



## Multi-element method for determination of trace elements in sunscreens by ICP-AES

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### ABSTRACT

An inductively coupled plasma atomic emission spectrometric (ICP-AES) method was developed for multi-element analysis of sunscreen creams and lotions. The objective was the simultaneous determination of Ti ( $\text{TiO}_2$  being the only authorized inorganic UV filter in the European Union) and several minor, trace or toxic elements (Al, Zn, Mg, Fe, Mn, Cu, Cr, Pb and B) in the final products. Two alternative pretreatment procedures were examined: (i) total acid digestion in closed pressurized vessels prior to sample introduction into the plasma and (ii) direct introduction of sample in the form of emulsified slurry. The latter was proved inefficient for several types of creamy samples due to their high viscosity and insolubility. Several acid mixtures were examined for wet digestion because of the complex and fatty matrix of creams and lotions. Plasma parameters like nebulizer argon gas flow rate and radiofrequency incident power were optimized in order to improve the atomization. The recovery of the proposed acid digestion method was evaluated using spiked samples. The calculated recoveries were 95.0% for Ti, 98.2% for Zn and 101.3% for Fe, and the detection limits were  $0.2 \mu\text{g g}^{-1}$  for Ti,  $0.2 \mu\text{g g}^{-1}$  for Zn and  $0.5 \mu\text{g g}^{-1}$  for Fe, respectively. Possible interference from the presence of Ti on the sensitivity of each analyte was examined. Finally the method was applied successfully to several commercial sun protection products and the results were compared with those obtained by atomic absorption spectrometry as reference method.

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### 1. Introduction

Sunscreen products are widely used to prevent sunburn, reduce premature photo-ageing and skin cancer risk and allow tanning and longer exposure to sunlight [1,2]. The active sunscreen agents are classified in two categories (i) inorganic UV filters which reflect scatter or absorb broadband the UV radiation and (ii) organic UV filters which attenuate solar UV rays by absorbing the radiation and are classified in two groups as UVA and UVB filters [3–5]. Various formulations containing combinations of inorganic and organic UV filters were developed aiming to improve the protective effect and sunscreen efficacy against both UV-B (290–320 nm) and UV-A (320–400 nm) radiation.

The regulatory authorities in the European Union and USA [6–8] have established lists of the authorized UV filters and the corresponding maximum allowed concentrations in the final products [9]. In these lists, only titanium dioxide is an inorganic UV filter, sometimes called physical UV filter, and it is applied in the form of micronised pigment of  $\text{TiO}_2$  which is easily incorporated in emulsions.

The analysis of the sunscreen cosmetics is required since sun protection factor (SPF) is related to the content of UV filters in the commercial products [10]. There is also necessity to ensure that the concentration levels of metals and oxides are lower than the established limits, since there are several known undesirable dermatological side-effects mainly from organic UV filters [1,5].

For inorganic UV filters like titanium dioxide, Schulz et al. [11] found that there is no evidence of skin absorption. Although titanium and zinc oxides are considered as inert substances without ability to penetrate stratum corneum [2,12] several other reports are contradictory [5]. There is a concern about the photocatalytic activity of titanium or zinc oxides, which facilitates the generation of reactive oxygen and hydroxide radicals. The research in the field of inorganic UV filters is continuous towards deactivation of titanium oxide by coating with  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  [5], while Yabe and Sato [13] investigated cerium oxide as an alternative to titanium and zinc oxides inorganic UV filter.

Many products containing titanium dioxide and zinc oxide have been commercialised, and several sunscreens can also include iron oxide in order to improve the skin color appearance. As it is mentioned above, it is generally assumed that the sun protection factor (SPF) of a sunscreen is dependent on the amount of product applied and the percentage of active ingredient(s) [10]. Analytical control of the final composition is a matter of great interest because the raw materials employed in sunscreen formulations may sometimes not

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be carefully purified [4]. Consequently, reliable and fast methods are required to check whether they conform to existing legislation and also for quality control purposes. There are no official methods to determine these inorganic constituents in sunscreen cosmetics. In addition to Ti and Zn, other metals like Cr, Cu, Mn, Pb, etc. are also of importance and must be determined in such skin products due to their allergic or toxic properties. It is interesting that not more than 80 papers have been published for all types of sun care products analysis in the period 1976–2004 as described in a critical review by Salvador and Chisvert [1]. However, the majority of the reports refer to organic UV absorbers by liquid chromatographic (LC) methods [1,8,9,14–17] and very few to inorganic UV filters [4,18–20].

Despite of the fact that sunscreen products contain usually more than one metal oxides either as inorganic filters or other constituents, few analytical methods have been reported in the literature for multi-element analysis of commercial sunscreens. Inductively coupled plasma techniques (ICP-AES and ICP-MS) are very convenient multi-element tools for routine analysis applicable to a wide variety of applications including cosmetic and pharmaceutical, because they offer the significant advantage of improved sensitivity and selectivity as compared to other techniques [20–24].

