Trimethylsilyl Derivatives for the Study of Silicate Structures. Part 6.[1] Identification of Fluorosilicate Ions from a Lead(II) Oxide–Lead(II) Fluoride–Silicon(IV) Oxide (3/1/1) Glass

By **Harry P. Calhoun, W. David Jamieson,** and **Charles R. Masson,*** Atlantic Regional Laboratory, National Research Council of Canada, Halifax, Nova Scotia, Canada B3H 3Z1

A direct method of trimethylsilylation developed previously has been applied to a glass of composition 3PbO–PbF_2–SiO_2. The major products are the trimethylsilyl derivatives of $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, and $[Si_3O_{10}]^{8-}$, together with smaller amounts of the trimethylsilyl derivatives of $[SiFO_3]^{3-}$, $[Si_2FO_6]^{5-}$, $[Si_3FO_9]^{7-}$, and $[Si_4FO_{11}]^{7-}$. Trimethylsilyl derivatives of higher silicate and monofluorosilicate ions and of ions containing more than one fluorine atom have also been detected. The results provide direct evidence for the presence of Si–F bonds in glasses of this type.

THE trimethylsilylation [2] of silicate ions has been shown to be a useful technique for the study of silicate minerals and glasses. In this method silicate anions are extracted as their trimethylsilyl ($SiMe_3$) derivatives which are separated by gas–liquid chromatography and identified by mass spectrometry. One disadvantage of the method is the occurrence of side reactions which prevent accurate representation of the original silicate structure. However, a series of studies [2c–e] using silicate minerals of well defined structure has shown that while side reactions cannot be completely eliminated they can be minimized by careful choice of reagents and reaction conditions. This method is particularly useful for the study of silicate glasses which, because of their amorphous nature, cannot be easily studied by ordinary *X*-ray diffraction techniques. It has been used to study lead orthosilicate glass,[3] borate ($SiO_2 + B_2O_3$) and lithium borate ($SiO_2 + LiBO_2$) glasses,[4] and cobalt silicate slags.[5]

In a recent study [6] of the thermodynamic properties of PbO–PbF_2–SiO_2 melts, the results were interpreted in terms of a theory in which the anionic constitution of the melts was represented by O^{2-}, F^-, and an array of silicate and fluorosilicate ions in thermodynamic equilibrium. The purpose of the present work was to assess the general validity of this treatment by applying the method of trimethylsilylation to a glass of composition within the range covered by the thermodynamic investigations. A glass of composition 3PbO–PbF_2–SiO_2 was chosen for study.

EXPERIMENTAL

Materials.—Yellow lead(II) oxide (Fisher 'purified,' 99.25%) and lead(II) fluoride (B.D.H., 'extra pure') were used as received. Silicon(IV) oxide was prepared by firing Mallinckrodt reagent-grade silicic acid. Chlorotrimethylsilane (Pierce Chemical Co.), hexamethyldisiloxane (Columbia Organic Chemicals Co.), and isopropyl alcohol (Fisher) were purified as described previously.[7]

Preparation of 3PbO–PbF_2–SiO_2 *Glass.*—Silicon(IV) oxide (3.0495 g, 0.050 76 mol), PbO (33.9887 g, 0.152 27 mol), and PbF_2 (12.4451 g, 0.050 76 mol) were mixed, placed in a Pt–20% Rh crucible, and heated in air to 710 °C for 20 min. The melt was quenched between brass plates. The resulting glass was ground to pass a 100-mesh screen. The glass was shown to be uniformly non-crystalline by microscopic examination and *X*-ray diffraction. The lead content of the glass was determined by a standard gravimetric procedure, by precipitation as the sulphate (Found: Pb, 84.95. Calc. for 3PbO–PbF_2–SiO_2: Pb, 85.0%).

Trimethylsilylation.—The 3PbO–PbF_2–SiO_2 glass (1 g), hexamethyldisiloxane (18 cm^3), and Pr^iOH (2 cm^3) were placed in a glass jar (60 cm^3 capacity) with a Teflon-lined cap. The mixture was stirred with a Teflon-coated magnetic stirring bar at 28 °C for 2 min, then chlorotrimethylsilane (4 cm^3) was added and the mixture was stirred vigorously for 3 h. The hexamethyldisiloxane (upper) layer was removed with a micropipette, clarified by centrifugation, and distilled to a column temperature of 98 °C to remove unchanged $SiMe_3Cl$. The residue was stirred with Amberlyst 15 ion-exchange resin (2 g) for 40 h to complete the trimethylsilylation.

Gas Chromatography.—Both packed and open tubular (capillary) columns were used for analysis of the extracts.

