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DETERMINATION OF SILICATE ANIONS BY GAS CHROMATOGRAPHIC SEPARATION AND MASS SPECTROMETRIC IDENTIFICATION OF THEIR TRIMETHYLSILYL DERIVATIVES*

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SUMMARY

The trimethylsilyl derivatives of the anions SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$, $\text{Si}_3\text{O}_9^{6-}$, $\text{Si}_3\text{O}_{10}^{8-}$ and $\text{Si}_4\text{O}_{12}^{8-}$ were resolved below 290° on SE-30 (methylpolysiloxane) liquid phase using a temperature-programmed operation and were identified by high-resolution mass spectrometry. The cracking pattern of these derivatives in the mass spectrometer is discussed.

INTRODUCTION

Chromatographic methods have only recently been developed for silicates, due largely to the labile nature of the silicate anion in aqueous solution.

WIEKER AND HOEBBEL¹ used a paper chromatographic method to separate silicate anions in aqueous solution. A method for the gas chromatographic separation of silicate anions was first described by LENTZ^{2,3}. This technique is based on the resolution of trimethylsilyl (TMS) derivatives of silicate anions by gas-liquid partition chromatography (GLPC). Under the conditions described by LENTZ it is possible to separate the TMS derivatives of SiO_4^{4-} and $\text{Si}_2\text{O}_7^{6-}$ anions and to obtain a partial separation of the derivatives of the anions $\text{Si}_3\text{O}_{10}^{8-}$ and $\text{Si}_4\text{O}_{12}^{8-}$.

To apply the TMS method to the study of silicate structures it was necessary to obtain an improved separation of the higher anions. The technique developed is described below. High-resolution mass spectrometry was used to identify the separated TMS derivatives.

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EXPERIMENTAL

Apparatus

Gas chromatograph. A Hewlett-Packard Model 5750 dual column chromatograph, operated as a single-column instrument, with flame ionization detector, was used. The column, of stainless steel 12 ft. long and 1/8 in. I.D., was packed with methyl silicone gum rubber, SE-30 Ultraphase (Hewlett-Packard), 3%, on Chromosorb W, 80-100 mesh.

For collecting samples of the separated TMS derivatives, the collection vent of the instrument had to be modified. In the original design, the thermocouple was located near the hotter end (oven side) and the temperature profile along the collection tube was so sharp that condensation of the dimeric derivative inside the tube always occurred and only a portion of it passed through to the collecting glassware. Worse, the higher constituents were always contaminated with the dimeric derivative.

The modified collection vent is illustrated in Fig. 1. It was located between the