Titanium was determined in sunscreen creams for first time by Mason [18]. Atomic absorption spectrometry (AAS) was applied and the samples were decomposed with a mixture of sulphuric acid, ammonium sulphate and hydrogen peroxide. Based on ICP-AES determination, several acidic mixtures including nitric, phosphoric or hydrofluoric acids were comparatively tested for their efficacy in dissolving titanium dioxide [19]. Titanium could be also determined by ICP-AES after acid digestion in a microwave oven, followed by fusion of the titanium dioxide with  $\text{KHSO}_4$ , and finally dissolving the residue in concentrated sulphuric acid [4]. Zinc and iron were determined independently by flame AAS after emulsion formation of the samples with isobutyl methyl ketone (IBMK) and Nemol as surfactant [4]. XRF compared to ICP-AES was also used for titanium in cosmetic products [20].

Direct introduction of solid or oily matrices in the form of a slurry or an emulsion is an alternative technique to the acid digestion of the sample, and sometimes offers significant advantages [21–22]. Time-consuming digestion steps and possible losses or contamination are avoided by slurry introduction. The slurry introduction technique requires a suitable nebulization system and careful adjustment of plasma parameters in order to achieve robust conditions. However this is not always possible for emulsion-type slurries, like those obtained from sunscreen creams.

The objectives of this work were to develop and optimize methods of simultaneous determination of the most common inorganic UV sunscreen agents like titanium, zinc and iron as well as several other elements likely to be found in sunscreen cosmetics. Also there is a constant interest to monitor any trace of toxic elements in commercial products, and for this reason, the developed method included the determination of toxic heavy metals, e.g. lead and chromium, which must not be present in cosmetics [25]. The performance of three digestion procedures was examined for quantitative multi-element analysis of sunscreen creams. Alternatively direct introduction of the sample as emulsified slurry into the nebulization system of inductively coupled plasma was studied. The performance characteristics of the proposed method were evaluated and compared to the results obtained after conventional acid digestion of the sunscreen creams.

## 2. Experimental

### 2.1. Instrumentation

An axial plasma spectrometer model PerkinElmer Optima 3100 XL was used according to the operating conditions described in

**Table 1**  
Operating conditions and instrumentation of the ICP-AES.

Parameter	Value
RF generator	40 MHz, free-running
RF incident power	Optimized (1500 W)
Torch type	Fassel type
Injector, id	Alumina, 2.0 mm
Viewing mode	Axial
Auxiliary argon flow rate	0.50 l min <sup>-1</sup>
Nebulizer argon flow rate	0.80 l min <sup>-1</sup> (optimized)
Plasma gas flow rate	15 l min <sup>-1</sup>
Spray chamber type	Cyclonic
Sample propulsion	Peristaltic pump, three channel
Sample uptake flow rate	2 ml min <sup>-1</sup>
Detector	Segmented-array charge-coupled (SCD)

**Table 1.** The injector was made from alumina, which is sufficiently resistant to acidified and hydrofluoric solutions. Otherwise such solutions may deteriorate the injector tube and impact the final results. A peristaltic pump was used to introduce sample solutions into the ICP-AES at a flow rate of 2 ml min<sup>-1</sup>. Tygon type PVC peristaltic pump tubes were used for sample delivery. A cyclonic spray chamber with a cross-flow nebulizer was employed to allow higher rates of sample introduction into the plasma. Several analytical wavelengths were investigated for each analyte, as they are listed in Table 2. Yttrium at a concentration of 2 mg l<sup>-1</sup> was added in aqueous standards, spiked and not spiked samples and was used for internal standardization. Three yttrium spectral lines were examined as given in Table 2, and all of them were more than 2 nm far from any analyte spectral line. Among them, the yttrium line at 371.029 nm was finally selected. All results were corrected by reference to yttrium emission.

A PerkinElmer 5100 atomic absorption spectrometer was employed for independent measurement of metal content of sunscreens, using for each analyte the flame conditions recommended by the manufacturer (oxidizing flame for all analytes except Cr for which a reducing flame is needed). The instrument could be operated either with flame atomization (FAAS) for Mg or with electrothermal atomization (ETAAS) for Ti, Al and Zn, respectively. In ETAAS mode the Zeeman background correction method was employed. Transversely heated graphite tubes were used, 300 ml min<sup>-1</sup> argon flow rate and stopped-flow mode during atomization step. Magnesium, titanium, aluminum and zinc were measured using the following analytical lines 285.2, 365.4, 309.3 and 213.9 nm, respectively. The drying step was fixed to 130 °C (15 s hold time). The charring temperatures in the graphite furnace were Al/1300 °C/25 s hold time, Ti/1200 °C/25 s hold time and Zn/1200 °C/25 s hold time. Finally, the atomization temperatures in the graphite furnace were 2600, 2700 and 2500 °C for Al, Ti and Zn, respectively and a 7 s read time was adjusted for measurements at stopped-flow mode of argon gas.

