

## Evolution of the compositions of commercial glasses 1830 to 1990. Part I. Flat glass

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More than 500 analyses of flat glasses made since 1830 in seventeen countries have been analysed statistically. They include samples made by all the commonly used processes. The purpose of the analysis was to investigate differences related to type of process, region of manufacture, and the passage of time. Changes in the use of the various important constituents are demonstrated and commented on. In the early years of the twentieth century only sulphate was used as refining agent and high  $\text{SO}_3$  contents were found until around 1960. Other constituents, such as  $\text{BaO}$  and  $\text{B}_2\text{O}_3$ , were tried but did not gain acceptance. As time went by variations within any company decreased and compositions of all flat glasses converged. Differences in flat glass compositions produced by different processes were rather random as were differences between various countries.

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### 1. Introduction

Each type of glass has its own history, changes in composition being related to the processes used, the raw materials available and the customer's requirements. The development of compositions of modern glasses for special purposes was described by Kurkjian and Prindle [1]. However, the development of the common types of glasses made on a very large scale has until now received little attention. This paper deals with the compositions of flat glasses over the past century and a half; subsequent ones will treat container and pressed glasses. The possible influences of process, time, and geography are considered together with the reasons for any significant differences.

### 2. Research methodology

The data collected for statistical analysis include only chemical analyses of glasses given in the published literature or available in company archives. Thiene's monograph [2] was the main source for analyses published up to 1937, many of his original sources being now difficult to consult. A number of analyses of Czech flat glasses and those made in other countries were available from the archives of the Mühlig company [3]. Analyses of glasses made after the Second World War were taken from archives of the Czech research institute VÚSU [4]. Analyses were also taken from a range of other sources [5 to 13]. Only analyses of the basic glass types were used in the statistics; coloured glasses or other special glasses were not included. A total of 570

analyses of flat glasses were used. When sets of analyses showed that average compositions had clearly not changed over a period, as in regular factory control procedures, only one result was taken.

It is generally assumed (see e.g. Wendler [7], Jebsen-Marwedel [14]) that every forming technology needs its own particular properties and hence composition. The analyses were classified according to the process used: hand-made, cast, Fourcault, Pittsburgh, Colburn, and float. Within each of these groups analyses were classified according to country of origin and also arranged chronologically. The data set for each country was divided into periods of similar compositions. These sub-sets generally covered three to ten analyses of glasses made over a period of five to ten years. Average composition and corresponding variations within the group expressed by standard deviations which were calculated for each group are basic data for further processing. This method of so-called "data nests" decreases the effect of extreme samples as well as of analytical errors and inexact glass dating.

Tables 1 to 7 show compositions of particular groups, where  $n$  is the number of analyses within the group,  $\text{RO} = \text{CaO} + \text{MgO} + \text{BaO}$ ,  $\text{R}_2\text{O} = \text{Na}_2\text{O} + \text{K}_2\text{O}$ . All data are given in weight percentages. If no  $\text{K}_2\text{O}$  content has been given, any small amount of potassium in the original analysis has been included in the  $\text{Na}_2\text{O}$  content. Likewise where  $\text{Fe}_2\text{O}_3$  was not been given in older analyses, it is included in the  $\text{Al}_2\text{O}_3$ . Data in italics were obtained from smaller numbers of analyses than other data, so they must be given less weight.

The sum  $\text{RO} + \text{R}_2\text{O}$  is a practical criterion for evaluation of the glass composition and was first applied by Dietzel [15] for this purpose.

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The graphs in figures 1 to 4 show the evolution of the basic glass types. Average composition of the group is plotted for the middle of its period. Data from individual countries are distinguished and fitted by an approximate average line.

To make possible numerical evaluation of composition change in time, averages of all groups from all countries were calculated for each process and for selected longer periods regardless of country of production. Generally, periods were chosen as follows:

- up to 1835 = the oldest period, glassworks had not yet specialized, analyses were inaccurate;
- 1840 to 1880 = specialization had occurred, glass was melted on pots, analyses were more accurate;
- 1880 to 1914 = off-hand manufacture predominated, but the first machines had been introduced to draw cylinders, melting in tank furnaces became predominant, analyses were more reliable;
- 1919 to 1939 = machine production of flat drawn sheet had become almost universal, glass was melted only in tank furnaces, batch houses and raw materials had been modernized, glass science had entered into glass works;
- after 1945 = glass production was automated, dimensions and output of furnaces were greater and their control made more precise.

### 3. Hand-blown flat glass

Table 1 and figure 1 show the data. German glasses made around 1870 to 1879 were divided into two distinct groups – potash glasses and soda glasses. Hand-made crown glasses being produced by spinning, mostly from England, are mentioned.

The earliest analyses (about 1830) did not differ much from other glasses. Largely due to impure sand they had higher alumina contents, which replaced some of the silica. In the 1870s one third of German, half of Russian and possibly all Czech glasses were melted with potash. After 1880, the  $K_2O$  content diminished to less than 0.5 % and saltcake was used for glass melting. Alumina contents decreased and silica increased correspondingly because better quality sands were used. However, most hand-made glasses maintained about 1 %  $Al_2O_3$ . This fact together with average content of 12 %  $CaO$  and generally around 13 % alkali yielded good corrosion resistance of such glasses.

The sum  $RO+R_2O$  was fairly constant at about 26.5 %. Only two groups of glasses dating from 1879 (Russian and English glasses) exceeded these values significantly. German glasses mostly had higher than average alkali contents, whereas those of Czech and English glasses were lower. Extreme alkali contents (even 25 %) were seen in two groups of German and Russian glass from 1879.  $RO$  content always changed in the opposite sense to the alkali content. Magnesia occurred in hand-made glasses only as an impurity; other elements were not found at significant levels.

Iron content was reported only sporadically: values about 0.4 %  $Fe_2O_3$  were not rare; until the end of hand-made production flat glass contained about 0.17 %  $Fe_2O_3$ . Glass staining caused by iron was removed by decolorizing with manganese. Manganese was only reported in Czech

glasses after 1906; its content was generally around 0.12 %  $MnO$  but occasionally even more.  $SO_3$  content was only rarely determined. As the glass was melted using saltcake, high  $SO_3$  contents about 0.5 %, sometimes up to 0.8 %, were not surprising.

The ranges shown by average analyses decreased continuously, so that the composition of hand-made flat glasses eventually was the same throughout Europe. Hand-made crown glass differed from flat glasses of its time only by inclusion of about 4.6 %  $K_2O$ .

### 4. Cast and rolled glasses

Older pot glasses and those produced by the Bicheroux process are included as well as continuously rolled glasses. They include so-called mirror, plate, patterned, and wired glass, but only nominally colourless ones. The composition survey is given in table 2 and on figure 2.

These, like compositions of blown glasses, and compositions from the first half of 19<sup>th</sup> century, were at first related to the so-called “forest glasses” and were characterized by significant potash contents, occasionally up to 22 %  $K_2O$ . After 1880, additions of potash were generally given up, only German glasses had about 0.8 %  $K_2O$  early in the twentieth century. Average  $SiO_2$  content decreased but progressively more slowly. It is uncommon that the content of aluminium decreased very regularly to values about 0.9 % except during the Second World War when lower values were common.

