Technical

Determination of Titanium Dioxide in Soaps by Furnace Atomic Absorption Spectrometry

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ABSTRACT

A procedure for the determination of titanium dioxide in soaps by furnace atomic absorption spectrometry is described. The method has the advantage of being rapid and simple. After the soap is dispersed in water, the titanium dioxide content is determined directly without any preliminary treatment with acids and bases to solubilize the titanium dioxide.

Toilet and hard soaps are often formulated with titanium dioxide (TiO_2) for the purpose of making the color tonality of the product uniform and, in the case of white soaps, of increasing the whiteness.

Variables amounts of TiO_2 are generally used, but the optimal concentration range is usually from 0.02 to 0.4% by weight. The quantitative determination of titanium dioxide in soaps is a time-consuming procedure, for the following reasons: first of all it is necessary to separate titanium dioxide from the soap. This is normally accomplished by exploiting its insolubility in alcohol (1). This operation would be sufficient if titanium dioxide were the only substance insoluble in alcohol. In practice, however, other alcohol-insoluble materials are also contained in soap formulations, i.e., carbonates, borates, sulfates, silicates, phosphates, starch, casein, cellulose derivatives and alginates, which are also insoluble in alcohol.

Furthermore, after having separated the alcohol-insoluble matter, titanium dioxide must be digested with strong acids or bases prior to analysis by atomic absorption (2,3) or by colorimetry with hydrogen peroxide or chromotropic acid (4). The analytical method reported herein allows for the quantitative determination of TiO_2 by furnace atomic absorption spectroscopy in a precise and accurate way, without any preliminary separation or acid and/or base digestion.

TABLE I

Graphite Furnace Heating Conditions for Determination of TiO_2

	Program steps					
	1st	2nd	3rd	4th	5th	6th
Temperature (C)	110	800	1000	2800	250	2800
Ramp time (sec)	10	15	2	0	10	2
Hold time (sec)	15	15	10	6	10	5
Integral gas flow (mL/min)	260	260	40	40	–	–
Recorder (sec)				−20		
Baseline				−10		

1st step: sample drying; 2nd and 3rd steps: burning; 4th step: atomization; 5th step: cooling; 6th step: washing of graphite tube.

EXPERIMENTAL SECTION

Apparatus

All atomic absorption measurements were made with a Perkin Elmer Model 360 spectrophotometer at a wavelength of 364.2 nm. Heating of the samples was carried out with a Perkin Elmer graphite furnace HGA 500. Aliquots (20 μl) of sample were delivered to the furnace by means of a precision pipette. Pyrolytic graphite coated tubes were used exclusively. Tubes could be used for more than 60 firings without any visible sign of deterioration but, for safety reasons, only 30 firings per tube were carried out, in order to avoid the accumulation of salts from the sample. Atomic absorption signals were recorded on a Perkin Elmer Model 56 potentiometric recorder.

Reagents

High purity water was used in this work. Solutions were acidified with analytical grade (for atomic absorption) hydrochloric acid. Calibration curve was constructed by means of a standard solution of titanium chloride containing 1 g TI^{4+}.

Procedure

Preparation of titanium standard solution (1000 μg/mL Ti^{4+}). A standard solution containing 1 g Ti^{4+} was adjusted to one liter with 50% (v/v) HCl in a volumetric flask. The solution was stored in polyethylene containers.

Preparation of calibration standard solutions. The standard solution was suitably diluted with water in order to obtain the following concentrations: 0.25 μg/mL, 0.5 μg/mL and 0.75 μg/mL. Analytical operating parameters are shown in Table I.

Preparation of the samples to be analyzed. 1.5–10 g of soap, depending on titanium dioxide content (see Table II), were weighed into a 250 mL beaker and heated with

TABLE II

Indicative Amounts of Soap to be Weighed as a Function of the TiO_2 Content

Soap (g)	%TiO_2
10.0	0.02
5.0	0.04
2.0	0.1
1.5	0.4

TABLE III

Absorbance Value Read for Calibration Curve

Solution µg/mL	Absorbance	Standard deviation (s)
0.25	0.122	0.002
	0.120	
	0.121	
	0.124	
0.50	0.250	0.005
	0.252	
	0.260	
	0.257	
0.75	0.378	0.004
	0.375	
	0.372	
	0.380	

TABLE IV

Percentages, Experimentally Found in Soaps at Known TiO_2 Contents

% Theoretic	% Found	Standard deviation (s)
0.04	0.037	0.004
	0.041	
	0.044	
0.1	0.107	0.003
	0.102	
	0.104	
0.3	0.315	0.017
	0.308	
	0.282	

200 mL at 60 C, with continuous stirring by a magnetic stirrer. The soap solution was transferred into a 5000 mL graduated flask, filled to the mark with water and stirred for 1 hr by a magnetic stirrer. Fractions of 20 µL were taken, at room temperature. The analysis must be carried out under stirring, as TiO_2 is dispersed in a water solution.

Spectrophotometric measurements. After calibration of the instrument, the calibration curve was constructed by introducing 20 µL of each of the standard solutions and relative absorbance values recorded. The unknown samples were then analyzed and, immediately afterwards, for improving the accuracy, the standard solution with the absorbance value closest to that reading for the sample was read again.

The percentage of TiO_2 is obtained from the following expression:

$$\%TiO_2 = \frac{C \times 5000 \times 1.668}{10^6 \times P} \times 100$$

where P = weight (g) of sample, and C = titanium concentrations (µg/mL) of the sample, interpolated on calibration curve.

RESULTS AND DISCUSSION

Absorbance values, obtained for the calibration curve, are reported in Table III. Each standard solution was repeated four times. Relative standard deviation value(s) are reported in the third column of Table III. Values of TiO_2, found in the soaps made in our laboratories and containing known amounts of titanium dioxide, are reported in Table IV. Three analyses were carried out for each sample.

The results show a restricted s values range, considering the low percentage of TiO_2 in the soap product. This variation of the accuracy may be due to the nonhomogeneity of the sample as the drawing of the sample was carried out from a solution in which the insoluble titanium dioxide was kept in suspension by the soap itself. During our experimental work, we realized that titanium dioxide is dispersed in water solutions at very different soap concentrations as a function of the initial weighing of the sample. This situation leads to variations of viscosity and surface tension of the solutions to be analyzed and therefore to the possibility of a nonaccurate drawing of the 20 µL aliquot.

Trials have been carried out in this connection, weighing with an analytical balance, to the sixth decimal place, the amounts of TiO_2 seen in Table II. The results have shown a moderate influence of variations of viscosity and surface tension of the utilized solutions.

A further problem was to verify the validity of the calibration curve made with Ti^{4+} standard solutions in the absence of soap. In other words, we wanted to check the eventual presence of a matrix effect between the readings made with the standard solutions and those of the samples, that obviously contain considerable amounts of sodium ion coming from the soap. Studies carried out on this subject were based on the construction of a calibration curve as previously related, and of another, in which the same amounts of TiO_2 were dispersed in a water solution of soap at an average concentration of 5 g/5000 mL.

The experimental results have confirmed the perfect coincidence of the two curves and this proves the absence of a matrix effect.

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