Quantitative Determination of Titanium in a Commercial Sunscreen Formulation by Atomic Absorption Spectrometry

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Received May 7, 1979, from *Texas Pharmacal Company, San Antonio, TX 78296.* Accepted for publication June 29, 1979.

Abstract □ An atomic absorption spectrophotometric method was developed for the determination of titanium in a sunscreen formulation containing iron oxides and a complex organic base. Matrix matching between the samples and the standard was essential. A recovery study was conducted using a placebo base. Standard absorbance–concentration curves were linear in the 0–120-ppm range.

Keyphrases □ Titanium—analysis, atomic absorption spectrometry, sunscreens □ Atomic absorption spectrometry—analysis, titanium in sunscreens □ Sunscreens—titanium, analysis, atomic absorption spectrometry

Titanium dioxide is an effective sunscreen (1) for the prevention of sunburn and suntan. It reflects and scatters UV and visible light rays, providing a protective physical barrier against the damaging effects of the sun. The increasing use of sunscreens, along with the stringent and changing regulations on their use, makes a simple method for quantitating titanium dioxide desirable.

The commercial formulation[1] examined was a viscous, oil-in-water cream tinted with synthetic iron oxides. The analysis of titanium dioxide in the presence of iron oxides and a complex organic base requires either an intricate separation or a highly specific method to obtain significant results. Atomic absorption spectrometry promises a simple and specific analytical technique for pharmaceutical analyses. This technique offers an accurate and precise alternative to the titrimetric (2) and colorimetric (3) methods used to analyze titanium compounds. No atomic absorption spectrophotometric method was reported previously for the determination of titanium in pharmaceuticals.

EXPERIMENTAL

Equipment—The atomic absorption spectrophotometer[2] was equipped with a heavy solids, nitrous oxide burner head and a single-element titanium hollow cathode lamp[3]. The instrument settings were: wavelength, 364.3 nm; spectral band width, 0.3 nm; lamp current, 10 mamp; nitrous oxide flow, 10 SCFH; and acetylene flow, 9 SCFH.

Reagents—All reagents were ACS or USP grade. Purified water, USP grade, was used to make the solutions and to rinse the glassware.

Titanium Stock Solution—A standard stock solution containing 1000 ppm of titanium was prepared by heating vigorously 1.6681 g of titanium dioxide[4] with 40 g of ammonium sulfate and 200 ml of concentrated sulfuric acid until dissolution was complete. The solution was transferred to a 1000-ml volumetric flask and diluted to volume with purified water.

Iron Stock Solution—A stock solution containing 1000 ppm of iron was prepared by dissolving 0.50 g of iron wire in 20 ml of dilute nitric acid (1:1) and diluting to 500.0 ml with purified water.

Titanium Standards—The titanium stock solution was diluted to 80.0, 100.0, and 120.0 ppm. All standards were made to contain 0.8% (w/v) ammonium sulfate and 16 ppm of iron by the addition of appropriate quantities of ammonium sulfate and the iron stock solution.

[1] A-Fil Cream, Dark, Texas Pharmacal Co., San Antonio, Tex.
[2] Model 651, Instrumentation Laboratory.
[3] Intensitron, Perkin-Elmer.
[4] Pure Atlas White (99.6% pure), H. Kohnstamm and Co.

Table I—Absorbance Data for Standard Titanium Solutions

Solution	Titanium, ppm	Absorbance Trial 1	Trial 2	Trial 3
1	0	0.000	0.000	0.000
2	80	0.175	0.172	0.154
3	100	0.211	0.201	0.182
4	120	0.253	0.237	0.221
Correlation coefficient		0.9996	0.9980	0.9993

Table II—Titanium Dioxide Recovery from Placebo

Sample	Titanium Dioxide, mg Theoretical	Experimental	Recovery, %
1	47.5	48.0	101.0
2	39.6	39.5	99.7
3	49.0	47.9	97.8
4	34.7	35.6	102.6
5	43.3	42.2	97.5
6	37.3	37.3	100.0
Mean			99.8
RSD			1.9

Placebo—A placebo was prepared utilizing the ingredients and the manufacturing procedure prescribed for the commercial product but omitting the titanium dioxide.

Sample Preparation—Known titanium dioxide quantities, 35–50 mg, were weighed into separate 250-ml erlenmeyer flasks. Approximately 800 mg of placebo was added to each flask to approximate the commercial product at various strengths. After the addition of 7 ml of concentrated sulfuric acid and 2.0 g of ammonium sulfate, each flask was subjected to wet oxidation (4) to destroy the organic matter.

Each sample was digested on a hot plate in a fume hood until charring began. After the sample was decomposed initially by the acid, 30% hydrogen peroxide was added, dropwise, until all organic matter was destroyed and the solution was not more than slightly brown[5]. Fifty milliliters of water was added, and the solution was filtered through filter paper[6] into a 250-ml volumetric flask and brought to volume with purified water.

Procedure—The instrument was allowed to warm up for a minimum of 1 hr or until a stable absorbance reading was obtained using the 100-ppm standard. The nebulizer flow, lamp position, fuel flow, and burner head position were adjusted for maximum absorption. The absorbances of the sample and standard solutions were determined alternately, using the 10 read-average mode and 1-sec integration time, to verify conformance with the standard curve.

Each solution was aspirated at least three times, and the absorbance values were averaged. The two-variable linear regression of the absorbance–concentration curve through zero was determined for the standards using a statistical calculator[7]. The calibration curve was redetermined for each sample run.

