indices of the glasses were then calculated according to the formula,

$$n_D = \sqrt{N_D^2 - \sin^2 i}.$$

where, n_D is the index of the glass.
N_D is the refractive index of the Pulfrich prism.
i is the angle read on the graduated circle of the instrument.

The angle i must be corrected by subtracting the "null-punkt" or null-point reading. Tables prepared especially for use with the Pulfrich prism gave the values of n_D for all values of i.

The instrument was used first in a laboratory partly darkened, then in a special dark room. The readings taken in the dark room are considered most trustworthy; only these, therefore, will be given. Glass 4B could not be measured owing to its very small size. Two pieces of 7B were tested, but as only the second gave a distinct edge visible in the Pulfrich telescope, the readings for the first piece were rejected as unreliable.

Number of Setting	Refractive Index, n_D				
	3½B	4½B	5B	6B	7B
1	1.53632	1.60088	1.62589	1.66935	1.71214
2	1.53623	1.60116	1.62615	1.66927	1.71214
3	1.53632	1.60070	1.62580	1.66927	1.71226
4	1.53614	1.60107	1.62562		
5	1.53632	1.60107	1.62607		
6		1.60088			
7		1.60088			
Simple mean	1.53627	1.60095	1.62591	1.66930	1.71218
Weighted mean	1.5363	1.6010	1.6259	1.6693	1.7121

With regard to the dispersion of these first glasses a great deal cannot be definitely stated. Glass 3½B was the only piece which gave any results at all. Settings were made on the C and F lines of the hydrogen spectrum, but the G^{1} line was too faint to permit readings to be taken. The following table gives

The values of mean dispersion, partial dispersions , and "V" value for each of the settings of the instrument.

Dispersion Values For Glass 3½ B.

SEtting No.	Refractive index(N_D)	Mean dispersion(F-C)	Partial dispersion(D-C)	Partial dispersion(F-D)	V.Value $\frac{N_D-1}{N_F-N_C}$
1	1.53632	.01102	.00322	.00780	48.7
2	"	.01094	.00326	.00768	49.1
3	"	.01150	.00346	.00804	46.6
4	"	.01109	.00329	.00780	48.4
5	"	.01159	.00329	.00830	46.2
6	"	.01166	.00329	.00737	49.5
7	"	.01106	.00334	.00772	48.5
8	"	.01063	.00315	.00748	50.6 &
Mean		.01119	.00329	.00777	48.5

Accurate measurements on the spectrometer. For the accurate measurement of refractive and dispersion, a good spectrometer is by far the best instrument. The glass to be tested has the form of a prism, the angle between two of whose faces is known. If now a beam of light be passed through the prism in such a way that the beam is deviated or bent from its straight path to the maximum extent, then the refractive index of the prism is given by th equation.

$$n = \frac{\sin\frac{1}{2}(A-D)}{\sin\frac{1}{2}A}$$

where n= refractive index of prism.
A= angle atwhich the faces of the prism meet.
D= angle of minimum deviation.

By employing a hydrogen tube as a source of light, the refractive indices for the C,F, and G ^{2} lines may be determined, and hence the dispersion of the glass.

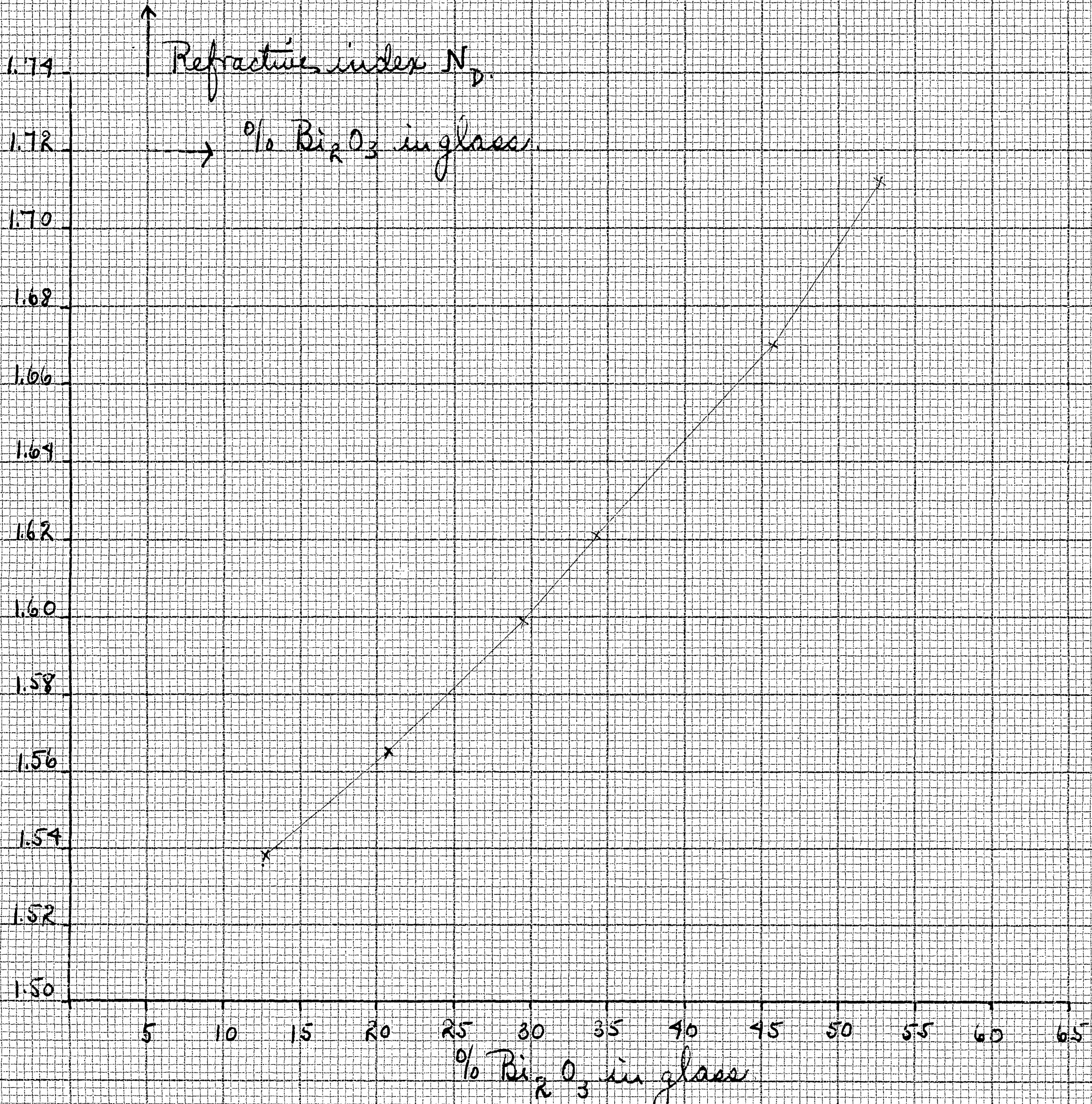
We were extremely fortunate in having the loan of the large spectrometer belonging to the Spencer Lens Company of Buffalo. This instrument had been carefully tested ans its scale checked over well, so that with it angles could be read to one second of arc.