The decrease of  $Al_2O_3$  and  $SiO_2$  corresponded to a rise of  $RO+R_2O$ , which rose from prior 20 to about 27 % (rarely 28 %). Cast glass has been cooled quickly during its production, so that danger of crystallization was low; that is why the composition could deviate from the assumed optimal sum of  $RO+R_2O = 26\%$ .

Up to 1900, alkali content decreased from 18 to about 14 % and such level has been held until the present time.

There was a considerable rise in alkaline earths after 1860, increasing from 6 % to reach 13 % by 1910. The manufacturers thereby lowered their costs whilst maintaining good fusibility, easy casting from the pots, and good chemical durability. For these types of glass the glass makers did not need to fear devitrification.  $MgO$  contents around 2.5 % were seen occasionally in Germany in 1925 and in USA in 1924 (Ford). Since then  $MgO$  additions have gradually spread and 2.9 %  $MgO$  has been used almost uniformly since 1958.

Iron contents up to 0.30 to 0.50 %  $Fe_2O_3$  were found in the oldest cast glasses but decreased in the interwar years to about 0.12 and 0.1 % after 1964. Cast glasses were presumably always decolorized by means of manganese. The analyses show it to have been usual in the period between the two World Wars when contents of 0.03 to 0.17 %  $MnO$  were found. After World War II use of manganese was abandoned, however one Italian sample from 1966 contained 0.17 %  $MnO$ .

As saltcake was used,  $SO_3$  contents around 0.70 % were found until the fifties but they decreased a little. Other oxide constituents were not quoted in published analyses, but 0.10 %  $Cl$  and 0.06 %  $F$  were reported in Czech cast glasses

Table 1. Cylinder glass (hand blown) – average composition (in wt%) of particular groups

period	<i>n</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	MnO	RO	R <sub>2</sub> O	Dietzel [15]
Germany:													
1849-1869	6	69.50	1.81	0.41	11.26		<i>9.94</i>	<i>13.76</i>			11.26	16.83	28.08
1870-1879	10	55.44	2.00		7.54	0.18	<i>2.31</i>	<i>23.85</i>		K-glass	7.72	24.53	32.26
	25	71.50	1.79	0.21	11.26	0.26	15.17	0.85		Na-glass	11.40	14.96	26.32
1888-1892	6	72.69	1.02	0.15	11.46	0.10	14.05	2.03			11.48	14.72	26.20
1909-1912	9	72.53	0.80	0.21	11.86	0.17	13.73	0.90	0.60		11.98	14.13	26.11
1924-1929	19	72.75	0.62	0.12	12.34	0.15	13.70	0.79	0.49		12.46	13.98	26.40
France:													
1830	6	68.77	4.67		13.08		13.48				13.08	13.48	26.56
1862-1896	3	70.83	1.59		13.98		13.61				13.98	13.61	27.59
Great Britain:													
1830	1	69.00	7.40		12.50		11.10				12.50	11.10	23.60
1867	1	70.71	1.92		13.38		13.25				13.38	13.25	26.63
1875-1897	4	70.89	3.05		12.68		12.52				12.68	13.52	26.20
1925-1934	5	71.52	1.20	0.17	13.08	<i>0.40</i>	13.59	<i>0.30</i>	0.16		13.32	13.65	26.97
Belgium:													
1864-1898	3	74.31	0.93		11.88		13.00				11.88	13.00	24.89
Russia:													
1875	5	66.12	1.80		6.82		<i>16.68</i>	<i>14.29</i>			6.82	25.25	32.06
Czechia:													
1846-1875	3	72.90	1.40		8.67			17.97			8.67	17.97	25.23
1906-1908	5	70.33	1.88	0.45	15.93	0.24	10.99			0.13	16.17	10.99	17.16
1909-1910	6	71.57	1.27	0.50	15.17	0.20	11.17			0.08	15.37	11.17	26.54
1913-1914	4	72.20	0.38	0.18	13.74	0.21	12.98		0.42	0.03	13.95	12.98	26.93
1919-1926	9	71.17	0.76	0.26	13.50	0.36	13.36		0.74	0.17	13.86	13.36	27.22
crown glass:													
1876 to 1892	5	73.42	0.66		13.95	0.32	12.84	4.65			13.18	13.06	26.25
average composition:													
until 1835	7	68.85	6.03		12.79		12.29				12.79	12.29	25.08
1846-1889	53	69.61	1.76	0.31	10.42	0.22	<i>11.82</i>	<i>14.14</i>			10.45	18.06	28.31
1880-1914	37	72.07	1.33	0.30	13.25	0.18	12.54	1.46	0.51	0.08	13.36	12.93	26.29
1919-1934	33	71.81	0.86	0.18	12.97	0.30	13.55	0.55	0.46	0.17	13.21	13.66	26.86

Note: Data in italics were obtained from smaller numbers of analyses than the other data.

from 1958 to 1960; the chloride came from chlorides in the soda ash or from NaCl used as a refining agent, the fluoride from fluoride accelerators that were very popular in the 1950s and 60s.

The nature of pot production and competition between individual manufacturers may have been responsible for bigger variations in compositions both within a group and a period. Over time the variations in cast glasses decreased and compositions converged. Three Czech cast glasses (Weinmann Chudeřice) from 1943 to 1944 were outside the group; despite their scarcity 19.3 % of alkalis were used, and only 5.7 % of RO but the glasses had very little alumina.

Over quite a long period [%RO] + [%R<sub>2</sub>O] was higher in Belgian but lower in English glasses. [%RO] content varied between countries and over time (especially in the earlier years).

## 5. Lubbers glasses

The Lubbers process mechanically drew long cylinders and persisted for about twenty-five years but was then replaced by the familiar processes for vertically drawn sheet. Average analyses from Czechia (Třemošná glassworks), from Ger-

many and from the USA are given in table 7 (see section 10): all compositions were similar. Czech glasses contained more Fe<sub>2</sub>O<sub>3</sub> and SO<sub>3</sub> and they were decolorized by manganese. The Lubbers glasses differed little from hand-made glasses of that time mostly having rather lower [%RO] + [%R<sub>2</sub>O] with alkali lower by 0.80 % and higher RO content. Contents of MgO and Fe<sub>2</sub>O<sub>3</sub> were also greater but the differences unimportant.

## 6. Fourcault glasses

The first reasonably successful drawing of flat glass was achieved, after several years of trials, in 1914 at Dampremy (Belgium). The process was introduced in 1919 in Hostomice (Czechia), and considerable effort was devoted to finding the best glass composition to avoid devitrification. These trials were recorded and summarized by Mühlig [8], who was very experienced in drawing processes. Fourcault started from usual composition of flat glass for hand blowing, but such glass devitrified very readily in the débiteuse. As a result the RO content was decreased to 9 to 11 % and the R<sub>2</sub>O content increased to 16 to 18 %. This glass was melted and drew well but it had poor chemical durability and its surfaces often became misty during storage. So 3 to

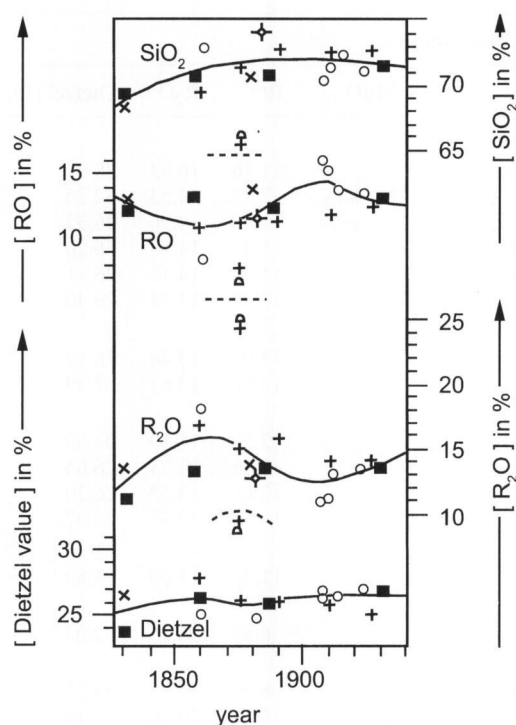


Figure 1. Development of the compositions of hand-blown flat glasses 1830 to 1930; average composition in partial groups is plotted: +: Germany, ×: France, ■: England, ◇: Belgium, ○: Czechia, △: Russia.