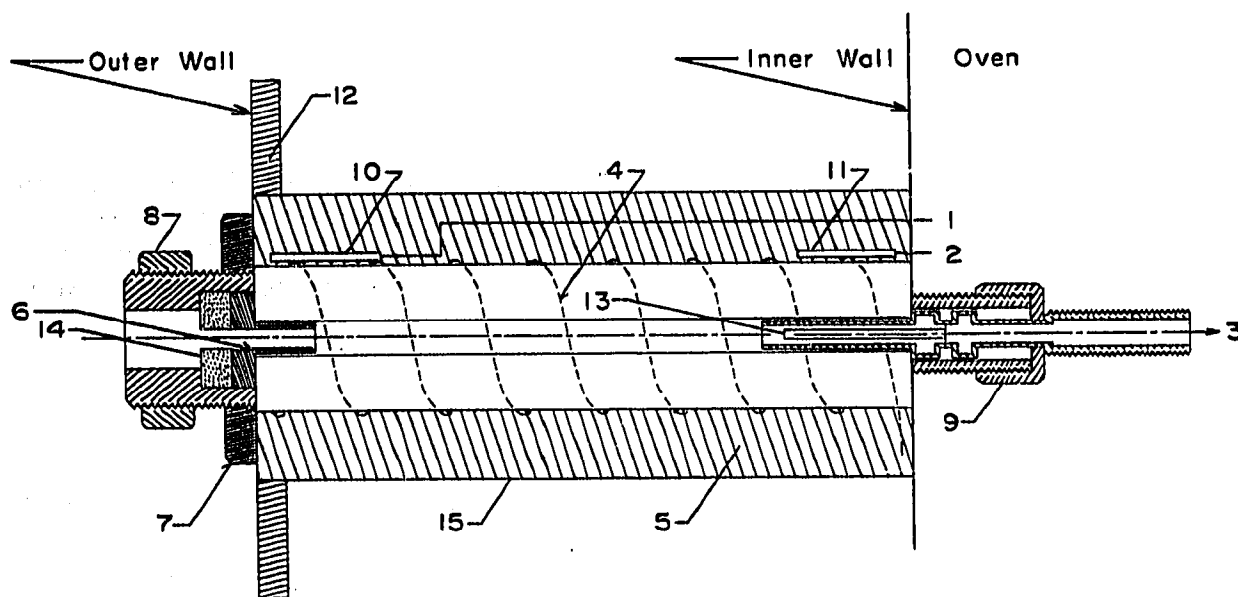


Fig. 1. Modified collection vent. 1, 2 = thermocouple leads; 3 = to column and splitter; 4 = Nichrome winding; 5 = asbestos insulation; 6 = capillary guide-block; 7 = mounting nut; 8, 9 = Swagelok fittings; 10, 11 = protective sheaths for thermocouple junctions; 12 = insulation; 13 = hypodermic needle; 14 = septum; 15 = outer stainless steel housing.

inner and outer walls of the oven. To obtain access to it for collection of samples, the instrument was operated with the outer panel removed.

The vent consisted of a stainless steel block approx. 2 in. long \times 1/2 in. O.D. through which a hole 1/8 in. diameter was drilled axially to receive the collecting tube. The block was lagged with asbestos paper and heated by a Nichrome winding. Samples were collected in pyrex melting-point capillary tubes inserted through a septum and guide-tube on the panel side. The carrier gas issued through a hypodermic needle 13, mounted axially inside a second guide-tube. The needle formed a sliding fit inside the melting-point capillary which, in turn, fitted snugly inside the guide-tube.

Except for the monomeric derivative, which was liquid at room temperature

and was collected in a U-shaped trap, all derivatives were solid and condensed in the straight portion of capillary which projected from the vent. Capillaries were sealed and transferred to the mass spectrometer.

Mass spectrometer. The mass spectrometer was a Bell and Howell/C.E.C. Model 21-110B with electron impact ionization source and ion detection by either photographic plate or collector electrode with electron multiplier. The magnetic scanning mode was modified to have linear m/e vs. time characteristics⁴. The latter feature proved valuable for identification of ions of $m/e > 1200$, *i.e.* beyond the range of the commercially available internal standards used for calibration.

Samples (2–15 μg) were inserted directly into the source using a probe equipped with a heat exchanger⁵ to keep the sample at a temperature (25–150°) such that the steady-state pressure of sample vapour within the ionization chamber would be about 10^{-6} torr. The temperature of the ionization chamber was independently controlled, in the range 150–180°.

The resolution when scanning was 1500–2000. When using the photoplate, or electrical detection for Beynon's "peak-matching" technique, the resolution was approx. 15000. The uncertainty in m/e measurements was within ± 5 p.p.m. when determined by electrical detection and ± 20 p.p.m. from photoplate recorded spectra.