The two best pieces of glass from each of the large melts were ground to the approximate shaped prisms, which were then finished and polished so that the two faces to be used ~~for~~ were accurately plane. The prisms were then tested on the instrument, after preliminary adjustments, such as adjusting each face exactly perpendicular to the plane of the collimater and telescope, has been made. It was found that, if the angle of minimum deviation could be read with an error not exceeding 10 seconds of arc, the values for refractive index found would not vary in the fifth decimal place. Several settings were made so that the angle of the prism was known accurately.

Curve II

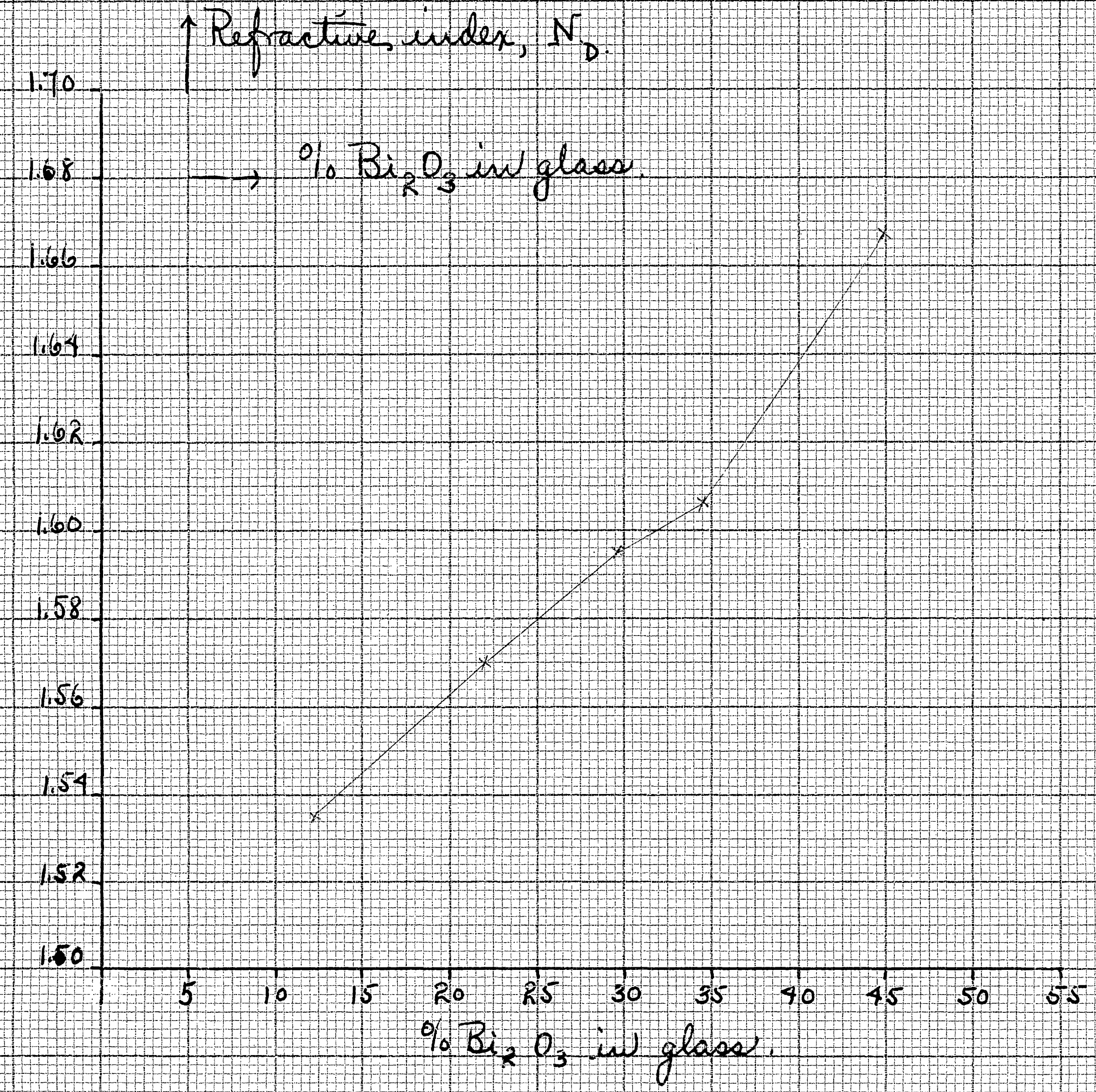
Refractive index plotted against % Bi_2O_3