**Table 2**  
Spectral wavelengths studied for ICP-AES measurements.

Element	Spectral line (nm)			
Al	237.313	308.215	309.271	394.401
Ti	334.940	336.121	337.279	368.519
Zn	213.857	202.548	206.200	334.501
Mg	279.077	280.271	285.213	279.553
Fe	238.204	259.939	234.349	
Cu	324.752	224.700	327.393	213.597
Mn	257.610	259.372	260.568	294.920
Cr	283.563	284.324	267.716	357.869
Pb	220.353	217.000	283.306	
B	249.772	249.677	182.589	208.957
Y	371.029	360.073	361.104	

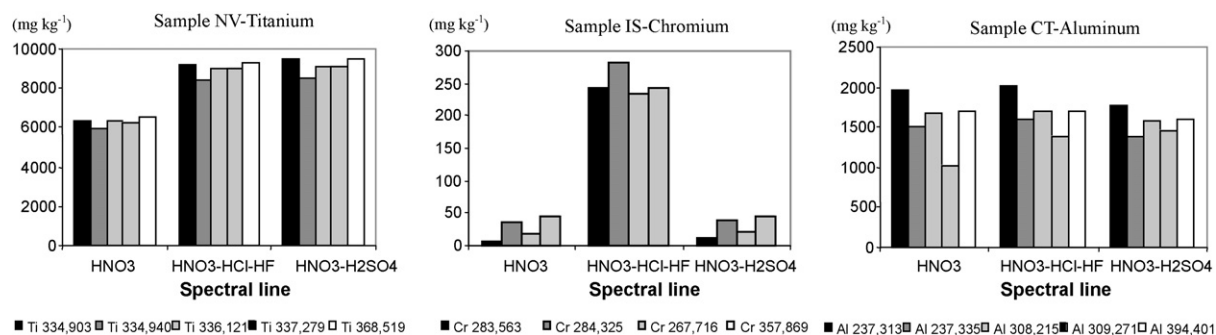


Fig. 1. Study for the effectiveness of wet-acid digestion using various acid mixtures. Representative results from three commercial suncare products spiked with 10.00 mg g<sup>-1</sup> Ti, 250 μg g<sup>-1</sup> Cr and 2000 μg g<sup>-1</sup> Al.

## 2.2. Reagents and solutions

Ultra pure water of Milli-Q quality (18.2 MΩ, Millipore, Bedford, USA) was used. Concentrated HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> and HF used for wet digestion were of analytical grade and were obtained from Merck (Darmstadt, Germany). The single-element standards used for preparation of multi-element standards were NIST traceable. Triton X-100 was used as surfactant for slurry formation. A working standard solution containing 10 mg l<sup>-1</sup> of all the above listed analytes was prepared by mixing suitable aliquots of single-element stock solutions (Merck) containing Al, B, Cr, Cu, Fe, Mg, Mn, Pb, Ti, Zn, 1000 mg l<sup>-1</sup> each and appropriate dilutions. All solutions were stored in polyethylene bottles in the refrigerator. The above solution was further diluted in 0.5 M HNO<sub>3</sub>, to obtain a series of lower concentration standards (0, 10, 50, 100, 200, 500, 1000, 2500, 5000, 10000 μg l<sup>-1</sup> for each analyte). The compatibility and storage stability of the above elements multi-element standard solution was checked for a period of 48 h, and no precipitation or turbidity was observed. Finally, a calibration test of the stored multi-element standard against a freshly prepared one showed no analyte losses. Six-point calibration curves were prepared.

The performance of the standard additions procedure was examined by using aqueous standards as diluents for preparation of emulsified slurries. The slope of the regression lines was used to estimate the sensitivity in all cases. Furthermore, a series of matrix-matched standards with similar analyte concentration range and acidity was prepared. These standards contained 4.0% (m/m) glycerol, 3.0% cetyl alcohol and 2.0% (m/m) stearic acid (Merck, Darmstadt, Germany), respectively, in de-ionized water. Yttrium was added in a final concentration of 2.00 mg l<sup>-1</sup> to act as an internal standard.