Materials

Hexamethyldisiloxane was purchased from the Columbia Organic Chemicals

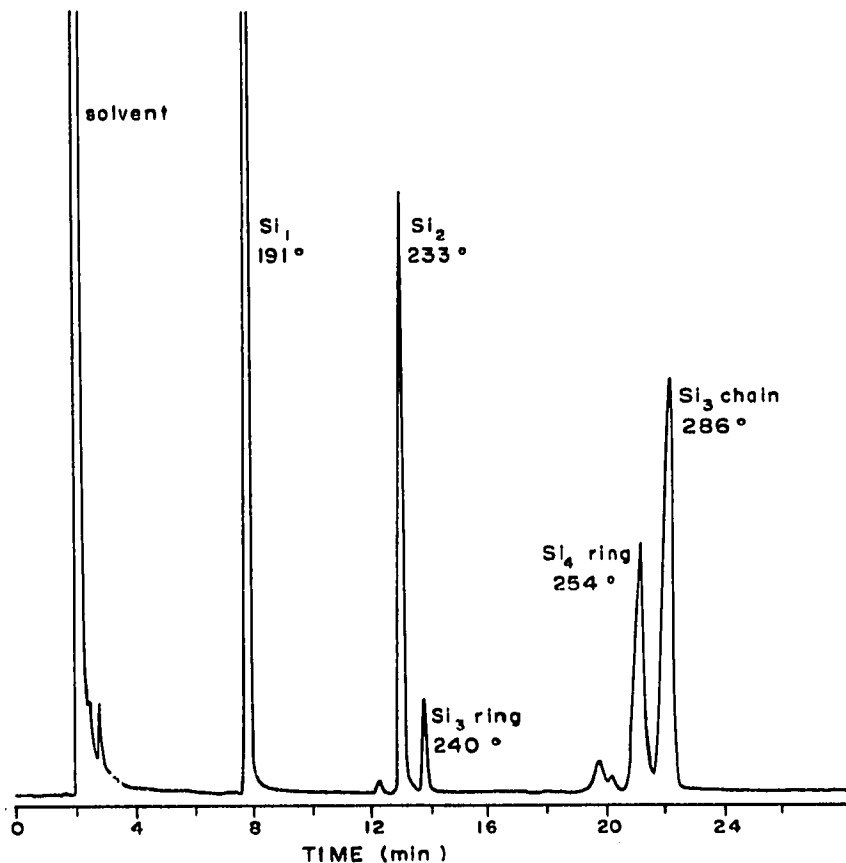


Fig. 2. Separation of TMS derivatives of silicate anions by GLPC.

Co., Columbia, S.C. Isopropanol, from Fisher Scientific Co., was ACS Certified grade. The Amberlyst 15 ion-exchange resin was from Rohm and Haas, Philadelphia, Pa. The source of silicate derivatives was a specimen of natural natrolite, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ from Springfield, Ore., supplied by Wards Natural Science Establishment, Inc., Rochester, N.Y.

Helium carrier gas (Airco) for the chromatograph was passed through a Koby air purifier (Koby Corporation, Melrose, Mass.) to remove water and other contaminants. Hydrogen and air, supplied to the flame ionization detector, were similarly purified.

Procedure

Preparation of TMS derivatives. Derivatives were prepared by the method of LENTZ². Pieces of crystalline natrolite free from base material were ground to pass 100 mesh; 20 g of the powder were added to a reaction mixture of 125 g ice, 150 ml conc. HCl (36%), 300 ml 2-propanol and 200 ml hexamethyldisiloxane which had been stirred at room temperature for 1 h. After adding the natrolite, the reaction mixture was stirred for a further 16 h at room temperature. The mixture was filtered and the siloxane (upper) layer was separated, washed with water, stirred with 2.5 g Amberlyst 15 for 1 h, filtered and stripped to a pot temperature of 115°. The liquid residue in the flask was analysed by GLPC.

Chromatographic analyses. Samples (1–2 μl), were injected directly into the chromatograph. The following conditions were employed:

Helium flow rate	9.1 ml/min
Air flow rate	250 ml/min
Hydrogen flow rate	40 ml/min
Injection port temperature	370°
Flame detector block temperature	430°
Electrometer range	10 ²
Electrometer attenuation	16 to 24