[small melts]

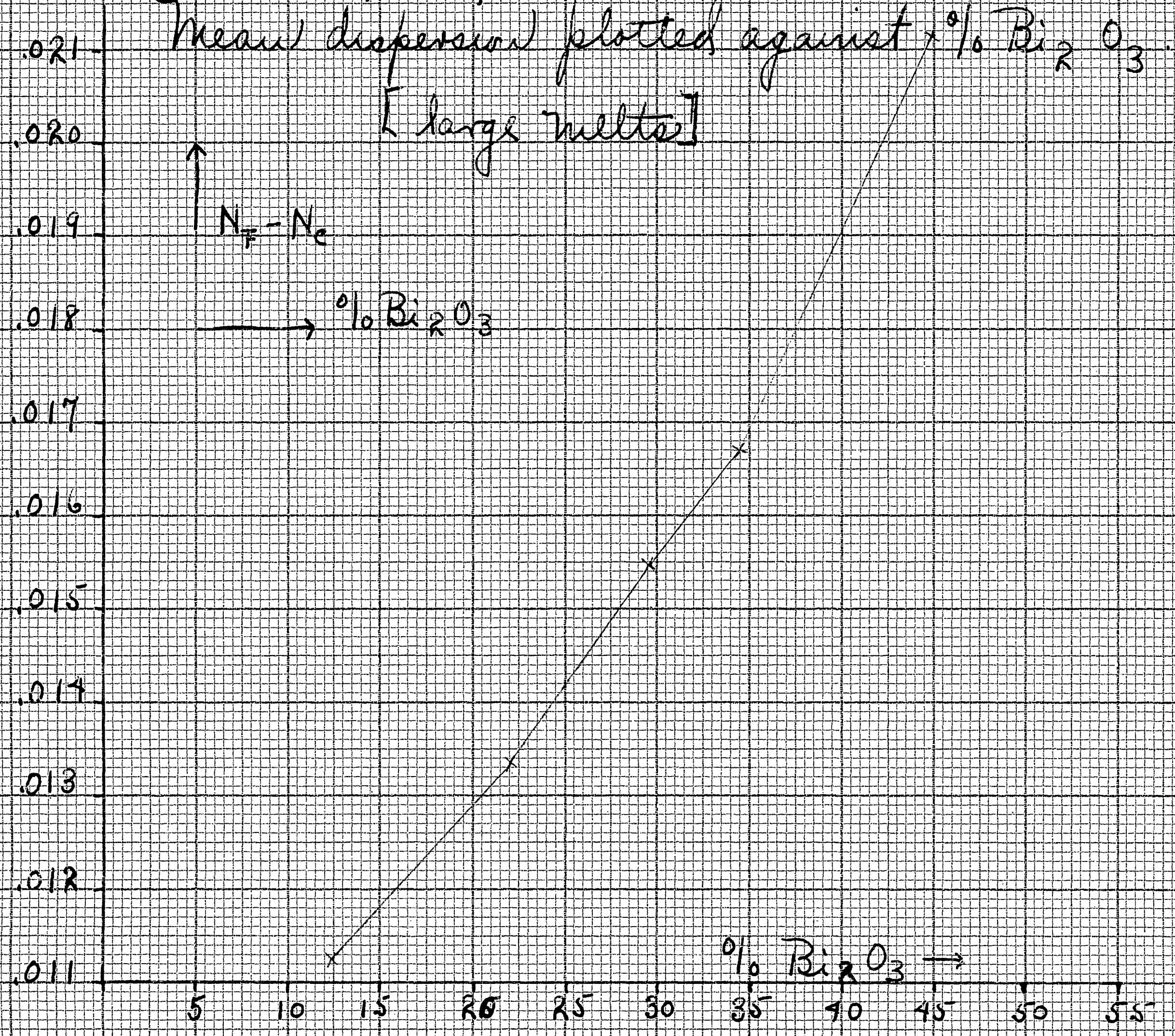


Curve III

Refractive index plotted against % Bi_2O_3.
[large melts]