## 2.3. Wet-acid digestion of sunscreen creams

Samples of sunscreen creams or lotions were collected from the market (coded as NA, NV, CT, IS, GN, KR, SB, AF, OS), and the ingredients written on the label were recorded. The samples were acid digested in closed poly-tetrafluoroethylene (PTFE) vessels. Three acid digestion mixtures were tested: (i) 6 ml of concentrated HNO<sub>3</sub>, (ii) 3 ml of concentrated HNO<sub>3</sub>, 3 ml of concentrated HCl and 1 ml of HF and (iii) 5 ml of concentrated HNO<sub>3</sub>, 1 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. An accurately weighed portion of the sample, ca. 100–150 mg, was placed into PTFE vessel, with the subsequent addition of the acid mixture. The vessels were closed, placed into a steel pressurized bomb and heated up to 125–130 °C for 2 h. The final digest was diluted to volume with 0.5 M HNO<sub>3</sub>. The final solutions were analyzed by ICP-AES against acidified aqueous standards. All glassware and digestion vessels were soaked in freshly prepared 10% (v/v) HNO<sub>3</sub> all night, and finally washed five times with Milli-Q quality water.

## 2.4. Emulsified slurry formation of sunscreen creams

Slurry emulsions of the samples were prepared in 0.5 M HNO<sub>3</sub> diluent solution, containing 1% (m/v) sunscreen cream and 0.5% (v/v) of Triton X-100 as surfactant. After homogenization by stirring at 800 rpm the emulsified slurry was sonicated for 15 min and then introduced during continuous stirring into the nebulization system using a peristaltic pump. The delivery of the emulsified slurry through the pump tubing should be attended because in some sunscreen samples with increased oily content, the emulsion phases tend to separate in the tubing.

## 3. Results and discussion

### 3.1. Performance of slurry introduction

An alternative which is faster than the wet-acid digestion procedure is the slurry introduction to the nebulization system and finally to the plasma. However, when high slurry concentrations of sunscreen creams are introduced into the plasma the stability and the nebulization efficiency may deteriorate significantly, possibly due to the presence of the organic matter or variable viscosity of the delivered sample. In preliminary experiments with introduction of 3.0% (m/v) slurry suspensions of sunscreen lotions, plasma was unstable or extinguished, independently of the radiofrequency (RF) power (1100–1500 W) and the nebulizer argon flow rate (0.7–1.0 l min<sup>-1</sup>) used. In addition to the presence of oily mass, another possible cause may be the improper diameter of the employed alumina injector. As a result, introduction of acid digested samples was selected for further study.

### 3.2. Effectiveness of wet-acid digestion

The results of the comparative study of the ability of three acid mixtures for quantitative sunscreen cream digestion are illustrated in the bar charts of Fig. 1. Considering as a reliable criterion the recovery of analytes it was proved that the mixture of HNO<sub>3</sub>-HCl-HF was the most efficient one among the three to achieve complete dissolution and was used in further study.

### 3.3. Optimization of ICP parameters

The effect of the plasma incident power was examined in the range 1100–1500 kW. It was proved that the signal to noise ratio of several analytes was slightly increased at higher power, thus 1500 W was finally selected, in order to ensure robust atomization conditions. Another critical factor is the nebulizer gas flow rate, which affects seriously the solution transportation into the ICP and also the atomization performance. Accordingly, the nebulizer gas flow rate was studied in

