

Analytical methodologies for atomic spectrometric determination of metallic oxides in UV sunscreen creams

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Abstract

In this study, methodologies for determining titanium oxide, zinc oxide and iron oxide are proposed and assayed in commercial sunscreen products. The proposed methodology for TiO₂ determination in sunscreens is based on a microwave-assisted treatment for digesting the organic components in a closed teflon reactor in presence of HNO₃ and HCl. Titanium is determined by inductive coupled plasma emission spectrometry (ICP-AES). The proposed methodologies for measuring ZnO and Fe₂O₃ are based on a sample emulsification in water with a non ionic tensioactive and IBMK, followed by Zn and Fe determination by flame atomic absorption spectrometry (FAAS). The methodologies allow a precise and accurate determination of metallic oxides in UV sunscreen creams, where the sample treatment is less time-consuming than in the classic methods. To our knowledge this is the first study focused to the determination of metallic oxides in commercial sunscreen products. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The increase in UV irradiation on earth due to the stratospheric ozone depletion represents the major environmental threat to the skin because it increases the risk of photooxidative damage by UV-induced reactive oxygen species [1]. An in-

creased reactive oxygen species load has been implicated in several pathological states, including photoaging and photocarcinogenesis of the skin. A decrease in this species load by efficient sunscreens and/or other protective agents may represent a promising strategy to prevent or minimise induced cutaneous photological states.

Titanium dioxide is the most important physical UV sunscreen currently used because it provides a high level of protection against UVB irradiation and also significant UVA protection.

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Products combining the high UVB protection of titanium dioxide with the high UVA protection of zinc oxide have been also commercialised. Such filters attenuate the UV irradiation by scattering and absorption of the radiation. Sunscreens can also include iron oxide, used to provide colour to the product or sometimes as impurity of rainbow materials. Other formulations seek to increase their protective effect by combining metallic oxides and organic compounds to absorb UV radiation.

The sun protection factor (SPF) of a sunscreen is critically dependent on the amount of product applied and the adequate percentage of active ingredient [2,3]. As the raw materials employed in sunscreen formulations may sometimes not be carefully purified, control of the final composition is a matter of great interest. In spite of that, we found no references to the determination of metallic oxides in commercial samples in the analytical literature. A determination of titanium in synthetic formulations has been published [4]. Such synthetic samples were prepared by addition of TiO_2 to a TiO_2 free placebo cream. The determination was based on a wet oxidation with H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and H_2O_2 , and measurement of atomic absorption using a $\text{N}_2\text{O}/\text{C}_2\text{H}_2$ flame. This is a time-consuming method, but it offers a good recovery.

Microwave-assisted procedures have been described in the literature as a successful pre-treatment of samples. They have been used to accelerate certain organic reactions, such as hydrolysis [5,6], and to improve the digestion of samples [7–10]. We propose here a procedure for digesting sunscreen samples for organic matter destruction by microwave-assisted acid treatment that makes it possible to obtain an inorganic residue easily soluble by acid fusion. Inductive coupled plasma atomic emission spectrometry (ICP-AES) was used to determine titanium.

On the other hand, sample emulsification has been proposed in the atomic absorption spectrometric determination of metallic elements in different types of liposoluble samples, such as oils [11,12] or gasolines [13,14]. Introducing samples and standards into the atomisation systems as emulsions is a compromise between the direct

introduction of organic solutions and prior mineralization [15]. This strategy allows a direct and rapid analysis of samples, avoids the use of large quantities of organic solvents and, moreover, permits inorganic salts or metallic elements to be used in the preparation of standards. Our bibliographic search revealed no references on the use of emulsions in the analysis of sunscreen products. A rapid procedure to determine ZnO and Fe_2O_3 in sunscreen samples based on the emulsification of the sample and air/ C_2H_2 FAAS is proposed here.

2. Experimental

2.1. Instrumentation

A Perkin Elmer, Plasma 2000, inductive coupled plasma atomic emission spectrophotometer equipped with a Technologies Inc., V-6000, ultrasonic nebulizer, was used for titanium determination. The experimental conditions were wavelength, 334.941 nm; plasma height, 15 mm; photomultiplier gain, 600 V; power, 1200 W; ultrasonic nebulizer flow, 0.650 l min^{-1} ; auxiliary flow, 0.5 l min^{-1} ; plasmogen flow, 15 l min^{-1} ; pump flow, 2.5 ml min^{-1} .