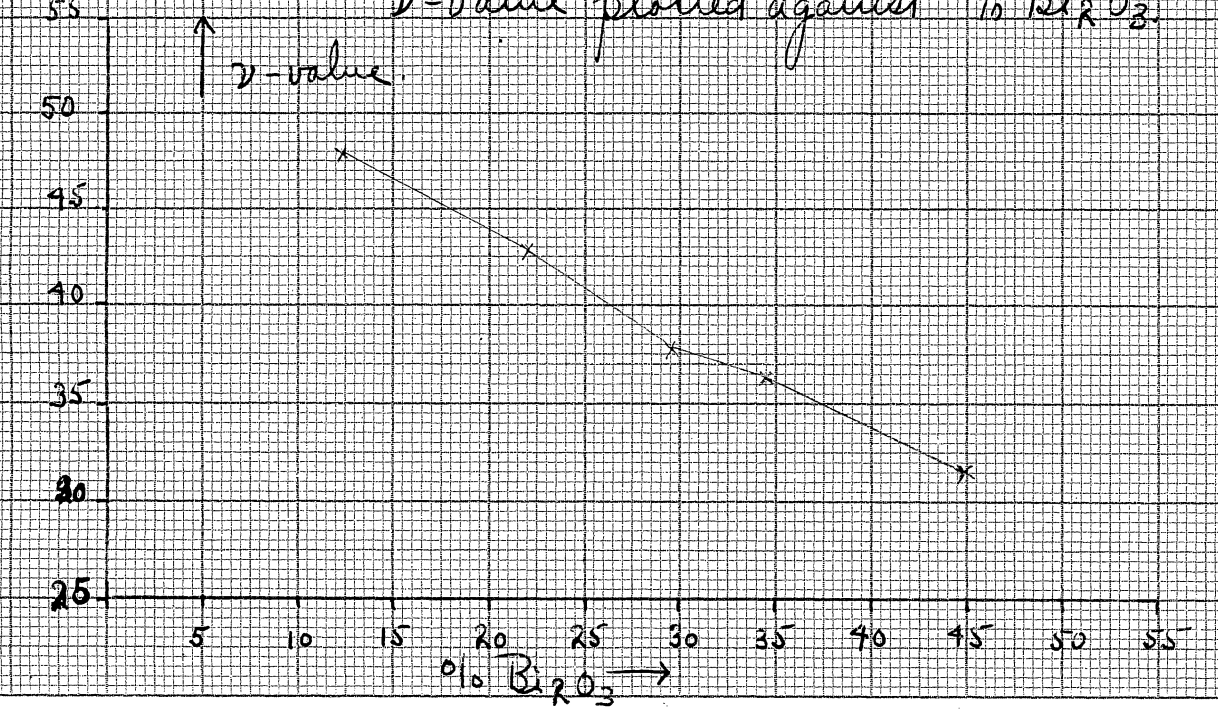


Curve IV



Mean dispersion plotted against % Bi_2O_3 [large melts]

Curve VI



ν-value plotted against % Bi_2O_3.

Conclusions from curves 11 and 111- The form of curve 11 makes it clear that, not only does increase of bismuth content cause an increase in index of refraction, but that the rate of increase of the property becomes greater as we ascend the series. Company our figures with those Peddle (Jour. Soc. Glass Tech. no.16,299,1920) we see that, not only do bismuth-soda silicates have a greater refractive index than the corresponding lead-soda silicates, but that the difference increases in general, as we ascend the series. These facts are bought out in the following table,

N_D of bismuth glasses	N_D of lead glasses	Difference.
1.5363	1.5299	.0064
1.5650	1.5558	.0042
1.6010	1.5761	.0249
1.6259	1.5927	.0332
1.6693	1.6219	.0474
1.7121	1.6471	.0650

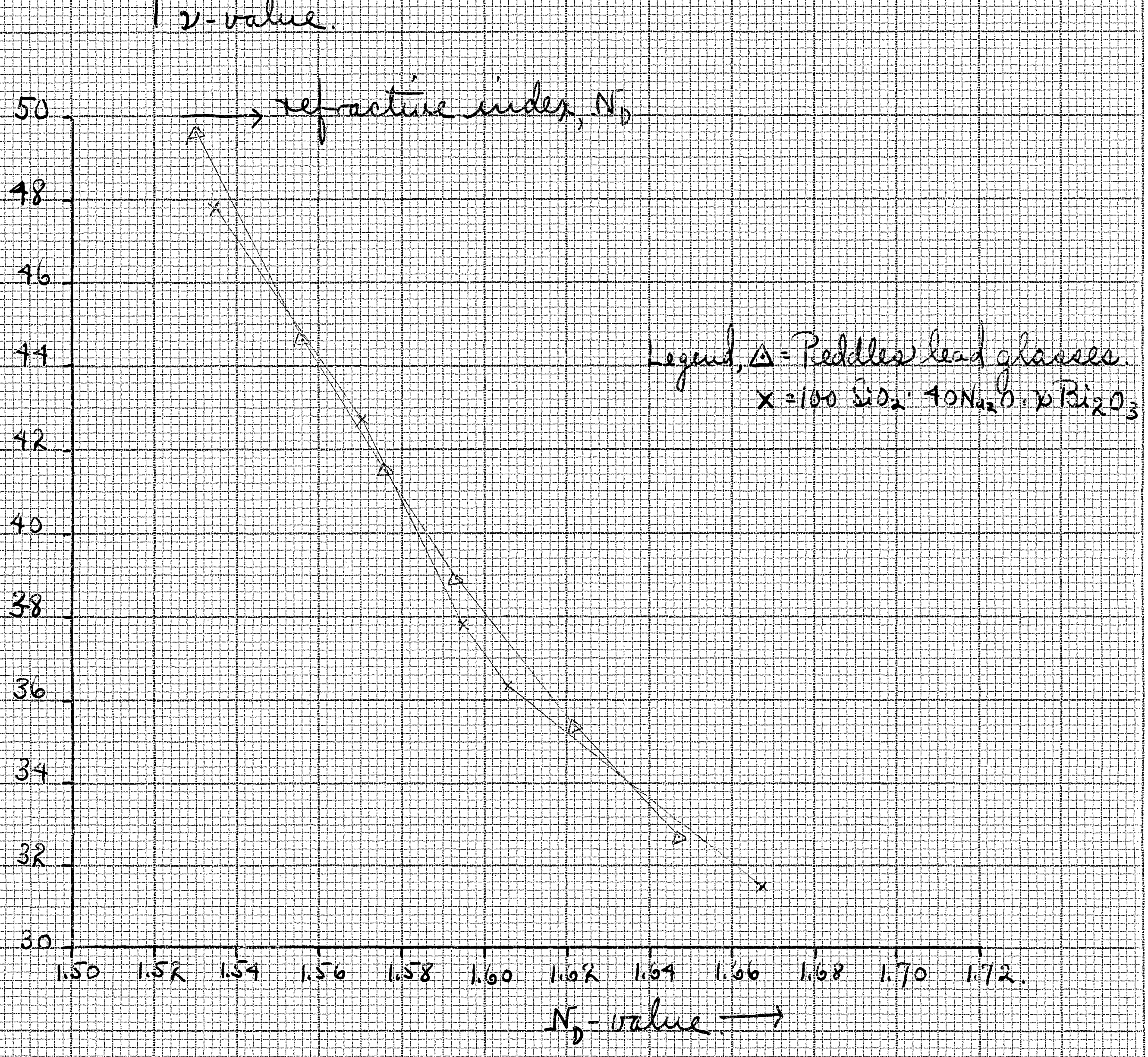
The same conclusions cannot be drawn from curve 111. Though the index of refraction increases with Bi_2O_3 content, it does so in an erratic manner. There is a verysmall rise in N_D from glass 4½B to 5B. Now we see from comparison of the analyses of the small and large melts that, while the bismuth figures are nearly identical in the two 5B glasses, the sodium figures differ greatly. In the small 5B sample, the sodium oxide content is 3.24% higher than in the 5B glass of the large melts. Peddle has found that addition of Na_2 to lead glasses containing more than 20 mols of PbO causes a decrease in N_D. It would appear, then, that bismuth glasses are unique, in that increase of however, be drawn at this time.