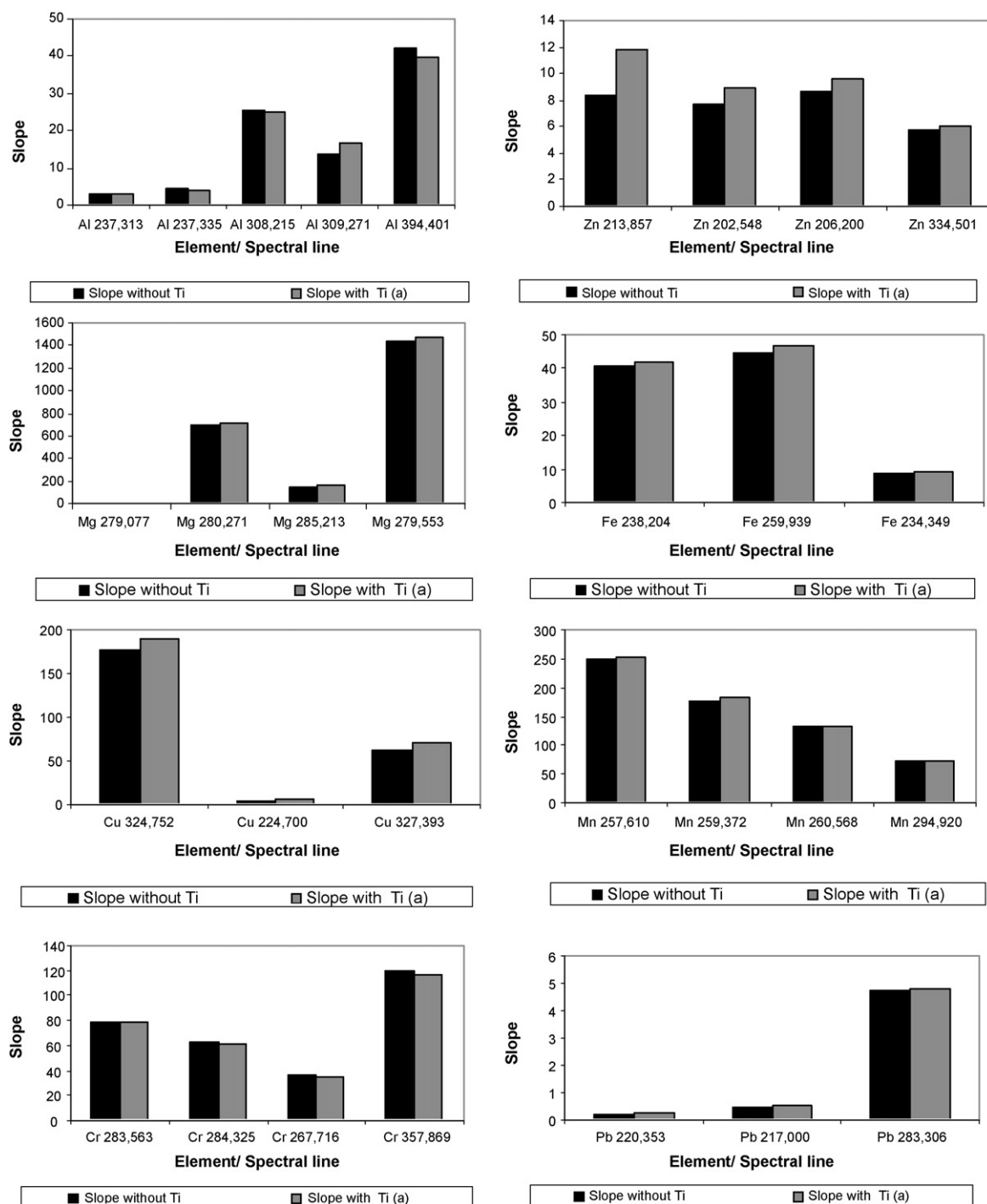


Fig. 2. Effect of the presence of titanium at  $20.00 \text{ mg l}^{-1}$  concentration level on the sensitivity of several analytes using various spectral lines.

the range  $0.7\text{--}1.1 \text{ min}^{-1}$  and showed maximum performance at  $0.7\text{--}0.8 \text{ min}^{-1}$ . Finally, a  $0.8 \text{ min}^{-1}$  flow rate was adopted throughout this research.

#### 3.4. Studies of potential interference from Ti

The next step was to study if high concentration of titanium, which is likely to be present in several commercial sunscreen products, may produce interference in the determination of other analytes by ICP-AES. Consequently, the effect of a high Ti concentration on the sensitivity of the determination of the other analytes was investigated. The slopes of the calibration curves were calcu-

lated for each analyte and the results are presented comparatively in Fig. 2. The first bar presents the slope in absence of titanium and the second bar the corresponding slope in presence of  $20.00 \text{ mg l}^{-1}$  Ti. It was shown that the presence of Ti at this concentration did not cause important alteration to the sensitivity of the analytes, although in case of even lower trace analytes this possibility should be always examined. The above observation was further tested by a paired *t*-test between the slopes obtained in both cases. Up to 37 analytes/spectral lines were tested and the results of the significance test are presented in Table 3. It was confirmed that at 99% confidence level the difference was not statistically significant ( $t_{\text{exp}} < t_{\text{crit}}$ ).

**Table 3**

Student's paired *t*-test for the significance of differences between slopes obtained for each analyte in presence or absence of high titanium concentration (20.00 mg l<sup>-1</sup>).

Parameter	Value
Number of analytes and spectral lines	37
Confidence level	99%
Degrees of freedom	36
Correlation coefficient	0.99993
<i>T</i> – critical (99%)	2.7194
<i>T</i> – experimental	2.6330

### 3.5. Calibration studies

A compromise between the most sensitive spectral line (higher slopes and  $r > 0.99$ ) of each analyte and the lower background was used to select the optimum spectral lines for further study. The selected lines are given in Table 4 together with the results of the regression and correlation analysis. The variation in calculated slopes between aqueous and matrix-matched standards is less than 3% for all analytes. Consequently it is proved that the use of matrix-matched standards for calibration was not necessary. The calibration study with aqueous standards was performed separately in presence or absence of equivalent concentration of Ti.

### 3.6. Performance of the proposed method

The performance of the developed method for variable sunscreen matrices and ingredients should be examined. Thus, under the above described recommended conditions, it was decided to test the performance of the method considering the sensitivity as a reliable indicator. The sensitivity was examined using: (i) the aqueous standards and (ii) the final digests from the standard addition procedure on various commercial sunscreens. The variation of sensitivities using real sample matrices (SB, AF, OS lotions) is illustrated in Fig. 3, together with those obtained from aqueous solutions. It was proved that for the majority of the analytes small scale sensitivity alterations are observed thus the effect of the sample matrix variability is not considered as important. Nevertheless, it is always recommended to use the standard addition procedure for the analysis because of the great variety of cream and lotions.