A Varian, SpectrAA-10, atomic absorption spectrophotometer was used for zinc and iron determinations. Instrumental parameters for zinc were wavelength, 213.9 nm; lamp current, 7 mA; slit width, 1 nm; burner height, 10 mm; air/ C_2H_2 flow ratio, 3.5:1.5. Iron absorbance was measured at these conditions wavelength, 248.3 nm; lamp current, 7 mA; slit width, 0.2 nm; burner height, 5 mm; air/ C_2H_2 flow ratio, 3:1.

An Ignis AKL530/IG/WH microwave oven, with rotating turntable, 2450 MHz magnetron and a nominal exit power of 800 W was employed to digest the samples. A 20 ml capacity Macharey-Nagel PTFE microwave reactor (provided by Aquatecnica S.A.) with security expansion chamber sealed with PFA and PTFE dishes was used to irradiate samples; this system makes it possible to avoid breaks in the reactor or leaks if overpressure occurs during the experiments.

2.2. Reagents and samples

A Titrisol 1000 mg l⁻¹ titanium stock solution was used to provide standard calibration solutions.

Zinc (1000 mg l⁻¹) and 1000 mg l⁻¹ iron stock solutions prepared from the metallic elements (Merck) were used to provide standard calibration solutions.

Analytical-reagent grade HNO₃, HCl, KHSO₄ and H₂SO₄ were used in the digestion and acid fusion of the samples.

Nemol K-39 (Massó y Carol) and isobutyl methyl ketone (IBMK) (Scharlau) were used for sample emulsification.

The commercial sunscreen samples analysed were (1) Protectrem (Lab. OTC Ibérica); (2) Fotoprotector Isdin, extrem (Lab. Isdin); (3) Sensilis (Lab. Dermofarm); (4) Lutsine (Lab. Lutsia); (5) Avène, crème écran extrême (Lab. Dermatologiques Avène); (6) Helioderm dermatica (Lab. Isdin). The composition of these creams is very complex, because they contain a great number of ingredients. All the samples contain TiO₂. Samples 1, 5 and 6 also contain ZnO and Fe₂O₃.

2.3. Reference procedure

A classic sample treatment procedure was used as a reference to test the accuracy of the proposed methodologies. Considering that the commercial samples to be analysed have a large organic matter content, and that TiO₂ must be desegregated in order to assure its solubilization and satisfactory atomisation, two pre-treatments were carried out; digestion of the organic matter and desegregation in the case of samples containing TiO₂. However, for free TiO₂ samples only digestion was considered necessary. The reference procedure used for comparative purposes was as follows. Sunscreen (0.5 g) was weighed in a porcelain crucible, and heated on a low Bunsen flame (for approximately 50 min). The intensity of the flame was increased and heating continued to obtain a carbon-free ash (approximately 30 min). Concentrated HNO₃ (1 ml) was added, evaporated and then the crucible was introduced into an electric

furnace at 500°C for 1 h. The crucible was let to cool, 1 ml of concentrated HCl was added and the mixture was heated for a few minutes with a Bunsen burner. For free TiO₂ samples, this residue was let to cool and diluted appropriately to carry out the determination. If TiO₂ was present, after HCl addition, the residue was evaporated, 2 g of KHSO₄ was added and fusion was done at the Bunsen flame in a few minutes; the molten product was dissolved in hot concentrated H₂SO₄ and diluted to carry out the determination. Ti was determined by ICP-AES and the determinations of Zn and Fe were done by FAAS. Aqueous solutions of these elements were used as standards. It should be pointed out that due to the large percentage of organic matter in the samples, initial heating of the samples should be gently done because an abrupt increase in the temperature can cause projections of the samples.

2.4. Microwave procedure

Sample (0.15 g) was weighed into a PTFE reactor for microwave-assisted digestion, 0.5 ml of concentrated HNO₃ was added, and the mixture was irradiated at 600 W for 1 min. The reactor was let to cool, 0.5 ml of concentrated HCl was added and an irradiation of 1 min was carried out again at the same power. The reactor was let to cool, and other step of irradiation during one more minute under the same conditions was done. The digestion product was transferred to a porcelain crucible, 0.5 g of KHSO₄ was added and the mixture was heated with a Bunsen flame during a few minutes for fusion, the molten was dissolved in concentrated H₂SO₄ and the solution was diluted appropriately with deionized water to carry out the determinations of Ti by ICP-AES.

2.5. Emulsification procedure

A sample (0.04–0.2 g) was weighed, 2 ml of IBMK and 0.8 g of Nemol K-39 were then added, the mixture was shaken and diluted up to 50 ml with deionized water. Zn and Fe were determined by FAAS using aqueous standards.