For the packed column a Hewlett–Packard model 5750 gas chromatograph, equipped with flame-ionization detector, was employed. Peak areas were measured with a model 3370-A electronic integrator. The stainless-steel column (3.6 m long × 3.2 mm diameter) was packed with 3% SE-30 on Chromosorb W, AWDMCS. Helium was used as the carrier gas. Operating conditions: injection-port temperature, 325 °C; flame-detector block temperature 325 °C; helium flow rate, 66 cm^3 min^{-1}; air flow rate, 375 cm^3 min^{-1}; hydrogen flow rate, 28 cm^3 min^{-1}. The column was cooled to 85 °C prior to injection of the sample. After 6 min the temperature was increased at 8° min^{-1} until $Si_2O_7(SiMe_3)_6$ was evolved (*ca.* 190 °C), and thereafter at 2° min^{-1} until the final temperature (240 °C) was reached. This temperature was then held constant for the remainder of the chromatogram. Samples for mass-spectrometric examination were collected in glass capillary tubes with the aid of a modified collection vent similar to that described elsewhere.[2b]

For the capillary column a Perkin-Elmer model 910 gas chromatograph, equipped with flame ionization detector and wall-coated all-glass open tubular column, was used. The column (25 m long × 0.27 mm internal diameter) was coated with OV-101. Helium was used as the carrier gas. Operating conditions: injection-port temperature, 280 °C; flame-detector block temperature, 280 °C; injector carrier-gas pressure, 54 lbf in^{-2}; pre-column flow rate, 60 cm^3 min^{-1}; auxiliary carrier-gas inlet pressure, 24 lbf in^{-2}; make-up gas flow rate, 40 cm^3 min^{-1}; air pressure, 50 lbf in^{-2}; hydrogen

---

† Throughout this paper: 1 lbf in^{-2} ≈ (9.8 × 4 536/6.45) Pa; 1 Torr = (101 325/760) Pa.

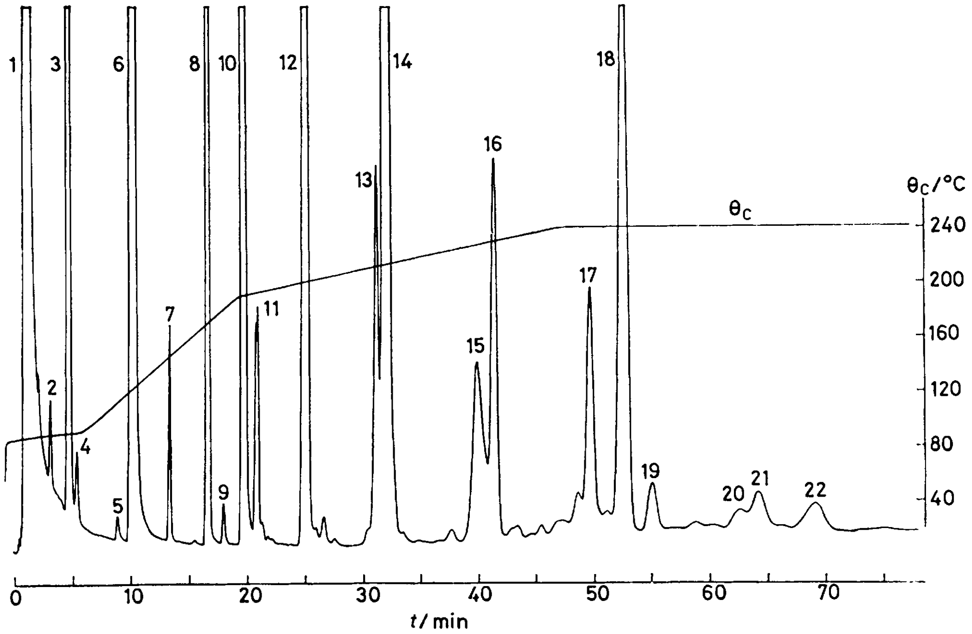

FIGURE 1 Gas chromatogram of the silylation product of the $3PbO–PbF_2–SiO_2$ glass obtained by using the packed column. For identity of peaks see Tables 1 and 2

pressure, 20 lbf in^{-2}. Temperature program: 70 °C for 6 min, then 5° min^{-1} to 240 °C; held at 240 °C for remainder of chromatogram.

Mass Spectrometry.—The mass spectrometer, of Mattauch–Herzog design, was a Dupont/CEC model 21-110B, with an electron-impact ionization source and equipped for ion detection by either photographic plate (Ionomet vacuum-deposited silver bromide) or electrode–electron multiplier. The magnetic-scanning circuitry had been modified to yield linear records of *m/e* against time by electrical detection. Two high-stability power supplies were installed as alternate sources of potential for the electrostatic analyser (Power Designs, Inc., model 2K-10). The voltage reference for the power supply of the ion accelerator was obtained either by means of the original circuitry or these high-stability supplies. The resolution of the mass spectrometer when scanning was *ca.* 2 000; it was adjusted to *ca.* 15 000 when spectra were recorded on photoplates.

Samples (2—15 μg) were sublimed directly into the ionization chamber of the source. The probe used for sample introduction (Masspec., Texas) allowed the temperature of the sample to be kept at an optimum value, in the range −70 to 150 °C, independent of the selected temperature (150—180 °C) of the ionization chamber itself. The temperature of the sample was adjusted to exert the minimum pressure (10^{-6}—10^{-5} Torr) required to yield a mass spectrum of adequate intensity. Higher pressures caused rapid deterioration in the ion-optical characteristics of the instrument, due, presumably, to accumulation of decomposition products on surfaces within the ionization chamber.