4 % MgO was added and alkalis were decreased to about 15 %  $R_2O$ . Magnesia decreased the tendency to devitrify, giving glasses that had liquidus temperatures of 950 to 990 °C [8]. Addition of about 1 %  $Al_2O_3$  increased the durability [8 and 9].

Data in the archives of the Mühlig company [3] allowed the evolution of its compositions to be followed from 1919 to 1943 (see figure 3). Particular points are averages of all analyses of drawn glass made each year (about 20 analyses on average). One to three tanks of load up to 100 t/d were in operation and they began with a softer composition than that used for hand-made glasses. Up to about 1923 various compositions were tried and  $RO+R_2O$  contents changed. Subsequently the development of composition became more regular (except for 1933 and 1941). Owing to steady regular increase of alkali content (1 % in 16 years) % $RO$  + % $R_2O$  also rose steadily,  $RO$  content being constant. Magnesia was introduced in 1924, at a level of about 2.1 % and by 1933 it had increased to 3.5%; further gradual rise occurred after 1939. Higher alumina content (up to 1.3 %  $Al_2O_3$ ) at the beginning of production was caused by clayey sand; when sand of good quality began to be used, alumina content decreased to about 0.3 %  $Al_2O_3$ . In 1932 feldspar was increased to yield 0.9 %  $Al_2O_3$  and it has remained at that level.

Iron content started at 0.35 %  $Fe_2O_3$ , decreased up to 1926, reaching about 0.05 %  $Fe_2O_3$ , then remained at this level. From the beginning the glass was decolorized with manganese, the  $MnO$  content being constant at (0.23±0.03) % but had to be abandoned when there was a shortage of manganese during World War II and was not afterwards resumed. Although soda ash was used during

most of this period, the  $SO_3$  content of the glass was high: 0.5 to 0.9 %  $SO_3$ . Melting in oxidizing conditions at lower temperatures might account for that. Other constituents were used only rarely: 1.0 %  $BaO$  in 1921, 0.5 %  $B_2O_3$  in 1931 to 1933; traces of  $ZnO$  were found in 1933. None of these was shown to be of benefit and they were abandoned.

A review of world-wide compositions of Fourcault glasses is shown in table 3 and figure 4. The compositions varied much less than those of hand-made and cast glasses.  $RO+R_2O$  decreased gradually, and reached the presumed optimal value for devitrification only after 1960. In Czechia and the USA  $MgO$  was added to sheet glass from 1924; it was introduced in Belgium in 1928 and in Germany in 1929. However, English glasses were made without  $MgO$  up to 1933. That is why averages for the interwar years are divided into two groups, with and without  $MgO$ . A maximum value of 4 %  $MgO$  was reached about 1940 and it has since remained there. Higher values are seen in Czech glasses because of good quality Slovak dolomite but Belgian and Swiss glasses were below average.

Alumina content varied up to 1933. Belgian, British and American glasses had higher alumina contents; most Czech glasses were melted without specific addition of aluminous raw materials. Content of  $Al_2O_3$  decreased to minimal values in all glasses in 1932 to 1940, then increased to about 1 %. Considerably higher alumina was seen in Russian glasses after 1950 (2.15 %  $Al_2O_3$ , the highest content seen for flat glass), as well as in Hungarian and Swiss glasses. Low content was found in Czech, Belgian and Finnish glasses.

Fourcault glasses were largely soda ones, small amounts of  $K_2O$  probably coming from fining agents or feldspar. Iron content decreased quite quickly to about 0.06 %  $Fe_2O_3$ ; decolorizing with manganese (0.15 %  $MnO$ ) followed the path already discussed.

Only a minority of Fourcault glasses were melted from saltcake, nevertheless, analyses up to 1940 showed on average 0.64 %  $SO_3$  but this decreased after 1946 to 0.34 %  $SO_3$ . Once again trials with other oxides such as  $BaO$  and  $B_2O_3$  failed to lead to their adoption.

## 7. Pittsburgh glasses

The technology of the Pittsburgh process, drawing without a *débiteuse*, required conditions in the drawing chamber to be maintained very precisely. From the beginning it was considered that a special composition was necessary [6]; the data are given in table 4. In all cases modern glasses were related to Fourcault glasses but they usually had about 1 % less soda. The rise of alumina was evident (1.76 %  $Al_2O_3$  in England in 1935; 1.91 %  $Al_2O_3$  in Russia in 1964), iron contents were mostly below 0.1 %  $Fe_2O_3$  (nevertheless, France had 0.12 %  $Fe_2O_3$  in 1976); magnesia content varied between 2.6 and 4.35 %  $MgO$  in all glasses.

$RO+R_2O$  rose to about 26.7 % in 1937 but after 1950 it decreased to 25.6 % owing to decreases of 0.2 % in alkali and up to about 1 % in  $RO$ . No glasses contained more than 0.2 %  $K_2O$ .  $SO_3$  contents and decolorizing with manganese followed the same trends as in Fourcault glasses.

Table 2. Cast and rolled glass – average composition (in wt%) of particular groups

