

Physicochemical Characterization and *In Vitro* Evaluation of the Sun Protection Factor of Cosmetic Products Made from Natural Clay Material

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ABSTRACT

Clay has been widely used as photo protectants in rural places of South Africa. Recently, there are wide range of products which are marketed in South Africa as clay cosmetics which are used for photo protection. In this work, *in vitro* determination of the sun protection factor (SPF) of newly formulated cosmetics produced from natural clay material from the Bizana region in the Eastern Cape Province of South Africa was performed by spectrophotometric means. The SPF values found for clay material, face cream, foundation, face mask and scrub were 1.18, 18.33, 13.71, 6.74 and 9.53, respectively. The same materials were characterized using thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS) and inductively coupled plasma (ICP). Based on FTIR, XRD, XRF and SEM-EDS results, kaolinite, goethite and quartz were the major minerals found in the clay. Toxic elements such as mercury and cadmium were not detected during ICP analysis; however, traces of lead (0.72–2.14 mg kg⁻¹) and arsenic (0.49–0.69 mg kg⁻¹) were found in cosmetic products. The results obtained in this study indicate that the cosmetic products manufactured from clay have sun protection ability.

KEYWORDS

Sun protection factor, cosmetic products, natural clay material.

1. Introduction

A large number of South African citizens from the rural areas use raw clay for sun protection. During this practice, the clay material is mixed with water and directly applied onto the skin. In the Eastern Cape Province of South Africa, clay soil is traditionally used for cosmetic applications, especially for cleansing, sunscreen and body beautification.¹ Globally, sunscreens are manufactured daily as they are able to provide protection against ultraviolet (UV) radiation. Ultraviolet radiation is a type of electromagnetic radiation with wavelengths ranging from 100 to 400 nm. Typically, UV radiation is divided into three types, namely; UV-A (320–400 nm), UV-B (290–320 nm) and UV-C (100–280 nm).² Some implications of UV-A radiation on the human skin includes ageing and erythema or sunburn, UV-B may cause DNA damage and skin cancer, whereas UV-C is known to be the highest energy and most dangerous type of UV radiation, but it is generally absorbed by the ozone layer in the atmosphere.³ Direct exposure to UV-C radiation for a long period of time is likely to destroy the skin.² While on a positive note, exposure to UV radiation can also result in the synthesis of vitamin D which is essential in the human skin.⁴

In the context of the scope presented above, sunscreen products are formulated with organic and inorganic compounds for UV protection. Titanium dioxide (TiO₂) and zinc oxide (ZnO) are inorganic compounds that are widely used as physical UV filters. These two inorganic oxides have the ability to reflect UV light and block out sunlight.⁵ Organic UV filters are classified as

chemical filters that can absorb UV light and thus increasing UV protection. They are usually aromatic compounds that contain a carbonyl group such as cinnamates, benzophenones, etc.^{4,5} Organic filters are used less often, since they can be absorbed into the skin and lead to unwanted reactions.

Cosmetic products are produced with high sun protection factors (SPF) for the purpose of UV protection. SPF is the number that describes the efficiency of the sunscreen product for UV protection. The SPF number can be further explained as the ratio of the least amount of ultraviolet energy required to produce a minimal erythema on sunscreen protected skin, to the amount of energy required to produce the same erythema on unprotected skin.⁶ Analytical methods that have been previously reported for the *in vitro* determination of SPF include the use of UV spectrophotometer,² mass spectrometry,⁷ and ultraviolet transmittance analyzer.⁸ Based on ease of operation, affordability, availability and small sample size required, UV spectrophotometer was selected as a technique of choice in the current study for the rapid determination of SPF in natural clay material and clay-based formulated cosmetic products.

Therefore, the objective of this work was to determine the SPF of newly formulated cosmetic products made from natural clay material. The study also focused on the characterization of natural clay material collected from the Bizana region of the Eastern Cape Province in South Africa. This natural resource from Bizana is of importance as it is widely used by people in the Eastern Cape Province for various traditional activities that include Xhosa weddings and initiation ceremonies.⁹ Regardless

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of the high importance and usage of this natural resource, there is currently no available data on its characterization and sun protection ability. Furthermore, there are currently no toxicological data for the determination of the risks/health effects associated with the usage of clay material for traditional activities or cosmetic applications. Moreover, most people in rural areas in the Eastern Cape Province cannot afford the expensive cosmetic products that are currently marketed in South Africa, therefore, they tend to use this natural resource for sun protection and beautification.

