

# Trimethylsilylation of $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ : Cyclisation of the Linear Chain Anion $\text{Si}_4\text{O}_{13}^{10-}$

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**Summary** Trimethylsilylation of  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  by a modified 'direct method' yielded the trimethylsilyl (TMS) derivative of the linear chain ion  $\text{Si}_4\text{O}_{13}^{10-}$  as the major product, this ion readily undergoes cyclisation in acidic aqueous media to yield the cyclic tetramer  $\text{Si}_4\text{O}_{12}^{8-}$  and the presence of linear and branched chain isomers of the TMS derivative of  $\text{Si}_4\text{O}_{13}^{10-}$  was confirmed in the trimethylsilylation of lead fluorosilicate glass

In a recent communication by one of the authors<sup>1</sup> the first synthesis of a linear chain tetrasilicate,  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ , was reported. The tetrasilicate ion  $\text{Si}_4\text{O}_{13}^{10-}$  has previously been identified, as its trimethylsilyl (TMS) derivative, in extracts of silicic acid solutions,<sup>2</sup> metallurgical slags,<sup>3</sup> and lead fluorosilicate glass.<sup>4</sup> The derivative has also been prepared<sup>5</sup> from decachlorotetrasiloxane  $\text{Si}_4\text{O}_3\text{Cl}_{10}$  and its chromatographic characteristics<sup>5,6</sup> and  $^{29}\text{Si}$  n.m.r. spectrum reported.<sup>7</sup>

In the study of lead fluorosilicate glass<sup>4</sup> the TMS derivatives of two silicate ions were detected whose mass spectral characteristics corresponded to the formula  $\text{Si}_4\text{O}_{13}(\text{TMS})_{10}$ . It was concluded that these were due to the linear and branched chain isomers (peaks 18 and 19 in Figures 1 and 2)<sup>4</sup> one of which (peak 18) predominated in the extract.

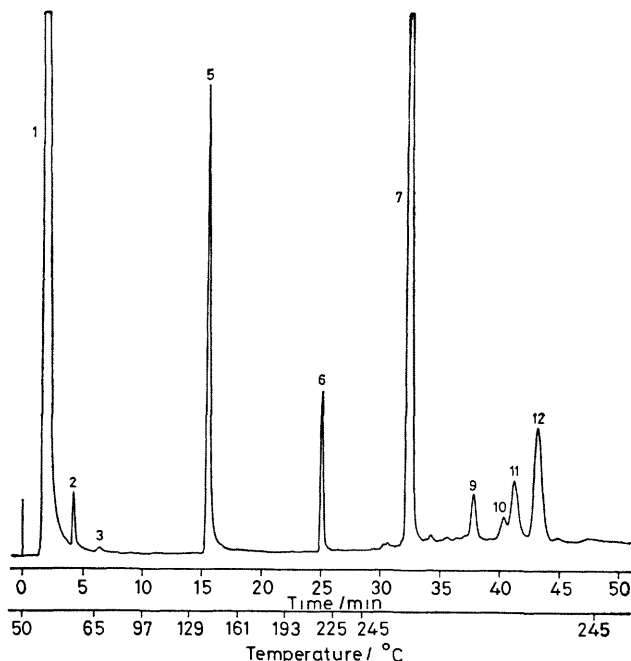


FIGURE 1 Chromatogram of the product of trimethylsilylation of  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  by the Lentz method. Peaks correspond to (1),  $\text{O}(\text{SiMe}_3)_2$ , (5),  $\text{SiO}_4(\text{SiMe}_3)_4$ , (6),  $\text{Si}_2\text{O}_7(\text{SiMe}_3)_6$ , (7),  $\text{Si}_4\text{O}_{12}(\text{SiMe}_3)_8$ , (12),  $\text{Si}_4\text{O}_{13}(\text{SiMe}_3)_{10}$ . Other peaks were not identified.