period	<i>n</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	MnO	RO	R <sub>2</sub> O	Dietzel [15]
Germany:													
1855-1859	3	74.21	2.26		5.90		9.46	<i>22.31</i>			5.90	16.90	22.80
1875-1879	5	71.66	1.37		11.50	0.30	13.87	3.34	0.70		11.83	14.77	26.59
1885-1910	5	70.27	3.45	0.30	12.29	0.17	14.17	0.91			12.35	14.35	26.71
1925-1933	35	71.94	0.73	0.13	13.11	0.57	13.14	0.60	0.76		13.33	13.29	26.63
1960	3	72.37	0.71	0.14	9.08	2.68	14.52	0.20			11.73	14.66	26.40
France:													
1830	2	74.87	3.15		4.70		14.78	<i>5.50</i>			4.70	17.52	22.18
1867-1879	7	72.69	1.73	0.52	13.72	0.32	12.08	3.60			13.82	12.61	26.41
1885-1898	6	74.50	1.07		10.69		14.19				10.69	14.19	24.88
1964-1976	5	71.17	0.80	0.08	10.95	2.91	13.60	0.17	0.36		13.86	13.70	27.56
Great Britain:													
1850	3	77.98	2.39		5.42		12.32	2.02			5.42	14.37	19.79
1875-1886	5	75.71	1.17		7.58		15.46				7.58	15.46	23.03
1929-1932	3	71.92	1.20	0.23	9.03	2.11	14.93		0.65	0.09	11.15	14.93	26.08
1964	2	70.07	1.82	0.12	10.98	3.10	13.12				14.09	13.14	27.24
Belgium:													
1921-1935	3	71.76	0.40	0.29	14.25	0.94	11.89		0.59		15.19	11.89	27.08
1960-1964	4	69.93	0.63	0.06	11.38	3.32	13.32	0.44			14.70	14.07	28.76
USA:													
1916-1931	6	71.43	0.44	0.09	12.26	1.43	14.52		0.58	0.03	12.98	14.52	27.50
Japan:													
1963-1964	2	71.71	1.80	0.17	7.98	3.82	13.82				13.81	13.82	25.62
Poland:													
1963-1964	3	73.59	0.69	0.08	9.91	1.07	14.35				10.98	14.35	25.32
Russia:													
1964	1	72.00	1.10		9.10	3.00	13.80				12.10	13.80	25.99
Italy:													
1966	1	70.52	1.07	0.10	10.46	3.18	13.66			0.17	13.64	13.83	27.49
Czechia:													
1921-1928	6	71.90	0.80	0.24	11.92	0.52	14.23		0.78	0.05	12.45	14.23	26.68
1935-1938	6	72.25	0.96	0.07	9.09	3.25	14.96	0.21	0.43	0.10	12.33	14.96	27.32
1943-1944	3	73.83	0.34	0.03	5.34	0.35	19.34		0.63		5.69	19.34	25.03
1958-1960	4	72.83	0.72	0.08	8.64	2.99	14.26		0.38		11.63	14.26	25.89
1961-1966	12	70.41	0.84	0.07	10.85	2.76	14.49		0.57		13.62	14.49	28.11
1971-1990	4	71.47	0.59	0.06	9.68	3.88	13.69	0.18	0.37		13.56	13.87	27.43
average composition:													
until 1835	2	74.87	3.15		4.70		14.78	<i>5.50</i>			4.70	17.52	22.18
1855-1880	23	74.45	1.78	0.52	8.82	0.31	12.64	<i>7.20</i>	0.70		8.91	14.82	23.72
1880-1910	11	72.38	2.26	0.30	11.49	0.17	14.18	0.91			11.52	14.27	25.80
1916-1938	59	71.87	0.75	0.17	11.61	1.47	13.95	0.40	0.63	0.07	12.90	13.97	26.88
1943-1944	3	73.89	0.34	0.03	5.34	0.35	13.34		0.63		5.69	19.34	25.03
1958-1990	41	71.46	0.98	0.10	9.91	2.97	13.92	0.25	0.42	0.17	12.88	14.00	26.89

Note: Data in italics were obtained from smaller numbers of analyses than the other data.

## 8. Libbey-Owens glass

The Libbey-Owens process spread from the USA into Europe in the years between the two World Wars but after the World War II it was replaced by the Pittsburgh process. Fourteen analyses given in table 5 came from the years between World Wars. The compositions fell into a small range with little variability between groups. All glasses had low alumina contents, below 0.9% Al<sub>2</sub>O<sub>3</sub>, American glasses from 1922 having only 0.28% Al<sub>2</sub>O<sub>3</sub>.

RO+R<sub>2</sub>O was generally close to 26.7% but American glasses had up to 28.0%. A greater tendency to devitrify was less important in processes operating without a débiteuse and with rapid cooling. All glasses except the earliest ones contained sufficient MgO. Belgian glasses had less

than average and the first American glasses a record amount of 5.62% MgO. Iron content was moderately high – around 0.1% Fe<sub>2</sub>O<sub>3</sub>. The glasses were decolorized by relatively low amount of manganese (0.1% MnO) but it was absent from English glasses and an American glass made in 1937.

## 9. Float glasses

Since 1960 annual production of float glass has been many millions of tons but only a few analyses are available, see table 6. That is not very important as it seems that the compositions of float glasses from different countries are quite similar. Differences in alumina content are evident – also

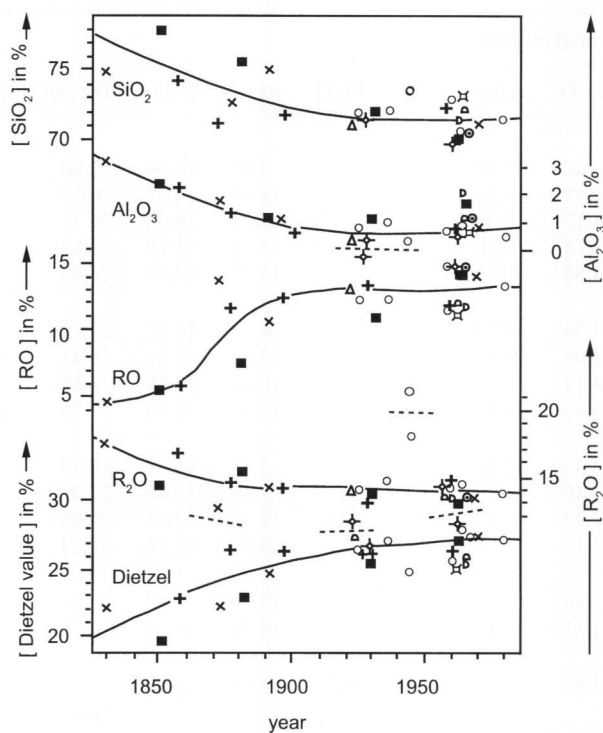


Figure 2. Development of the composition of cast glass 1830 to 1980; average composition in partial groups is plotted: +: Germany, ×: France, ■: England, ◆: Belgium, ○: Czechia, ▽: Russia, ▤: Japan, ⌘: Poland, △: USA, ⊙: Italy.

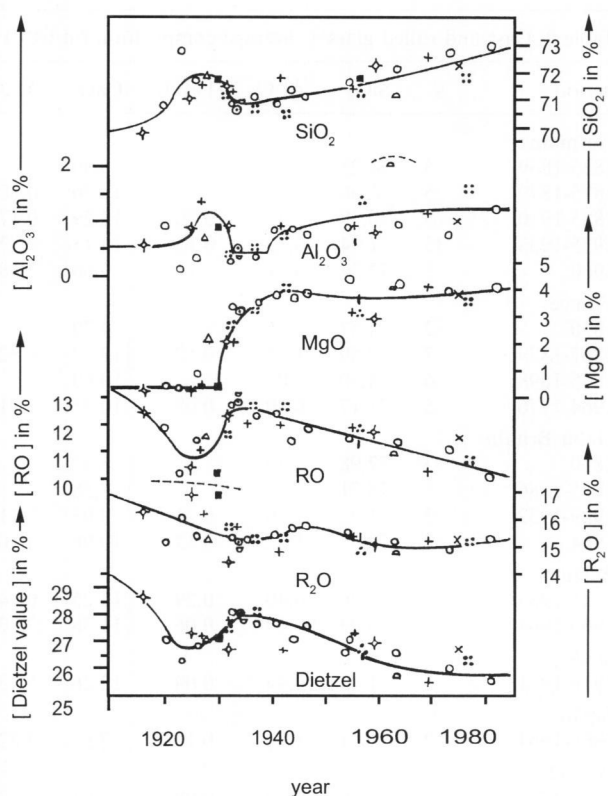


Figure 4. Development of Fourcault drawn glass between 1915 to 1983; average composition in partial groups is plotted: +: Germany, ×: France, ■: England, ◆: Belgium, ○: Czechia, ▽: Russia, ⬢: Hungary, △: USA, ◐: Austria, ⬤: Switzerland, I: Finland, ⊙: Italy.

