

Determination of Silicon in a Commercial Hand Lotion by Atomic Absorption Spectroscopy

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A procedure for the extraction and quantitative determination of silicon by atomic absorption spectroscopy in a commercial hand lotion is described. After the complete removal of water, benzene is used to extract the silicon derivative (dimethylpolysiloxane) from the sample. The benzene extract is then analyzed by atomic absorption spectroscopy utilizing a nitrous oxide/acetylene flame. The method was verified by the addition of known quantities of octaphenylcyclotetrasiloxane to samples of known silicon content prior to extraction. Standard curves obtained by plotting absorbance *versus* p.p.m. silicon were found to be linear in the range of 0 to 120 p.p.m. silicon.

THE RAPIDLY INCREASING utilization of silicone fluids in commercial beauty aids for skin protection has pointed up the need for a more rapid and accurate method to analyze these products for silicon content. The classical acid digestion methods (1) are rather time consuming, and high temperatures are required to convert the silicon completely to silicon dioxide. The infrared methods (2) require considerable sample clean-up and introduce the usual variables encountered with quantitative infrared determinations. This paper describes the suitability of atomic absorption spectroscopy for the determination of silicon in a commercial hand lotion containing approximately 85% water. The method offers both speed and accuracy.

EXPERIMENTAL

Apparatus—A Perkin-Elmer model 303 atomic absorption spectrophotometer was utilized with a fuel mixture of nitrous oxide and acetylene. The high temperatures achieved with this fuel mixture were necessary since silicon is a refractory element. The nitrous oxide flow rate was held at approximately seven at the flowmeter and the pressure regulated to 30 psig at the tank regulator. The acetylene flow rate was held at approximately six using the lower ball in a double ball flowmeter and the pressure regulated to 8 psig at the tank regulator. The flame was considered suitable when the red inner cone attained a height of approximately 1 in. (2.54 cm.). A hollow-cathode silicon lamp was used as the source of emission. The measurement wavelength was approximately 251 μ (maximized) in the ultraviolet region. The instrument was operated with a slit setting of three and a meter response setting of four. These parameters are dimensionless and will therefore vary from instrument to instrument.

Materials—The commercial samples examined in this study were prepared with dimethylpolysiloxane.¹ The dimethylpolysiloxane used in the specific lot of commercial material discussed in this paper was analyzed by atomic absorption spectroscopy and found to contain 38.25% silicon. Octaphenylcyclotetrasiloxane² was used as the internal standard. This material is currently used by the National Bureau of Standards as a primary standard for atomic absorption studies involving silicon. The

material was certified to contain 14.15% silicon. Analytical reagent grade benzene was used throughout this study.

Methods—Samples of hand lotion containing approximately 400 mg. of silicon were weighed accurately into a 250-ml. flat-bottom Pyrex flask equipped with a ground-glass neck. Several glass beads were added and a suitable glass elbow adapter affixed to the flask. The mixture was heated gently until *all* water was volatilized. The residue remaining varied in color from light amber to colorless depending on the rate of heating. The sample was allowed to cool and 100 ml. of benzene was added. The flask was stoppered and the sample extracted for 60 min. on a mechanical shaker. The extract was decanted through a cotton pledget into a 200-ml. volumetric flask. An additional extraction using 50 ml. of benzene was performed for 30 min. in the same manner. This extract was added to the 200-ml. volumetric flask as described above and the flask and cotton pledget were rinsed with sufficient benzene to obtain 200 ml. Three milliliters of this solution was pipeted into a 100-ml. volumetric flask and diluted to volume with benzene. Standards, from which a linear calibration curve was obtained, were prepared by dissolving known amounts of octaphenylcyclotetrasiloxane in benzene.

Internal recovery standards were prepared by mixing samples of hand lotion containing approximately 400 mg. of silicon with known amounts of the octaphenylcyclotetrasiloxane standard. These internal recovery standards were heated to remove all water and extracted with benzene as described above.

The samples and standards were read in an alternate manner throughout this study to verify conformance with the standard curve. The solvent (benzene) was aspirated after each test solution. Each test solution was aspirated three times and the absorbance values averaged.

RESULTS AND DISCUSSION

Table I contains the absorbance data obtained

TABLE I—CALIBRATION DATA FOR P.P.M. SILICON
versus ABSORBANCE

Sample No.	p. p. m. Silicon	Absorbance
1	14	0.0801
2	36	0.2034
3	57	0.3233
4	71	0.4034
5	85	0.4763
6	106	0.5901
7	120	0.6720

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¹ Marketed as SF-96 350 by General Electric Silicone Products Department, Waterford, N. J.

² The authors acknowledge with thanks receipt of this standard material from Dr. R. A. Mansfield of General Electric, Waterford, N. J.

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	56.8
2	57.0	4.3	61.3	62.0
3	57.0	10.6	67.6	67.4
4	57.0	21.2	78.2	78.0
5	57.0	42.4	99.4	99.0

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.

REFERENCES

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Keyphrases

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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 $\Delta \text{pH}/\Delta V$ 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).

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