Table 1
Effect of the acid microwave treatment on the accuracy of the results

Experiment	Step 1	Step 2	Step 3	E_r (%)	R (%)
A	0.5 ml HNO ₃ 600 W, 1 min	0.5 ml HNO ₃ 600 W, 1 min	–	14.3	83.2
B	0.5 ml HNO ₃ 600 W, 1 min	0.5 ml HCl 600 W, 1 min	–	9.3	89.4
C	0.5 ml HNO ₃ 600 W, 1 min	0.5 ml HCl 600 W, 1 min	600 W, 1 min	1.4	99.8
D	0.5 ml HNO ₃ 800 W, 1 min	0.5 ml HCl 800 W, 1 min	–	1.2	99.6

3. Results and discussion

3.1. Determination of TiO₂ by ICP-AES after microwave-assisted digestion of the sunscreens

3.1.1. Study of the microwave conditions

In order to optimise the experimental conditions for the microwave-assisted digestion, a study of the acidity (HCl and/or HNO₃) and the irradiation time was done.

A commercial sunscreen (sample 1) previously analysed by the reference method described above was used for comparative purposes. As can be seen in Table 1 (relative errors and recovery of the method), the best results were obtained with three irradiation steps — 1 min of irradiation with HNO₃ was followed by an addition of HCl and two irradiation steps of 1 min each. Volumes of 0.5 ml of each acid were enough to effect a complete destruction of the organic matter working at 600 W. Less than 3 min or less than 600 W did not give a good accuracy. Assays at 800 W (power limit of the oven) produced total mineralization in 2 min, but in some cases the safety dishes burst. For this reason more than 600 W is not recommended.

3.1.2. Analytical application

The mean recovery of the method for the six samples analysed by the proposed conditions was $101 \pm 4\%$.

Table 2 shows the results obtained for TiO₂ determination by both the reference and the proposed method.

The relative standard deviation of the TiO₂ content was in the 0.6–5% range.

A paired *t*-test [16] was applied to these data to evaluate the accuracy of the proposed method.

The confidence interval (tS_D/\sqrt{N}) was calculated, (where *t* is the Student's statistic for *N* – 1 degrees of freedom and a 95% confidence level, *N* the number of sunscreens analysed, and *S_D* the standard deviation of the mean of the differences \bar{D} , between the values obtained by the proposed and the reference methods). The value of the mean of the differences \bar{D} was lower than the confidence interval calculated, which indicates that the results obtained by the proposed method were comparable to those obtained by the reference method.

This indicates that other components of samples do not cause matrix interferences and the selectivity of the method is adequate for titanium determination.

Standard solutions from 0.2 to 2 µg ml⁻¹ were used for calibration. The sensitivity estimated from the slope of the calibration line of the ICP-AES determination of Ti, was in the order of 10^{+5} µg⁻¹ ml (Table 3).

The limit of detection of the ICP-AES determination of Ti was estimated as $3s_{y/x}b^{-1}$ (where *s_{y/x}* is the standard deviation of the calibration line and *b* the slope). It was in the order of 0.035 µg ml⁻¹ (Table 3).

Table 2
Determination of TiO₂ in commercial sunscreen samples

Sample	TiO ₂ (%) ^a	
	Reference method	Microwave method
1	2.81 ± 0.02	2.78 ± 0.04
2	1.368 ± 0.007	1.31 ± 0.03
3	0.65 ± 0.02	0.50 ± 0.01
4	1.61 ± 0.05	1.61 ± 0.01
5	10.88 ± 0.09	12.5 ± 0.3
6	4.91 ± 0.02	5.80 ± 0.03

^a Mean value ± standard deviation of the mean.

Table 3
Intercepts (*a*) and slopes (*b*) of the calibration lines

Determination	Intercepts ($a \pm s_a$)	Slopes ($b \pm s_b$)
ICP-AES, Ti	$3 \times 10^{+3} \pm 1 \times 10^{+3}$	$1 \times 10 \pm 2 \times 10^{+3}$
AAS, Zn	$8 \times 10^{-3} \pm 2 \times 10^{-3}$	$2 \times 10 \pm 3 \times 10^{-3}$
AAS, Fe	$6 \times 10 \pm 3 \times 10^{-4}$	$8 \times 10 \pm 8 \times 10^{-5}$

From our results it can be concluded that the proposed microwave-assisted digestion methodology permits a large decrease in the sample treatment time as compared with the classical organic matter destruction procedures, and provides accurate results.