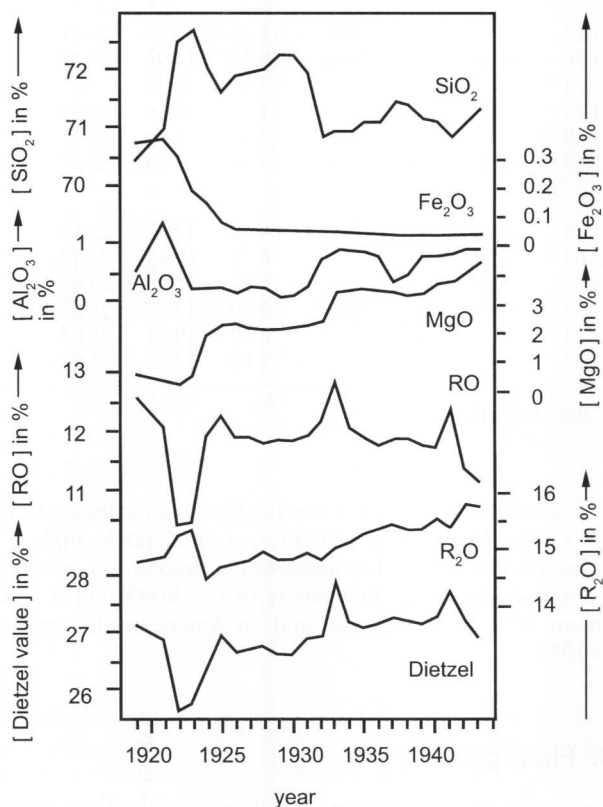


Figure 3. Development of average composition of Fourcault flat glass as melted at Mühligg company in Teplice between 1919 to 1943; year averages of the glass melted on one to three tanks are plotted.

prestigious producers use no more than 0.5 %  $Al_2O_3$ . Only four producers (from England, Italy, Sweden, and Japan) used more than 1.0 %  $Al_2O_3$  with a maximum of 1.77 %. Iron contents were relatively high — around 0.1 %  $Fe_2O_3$ , Czech glasses had half as much iron owing to the tradition of using purer sands.

$RO+R_2O$  varied slightly, the highest value of 27.6 was found in French, Belgian and Dutch glasses. Contents of alkali and alkaline earths were almost identical. All glasses contained around 4.0 %  $MgO$ .  $K_2O$  contents were up to 0.75 %, generally introduced by feldspar.  $SO_3$  contents varied but were lower than in other types of glass because of the melting temperatures used.

### 10. Comparison of flat glasses

The 517 analyses of flat glasses were divided into 119 groups using seven methods of manufacture made in sixteen countries. To be able to appreciate the influence of technology on glass composition, average compositions were calculated for each period and process irrespective of country of origin as given in tables 7 and 8. Note that Fourcault glasses without  $MgO$  are marked “Fourcault a” and those with  $MgO$  as “Fourcault b”; the average of all Fourcault compositions in a given period is “Fourcault Ø”.

Up to 1914, only hand-blowing and casting were widely used. From beginning of observation the compositions of

Table 3. Fourcault glasses = average composition (in wt%) of particular groups

period	<i>n</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	MnO	RO	R <sub>2</sub> O	Dietzel [15]
Germany:													
1925-1929	6	71.66	1.34	0.11	10.59	0.38	15.56	1.00	0.53		10.97	16.05	27.03
1930-1935	4	71.34	0.37	0.07	9.99	1.97	15.60		0.57	0.18	11.95	15.60	27.56
1939-1944	5	71.88	0.92	0.06	8.94	2.88	14.70		0.52	0.09	11.82	14.70	26.53
1955-1957	5	71.40	0.89	0.04	8.75	3.07	15.33				11.83	15.33	27.16
1964-1975	4	72.73	1.15	0.09	6.17	4.01	14.51	0.61	0.19		10.19	15.12	25.30
France:													
1976	2	72.30	1.02	0.09	7.52	3.90	14.70	0.47	0.20		11.43	15.19	26.64
Great Britain:													
1926-1933	4	71.81	0.81	0.11	9.81	0.38	16.83		0.72	0.11	10.10	16.83	26.93
Belgium:													
1913-1920	4	69.89	0.63	0.23	12.15	0.31	15.98	0.28	0.70	0.09	12.46	16.12	28.58
1924-1926	5	71.18	0.86	0.25	10.20	0.26	16.81		0.74	0.05		10.33	16.81
1928-1935	3	71.69	0.93	0.09	10.35	2.04	14.33		0.67	0.15	12.39	14.33	26.72
1956-1964	3	72.41	0.83	0.07	8.76	2.97	14.88	0.56			11.73	15.07	26.80
USA:													
1924-1933	7	72.01	0.71	0.09	9.34	2.24	15.28		0.50		11.55	15.28	26.96
Italy:													
1933-1935	2	70.66	0.52	0.07	9.74	3.14	15.00		0.69	0.18	12.88	15.00	27.88
Hungary:													
1931-1934	4	71.58	0.44	0.06	8.89	2.78	15.70		0.55		11.67	15.70	27.37
1937-1938	6	70.64	0.52	0.06	9.41	3.32	15.32		0.60	0.13	12.73	15.32	28.05
1943	1	70.48	0.72	0.06	8.61	4.15	15.34		0.54	0.06	12.76	15.34	28.10
1978	1	71.97	1.47	0.05	7.13	3.63	15.35		0.20		10.76	15.52	26.28
Austria:													
1931-1936	4	70.94	0.33	0.06	10.32	2.69	14.87		0.66	0.11	13.01	14.87	27.88
Switzerland:													
1956-1957	2	71.26	1.38	0.05	8.67	3.15	14.67				11.82	14.67	26.49
Russia:													
1964	1	71.12	2.15	0.07	6.75	4.04	14.67				10.79	14.67	25.46
Finland:													
1957	1	71.97	0.60	0.11	7.66	3.55	15.23	0.13			11.21	15.23	26.44
Czechia:													
1919-1921	4	70.85	0.91	0.43	11.45	0.40	15.06		0.76	0.14	11.85	15.06	26.91
1922-1923	12	72.91	0.17	0.21	9.76	0.33	15.94		0.44	0.13	10.09	15.94	26.03
1924-1928	15	71.80	0.32	0.09	10.49	0.82	15.30		0.76	0.24	11.33	15.30	26.72
1931-1934	20	70.82	0.34	0.06	9.35	3.35	15.20		0.65	0.22	12.75	15.20	27.95
1935-1938	12	71.16	0.35	0.06	8.70	3.49	15.26		0.60	0.25	12.33	15.26	27.56
1939-1942	12	70.95	0.86	0.05	8.40	3.82	15.35		0.54	0.18	12.31	15.35	27.50
1943-1945	15	71.40	0.88	0.05	7.61	3.68	15.56		0.54		11.29	15.56	26.85
1946-1949	3	71.16	0.75	0.06	7.98	3.84	15.65		0.46	0.13	11.79	15.66	27.46
1951-1960	15	71.64	0.87	0.06	7.50	3.96	15.48		0.37	0.09	11.45	15.48	26.04
1962-1966	11	72.21	0.96	0.06	7.15	4.17	15.08		0.58		11.32	15.08	26.40
1971-1976	3	72.86	0.74	0.07	7.10	3.96	14.55	0.22	0.35		11.07	14.77	25.83
1977-1990	2	73.15	1.01	0.06	5.97	4.10	14.65	0.55	0.35		10.07	15.20	26.27
average composition:													
1913-1928 <sup>1)</sup>	50	71.44	0.72	0.20	10.64	0.41	15.93	0.64	0.66	0.13	11.02	16.02	27.05
1924-1938 <sup>2)</sup>	69	71.20	0.50	0.07	9.57	2.76	15.17		0.61	0.17	12.42	15.17	27.55
1939-1945	33	71.18	0.85	0.05	8.39	3.63	15.24		0.53	0.11	12.04	15.24	27.25
1946-1990	53	72.01	1.06	0.07	7.47	3.72	14.98	0.42	0.34		11.19	15.15	26.34