Conclusions from curves 1V and V- As regards the relation of mean total dispersion and 2 value to the composition of the glasses, the following conclusions may be drawn,

1. As the bismuth content of the glass increases, its total -

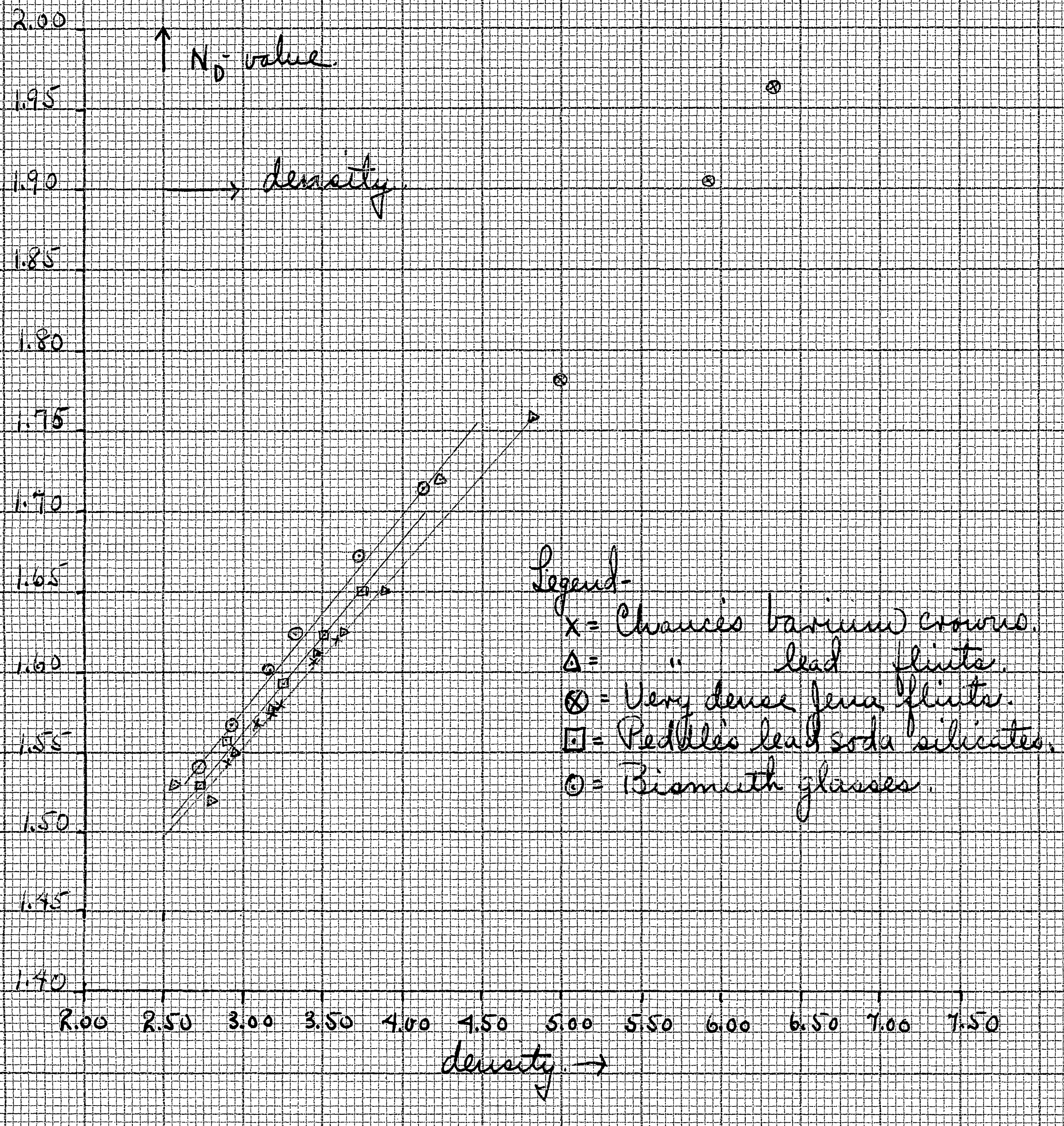
Curve VI

ν-value plotted against N_D for bismuth glasses and Peddle's 100 SiO_2 : 40 Na_2O : x PbO series.