RESULTS

Chromatograms of the product of trimethylsilylation of $3PbO–PbF_2–SiO_2$ glass obtained on the packed and open tubular columns are presented in Figures 1 and 2 respectively. The identity of the peaks is shown in Table 1 and Table 2 gives the relative peak areas for the packed column, each expressed as a percentage of the total (excluding solvent).

In both chromatograms peak 1 was attributed to the solvent, $O(SiMe_3)_2$, identified by its retention time. The remaining peaks were identified by mass spectrometry. Comparison of Figures 1 and 2 illustrates the improvement in resolution with the open tubular column. Material collected from the packed column corresponding to peaks 11, 12, 13, and 15 was shown by mass spectrometry to be mixtures of various trimethylsilyl derivatives. The components of these mixtures could be completely resolved on the open tubular column.

TABLE 1

Identity of peaks in Figures 1 and 2

Peak no.	Identity of parent ion	*M* of trimethylsilyl derivative
1	O^{2-}	162
2	unidentified	
3	$[SiFO_3]^{3-}$	314
4	unidentified	
5	unidentified	
6	$[SiO_4]^{4-}$	384
7	$[Si_2F_2O_5]^{4-}$	466
8	$[Si_2FO_6]^{5-}$	536
9	$[Si_3F_3O_7]^{5-}$	618
10	$[Si_2O_7]^{6-}$	606
11a	$[Si_4F_2O_{10}]^{6-}$	748
b	$[Si_3F_2O_8]^{6-}$	688
c	$[Si_3O_9]^{6-}$	666
12a	$[Si_4FO_{11}]^{7-}$	818
b	$[Si_3FO_9]^{7-}$	758
13a	$[Si_4O_{12}]^{8-}$	888
b	$[Si_5F_2O_{13}]^{8-}$	970
c	$[Si_4F_2O_{11}]^{8-}$	910
14	$[Si_3O_{10}]^{8-}$	828
15a	$[Si_6FO_{16}]^{9-}$	1 100
b	$[Si_5FO_{14}]^{9-}$	1 040
c	$[Si_4FO_{12}]^{9-}$	980
d	$[Si_4FO_{12}]^{9-}$	980
16	$[Si_4FO_{12}]^{9-}$	980
17	mainly $[Si_5O_{15}]^{10-}$	1 110
18	$[Si_4O_{13}]^{10-}$	1 050
19	$[Si_4O_{13}]^{10-}$	1 050

TABLE 2

Percentage peak areas obtained by using the packed column

Peak no.	Trimethylsilyl derivative	Percentage of total area [excluding $O(SiMe_3)_2$]
2	unidentified	0.06
3	$SiFO_3(SiMe_3)_3$	3.84
4	unidentified	0.05
5	unidentified	0.04
6	$SiO_4(SiMe_3)_4$	45.05
7	$Si_2F_2O_5(SiMe_3)_4$	0.24
8	$Si_2FO_6(SiMe_3)_5$	5.80
9	$Si_3F_3O_7(SiMe_3)_5$	0.05
10	$Si_2O_7(SiMe_3)_6$	24.25
11	$Si_4F_2O_{10}(SiMe_3)_6$ $+Si_3F_2O_8(SiMe_3)_6$ $+Si_3O_9(SiMe_3)_6$	0.24
12	$Si_4FO_{11}(SiMe_3)_7$ $+Si_3FO_9(SiMe_3)_7$	4.52
13	mainly $Si_4O_{12}(SiMe_3)_8$	0.93
14	$Si_3O_{10}(SiMe_3)_8$	9.46
15	$Si_6FO_{16}(SiMe_3)_9$ $+Si_5FO_{14}(SiMe_3)_9$ $+Si_4FO_{12}(SiMe_3)_9$	1.01
16	$Si_4FO_{12}(SiMe_3)_9$	0.83
17	mainly $Si_5O_{15}(SiMe_3)_{10}$	0.75
18	$Si_4O_{13}(SiMe_3)_{10}$	2.74
19	$Si_4O_{13}(SiMe_3)_{10}$	0.14
20	unidentified	trace
21	unidentified	trace

In all cases the major structurally significant ion in the mass spectra of the trimethylsilyl derivatives was that corresponding to loss of $CH_3^{\bullet}$ from the molecular ion. Also of importance for identification purposes were the immediate products of fragmentation of the $[M-15]^+$ ions. In the case of the fluorosilicate derivatives, these reactions proceed mainly by loss of 92 *m/e* units, presumably $SiMe_3F$, and in the case of the silicate derivatives, by loss of 88 *m/e* units previously ascribed[7] to $SiO(CH_3)_2CH_2$ and/or $SiMe_4$. The mass-spectral pattern in the range below *m/e* 200 is not very useful for identifying trimethylsilyl derivatives. The most abundant ion signal (' base peak ') in most spectra was at *m/e* 73 and was predominantly due to $[SiMe_3]^+$.

Material corresponding to peak 3 was identified as $SiFO_3(SiMe_3)_3$ based on the mass spectrum shown in Figure 3. For this derivative the molecular ion is not observed. The $[M-15]^+$ ion is at *m/e* 299. Loss of $SiMe_3F$ from the $[M-15]^+$ ion results in the peak at *m/e* 207. The ' base peak ' occurs at *m/e* 73.