RESULTS AND DISCUSSION

Table I contains the absorbance data obtained for three typical standard curves; the relationship of titanium to absorbance was linear in the 0–120-ppm range. This linearity permits the use of these data in determining the titanium in unknown samples, provided the instrument conditions remain unchanged.

Table II contains the titanium dioxide recovery data obtained from

[5] The solution was orange until all hydrogen peroxide was removed.
[6] Whatman No. 1.
[7] Monroe 1860.

0022-3549/80/0100-0101$01.00/0

Table III—Iron Interference on 100 ppm of Titanium

Iron, ppm	Absorbance Increase, %
25	2
50	4
100	7
300	11
500	13
1000	13
3000	26

samples of placebo-prepared sunscreen product. In all samples, the placebo weight was the same.

Iron in the presence of sulfuric acid concentrations below 1 *N* was reported to depress titanium absorption (5). Iron at 2000 ppm in the presence of 2% HF enhanced titanium absorption, while iron at 200 ppm had no detectable effect (6). A third study indicated no interference on the absorbance of a 100-ppm titanium sample by 50 ppm of iron but a depression of absorbance by iron above 200 ppm (7). Attempts to determine the degree of interference caused by the presence of iron yielded the results in Table III. The iron amount present in the final dilutions varied from 11 to 22 ppm, depending on the shade[8] of the sunscreen. Iron, 16 ppm, was added to the standards to approximate the quantity in the samples to match the matrix and to minimize enhancement.

[8] Neutral and dark shades; iron levels were determined by the atomic absorption spectrophotometric method.

Examination of the effects on titanium absorption caused by a difference in the ammonium sulfate or sulfuric acid levels between the standards and the samples showed that a twofold increase in sulfuric acid produced a 2% enhancement of absorbance while a twofold increase in ammonium sulfate produced a 3% enhancement.

The fuel to oxidizer ratio was verified to be critical (5); when the flow rate of one gas varied slightly, the flame condition and the titanium absorption value changed significantly.

The described atomic absorption spectrophotometric method for the determination of titanium is simple, reliable, and accurate. The procedure, including standard preparation, can be performed in ~3 hr.

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ACKNOWLEDGMENTS

The author thanks E. L. Anderson for valuable discussions.

Surface Activities of Barbital, Phenobarbital, and Pentobarbital and Their Interaction Energies with Phospholipid Monolayers

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Received December 18, 1978, from the *College of Pharmacy, University of Florida, Gainesville, FL 32610.* Accepted for publication July 3, 1979.

Abstract □ The adsorption free energies of barbital, phenobarbital, and pentobarbital at the air–water interface were estimated from plots of the surface pressure ($\pi \leq 5$ dynes/cm) against the bulk concentration. Their energies of interaction with dipalmitoylphosphatidylethanolamine and dipalmitoyllecithin monolayers spread at the air–water interface were estimated from the surface pressure increase with increasing concentrations of the subphase-injected barbituric acid derivatives. Adsorption free energies and interaction energies were barbital < phenobarbital < pentobarbital, which correlate with their nerve blocking concentration.

Keyphrases □ Barbiturates—adsorption free energy, phospholipid monolayers, barbital, phenobarbital, pentobarbital □ Free energy—adsorption, barbital, phenobarbital, pentobarbital, phospholipid monolayers □ Phospholipid monolayers—adsorption free energy, barbital, phenobarbital, pentobarbital □ Surface activity—barbital, phenobarbital, pentobarbital, interaction with phospholipid monolayers

The interaction energies of procaine, lidocaine, and tetracaine with phospholipid monolayers were correlated recently with their anesthetic and nerve conduction blocking potencies (1).

The present work concerned the surface activities of barbital, phenobarbital, and pentobarbital at the air–water interface and their interaction energies with dipalmitoylphosphatidylethanolamine and dipalmitoyllecithin monolayers spread at the air–water interface.

EXPERIMENTAL

Reagents—Sodium salts of barbital[1], phenobarbital[1], and pentobarbital[1] were used without further purification. Dipalmitoyllecithin[2], dipalmitoylphosphatidylethanolamine[3], the hexane[4] used to prepare the phospholipid spreading solutions, and the water used to prepare the solutions fulfilled the requirements previously specified (2, 3). Analytical reagent grade sodium chloride[1] was roasted for 6 hr at 700° prior to preparation of the aqueous solutions to remove surface-active impurities.

Instruments and Methods—The instruments and methods for the measurement of the surface tension of aqueous solutions (γ) and of the surface pressure change ($\Delta\pi$) of the phospholipid monolayer after drug injection in the subphase already were described (2, 3). The experiments reported here were performed in 0.15 *M* NaCl at 20 ± 1°. In the injection experiments, the initial surface pressure of the phospholipid monolayer was 5 dynes/cm (±0.1 dyne/cm). Surface pressures (π) of the 0.15 *M* NaCl drug solutions were fitted to a function of the logarithm of the drug concentration, *C*, by digital-computerized, nonlinear regression (1, 4). Drug solution densities were determined using 10-ml specific gravity bottles.

RESULTS

Adsorption at Air–Aqueous Interface—Typical plots of the surface pressure (π) against the logarithm of the concentration (*C*, moles per liter)

[1] Mallinckrodt Chemical Works, St. Louis, Mo.
[2] Applied Science Laboratories, State College, Pa.
[3] Schwarz-Mann Research Laboratories, Orangeburg, N.Y.
[4] J. T. Baker Chemical Co., Phillipsburg, N.J.

0022-3549/80/0100-0102$01.00/0