Curve VI

N_D plotted against density for various glasses on the market, and for Peddle's series $100\,SiO_2 \cdot 40\,Na_2O \cdot x\,PbO$.



ispersion rises and its V value falls.

2. The rate of increase of total dispersion with Bi_2O_3 content ecomes greater, while the rate of decrease of the V value decreases, s we ascend the series.

Curve VI shows the relation between N_D and V values for both soda-bismuth silicates and soda-lead-silicates. It is seen that, in general he bismuth glasses have a lower V value for a given value of N_D THAN the lead glasses. The rate of decrease of the V value for bismuth glasses s less than the rate of decrease for lead glasses, at N_D values greater han 1.60.

If we plot density against N_D VALUE FOR The bismuth glasses f the small melts, we get practically a straight line. By plotting density gainst N_D value for the commercial crown and flint glasses we get a eries of points through which a straight line may be traced. The graph or Peddle's lead-soda glasses is a straight line. These facts are brought ut in the accompanying graph. The following conclusions may be drawn,

1. For any given density value, the bismuth glasses have a higher efraction index than any other commerical glass, whether flint or crown.

2. This difference in refractive index becomes relatively larger as lasses of higher and higher density are considered.

Inspection of the FtoG partial dispersions of the bismuth glasses rings to light an extremely interesting and important fact, These partial ispersions are abnormally small as compared with the total dispersion eing ~~xmxkx~~ only about half of the usual values for the general mun of ommerical flints. Among Chances glasses, only the hard crowns have a partial ispersion near this value. The borosilicate and fluor crowns have a artial dispersion lower than that of the bismuth glasses, but they also ave a corresponding very low index of refraction and total dispersion. he bismuth glasses appear to be very unique inthis one respect. It is -

hoped that, in the very near future, larger melts of glass may be made, so that the partial dispersions may be determined with the utmost certainty.

<u>The refractivities of bismuth glasses</u>- In a solution, or homogeneous mixture of liquids, the components of which do not combine chemically, the specific refractive power, is an additive function of the repective refractivties of the components present.[1]Thus,

$$K- \frac{p_. k.}{100} - \frac{p_2 K_2}{100} - \frac{p3\ k_3}{100} - -$$

Where,

K- specific refractive power of the mixture.

$K.$, K_2 etc. are the refractivities of the components,

$p.$, p_2 etc. are the percent of components 1,2, etc. present.

Tillotson applied this formula to the study of glasses which, in general, are not true chemical compounds, but homogeneous, supercooled liquids. To obtain the specific refractive power of the glass, Tillotson used the well-known Lorenz-Lorentz formula,

$$K- \frac{N_2 -1}{N_2 -2} \quad \frac{.1}{d}$$

where, ~~n~~ N is the refractive index of the glass for ~~white~~ sodium light.

and, d is the density of the glass.

By substituting for d the density of silica in the combined state, Tillotson was able to calculate the refracturty of this component.

By determining the density and refractive index of sodium silicate, the specific refractivity of this compent could be calculated. Tillotson then determined the refractive index and density of calcium silicate and thus found the specific refractivity of Ca0. He then studied a series of soda-lime- silicates, using the known figures for percentage composition, density, and specific refractivity of the components to calculate the refractive index of the glasses.

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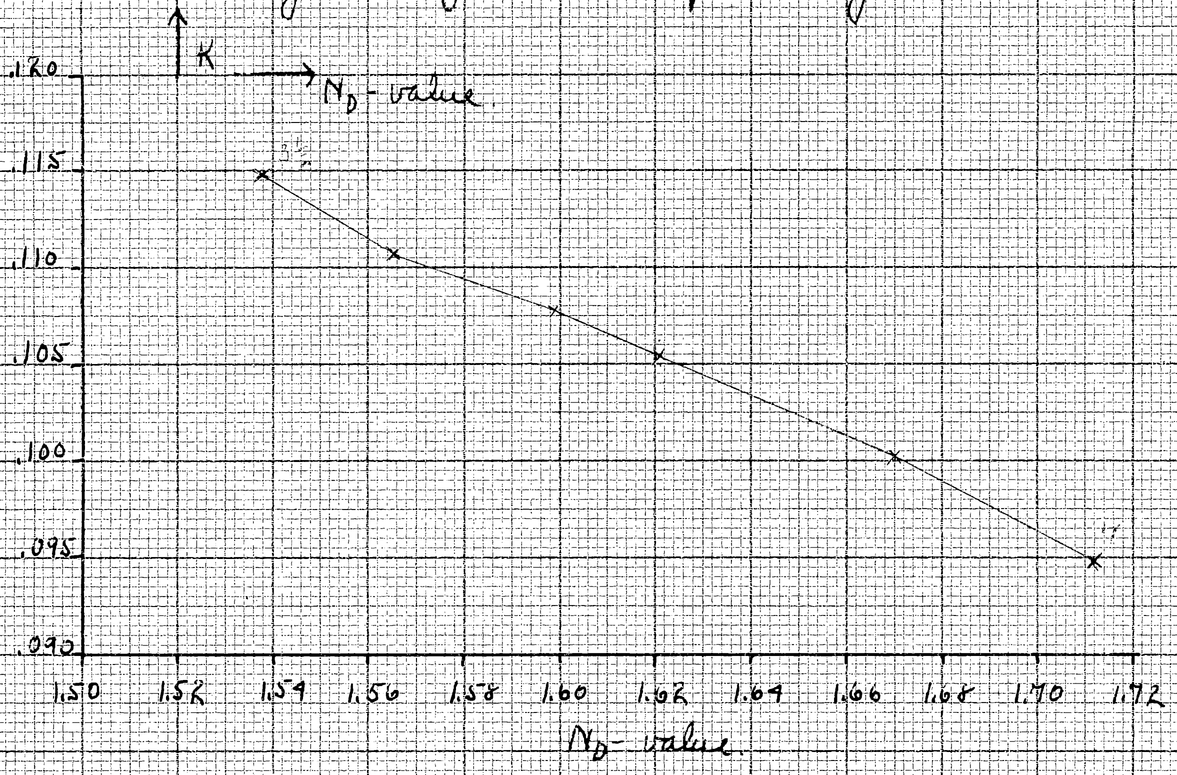
[2] E. W. Tillotson-J.Sud.Eng.Chem. 1912,p246.