The temperature of the column was programmed as follows:

from 70 to 170°	20°/min
from 170 to 240°	8°/min
from 240 to 300°	2°/min

RESULTS AND DISCUSSION

A typical chromatogram is shown in Fig. 2. The TMS derivatives of the following anions, in the order in which they appeared in the chromatograms, were identified: monomer SiO_4^{4-} ; dimer $\text{Si}_2\text{O}_7^{6-}$; trimeric ring $\text{Si}_3\text{O}_9^{6-}$; tetrameric ring $\text{Si}_4\text{O}_{12}^{8-}$; and trimeric chain $\text{Si}_3\text{O}_{10}^{8-}$. The peaks were sharper than in the original work of LENTZ³ and the resolution of the trimeric chain and tetrameric ring derivatives was considerably improved. Extremely low column bleeding was observed, as indicated by the absence of baseline drift and the absence of detectable amounts of material in mass spectral examination of blanks collected for up to 17 h.

The temperatures at which the various derivatives appeared are shown in Fig. 2. The first part of the time scale corresponds closely to the instrument settings of 20° and 8°/min, but after 240° (14 min) the rate of increase was higher than the setting of 2°/min, due to thermal inertia.

The 70-eV mass spectra of the TMS derivatives of the trimeric chain $\text{Si}_3\text{O}_{10}^{8-}$ and the tetrameric ring $\text{Si}_4\text{O}_{12}^{8-}$ are shown in Figs. 3 and 4. Mass spectra of the other

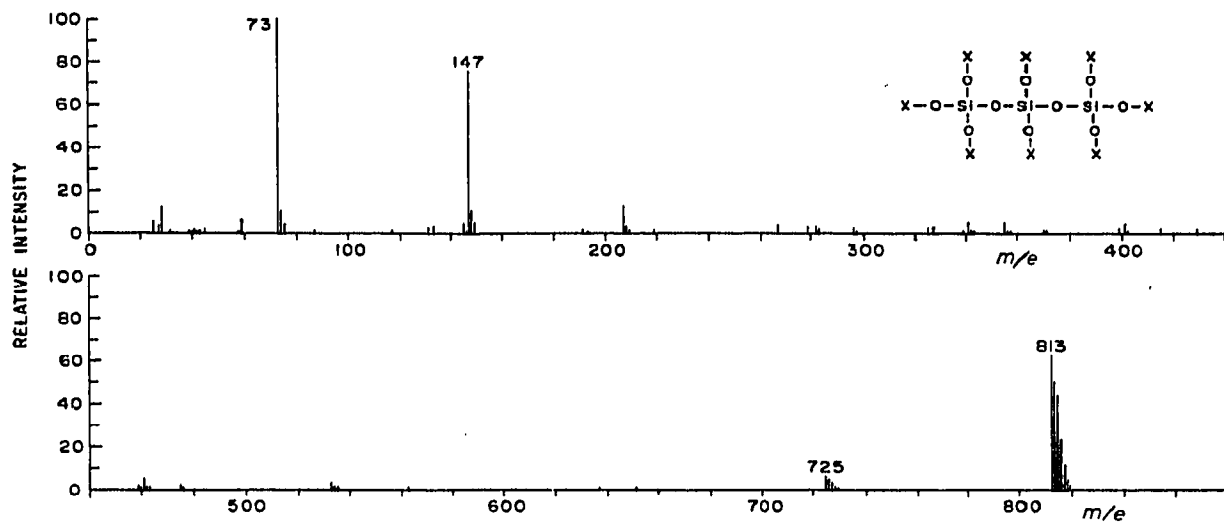


Fig. 3. Mass spectrum of the TMS derivative of $\text{Si}_3\text{O}_{10}^{8-}$. X denotes $\text{Si}(\text{CH}_3)_3$.

