TABLE II—P.P.M. SILICON IN COMMERCIAL HAND LOTION

Sample No.	p.p.m. Silicon (Theory)	p.p.m. Silicon Added	Total p.p.m. Silicon (Theory)	Total p.p.m. Silicon (Found)	
1	57.0	None	57.0	56.2	56.8
2	57.0	4.3	61.3	62.0	62.0
3	57.0	10.6	67.6	67.6	67.4
4	57.0	21.2	78.2	80.0	78.0
5	57.0	42.4	99.4	99.0	97.4

from seven samples of octaphenyltetrasiloxane in benzene containing known amounts of silicon (p.p.m.) in the range of 0 to 120 p.p.m. As can be seen in Table I, the relationship of p.p.m. silicon to absorbance is linear in the range described. This linear relationship permits the use of these data in determining the silicon content of unknown samples provided the instrument conditions remain unchanged. Table II contains the data obtained from five samples (each performed in duplicate) of the same lot of hand lotion. In all samples shown, the initial weight of hand lotion was the same. Samples 2 through 5 contain additional known quantities of silicon resulting from the addition of octaphenylcyclotetrasiloxane to the original hand lotion prior to heating and extraction with benzene.

The removal of all water from the sample prior to benzene extraction is necessary since the organic extract exhibits turbidity if water is present during extraction. This turbidity renders the benzene extracts unacceptable for aspiration and results in a $\pm 10\%$ variation for p.p.m. silicon. The ratio of fuel to oxidizer is critical for minimizing background signal and optimizing flame temperature. When the ratio of gases is not optimal, linearity between

p.p.m. silicon and absorbance is lost above 75 p.p.m. silicon. This loss of linearity may be due to the formation of refractory oxides of silicon within the flame during aspiration.

As can be seen in Table II, the method is very reliable and accurate. The heating step to remove water (about 85% in the product examined) requires approximately 30 min. The overall procedure including standard preparations can be performed in approximately 3 hr.

SUMMARY AND CONCLUSION

A rapid, accurate method for the determination of silicon in a commercial hand lotion has been developed utilizing atomic absorption spectroscopy. In concentrations up to 120 p.p.m., silicon absorbance is linear with respect to p.p.m. Critical parameters are the flow rates of fuel and oxidizer, the appearance of the flame, the requirement of complete removal of water prior to extraction with benzene, and the need for frequent aspiration of pure solvent (benzene) to prevent instrument memory.

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☞ *Keyphrases*

Silicon analysis
Dimethylpolysiloxane—determination in lotions
Atomic absorption spectroscopy—analysis
Octaphenylcyclotetrasiloxane—standard

Mannich Bases of Vanillin Oxime

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Synthesis of a group of 5-cycloalkyl- and 5-dialkylaminomethyl derivatives of vanillin oxime is reported. Results of microbiological tests are cited.

PHENOL AND CRESOLS are well-known antibacterial agents of long standing. It has previously been shown that α-dialkylamino-*o*-cresols exhibit significant activity against both bacteria and protozoa (1, 2). From these reports it was postulated that Mannich bases derived from vanillin oxime might fit the structural requirements necessary for possession of some degree of bacteriostatic effect.

Mannich bases were obtained from reaction of the oxime of vanillin with paraformaldehyde and various secondary amines.

EXPERIMENTAL

Vanillin oxime was prepared after the general method stated by Shriner and Fuson (3) and recrystallized from ethanol–water, m.p. 115–117°. Synthesis of phenolic Mannich bases was achieved by the procedure of Burckhalter *et al.* (Procedure I) (2). The hydrochloride salts were recrystallized from solvents listed in Table I.

In the case of compound No. 4, Table I, the solid free base was obtained from the reaction mixture and recrystallized from ethanol, m.p. 181–184°. It gave a correct elemental analysis and was converted to its hydrochloride by treating an ether solution of the amine with ethanolic HCl. The other bases were oils.

pKa values were determined by differential plots of Δ pH/Δ V versus volume of 0.1 N NaOH titrant using approximately 50 mg. of the salt (4).
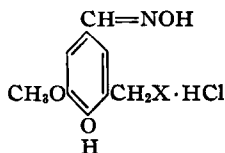
Antimicrobial activity was measured on *E. coli* (A.T.C.C. No. 8739) after a slight modification of the turbidimetric assay method of Eisman and co-workers (5).