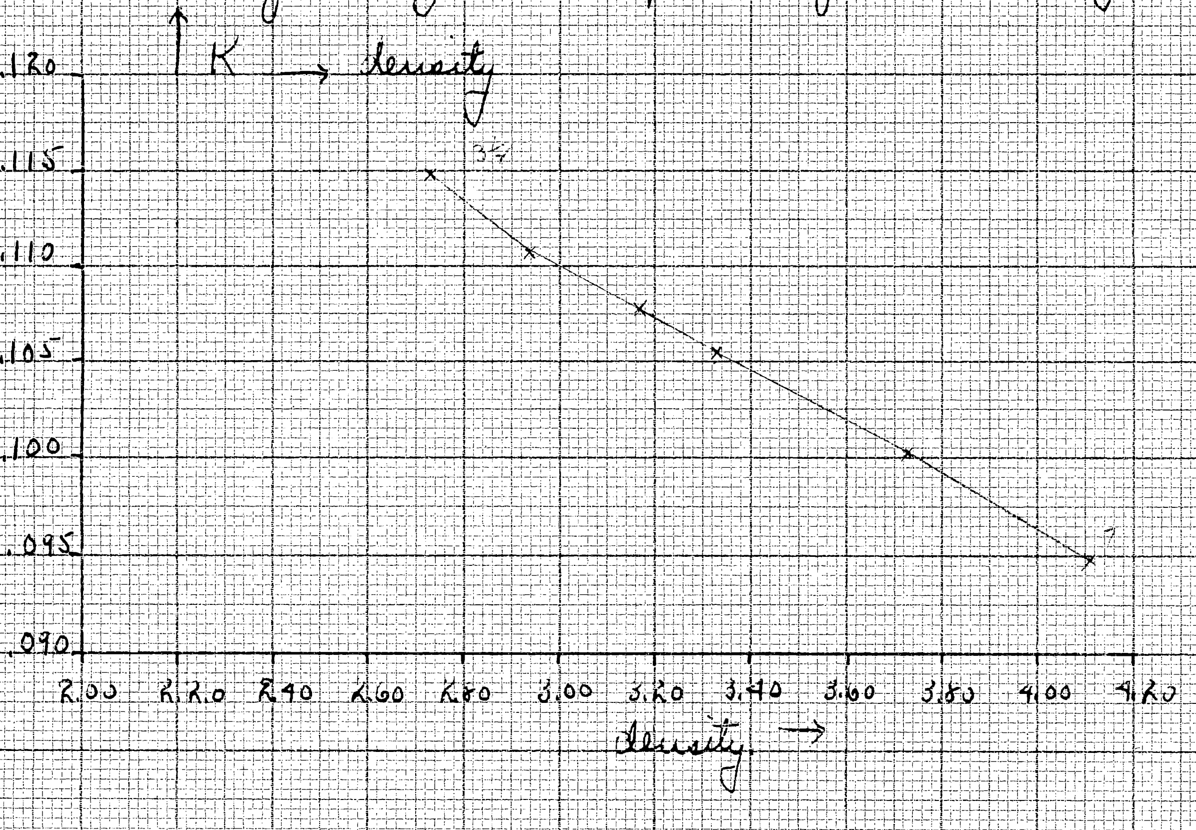
Curve VII

The Lorenz-Lorentz constant plotted against N_D value.



Curve VIII

The Lorenz-Lorentz constant plotted against density.



The calculated values for refractive index agreed well with the observed values.

Using the density and refractive index for the small melts, the Lorenz- Lorentz constant was calculated for each glass, the results being given in the following table,

Glass	Density	N_d	K
$3\frac{1}{2}$B	2.725	1.538	.1142
4 B	2.941	1.565	.1106
$4\frac{1}{2}$B	3.171	1.599	.1075
5B	3.333	1.621	.1055
6B	3.732	1.670	.1001
7B	4.110	1.712	.09481

The values of K are plotted against density in the following graph. It is seen that the relation is approximately linear(curve VIII). In curve VII, K is plotted against N_D.