The availability of the compound  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  allows us to confirm these conclusions and to establish that the dominant peak observed previously is due to the linear chain isomer.

It has further been shown that the linear chain ion  $\text{Si}_4\text{O}_{13}^{10-}$  readily undergoes cyclisation during trimethylsilylation to yield the cyclic tetramer  $\text{Si}_4\text{O}_{12}^{8-}$ . This cyclisation occurs so readily in acidic aqueous media that the  $\text{Si}_4\text{O}_{13}^{10-}$  derivative was only a minor product when trimethylsilylation of  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  was performed under the conditions originally described by Lentz.<sup>8</sup> Cyclisation was minimized, though not entirely suppressed, when a modified version of the technique of direct trimethylsilylation<sup>9</sup> was used. In this technique the reaction is allowed to proceed in the presence of ethyl alcohol and dilute nitric acid, with trimethylchlorosilane as the derivatizing agent.

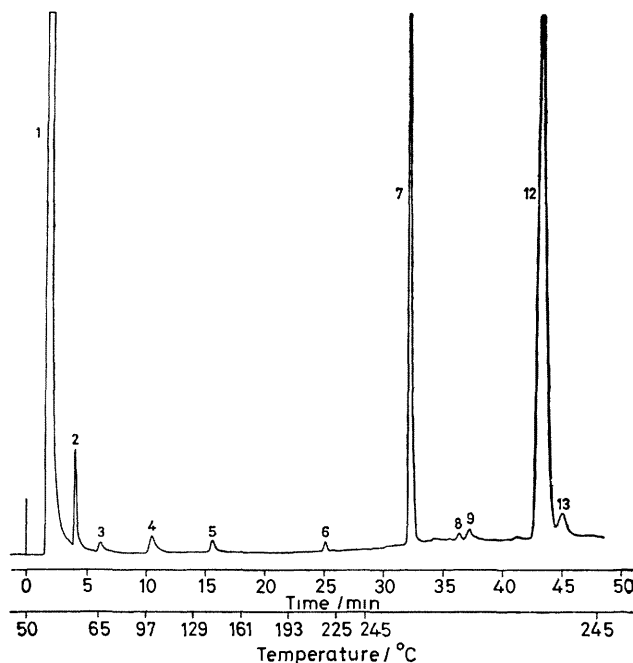


FIGURE 2 Chromatogram of the product of trimethylsilylation of  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  by the modified direct method. Peaks correspond to (1),  $\text{O}(\text{SiMe}_3)_2$ , (5),  $\text{SiO}_4(\text{SiMe}_3)_4$ , (6),  $\text{Si}_2\text{O}_7(\text{SiMe}_3)_6$ , (7),  $\text{Si}_4\text{O}_{12}(\text{SiMe}_3)_8$ , (12),  $\text{Si}_4\text{O}_{13}(\text{SiMe}_3)_{10}$ . Other peaks were not identified.

These results show that detection of  $\text{Si}_4\text{O}_{12}(\text{TMS})_8$  in the products of trimethylsilylation of silicates does not necessarily establish the presence of the cyclic ion  $\text{Si}_4\text{O}_{12}^{8-}$  in the original material. For example, with the modified technique described above, this ion was not detected in the trimethylsilylation of lead orthosilicate glass, although its presence has been reported by several investigators.<sup>10-13</sup>