Note: Data in italics were obtained from smaller numbers of analyses than the other data.

<sup>1)</sup> Without MgO; <sup>2)</sup> with MgO.

both groups approached each other closely. Hand-blown glass had higher RO and thus higher RO+R<sub>2</sub>O contents it also contained more K<sub>2</sub>O than cast glass. In the period 1880 to 1914 differences between these two groups ceased to be statistically significant (90 % level). These glasses changed very little up to 1938 but MgO was sometimes used in more modern glasses. Lubbers glasses differed from hand-made glasses in lower alkali and in higher RO contents (particu-

larly CaO). Fourcault glasses made between the World Wars differed from hand-made glasses in slightly increased RO+R<sub>2</sub>O, higher alkali, and lower RO contents and, of course, in the introduction of MgO. Both kinds had low alumina contents. Pittsburgh glasses from years between the World Wars differed from Fourcault glasses in having about 1.5 % lower alkali but about 1.0 % more RO and thus somewhat lower RO+R<sub>2</sub>O. These glasses had about 1.5 % higher

Table 4. Pittsburgh glasses – average composition (in wt%)

period	<i>n</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	MnO	RO	R <sub>2</sub> O	Dietzel [15]
Germany:													
1930-1933	4	72.14	0.43	0.07	10.32	2.60	13.85		0.69	0.10	12.95	13.65	26.60
1936-1937	2	71.98	0.50	0.08	9.93	3.07	13.66		0.67	0.17	12.98	13.66	26.64
1960-1966	3	72.90	0.90	0.08	8.38	3.81	13.18	0.19			12.19	13.36	25.55
France:													
1976	2	72.80	1.00	0.12	8.20	3.75	13.80	0.18	0.22		11.95	13.98	25.92
Great Britain:													
1935-1936	2	71.46	1.76	0.17	9.34	2.91	14.40		0.51	0.17	12.42	14.40	26.65
1956-1964	2	73.02	0.82	0.09	9.18	2.81	13.61				11.98	13.61	25.60
Belgium:													
1933	3	71.57	0.67	0.07	9.68	2.27	13.95		0.60	0.16	13.05	13.95	27.00
1937	1	71.72	1.23	0.13	8.75	3.99	13.75		0.46	–	12.74	13.75	26.49
1964	1	71.30	1.52	0.09	7.90	3.89	13.81				11.77	13.81	25.58
USA:													
1930-1933	2	72.28	0.43	0.08	10.15	2.66	13.56		0.68	0.07	12.81	13.56	26.37
1935-1937	3	72.00	0.76	0.09	9.55	3.05	14.16		0.63		12.56	14.16	26.64
1964-1966	2	72.60	1.08	0.09	8.11	3.70	13.50	0.20			11.81	13.60	25.40
Poland:													
1964-1965	2	73.46	1.24	0.10	7.68	3.29	13.28	0.18			11.46	13.45	24.91
Russia:													
1964	1	71.80	1.91	0.08	7.73	3.70	13.53				11.43	13.53	24.96
Hungary:													
1977	1	71.85	1.15	0.05	7.01	4.10	15.05	0.18		0.23	11.11	15.23	26.34
Czechia:													
1933-1934	2	71.02	0.42	0.07	8.66	3.89	14.99		0.65	0.24	12.55	14.99	27.54
1952-1960	8	72.54	0.90	0.07	8.21	3.83	13.77		0.39	0.03	12.04	13.77	25.81
1961-1966	13	72.54	0.91	0.07	7.43	4.33	14.08	0.17	0.39	–	11.77	14.09	25.86
average:													
1930-1937	19	71.77	0.77	0.09	9.55	3.20	14.01		0.60	0.15	12.75	14.01	26.75
1952-1977	35	72.48	1.13	0.08	7.98	3.72	13.76	0.18	0.31	0.03	11.75	13.84	25.59

Table 5. Libbey-Owens glasses – average composition (in wt%)

period	<i>n</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	MnO	RO	R <sub>2</sub> O	Dietzel [15]
Germany:													
1927-1930	4	71.75	0.45	0.08	10.21	2.94	13.52		0.63	0.11	13.15	13.52	26.67
1932-1935	5	71.99	0.81	0.07	10.12	2.87	13.24		0.62	0.17	12.99	13.24	26.23
1936-1940	4	72.39	0.89	0.08	10.08	2.68	13.18		0.60	0.10	12.76	13.18	25.94
Great Britain:													
1926-1930	4	71.81	0.75	0.11	10.92	2.46	13.48				13.39	13.48	26.86
Belgium:													
1923-1926	8	71.77	0.61	0.20	11.87	1.15	13.59		0.88	0.01	13.01	13.59	26.56
1931-1937	6	72.50	0.60	0.08	10.08	2.94	13.16		0.60	0.10	13.01	13.16	26.17
USA:													
1922	2	70.93	0.28	0.21	8.53	5.62	13.40		0.62	0.11	14.15	13.40	27.55
1927	1	70.22	0.68	0.08	10.01	4.35	13.62		0.70	–	14.36	13.62	27.98
average:													
1923-1940	34	71.67	0.63	0.11	10.23	3.13	13.40		0.66	0.10	13.55	13.40	26.75
± <i>s</i>		0.76	0.20	0.06	0.93	1.33	0.18		0.10	0.06	0.59	0.18	0.70

MgO contents and higher alumina content than Fourcault glasses because these glasses evolved later. Libbey-Owens glasses had 1.6 % less alkali and 1.8 % more RO than Fourcault glasses and high MgO contents were used. All glasses from the above-mentioned period were decolorized by manganese.