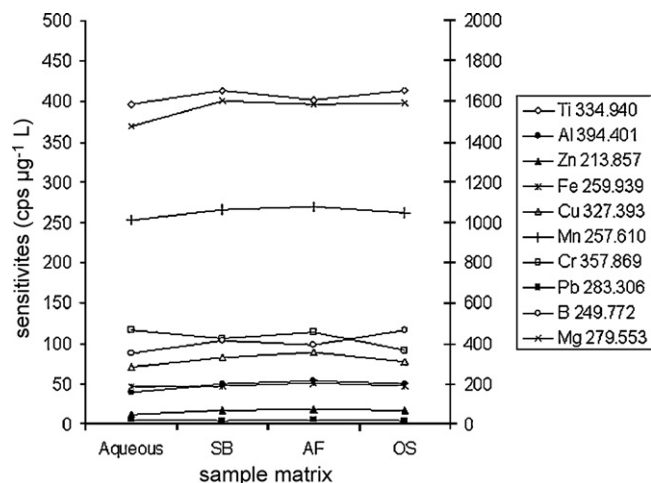
### 3.7. Detection limits, accuracy and precision of the method

Under the above described optimum and recommended conditions, the detection limits (LOD,  $\mu\text{g g}^{-1}$ ) were calculated using the 3 *s* criterion (three times the standard deviation of 10 blank measurements), taking into account that a typical amount of 100 mg sample mass is used for analysis. The detection limits for the most sensitive spectral line of each analyte are presented in Table 5. The

**Table 4**

Slope ( $\pm$  standard error) and correlation coefficients (*r*) between aqueous calibration in presence of 20.00 mg l<sup>-1</sup> and in absence of titanium, for each analyte at the selected spectral line. Comparative regression data for aqueous and matrix-matched standards.

Element/wavelength	Without Ti		With Ti		Matrix matched std.	
	Slope	<i>r</i>	Slope	<i>r</i>	Slope	<i>r</i>
Ti 334.940			397 $\pm$ 4.6	0.9994	386 $\pm$ 14.0	0.9989
Al 394.401	42.2 $\pm$ 1.6	0.9993	39.9 $\pm$ 1.3	0.9996	41.1 $\pm$ 4.6	0.9999
Zn 213.857	8.37 $\pm$ 0.5	0.9997	11.8 $\pm$ 0.4	0.9998	10.0 $\pm$ 0.6	0.9990
Mg 279.553	1436 $\pm$ 29	0.9981	1476 $\pm$ 38	0.9987	1412 $\pm$ 55	0.9995
Fe 259.939	44.6 $\pm$ 1.1	0.9997	46.5 $\pm$ 2.0	0.9999	43.9 $\pm$ 3.3	0.9992
Cu 327.393	62.9 $\pm$ 3.1	0.9993	71.2 $\pm$ 1.7	0.9990	68.4 $\pm$ 5.5	0.9988
Mn 257.610	247 $\pm$ 7.5	0.9995	253 $\pm$ 4.8	0.9998	240 $\pm$ 8.6	0.9997
Cr 357.869	119 $\pm$ 5.6	0.9996	116 $\pm$ 7.0	0.9994	111 $\pm$ 1.9	0.9991
Pb 283.306	4.75 $\pm$ 0.33	0.9994	4.79 $\pm$ 0.45	0.9993	4.52 $\pm$ 0.50	0.9990
B 249.772	86.1 $\pm$ 6.6	0.9997	87.3 $\pm$ 5.8	0.9994	85.2 $\pm$ 2.9	0.9999



**Fig. 3.** Effect of various sample matrices on the sensitivity of several analytes. Mg line is scaled according to the right y-axis.

**Table 5**

Analytical performance of the proposed method. RSD calculated at 250  $\mu\text{g l}^{-1}$  concentration level of each analyte. Mean recovery from  $n = 5$  measurements.

Analyte/spectral line	LOD ( $\mu\text{g g}^{-1}$ )	RSD (%)	Recovery (%)
Ti 334.940	0.2	5.1	95.0 $\pm$ 2.6
Al 394.401	0.4	4.0	95.7 $\pm$ 3.9
Zn 213.857	0.2	2.2	98.2 $\pm$ 2.0
Mg 279.553	0.5	6.2	97.8 $\pm$ 3.1
Fe 259.939	0.5	8.1	101.3 $\pm$ 4.4
Cu 327.396	0.9	6.0	100.2 $\pm$ 2.4
Mn 257.610	0.2	2.6	95.9 $\pm$ 3.0
Cr 357.868	0.6	4.4	94.6 $\pm$ 4.8
Pb 283.305	3.2	2.5	97.1 $\pm$ 2.2
B 249.772	0.8	3.0	102.8 $\pm$ 2.0

quantitation limits (LOQ) are nearly three-fold the corresponding detection limit for each analyte. It can be seen that for all analytes the capability of the method is satisfactory, and can be applied either as a quantitative method or as a screening one.