2. Experimental

2.1. Cosmetic Products, Clay Samples and Sampling Location

Natural clay sample which was used in the manufacture of cosmetic products was collected from rural location in Bizana which is a small town located in the Eastern Cape Province of South Africa. The rural location is situated approximately 55 km from Bizana town. The town itself is located at a distance of about 250 km south of Durban Metropolitan City. The samples were dug out using a spade and collected in a plastic container, thereafter they were transported into the laboratory. On arrival in the laboratory, mortar and pestle were used to grind the samples prior to analysis. Cosmetic products manufactured from natural clay and marketed as face cream, foundation, face mask and scrub were analyzed in this study. Such products were kindly donated by a local cosmetic manufacturing company. Commercially available cosmetic products purchased from local supermarkets in Durban, South Africa were used as control samples.

2.2. *In Vitro* Evaluation of the Sun Protection Factor

A sample of 1 g was transferred to a 100 cm³ volumetric flask followed by the addition of high performance liquid chromatography grade ethanol ($\geq 99.8\%$) from Sigma-Aldrich (Steinheim, Germany) to the calibration mark. The resulting solution was filtered through a Whatman number one filter paper from Whatman International Ltd (Maidstone, England). 10 cm³ of the sample was withdrawn from the initial solution and diluted to 200 cm³. Thereafter, the absorbance of 10 cm³ of the diluted solution was recorded in the wavelength range of 290–320 nm using a Varian Cary 50 ultraviolet/visible (UV/Vis) spectrophotometer from Agilent Technologies Co Ltd (California, United States). The SPF of natural clay material and cosmetic products was calculated using Equation (1):^{2,10}

$$\text{SPF} = \text{CF} \times \sum_{290}^{320} \text{EE}(\lambda) \times \text{I}(\lambda) \times \text{Abs}(\lambda) \quad (1)$$

where, CF is the correction factor, λ is the wavelength, EE is the erythral effect, I is the solar intensity spectrum and Abs is the absorbance of the diluted sample. Each analysis was performed in triplicate.

2.3. Physicochemical Characterization

Natural clay samples were crushed into fine powder and dried for 2 h in an oven set at 100 °C from Scientific Engineering (Pty) Ltd (Industria, South Africa). Elemental analysis was performed using a CHNS/O analyzer obtained from Perkin Elmer (Massachusetts, United States). X-ray diffraction (XRD) equipped with XRD commander for data collection and Eva software for processing was obtained from Bruker AXSD8 diffractometer (Karlsruhe, Germany). The diffractometer was coupled with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV, 40 mA in a 2θ range of 10° to 70°. Thermogravimetric analysis (TGA) equipment was sourced from Mettler (Greifensee, Switzerland).

Fourier-transform infrared spectroscopy (FTIR) equipped with attenuated total reflection from Perkin Elmer (Llantrisant, United Kingdom) was used. Natural clay and clay-based cosmetic formulations were analyzed without any sample pre-treatment.

Scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS) from Oxford Instruments (Abingdon, Oxfordshire) was used to study the elemental composition in a clay sample that was coated with gold for high resolution. Samples were further evaluated by independent external laboratories where elemental contents and oxides present in cosmetic products and clay material were determined. Elements were quantified with inductively coupled plasma (ICP) equipped with mass spectrometry detection after the drying and microwave digestion of the samples. Oxide analysis and loss of ignition were performed with x-ray fluorescence (XRF) equipment.

Physicochemical properties such as pH, electrical conductivity (EC), dissolved oxygen (DO), salinity, and total dissolved solids (TDS) were measured using a Bante900P multi-parameter meter from Bante instruments (Shanghai, China). Prior to the use, the equipment was calibrated for pH and conductivity in our laboratory using the calibration buffers of pH 4, 7 and 10, and also the conductivity solutions of 12.88, 84.0 and 1413 $\mu\text{S cm}^{-1}$ that were provided by the supplier. Prior to analysis, samples were treated using the optimized procedures reported in literature.^{1,11} This was done by preparing slurry solutions of 1:5 sample to deionized water ratio (by mass), followed by stirring the slurry at constant speed for 3 h.

3. Results and Discussion

3.1. *In Vitro* Determination of the Sun Protection Factor

Commercial cosmetic products with SPF of 15 and 50+ as indicated by respective manufacturers were used in order to determine the accuracy and precision of the proposed SPF method. Average SPF of 17.70 and 50.76 were obtained for such commercial products which indicated that the method used in this study is accurate. Whereas, the %RSD values of 3.40 and 3.01 are an indication of the good precision. Therefore, the current SPF method was applied in the analysis of newly formulated cosmetic products and natural clay material.