Between 1946 and 1990 differences between glasses made by the various processes progressively decreased. RO+R<sub>2</sub>O averaged 26.58 %, but Pittsburgh glasses were lower by 1.0 %. The alkali content of Fourcault glasses was more than 1.0 % higher than the others, the difference was balanced through RO contents. All glasses contained 3.4 %



Table 6. Average composition of float glasses (in wt%)

period	<i>n</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	RO	R <sub>2</sub> O	Dietzel [15]
Germany:												
1986-1987	3	72.31	0.46	0.080	8.55	4.45	13.75	0.12	0.26	13.00	13.86	26.86
1987-1999	3	72.55	0.56	0.102	8.76	3.97	13.54	0.22	0.16	12.72	13.77	26.49
France:												
1976-1983	2	71.26	0.37	0.081	9.62	4.08	14.10	0.12	0.37	13.69	14.22	27.91
Great Britain:												
1960-1999	3	72.61	1.19	0.128	8.67	3.60	13.05	0.62	0.24	12.27	13.47	25.74
Belgium:												
1983-1987	2	71.26	0.65	0.066	9.48	4.01	13.86	0.21	0.26	13.50	14.07	27.57
Italy:												
1983-1999	3	71.46	1.09	0.104	8.89	3.94	13.38	0.52	0.24	12.83	13.90	26.73
USA:												
1984	1	72.83	0.19	0.122	8.56	4.06	13.62	traces	0.48	12.62	13.62	26.24
Japan:												
1972-1980	2	71.84	1.77	0.102	7.12	3.96	13.72	0.75	0.28	11.08	14.48	25.56
Russia:												
1971-1987	4	73.13	0.92	0.093	8.56	3.53	13.12	0.24	0.27	12.09	13.36	25.46
Netherlands:												
1987	1	70.86	0.86	0.062	8.66	4.97	13.90	0.10	0.24	13.63	14.00	27.63
Sweden:												
1989	1	72.75	1.16	0.102	8.36	3.86	12.97	0.40	0.20	12.22	13.37	25.59
Czechia:												
1971-1990	12	72.60	0.76	0.049	8.45	3.88	13.65	0.32	0.24	12.34	13.97	26.31
average:												
1960-1999	37	72.12	0.83	0.091	8.64	4.03	13.56	0.31	0.27	12.67	13.84	26.51
± <i>s</i>		0.75	0.43	0.024	0.62	0.38	0.35	0.22	0.10	0.75	0.34	0.86

Table 7. Average composition of flat glasses (in wt%) – overview pursuant to periods and glass kinds

period	<i>n</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	MnO	RO	R <sub>2</sub> O	Dietzel [15]
until 1835:													
hand blown	7	68.85	6.03		12.79		12.29				12.79	12.29	25.08
cast	2	74.87	3.15		4.70		14.78	5.50			4.70	17.52	22.18
1846-1880:													
hand blown	53	69.61	1.76	0.31	10.42	0.22	<i>11.82</i>	<i>14.14</i>			10.46	18.06	28.31
cast	23	74.45	1.78	0.52	8.82	0.31	12.64	7.87	0.70		8.91	14.82	23.72
1880-1914:													
hand blown	37	72.07	1.33	0.30	13.25	0.18	12.54	1.46	0.51	0.08	13.36	12.93	26.29
cast	13	72.38	2.26	0.30	11.49	0.17	14.18	0.91			1.52	14.27	25.80
1919-1938:													
hand blown	33	71.81	0.86	0.18	12.97	0.30	13.55	0.55	0.46	0.17	13.21	13.66	26.86
cast	59	71.87	0.75	0.17	11.61	1.47	13.95	0.40	0.63	0.07	12.90	13.97	26.88
Oppermann	7	72.01	1.00	0.29	13.00	0.77	12.87		0.75	0.11	13.55	12.86	26.46
Fourcalt a.	50	71.44	0.72	0.20	10.64	0.41	15.93	0.64	0.66	0.13	11.02	16.02	27.05
Fourcalt b.	69	71.20	0.50	0.07	9.57	2.78	15.17		0.61	0.17	12.42	15.17	27.55
Fourcalt Ø		71.31	0.60	0.13	10.03	1.74	15.50		0.63	0.15	11.77	15.54	27.33
Pittsburgh	19	71.77	0.77	0.09	9.55	3.20	14.01		0.61	0.15	12.75	14.01	26.75
Libb.-Owens	34	71.67	0.63	0.11	10.23	3.13	13.40		0.66	0.10	13.55	13.40	26.75
1940-1944:													
cast	3	73.83	0.34	0.03	5.34	0.35	19.34		0.63		5.69	19.34	25.03
Fourcalt	10	71.18	0.85	0.05	8.39	3.63	15.24		0.53	0.11	12.04	15.24	27.25
1946-1990:													
cast	41	71.46	0.98	0.10	9.91	2.97	13.92	0.25	0.42	0.17	12.88	14.00	26.89
Fourcalt	53	72.01	1.06	0.07	7.47	3.72	14.98	0.42	0.34		11.19	15.15	26.34
Pittsburgh	35	72.48	1.13	0.08	7.98	3.72	13.76	0.18	0.31	0.03	11.75	13.84	25.59
float	27	72.12	0.83	0.09	8.64	4.03	13.56	0.31	0.27		12.67	13.84	26.51

Note: Data in italics were obtained from smaller numbers of analyses than the other data.

Table 8. Average composition of flat glass (in wt%) in particular periods

period	<i>n</i>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	MnO	RO	R <sub>2</sub> O	Dietzel [15]
average composition:													
until 1835	9	71.86	4.59		8.75		13.54	<i>5.50</i>			8.75	14.90	23.63
1846-1880	76	72.03	1.77	0.41	9.62	0.26	12.23	<i>10.98</i>	0.70		9.69	16.44	26.01
1880-1914	48	72.22	1.79	0.30	12.37	0.17	13.36	1.18	0.51	0.08	12.44	13.60	26.05
1919-1938	217	71.68	0.75	0.16	11.08	1.72	14.13	0.53	0.63	0.13	12.77	14.16	26.90
1943-1944	105	72.50	0.60	0.04	6.86	2.00	17.29		0.58		8.87	17.29	26.14
1946-1990	156	72.02	1.00	0.08	8.50	3.61	14.05	0.29	0.33		12.12	14.21	26.33
variability ( $\pm s$ ) between glass types:													
until 1835		4.25	2.04		5.72		1.68				5.72	3.70	2.05
1846-1880		3.42	0.02	0.15	1.13	0.06	0.58	4.47			1.09	2.29	3.25
1880-1914		0.22	0.67	0-	1.24	0.02	1.16	0.39			1.30	0.95	0.35
1919-1938		0.28	0.16	0.08	1.47	1.29	1.07	0.12	0.09	0.04	0.88	1.08	0.34
1943-1944		1.87	0.36	0.01	2.16	2.31	2.90		0.07		4.49	2.90	0.16
1946-1990		0.42	0.13	0.01	1.05	0.45	0.63	0.10	0.06		0.79	0.63	0.55

Note: Data in italics were obtained from smaller numbers of analyses than the other data.