TABLE I—MANNICH BASES OF VANILLIN OXIME

$$CH{=}NOH$$

$$CH_3O \quad CH_2X \cdot HCl$$

O
H

No.	X	Yield, %	M.p.,[a] °C.	Formula	pKa	Analyses[b] Calcd.	Found
1	N(CH₃)₂	22	197–199[c]	C₁₁H₁₇N₂ClO₃	7.21	C, 50.7 H, 6.6 N, 13.6	50.5 6.7 13.5
2	N(C₂H₅)₂	56	184–186[d]	C₁₃H₂₁N₂ClO₃	7.14	C, 54.1 H, 7.3 N, 12.3	53.8 7.4 12.0
3	NC₅H₁₀[e]	47	194–196[c]	C₁₄H₂₁N₂ClO₃	7.25	C, 55.9 H, 7.0 N, 9.3	55.6 7.4 9.0
4	NC₄H₈O[f]	62	189–192[d]	C₁₃H₁₉N₂ClO₄	6.52	C, 51.6 H, 6.3 N, 9.3	51.4 6.3 9.1

[a] Melting points are uncorrected. [b] Carbon, hydrogen, and nitrogen analyses are through the courtesy of Mr. Urs Stoeckli. [c] Recrystallized from absolute ethanol–petroleum ether. [d] Recrystallized from absolute ethanol–ether. [e] Piperidino. [f] Morpholino.
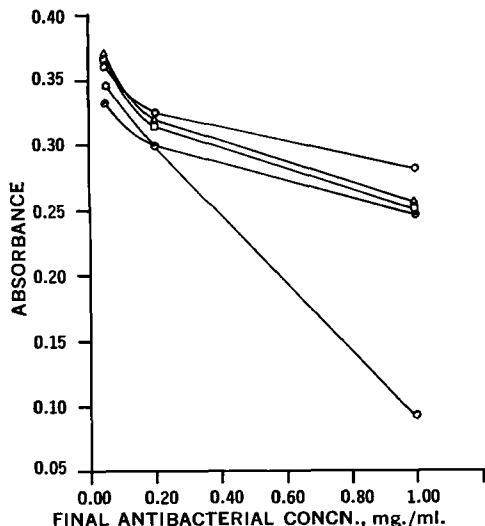

Fig. 1—Plot of absorbance of E. coli *suspension* versus *concentrations of antibacterial substances from Table I. Key:* ●, *compound 1;* □, *compound 2;* △, *compound 3;* ○, *compound 4;* ⊙, *chlorobutanol.*

A stock culture of *E. coli* was maintained on trypticase soy agar slants. The 24-hr. growth from these slants was suspended in sterile 0.9% saline and the suspension adjusted to 10–12% transmission at 580 mμ. A 1.5-ml. portion of this saline suspension was diluted with 100 ml. of trypticase soy broth.

Serial dilutions containing 4.0, 0.8, and 0.2 mg./ml. of the test compounds along with chlorobutanol were prepared in a pH 5.8 phosphate buffer

(USP XVII). Aliquots of these solutions (2.5 ml.) as well as a 2.5-ml. quantity of the pH 5.8 buffer for control were mixed with 7.0-ml. portions of the inoculated broth. The tubes were incubated at 37° until the controls reached an approximate absorbance of 0.350 at 530 mμ. At this point growth was terminated by addition of 0.5 ml. of formalin in water (1:3) to all tubes and the solutions read at 530 mμ. The graph in Fig. 1 shows computed values obtained from 12 determinations.

RESULTS

The four derivatives of vanillin oxime appear to exhibit some inhibitory effect on the test organism. The slopes of the linear portions (Fig. 1) indicate this inhibition to be similar for all four compounds and they are significantly less active than chlorobutanol.

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⊙➤ *Keyphrases*

Vanillin oxime derivatives—synthesis

Mannich bases—5–cycloalkyl, 5–dialkylaminomethyl vanillin oxime derivatives

Antimicrobial activity—vanillin oxime derivatives