It is worth mentioning that analytical methodologies based on the direct solution of liposoluble samples in an organic solvent require the use of organometallic compounds as standards and flame fluctuations are produced due to the high organic content of the solutions. Moreover, conventional creams can be dissolved, but those composed of metallic oxide particles in suspension, such as physical UV sunscreen creams can not. Other direct procedures such as slurry and/or emulsification of samples gave results for TiO₂ that were lower than the real ones due to the low atomisation yield. On the contrary, a methodology like the one proposed here constitutes a possible alternative to the classic procedures, rapid and accurate for analysis of TiO₂ in sunscreen samples.

3.2. Determination of ZnO and Fe₂O₃ by emulsification of the sunscreens and FASS

3.2.1. Study of the sample emulsification

In order to select the most adequate methodol-

ogy for preparing stable emulsions, different reagents and ratios were assayed.

Nonylphenol polyethylenglycol ethers are well known tensioactives, which provide good hydrophilic–lipophilic balances (HLB) [15] for emulsion prepared from different liposoluble matrices. Three commercial compounds (Nemol) of the same chemical family with different degrees of condensation were subjected to a preliminary assay. All of them provided stable emulsions during the time required to carry out the analysis. Nemol K-39 was used in the analysis of the commercial sunscreen creams.

The weight of samples assayed ranged from 0.01 to 0.2 g. No effect on the stability of the emulsions was observed.

The Nemol K-39 percentage assayed ranged from 0.4 to 2%. Up to 0.8% the emulsions were stable. The percentage of IBMK assayed was from 1 to 5%. It was found that for percentages lower than 2% the preparation of the emulsion was more difficult, but once the emulsion was formed, it was stable.

3.2.2. Analytical application

Table 4 shows the results obtained for ZnO and Fe₂O₃ determination by both the reference and the proposed method.

The relative standard deviation of the ZnO contents was in the 1–9% range, and for Fe₂O₃ it was 0.4–0.7%.

The same paired *t*-test [16] used for TiO₂ was applied to these data to evaluate the accuracy of the proposed method. The results obtained by the proposed method for ZnO and Fe₂O₃ were statistically comparable to those obtained by the reference method. Then, if the selectivity is adequate

Table 4
Determination of ZnO and Fe₂O₃ in commercial sunscreen samples

Muestra	ZnO (%) ^a		Fe ₂ O ₃ (%) ^a	
	Reference method	Emulsion method	Reference method	Emulsion method
1	3.40 ± 0.07	3.34 ± 0.07	0.76 ± 0.05	0.73 ± 0.04
5	2.20 ± 0.04	2.27 ± 0.07	0.186 ± 0.006	0.21 ± 0.01
6	0.213 ± 0.002	0.22 ± 0.02	0.104 ± 0.002	0.109 ± 0.002

^a Mean value \pm standard deviation of the mean.

for the zinc and iron determinations, the method is accurate.

These results show that aqueous solutions of Fe^{3+} and Zn^{2+} can be used as standards. This is particularly interesting from a chemical point of view in the case of iron. Unpublished results demonstrate that in emulsified samples, the atomisation yield of Fe^{3+} is higher than Fe_2O_3 particles, and consequently higher than the yield of Fe^{3+} in aqueous samples. From this fact it can be deduced that the atomisation yield of Fe^{3+} is affected by the emulsificant reagents, but this effect is not appreciable when the iron in the sample is in the form of Fe_2O_3 particles. For this reason, the study of the recovery is not feasible in this case because it could provide erroneous information about the accuracy of the method, since (a) aqueous standard solutions can not be used because their behaviour can not be compared to that of oxide particles present in the samples, (b) addition of pure oxide particles to the samples as standards is not possible either, because incorporation of the oxides to the final formulations does not provide stable dispersions. On the other hand, accuracy of the proposed method is well proved from the results obtained by the reference method.

Aqueous solutions from 0.1 to 1 $\mu\text{g ml}^{-1}$ were used as standards for Zn and from 0.5 to 4 $\mu\text{g ml}^{-1}$ for Fe. The sensitivity was in the order of 0.2 μg^{-1} ml for Zn and 0.08 μg^{-1} ml for Fe.

The limit of detection was 0.03 $\mu\text{g ml}^{-1}$ for Zn and 0.02 $\mu\text{g ml}^{-1}$ for Fe.

If the analytical features presented here are considered, the simplicity of the preparation of the emulsion, the low content of organic solvent required, and the fact that aqueous standards can be used, it can be stated that this emulsification procedure constitutes an advantageous and rapid alternative for analysis of ZnO and Fe_2O_3 in sunscreen samples.

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