Table 9. Average values of variability within group ( $\pm s$ )

period	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	RO	R <sub>2</sub> O	Dietzel [15]
until 1835	1.02	1.90		2.48		3.30		2.48	1.38	2.19
1846-1880	2.99	0.80		2.11	0.21	2.62	2.90	2.06	3.04	2.65
1880-1914	2.42	1.65	0.10	2.63	0.09	1.83	1.02	2.65	1.85	1.70
1919-1938	0.78	0.31	0.06	0.70	0.35	0.64	0.24	0.70	0.67	0.69
1943-1944	0.33	0.14	0.01	0.38	0.32	0.37	0.04	0.45	0.31	0.88
1946-1990	0.64	0.21	0.02	0.49	0.34	0.45	0.08	0.43	0.41	0.49
Jebsen-Marwedel [14]	0.26	0.20		0.50	0.45	0.34				
Mühlig [3]	0.23	0.07	0.01	0.15	0.14	0.14				
VÚSU [4]	0.24	0.09	0.01	0.20	0.10	0.17	0.06			

MgO and around 1.0 % Al<sub>2</sub>O<sub>3</sub>, float glasses having the lowest alumina contents. Although well-operated plants (Mühlig) were able to keep iron content between 0.04 to 0.05 % Fe<sub>2</sub>O<sub>3</sub> in the 1930s, float glasses had nearly twice as much iron. Potash was found in modern glasses only as an impurity from sand or from use of feldspar. Manganese is no longer used.

A particular process may have different requirements for the viscosity curve and tendency to devitrify. Devitrification may be seen as the biggest problem in Fourcault glasses and accounts for the higher alkali and lower RO content. The danger of devitrification did not affect cast glasses, Libbey-Owens or float glasses, so they have significantly lower alkali and higher RO contents. Pittsburgh glasses lie somewhere between the other two.

## 11. Variability of composition

Average deviations within particular periods were calculated from the ranges of composition found for particular glass groups (standard deviation *s*); the values are given in table 9. The table also gives average deviations of flat glasses produced in Germany, as given by Jebsen-Marwedel [14] in 1941. Hereafter average variance of analyses about the annual average of compositions was given for Fourcault

glasses melted by Mühlig (Teplice (Czechia)) in period 1919 to 1943 calculated according to data obtained from company file [3]. In the same way variation of compositions was calculated for seven Czech melting tanks producing flat glass during 1970 to 1990 (Fourcault, Pittsburgh, cast glass, float glass); calculated average value is given in last line of table 9 according to data from laboratory file [4]. On smaller tanks the variance was bigger, while on big float tanks, lower.

The variance in a group represents composition variance in one country and in relatively short period; it may be supposed that it includes both inevitable variations caused by fluctuation of raw materials or inaccurate batch plant operation, and changes caused by small composition modifications, for example of refining agents, in individual glassworks and by incidental differences between the glassworks. During observed 150 years such variance decreased all the time in all coefficients practically. The variability of 1919 to 1938 expressed as  $\pm 100$  average value for all observed oxides for other periods of time is given in table 10.

Before 1914 all flat glass was produced discontinuously and was melted in pots or small tanks. Fluctuations in glass composition were relatively unimportant: the glassmaker was able to cope with variations in viscosity. However, the change-over to continuous mechanical production after 1919 made it necessary to keep viscosity and composition

Table 10. Variability of composition for the years 1830 to 1990

period	variability $s$
up to 1835	$\pm 356$
1846 to 1880	$\pm 318$
1919 to 1938	$\pm 100$
1943 to 1944	$\pm 61$
1946 to 1990	$\pm 72$

within narrower limits. Average deviations at once decreased to a third. The data from 1943 to 1944 are not statistically representative, because they relate to only a few glassworks. Further decrease in variations of all oxides occurred after 1946, when new technologies (the float process) called for greater precision.

Comparing the variability of composition on one tank according to the statistics of Mühlig company from 1920 to 1940 with data for Czech flat glass tanks in 1970 to 1990, 50 years later, shows them to be very close; they prove how precisely the composition was kept in well-operated flat glass plants. Variations were very small; their effect on glass properties was calculated according to factors derived for industrial glasses [16]. The data show that variations in composition on a tank corresponded to the following differences in temperature:

- melting temperature  $\pm 3.3$  K, ( $\lg \eta = 2.0$  dPa s);
- drawing temperature  $\pm 6.2$  K, ( $\lg \eta = 4.0$  dPa s);
- liquidus temperature:  $\pm 4.7$  K.

## 12. Conclusion

The important parameters in making flat glass have always been [5]:

- lowest possible price of batch,
- easy melting, refining, and freedom from stones,
- low tendency to devitrification (especially for drawn sheet),
- good chemical durability, above all during storage [5 to 8, 14],
- suitable viscosity curve; especially once machines were used and it could enhance performance [14].

Early flat glass compositions were the same as those of common container glass but producers began to specialize early in the 19th century and adjust their compositions. By 1880 potash had been largely replaced as the main source of alkali, first by saltcake and then, from around 1920, by soda ash.

All kinds of flat glass have had RO+R<sub>2</sub>O contents almost constant at about 26.3 % since 1835, changes in alkali content being compensated by contrary changes in RO. This finding is surprising because Dietzel's work showing that value of RO+R<sub>2</sub>O to be desirable for lack of devitrification was not published until 1931 [37].

The earliest glasses contained around 4.5 % Al<sub>2</sub>O<sub>3</sub>, partly from use of impure sands and partly from corrosion of the pots. Alumina levels then soon fell to about 1.7 % Al<sub>2</sub>O<sub>3</sub> and remained there until about 1914; use of purer raw materials then led to a decrease to about 0.4%. In the 1920s and 1930s increases in alumina content were generally

made to improve chemical durability. Nevertheless, as the limited range of RO+R<sub>2</sub>O contents imply, SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> averaged ( $73.3 \pm 0.6$ ) % from 1846 to 1990. The crucial innovation was deliberate addition of MgO (as dolomite), which was the only cheap constituent able to decrease problems with devitrification in drawing sheet glass. Dimpleby and her colleagues [18] first pointed out the effects of MgO on glass properties in 1921. The first uses of significant MgO contents (23 %) were in Libbey-Owens, USA (1922), Fourcault and cast glass (1924). It seems that American experience was accepted in Europe.

Mühlig in Czechia was probably the first to add MgO to Fourcault glasses in Europe in 1924; the first regular use in Belgium dates from 1928, in Germany from 1929; however, magnesia was occasionally used in Germany from 1925. Fourcault glasses were still made in Great Britain without MgO. Experimental confirmation of the effects of MgO on glass properties was reported by Kamita [11] in 1935, and Schmidt [12] in 1938.

As purity of used sand and other raw materials improved, iron content naturally decreased from about 0.5 to 0.05 % Fe<sub>2</sub>O<sub>3</sub>. When windows were glazed with hand-blown flat glass of only 1.5 mm thickness, a darker green tint was not important.

Decolorizing by manganese was used until World War II but eventually abandoned. Most flat glasses were refined with sulphate. Over the years the SO<sub>3</sub> content has decreased from 0.7 to 0.3 %. As<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> is found only rarely, especially in the oldest cast glasses. Additions of other oxides (BaO, B<sub>2</sub>O<sub>3</sub>, ZnO and F) were tested, but use was only of limited duration.

The compositions of flat glasses produced by various processes and in different glassworks converged over the years but have not become identical. The differences persisting even in the second half of the 20th century may have owed much to tradition.

The large furnaces and closely controlled processes used for float glass have further reduced variability in particular plants but differences between individual producers remain.

At the present time new environmental requirements have to be satisfied; glass and filter dusts recycling have to be managed. Measures to reduce batch costs and achieve easier melting are actively pursued.

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