Figures 1 and 2 show the chromatograms obtained from  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  by the Lentz method and the modified direct method described above. The  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  was prepared as described previously.<sup>1</sup> For the Lentz method  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  (45 mg), hexamethyldisiloxane (4.5 cm<sup>3</sup>), isopropanol (3 cm<sup>3</sup>), distilled water (2 cm<sup>3</sup>), and concentrated HCl (2 cm<sup>3</sup>) were stirred for 20 h at room temperature, the upper layer was separated, washed with distilled water, then stirred with Amberlyst 15 ion exchange resin for ca. 20 h. For the modified direct method  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  (102.2 mg), hexamethyldisiloxane (27 cm<sup>3</sup>), and absolute ethanol (3 cm<sup>3</sup>) were stirred and cooled to  $-20^\circ\text{C}$ , then chlorotrimethylsilane (6 cm<sup>3</sup>) and 0.2 N  $\text{HNO}_3$  (0.75 cm<sup>3</sup>) were added. The solution was stirred at  $-20^\circ\text{C}$  for 5 h, then allowed to reach room temperature. Stirring was continued for 15 h at room temperature. The upper layer was separated, clarified by centrifugation, concentrated by distillation, and stirred with Amberlyst 15 for approximately 20 h. Both residues were

analysed by gas-liquid chromatography as described previously.<sup>14</sup>

In Figure 1 the dominant peak is due to the derivative of the cyclic ion  $\text{Si}_4\text{O}_{12}^{8-}$ , with lesser amounts of the  $\text{SiO}_4^{4-}$ ,  $\text{Si}_2\text{O}_7^{6-}$ , and  $\text{Si}_4\text{O}_{13}^{10-}$  derivatives. In Figure 2 the dominant peak is due to the expected derivative of the linear chain ion  $\text{Si}_4\text{O}_{13}^{10-}$ , which accounts for 71% of the total peak area of the products. In these experiments 32% of the silicon in the  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  was extracted as volatile derivatives by the modified method and 35% by the Lentz method.

Chromatographic analysis of an extract from lead fluoro-silicate glass mixed with a solution which contained the  $\text{Si}_4\text{O}_{13}^{10-}$  derivative from  $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$  showed that peak 18 in ref. 4 is due to the linear chain derivative. Peak 19 is therefore attributed to the branched chain isomer.

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<sup>1</sup> M. Jansen and H. L. Keller, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 464.

<sup>2</sup> G. Garzó, D. Hoebbel, Z. J. Ecsery, and K. Ujszászi, *J. Chromatogr.*, 1978, **167**, 321.

<sup>3</sup> C. R. Masson, W. D. Jamieson, and F. 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, 223.

<sup>4</sup> H. P. Calhoun, W. D. Jamieson, and C. R. Masson, *J. Chem. Soc., Dalton Trans.*, 1979, 454.

<sup>5</sup> D. Hoebbel and W. Wieker, *Z. Anorg. Allg. Chem.*, 1974, **405**, 163.

<sup>6</sup> G. Garzó and D. Hoebbel, *J. Chromatogr.*, 1976, **119**, 173.

<sup>7</sup> D. Hoebbel, G. Garzó, G. Engelhardt, H. Jancke, P. Franke, and W. Wieker, *Z. Anorg. Allg. Chem.*, 1976, **424**, 115.

<sup>8</sup> C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574.

<sup>9</sup> J. Götz and C. R. Masson, *J. Chem. Soc. (A)*, 1970, 2683; 1971, 686.

<sup>10</sup> J. Götz and C. R. Masson, *Int. Congr. Glass, Sci. Tech. Commun.*, 9th, Vol. 1, Institut du Verre, Paris, 1971, 261.

<sup>11</sup> J. Götz, C. R. Masson, and L. M. Castelliz, in 'Amorphous Materials,' eds. R. W. Douglas and B. Ellis, Wiley, New York, 1972, p. 317.

<sup>12</sup> J. Götz, D. Hoebbel, and W. Wieker, *Z. Anorg. Allg. Chem.*, 1975, **416**, 163; 1975, **418**, 29; *J. Non-Cryst. Solids*, 1976, **20**, 413; 1976, **22**, 391.

<sup>13</sup> R. M. Smart and F. P. Glasser, *Phys. Chem. Glasses*, 1978, **19**, 95.

<sup>14</sup> F. F. H. Wu, J. Götz, W. D. Jamieson, and C. R. Masson, *J. Chromatogr.*, 1970, **48**, 515.