Peaks 2, 4, and 5 could not be identified because of difficulties in collecting sufficient sample for the mass spectrometer. Peaks 6, 10, and 14 were assigned to $SiO_4(SiMe_3)_4$, $Si_2O_7(SiMe_3)_6$, and $Si_3O_{10}(SiMe_3)_8$ respectively. Mass spectra for these derivatives have been reported in an earlier communication.[2b]

The identity of peaks 7—9 was established on the basis of the *m/e* values of the $[M-15]^+$ ions. The mass spectrum of the material corresponding to peak 8, Figure 4, again shows the characteristic fragmentation pattern of the trimethylsilyl derivatives of the fluorosilicate ions. The peak at *m/e* 521 corresponds to loss of $CH_3^{\bullet}$ from the molecular ion, and that at *m/e* 429 to loss of $SiMe_3F$ from the $[M-15]^+$ ion. The molecular ion is not observed.

The mass spectrum of the material corresponding to peak 11 showed it to be a mixture of trimethylsilyl derivatives of the tetrameric ring ion $[Si_4F_2O_{10}]^{6-}$, the trimeric chain ion $[Si_3F_2O_8]^{6-}$, and the trimeric ring ion $[Si_3O_9]^{6-}$. These derivatives could be separated on the open tubular column and are labelled peaks 11a, 11b, and 11c in Figure 2. A mixture of the product and a hexamethyldisiloxane solution of pure $Si_3O_9(SiMe_3)_6$ prepared earlier showed that peak 11c could be assigned to $Si_3O_9(SiMe_3)_6$. Peak 11a is assigned to $Si_4F_2O_{10}(SiMe_3)_6$ and 11b to $Si_3F_2O_8(SiMe_3)_6$ on the basis that trimethylsilyl derivatives of the tetrameric ring ion

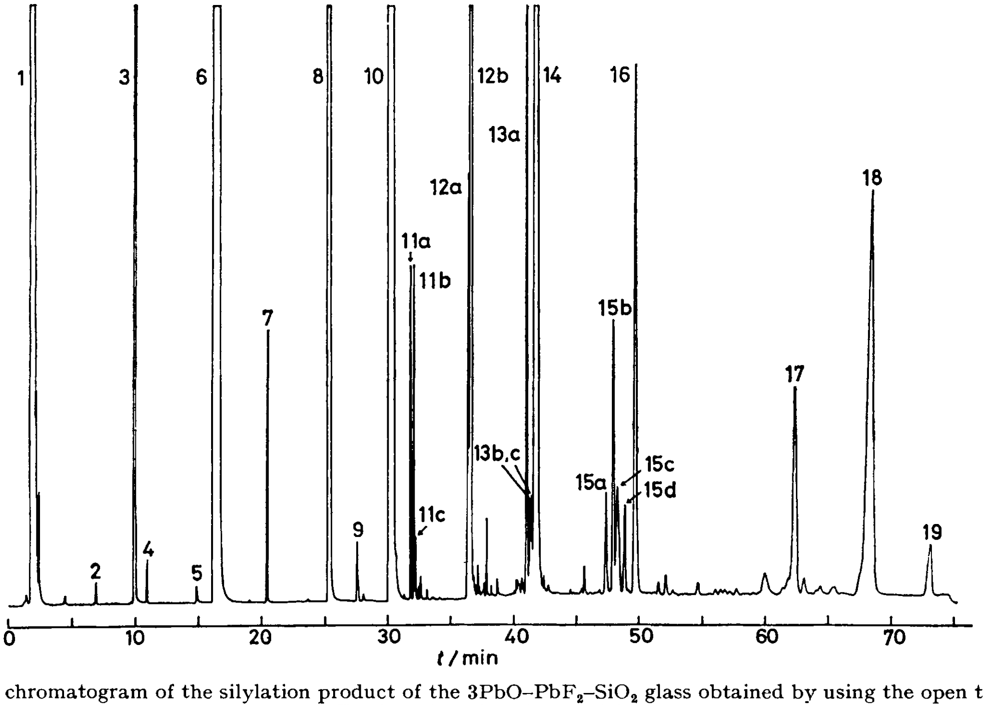

FIGURE 2 Gas chromatogram of the silylation product of the $3PbO-PbF_2-SiO_2$ glass obtained by using the open tubular column. For identity of peaks see Table 1