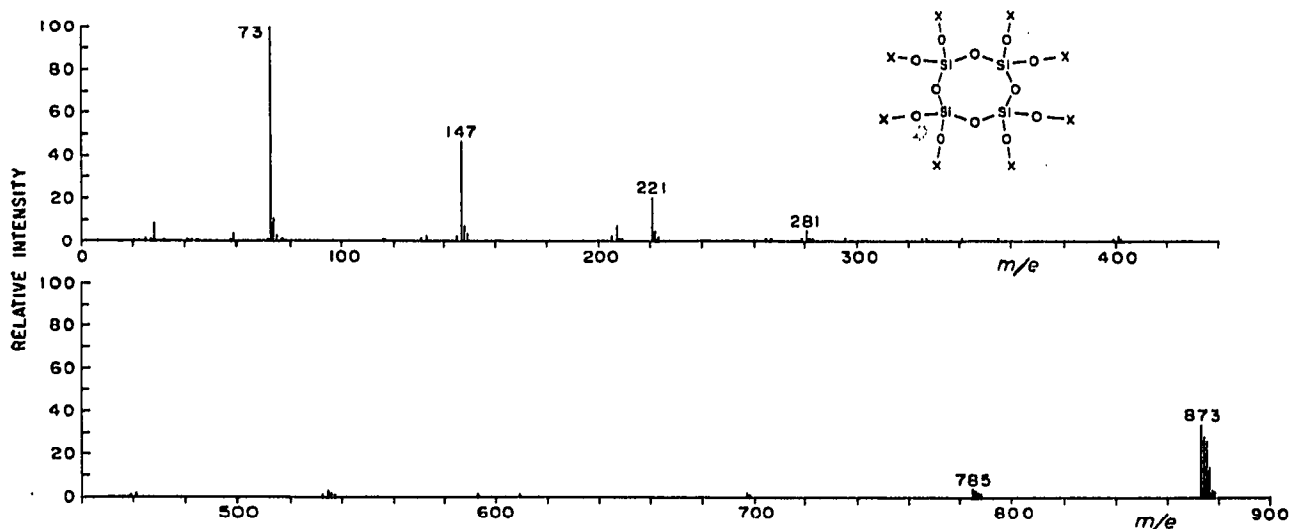


Fig. 4. Mass spectrum of the TMS derivative of $\text{Si}_4\text{O}_{12}^{8-}$. X denotes $\text{Si}(\text{CH}_3)_3$.

derivatives were analogous. Evidently, all these TMS derivatives of silicate anions undergo similar fragmentation following electron impact. The molecular ion is either of very low abundance or not detectable; the major structurally significant ion, 15 m/e units less than that of the molecular ion, is due to the loss of $\cdot\text{CH}_3$. The "base-peak" in these spectra is at m/e 73 [$\text{Si}(\text{CH}_3)_3$] $^+$. Neither this ion nor the abundant ion at m/e 147, due to $[(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_2]^+$, is very useful in identifying TMS derivatives. This is shown also, for example, by the work of BAKER *et al.*⁶ and DE-JONGH *et al.*⁷ for the TMS derivatives of other classes of compounds. Ions of low abundance but structural significance result from further fragmentation of the (M-15) $^+$ ion, either by successive loss of 88 m/e units [loss of $(\text{CH}_3)_2\text{CH}_2\text{SiO}$] and/or

162 *m/e* units [loss of $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$]. 'Metastable peaks' observed in the spectra confirm these reactions by which the $(\text{M}-15)^+$ ion fragments; no 'metastable peak' was observed which would confirm the reaction $\text{M}^{\cdot+} \rightarrow (\text{M}-15)^+ + \cdot\text{CH}_3$.

The combination of GLPC and mass spectrographic analysis offers a powerful tool for the structural elucidation of silicates.

The chromatogram in Fig. 2 does not correspond to that expected from the mineral natrolite, which might have yielded a single peak due to $\text{Si}_3\text{O}_{10}^{6-}$ had its structure been retained during preparation of the TMS derivative². The additional peaks in Fig. 2 are due to side reactions which occur during trimethylsilylation. In the present work the time of trimethylsilylation was deliberately prolonged to yield larger amounts of these by-products, in order to assess the separation procedure. A preliminary account of some of the factors which influence these side reactions, including the effects of time, temperature and acidity of the medium, has been reported elsewhere⁵, and further work with minerals of well-defined structure is in progress to develop a modified procedure in which these undesirable reactions are suppressed or eliminated.

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