The precision, expressed by means of relative standard deviation of ten replicates at 250  $\mu\text{g l}^{-1}$  concentration level of each analyte was also calculated and ranged between 2.2 and 8.1% for all analytes and the selected spectral lines. The accuracy of the proposed method was evaluated by recovery measurements after complete wet-acid digestion of spiked commercial sunscreens, because no reference material with a multi-element certification was commercially available. The comparative results concerning all analytes which can be quantitatively determined are also given in Table 5.

**Table 6**Analysis of commercial sunscreen products (mean concentrations expressed as  $\mu\text{g g}^{-1}$ ,  $n = 3$ ) and qualitative label information.

Element	Technique/compound listed on the product label	NA	CT	IS	GN	KR
Ti	ICP-AES	$8.13 \times 10^3$	$18.5 \times 10^3$	<0.2	<0.2	149
	ET-AAS	$7.70 \times 10^3$	$16.9 \times 10^3$	0.060	<0.05	128
	Titanium dioxide	x	x			x
Al	ICP-AES	22	$17 \times 10^2$	74	48	44
	ET-AAS	19	$18 \times 10^2$	79	39	38
	Alumina		x			
	Aluminum stearate Aluminum hydroxide		x		x	
Zn	ICP-AES	57	46	$5.5 \times 10^2$	<0.2	73
	ET-AAS	55	51	$5.0 \times 10^2$	<0.02	86
	Zinc oxide					x
Mg	ICP-AES	37	$9.7 \times 10^2$	$6.2 \times 10^2$	<0.5	$1.2 \times 10^2$
	FAAS	43	$10 \times 10^2$	$5.7 \times 10^2$	<3.5	$1.1 \times 10^2$
	Magnesium stearate		x			
	Magnesium glutamate					x
Fe	ICP-AES	$3.8 \times 10^2$	63	$1.5 \times 10^3$	50	43
Cu	ICP-AES	18	<0.9	$5.3 \times 10^2$	11	<0.9
Mn	ICP-AES	35	<0.2	$5.9 \times 10^2$	12	<0.2
Cr	ICP-AES	42	<0.6	$2.1 \times 10^2$	<0.6	<0.6
Pb	ICP-AES	<3.2	<3.2	<3.2	<3.2	<3.2
B	ICP-AES	663	378	376	54.0	40.0

"x" denotes presence of the substance in the product based on the product label information.

### 3.8. Application to commercial sunscreen products

Five sunscreen products, under the code names NA, CT, IS, GN, KR (sun protection factors SPF 15, 30, 10, 8, and 15, respectively) commercially available and containing various combinations of UV filters were assayed using the proposed ICP-AES method and standard addition. As a reference method, electrothermal or flame atomic absorption spectrometry was used for Ti, Al, Zn and Mg, although it is known that determination of titanium may be less effective by ETAAS in comparison to ICP-AES [24]. The results are presented in Table 6 together with the declared presence of each element according to the qualitative list of ingredients on the product label. Unfortunately, no useful quantitative information is given on the product label of the sunscreens. The data obtained showed a general qualitative compliance with the producer labels with some exceptions. The CT product contains titanium dioxide, and also aluminum in the form of alumina and aluminum stearate, as it is listed on the product label. Alumina is commonly used to improve the properties and skin compatibility of titanium dioxide [11,26]. This is not the case with the NA product which is also based on titanium dioxide UV filter, but without alumina. The high Mg concentration in CT product is probably due to its use as magnesium stearate in order to improve the dispersion properties of titanium dioxide. The sunscreen lotion IS showed increased concentrations of Zn, Mg, Fe, Mn and Cr as compared to the other examined samples, although not mentioned on the label, and also the cream NA showed increased concentrations for Fe and B. This fact proves the necessity for multi-element quality control of these products, because it is likely to find traces of elements not described in the formulation of the sunscreens or other cosmetics, as it is reported by several workers [25,27]. Finally, Pb was not detected in any of the commercial samples.