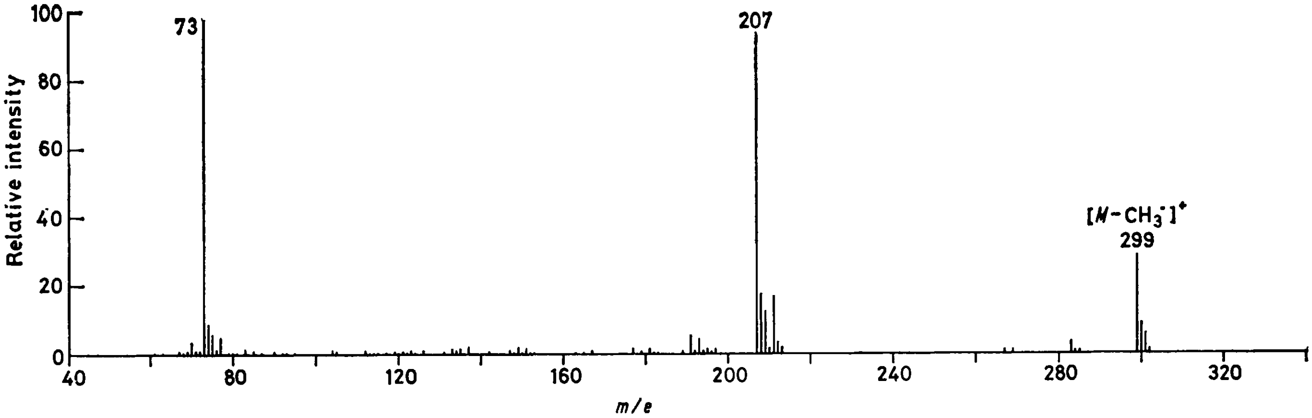

FIGURE 3 Mass spectrum of $SiFO_3(SiMe_3)_3$ (peak 3 in Figures 1 and 2)

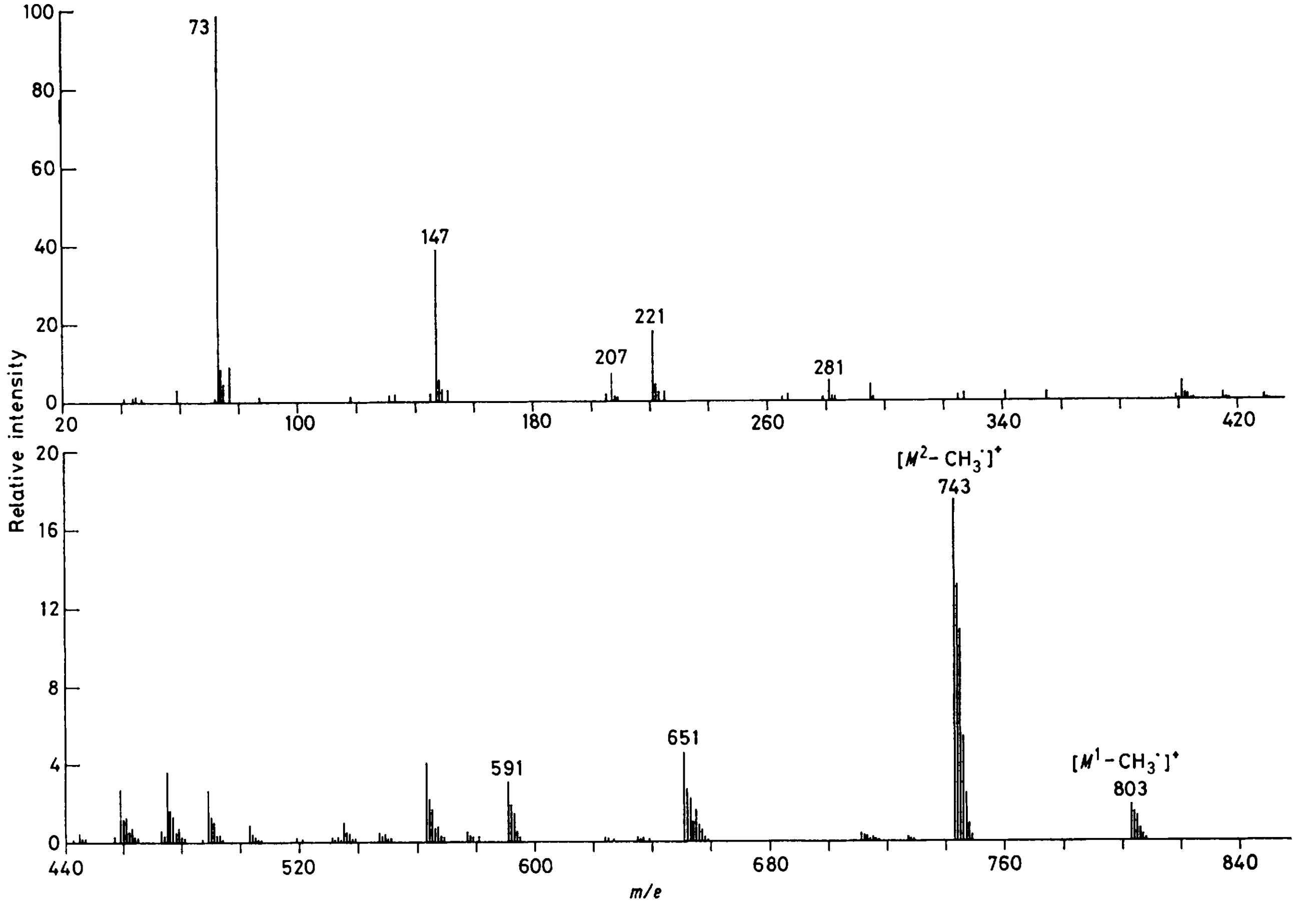

FIGURE 4 Mass spectrum of $Si_2FO_6(SiMe_3)_5$ (peak 8 in Figures 1 and 2)

generally pass through the column slightly ahead of derivatives of the trimeric chain ion.[2b]

The mass spectrum of the material corresponding to peak 12 is shown in Figure 5. It is consistent with that of a mixture of trimethylsilyl derivatives of the tetrameric ring ion $[Si_4FO_{11}]^{7-}$ and the trimeric chain ion $[Si_3FO_9]^{7-}$. These derivatives could be partially separated on the open tubular column and are labelled 12a and 12b in Figure 2. Peak 12a is assigned to the trimethylsilyl derivative of $[Si_4FO_{11}]^{7-}$ and peak 12b to the $SiMe_3$ derivative of $[Si_3FO_9]^{7-}$.