By plotting K against molar composition, Tillotson was able to prove the presence of the compound, 2 Na_2O· 3 CaO· 5 SiO_2 in one of the lime-soda silicates which he studied.

Solubility tests- To determine their relative durabilities, solubility tests were carried out on the glasses from the large melts. As mentioned some time previous, the glasses were ground as that they would pass a 150-mesh sieve but not one of 200-mesh. This sizing process eliminated all excessively five glass dust which would vitiate the results of a solubility determination. Pure water was decided upon as the best dissolving agent. It as decided at first to treat the glass with water, then estimate the amount undissolved by filtration. However, work by Peddle(J. Soc. Glass Tech. 14, 36-37, 1920) makes it abundantly clear that this method is not to be relied in the case of double silicates, owing to the fact that insoluble silicates may be formed by the reaction of the glass with the water. The Alkalinity of the filtrate from the glass is a much better indication of solubility. Peddle (loc. cit). digested 5 grams of glass with 100cc of water for one hour at 80°c. He then expressed the solubilities as number of milligrams of $H2So_4$ required to neutralize the alkali dissolved from 100g. of glass, and also as milligrams of alkali dissolved per 100g. of glass.

The procedure adopted for the bismuth glasses was as follows. About 5g of glass was treated in a pyrex flask with 50cc of water at 70-80°C. This temperature was maintained constant for one hour. The flask was then removed, the liquid decanted from the glass, the latter washed with 3 or 4 portions of 95% alcohol and the filtrate titrated with $\frac{N}{40}$-HCl using phenolphthalein as indicator. The pyrex flask was tested for soluability but yeiled a negative result. The following table gives the results obtained,-

Solubility Tests.

Glass No	Weight	Titration	Milligrams per gram	
			HCl required to neutralize filtrate	Na$_2$O dissolved from glass.
3½ B	.5038 g	27.95cc	50.50	
	.5020	29.81	54.05	
	.5075	23.47	42.10	
Mean			48.88	38.25
4 B	.5042 j	7.44cc	13.45	
	.5042	9.22	16.70	
Mean			15.08	12.83
4½ B	.5050 g	3.66cc	6.60	
	.5052	4.10	7.40	
Mean			7.00	5.97
5 B	.5017 g	2.10 gc	3.81	
	.5068	3.49cc	6.30	
Mean			5.06	4.315
6 B	.3806 g	.70cc	1.68	
	.6312	.49	.708	
	.5084	.67	1.23	
	.4996	.50	.912	
Mean			1.133	.963

The results for the individual glasses agree very poorly. It must be stated that every precaution was taken to perform these tests under identical experimental conditions. Even so, it is seen that sometimes less alkali was dissolved from a large sample than from a small sample of the same glass. Even samples identical in weight, and treated in the very same manner, gave widely varying titrations. The only explanation to be offered for this very peculiar behavior is that in small samples, the effect of surface is greater than in large samples Large samples may possess what might be called a greater probability of homogeneity. Peddle used 5 grams of glass for his tests. When still larger melts are available, it will be possible to perform the tests on bismuth glasses with 5 or more grams. It is hoped that more concordant results will be obtained.

Conclusions from solubility tests- The table makes it clear that sodium oxide has a marked effect on the solubility of bismuth glasses. Though the sodium content of the glasses varies within comparatively narrow limits, the solubility varies between wide limits. This may be partly due to the powerful restraining influence which Bi_2O_3 exerts on solubility. The question can be more fully decided when a second series of bismuth glasses of the formula 100 SiO_2. 20 Na_2O. X Bi_2O_3 have been studied. The small solubility of the bismuth glasses as compared with that of the lead glasses is shown in the following table?

Bismuth glass	Lead glass	Milligrams of Na_2O per gram of glass. Bismuth glass	Lead glass
3½ B	180 A	38.25	199.74
4 B	180 B	12.83	58.86
4½ B	180 C	5.97	26.32
5 B	180 D	4.315	21.67
6 B	180 E	.963	10.62

This would indicate that bismuth glasses might be employed for purposes for which lead glasses would be unsuited because of their susceptibility to weathering. If we compare the solubilities of the lead glasses 100 SiO_2. 40 Na_2O. XPbO, with the solubilities of the series 100SiO_2.Na_2O. XPbO, we are led to the conclusion that the bismuth glasses of the second series are very insoluble. Thus bismuth glass might find use in chemical glassware.

X Summary And General Conclusions.

1. Glasses containing soda, silica and Bismuth oxide as principal constituents have been prepared and studied.

2. The color of these glasses increases with their bismuth content, showing the powerful effect of Bi_2O_3 on pot attack.

3. A method for the determination of Bi_2O_3 and Na_2O in glasses has been developed.

4. Attempts have been made to employ the volatilization method for the determination of silica in bismuth glasses. Further work is be carried out in this direction.

5. The densities of bismuth glasses have been found to increase with increase of Bi_2O_3 content, the rate of increase becoming greater as one goes up the series studied. The densities of the bismuth glasses are greater than those of the corresponding lead glasses.

6. The refractive indices and dispersions values CtoF, C-D, and DtoF have been found to increase with the bismuth content of the glasses. The "V" value has been found to decrease with increasing bismuth content.

7. Bismuth glasses have been found to possess a higher refractive index for a given density value, than any other kind of glass.

8. Bismuth glasses have been found to shorten the violet region of the spectrum more than other any glass of equal refractive index.

9. Bismuth glasses have been found to possess a much lower solubility than the corresponding lead or lime glasses. More accurate solubility figures are to be obtained by using a sample of 5 or more grams of glass.