## 4. Conclusions

The wet-acid digestion technique including nitric, hydrochloric and hydrofluoric acids was proved an efficient procedure for quantitative recovery of inorganic sunscreen agents and other elements from sun care products despite of their complex matrix. The developed method can be used for simultaneous quantitative deter-

mination of Ti, Al, Zn, Fe, Mg, Cu, Mn, Pb, Cr and B down to the low  $\mu\text{g g}^{-1}$  level in commercial creams and lotions by ICP-AES. Nevertheless, because of very large expected variations in the composition of commercial products. The method of standard addition must be used to compensate for the effects of the complex fatty matrix. Inorganic analytes of interest can be determined in presence of higher titanium concentration without significant interference. Most of the commercial preparations that were studied showed generally good agreement to the ingredients listed on the product label, however, the quantitative composition found cannot be assessed because the product labels usually do not write it. Finally, the presence of elements not cited in the formulation given to the product label proves the necessity for multi-element quality control of these products.

## References

- [1] A. Salvador, A. Chisvert, *Anal. Chim. Acta* 537 (2005) 1–14.
- [2] S. Wahie, J.J. Lloyd, P.M. Farr, *Clin. Dermatol.* 32 (2007) 359–364.
- [3] S.C. Rastogi, *Contact Dermat.* 46 (2002) 348–351.
- [4] A. Salvador, M.C. Pascual-Marti, J.R. Adell, A. Requeñi, J.G. March, *J. Pharm. Biomed. Anal.* 22 (2000) 301–306.
- [5] N. Serpone, D. Dondi, A. Albini, *Inorg. Chim. Acta* 360 (2007) 794–802.
- [6] European Economic Community Council Directive 76/768/EEC, Annex VII, 1976, Amendment 31976L0768, <http://europa.eu.int/eurllex/en/lif/reg/en-register/133016.html>.
- [7] US Food and Drug Administration, Department of Health and Human Services, 21CFR Parts 310, 352, 700 and 740, RIN 0910-AA01, Sunscreen Drug Products for over-the-counter Human Use Final Monograph, Federal Register, Rules and Regulations, 1999, 64, 27666–27693.
- [8] A. Salvador, A. Chisvert, *Analysis of Cosmetic Products*, Elsevier, Amsterdam, 2007.
- [9] S. Simeoni, R. Tursilli, A. Bianchi, S. Scalia, *J. Pharm. Biomed. Anal.* 38 (2005) 250–255.
- [10] T. Maier, H.C. Korting, *Skin Pharmacol. Physiol.* 18 (2005) 253–262.
- [11] J. Schulz, H. Hohenberg, F. Pflucker, E. Gartner, T. Will, S. Pfeiffer, R. Wepf, V. Wendel, H. Gers-Barlag, K.-P. Wittern, *Adv. Drug Deliv. Rev.* 54 (2002) S157–S163.
- [12] A.O. Gamer, E. Leibold, B. van Ravenzwaay, *Toxicol. In Vitro* 20 (2006) 301–307.
- [13] S. Yabe, T. Sato, *J. Solid State Chem.* 171 (2003) 7–11.
- [14] Y. Shih, F.-C. Cheng, *J. Chromatogr. A* 876 (2000) 243–246.
- [15] C.G. Smyrniotakis, H.A. Archontaki, *J. Chromatogr. A* 1031 (2004) 319–324.
- [16] D.L. Giokas, A. Salvador, A. Chisvert, *Trends Anal. Chem.* 26 (2007) 360–374.
- [17] D.L. Giokas, V.A. Sakkas, T.A. Albanis, *J. Chromatogr. A* 1026 (2004) 289–296.
- [18] J.T. Mason, *J. Pharm. Sci.* 69 (1980) 101–102.
- [19] M. das Gracias, A. Korn, A.C. Ferreira, A.C.S. Costa, J.A. Nobrega, C.R. Silva, *Microchem. J.* 71 (2002) 41–48.
- [20] A. Kawachi, M. Ishida, I. Saitoh, *Spectrosc. Lett.* 29 (1996) 345–366.

- [21] T. Wang, X. Jia, J. Wu, *J. Pharm. Biomed. Anal.* 33 (2003) 639–646.
- [22] T. Wang, J. Wu, R. Hartman, X. Jia, R. Egan, *J. Pharm. Biomed. Anal.* 23 (2000) 867–890.
- [23] N. Lewen, S. Mathew, M. Schenkenberger, T. Raglione, *J. Pharm. Biomed. Anal.* 35 (2004) 739–752.
- [24] T.J. Einhauser, T.G. Pieper, B.K. Keppler, *J. Anal. At. Spectrom.* 13 (1998) 1173–1176.
- [25] F.L. Melquiades, D.D. Ferreira, C.R. Appoloni, F. Lopes, A.G. Lonni, F.M. Oliveira, J.C. Duarte, *Anal. Chim. Acta* 613 (2008) 135–143.
- [26] A. Rampaul, I.P. Parkin, L.P. Cramer, *J. Photochem. Photobiol. A: Chem.* 191 (2008) 138–148.
- [27] E.L. Sainio, R. Jolanki, E. Hakala, L. Kanerva, *Contact Dermat.* 42 (2002) 5–10.