The mass spectrum of the material corresponding to peak 13 showed it to contain mainly the trimethylsilyl derivative of the tetrameric ring ion $[Si_4O_{12}]^{8-}$, with minor contributions from $SiMe_3$ derivatives of the pentameric ring ion $[Si_5F_2O_{13}]^{8-}$ and the tetrameric chain ion $[Si_4F_2O_{11}]^{8-}$. These derivatives could be separated on the open tubular column and are labelled 13a, 13b, and 13c in Figure 2.

Figure 6 shows the mass spectrum, at high *m/e*, of the material corresponding to peak 15. The groups of peaks at *m/e* 965, 1 025, and 1 085 are consistent with this material being a mixture of trimethylsilyl derivatives of the fluorosilicate ions $[Si_{4+n}FO_{12+2n}]^{9-}$ ($n = 0$—2). These derivatives could be resolved on the open tubular column and are labelled 15a, 15b, 15c, and 15d in Figure 2. Four peaks were observed, suggesting that one of the above derivatives is present as two isomers. The mass spectrum of the material corresponding to peak 16 showed it to contain the trimethylsilyl derivative of the tetrameric chain ion $[Si_4FO_{12}]^{9-}$. The presence of $SiMe_3$ derivatives of the $[Si_4FO_{12}]^{9-}$ ion in both peaks 15 and 16 indicates that more than one isomer of this compound is present in the product.

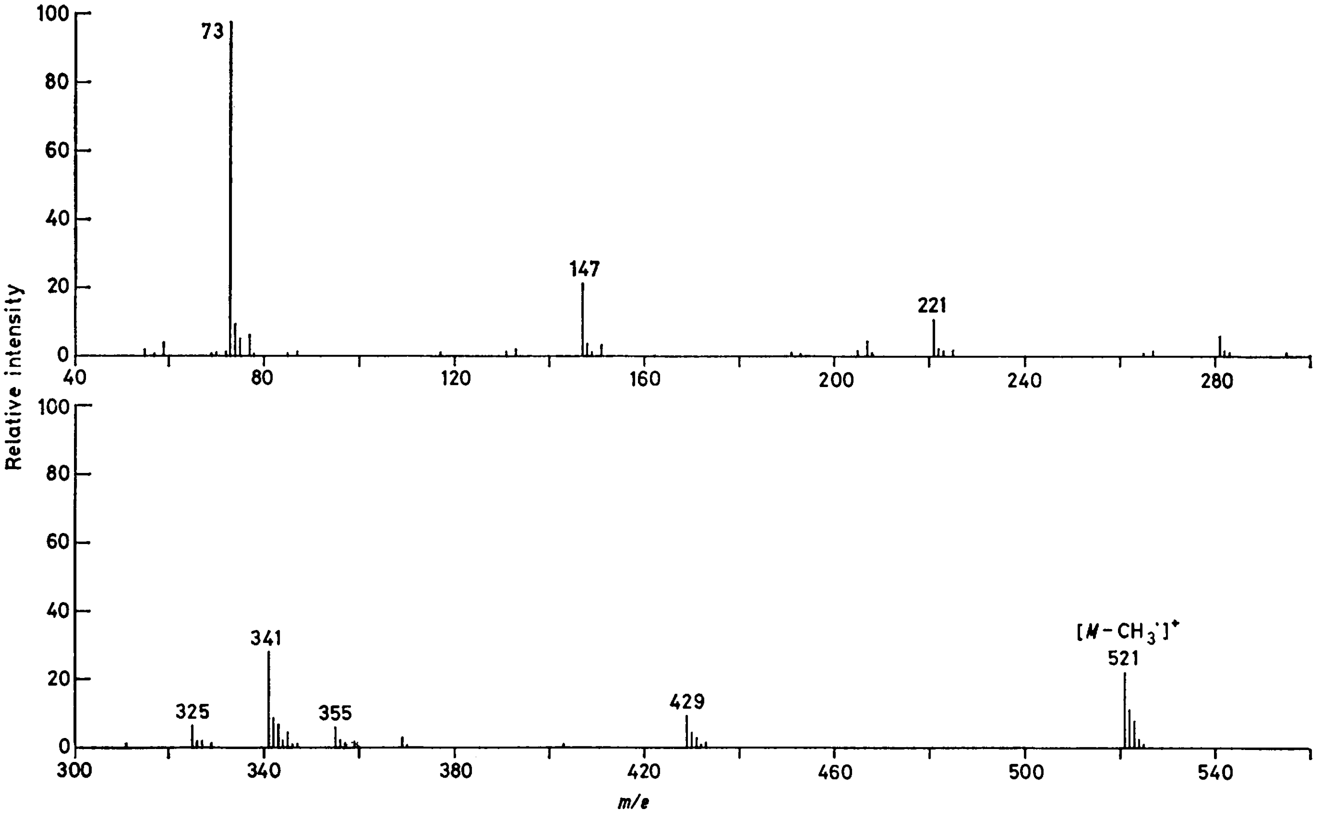

FIGURE 5 Mass spectrum of the material corresponding to peak 12 in Figures 1 and 2

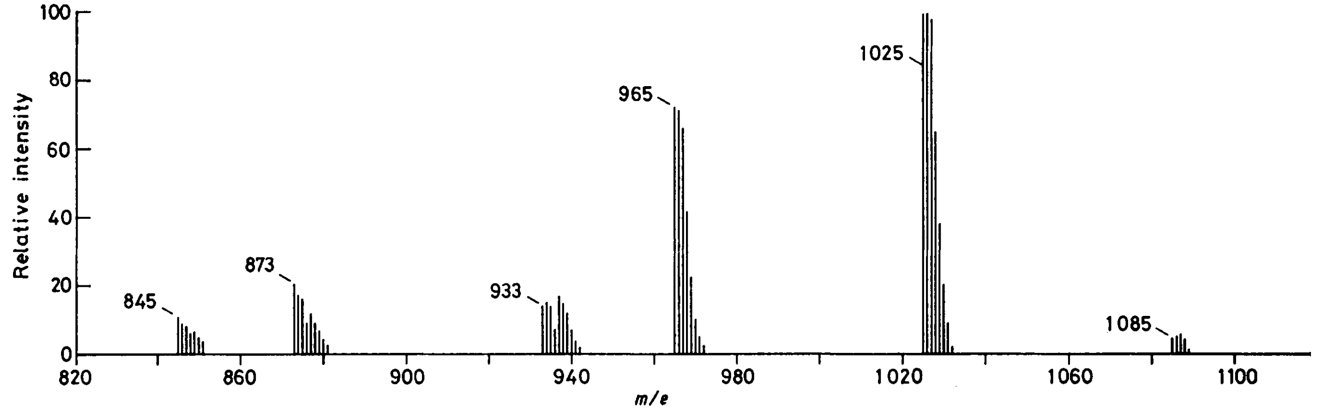

FIGURE 6 Mass spectrum of the material corresponding to peak 15 in Figures 1 and 2

The mass spectrum of the material corresponding to peak 17 showed it to contain mainly the pentameric cyclic derivative $Si_5O_{15}(SiMe_3)_{10}$ with minor contributions from $Si_6O_{17}(SiMe_3)_{10}$ (3.6%, based on equal mass-spectral sensitivity at the *m/e* value of the $[M - 15]^+$ ions), $Si_7O_{19}(SiMe_3)_{10}$ (1.8%), $Si_6F_2O_{16}(SiMe_3)_{10}$ (1.8%), and $Si_5F_2O_{14}(SiMe_3)_{10}$ (1.8%).

The mass spectra of peaks 18 and 19 showed them to contain the trimethylsilyl derivative of the tetrameric chain ion $[Si_4O_{13}]^{10-}$. These peaks correspond to the linear- and branched-chain isomers of $Si_4O_{13}(SiMe_3)_{10}$.

DISCUSSION

A summary of the trimethylsilyl derivatives formed in the trimethylsilylation of the $3PbO–PbF_2–SiO_2$ glass is given in Table 3. Derivatives of silicate ions account for 83.3% of the total peak area of Figure 1 and derivatives of fluorosilicate ions for 16.5% of the total peak area. Derivatives of the $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, and

TABLE 3

Ions identified as their trimethylsilyl derivatives in extracts of the 3PbO–PbF_2–SiO_2 glass

Silicate ions	Monofluoro-silicate ions	Difluoro-silicate ions	Trifluoro-silicate ions
$[SiO_4]^{4-}$	$[SiFO_3]^{3-}$		
$[Si_2O_7]^{6-}$	$[Si_2FO_6]^{5-}$	$[Si_2F_2O_5]^{4-}$	
$[Si_3O_9]^{6-}$			
$[Si_3O_{10}]^{8-}$	$[Si_3FO_9]^{7-}$	$[Si_3F_2O_8]^{6-}$	$[Si_3F_3O_7]^{5-}$
$[Si_4O_{12}]^{8-}$	$[Si_4FO_{11}]^{7-}$	$[Si_4F_2O_{10}]^{6-}$	
$[Si_4O_{13}]^{10-}$ [a]	$[Si_4FO_{12}]^{9-}$ [b]	$[Si_4F_2O_{11}]^{8-}$	
$[Si_5O_{15}]^{10-}$	$[Si_5FO_{14}]^{9-}$	$[Si_5F_2O_{13}]^{8-}$	
$[Si_6O_{17}]^{10-}$ [c]	$[Si_6FO_{16}]^{9-}$		
$[Si_7O_{19}]^{10-}$ [c]			
		$[Si_5F_2O_{14}]^{10-}$ [c]	
		$[Si_6F_2O_{16}]^{10-}$ [c]	

[a] Two isomers. [b] At least two isomers. [c] Trace amount.

$[Si_3O_{10}]^{8-}$ ions are formed in the largest relative amounts and account for 78.8% of the total peak area. The most abundant trimethylsilyl derivatives of fluorosilicate ions are those in which one oxygen of a given silicate ion is replaced by a fluorine. Derivatives of $[SiFO_3]^{3-}$, $[Si_2FO_6]^{5-}$, $[Si_4FO_{11}]^{7-}$, and $[Si_3FO_9]^{7-}$ ions account for 14.2% of the total peak area and 86.1% of the peak area attributed to fluorosilicate derivatives. Trimethylsilyl derivatives of fluorosilicate ions formed by replacement of more than one oxygen of the parent silicate ion by fluorine are present only in very small amounts.

These results are qualitatively in line with expectations from polymer theory [6] for a melt of this composition. Theory predicts that, on a molar basis, the silicate ions are more abundant than the corresponding monofluorosilicate ions which, in turn, are more abundant than the corresponding difluorosilicate ions, *etc*. According to theory, the $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, and $[Si_3O_{10}]^{8-}$ ions should account for 57.9% and the $[SiFO_3]^{3-}$, $[Si_2FO_6]^{5-}$, and $[Si_3FO_9]^{7-}$ ions 24.9% of the total on a molar basis. Further comparison of theory and experiment, which requires the preparation of standard solutions of the pure fluorosilicate derivatives, is beyond the scope of the present work, which was devoted mainly to the identification and characterization of the trimethylsilyl derivatives. It may be noted that the theory allows no predictions concerning the cyclic species $[Si_4O_{12}]^{8-}$, $[Si_5O_{15}]^{10-}$, $[Si_4FO_{11}]^{7-}$, *etc.*, observed in this work.

Trimethylsilyl derivatives emerge from the column in order of increasing charge of the parent ion. Derivatives of ions of charge greater than 8— are present only in small quantities. These are mainly trimethylsilyl derivatives of the silicate ions $[Si_5O_{15}]^{10-}$ and $[Si_4O_{13}]^{10-}$ and their corresponding monofluorosilicate ions $[Si_5FO_{14}]^{9-}$ and $[Si_4FO_{12}]^{9-}$. Trace amounts of the difluorosilicate derivatives $Si_5F_2O_{14}(SiMe_3)_{10}$ and $Si_6F_2O_{16}(SiMe_3)_{10}$ were seen in the mass spectrum of the material corresponding to peak 17. These are the derivatives of the pentameric chain ion $[Si_5F_2O_{14}]^{10-}$ and the hexameric cyclic ion $[Si_6F_2O_{16}]^{10-}$.

Mass spectra of the material corresponding to peaks 18 and 19 indicate that both peaks can be attributed to the trimethylsilyl derivative of the silicate ion $[Si_4O_{13}]^{10-}$. These are evidently due to isomers of this ion, one peak corresponding to the linear-chain ion and the other to the branched-chain ion. Isomers of $[Si_4FO_{12}]^{9-}$ were also detected, since both peaks 15 and 16 contain this species.

Conclusion.—The major products of the trimethylsilylation of the 3PbO–PbF_2–SiO_2 glass are trimethylsilyl derivatives of the silicate ions $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, and $[Si_3O_{10}]^{8-}$. Trimethylsilyl derivatives of silicate ions of charge 10— and an array of trimethylsilyl derivatives of fluorosilicate ions are present in smaller amounts in the product. The results provide direct experimental evidence for the presence of discrete silicate and fluorosilicate ions in the glass, in line with expectations from polymer theory.

[8/715 *Received*, 17*th April*, 1978]

REFERENCES

[1] Part 5, H. P. Calhoun and C. R. Masson, *J.C.S. Dalton*, 1978, 1342.

[2] (*a*) C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574; (*b*) F. F. H. Wu, J. Götz, W. D. Jamieson, and C. R. Masson, *J. Chromatog.*, 1970, **48**, 515; (*c*) J. Götz and C. R. Masson, *J. Chem. Soc.* (*A*), 1970, 2683; (*d*) *ibid.*, 1971, 686; (*e*) S. K. Sharma, L. S. Dent Glasser, and C. R. Masson, *J.C.S. Dalton*, 1973, 1324.

[3] J. Götz, C. R. Masson, and L. M. Castelliz, in 'Amorphous Materials,' eds. R. W. Douglas and B. Ellis, Wiley, New York, 1972, pp. 317—325.

[4] K. E. Kolb and K. W. Hansen, *J. Amer. Ceram. Soc.*, 1965, **48**, 439.

[5] I. B. Smith and C. R. Masson, *Canad. J. Chem.*, 1971, **49**, 683.

[6] W. F. Caley and C. R. Masson, *J.C.S. Faraday I*, 1978, 2952.

[7] C. R. Masson, W. D. Jamieson, and F. G. Mason, in 'Physical Chemistry of Process Metallurgy,' The Richardson Conference, eds. J. H. E. Jeffes and R. J. Tait, Institute of Mining and Metallurgy, London, 1974, pp. 223—231.