The results in Table 1 show the treatment of data in order to determine the SPF of the samples. Table 1 shows the data that was obtained during the determination of the SPF of a commercial available product. In each case, the absorbance values recorded at various wavelengths are given. The normalized product functions ($\text{EE} \times \text{I}$) used are those available in literature.^{12,13}

Table 1 SPF calculated for a commercial cream with an SPF of 15.

Wavelength (nm)	EE $\times$ I	ABS	SPF
290	0.0150	0.091	0.01365
295	0.0817	0.090	0.07353
300	0.2874	0.088	0.2529
305	0.3278	0.088	0.2885
310	0.1864	0.090	0.1678
315	0.0839	0.088	0.07383
320	0.0180	0.082	0.01476
SPF (diluted sample)			0.8849
SPF			17.70

CF = 10

Table 2 SPF and %RSD ($n = 3$) values of commercially available cosmetic creams, natural clay and cosmetic products formulated from natural clay material.

Sample	SPF
SPF 50+	50.76 $\pm$ 3.40
SPF 15	17.70 $\pm$ 3.01
Face cream	18.33 $\pm$ 0.45
Foundation	13.71 $\pm$ 1.00
Face mask	6.74 $\pm$ 6.52
Scrub	9.53 $\pm$ 3.17
Clay soil	1.18 $\pm$ 6.50

%RSD are given as $\pm$ values

Table 2 shows the SPF values determined for each formulated products including the control samples (SPF 15 and 50+). It was observed that the natural clay material from Eastern Cape which was used in the formulation of the cosmetic products has low SPF value of 1.18. Although the SPF for this material is low, it is widely used as it is known to have the ability to cleanse the skin and to absorb the oils from the skin. These results are in close agreement with the data in literature, for instance, the SPF of natural clay materials used for cosmetic purposes in Kenya is in the range of 1.46 to 5.59.¹⁴ SPF was improved to between 9.53 and 18.33 in newly formulated clay-based cosmetic products due to the introduction of inorganic compounds such as TiO₂ during their manufacturing process as shown in Table 2.

3.2. Characterization of Clay Material and Cosmetic Products

3.2.1. Thermal Analysis

The TGA data for natural clay material given in Fig. 1, shows the weight loss of the material as a function of temperature. The weight loss that occurred at around 100 °C was attributed to the loss of water molecules adsorbed at the surface of the natural clay material. Further weight loss was observed between 250 and 300 °C which was due to the conversion of goethite into hematite. As documented in literature,¹⁵ the weight loss above 450 °C corresponds to the dehydration of inorganic matter such as kaolinite, illite and chlorite. The obtained results from TGA curve were in agreement with the one published for clay that was sampled in Brazil.¹⁶

3.2.2. Physicochemical Parameters

Natural clay material was examined using CHN analyzer in order to confirm the presence of organic materials. The results

obtained from elemental analysis showed that the clay material contained 0.69, 1.58 and 0.04 % of carbon, hydrogen and nitrogen, respectively. Carbon and hydrogen contents are very low and are coherent with very low content of organic matter. This small amount of the organic matter correlate well with the decomposition between 250 and 300 °C in the TGA data (Fig. 1).

The studied physicochemical properties are presented in Table 3. A commercial cosmetic cream with SPF 15 was used as a reference and identified as the control sample. The pH obtained for natural clay material was 4.9 which is in agreement with the results obtained previously in another South African study, where the pH of soil samples from Eastern Cape Province ranged from 4.53 to 9.57.¹ The reported pH range for clay samples collected in southern Africa was 2–9.¹⁷ The pH for newly formulated cosmetic products from natural clay material ranged from 4.94 for scrub to 6.97 for face mask, whereas in a published work, the pH of about 6.6 was reported for anti-ageing cosmetic emulsions containing vitamin E acetate as active ingredient.¹⁸ Furthermore, these results agreed well with the pH of 6.6 obtained for emulsion cream that was formulated with natural plant extract.¹⁹ The electrical conductivity of natural clay material was 315 $\mu\text{S cm}^{-1}$, this value was unexpectedly low in all cosmetic products including the control sample which indicated that all the samples were non-saline. This was further confirmed in low salinity results of respective samples. Measuring the electrical conductivity in natural clay material and clay-based formulations is very important as this could allow for the estimation of the soluble salt concentration which in turn is related to the salinity.¹¹ TDS values were low when compared to the values reported for soils (246–455 mg L⁻¹) obtained from Libya.¹¹ Dissolved oxygen for the new cosmetic products matched well with those of the existing sample used as the control.

3.2.3. X-ray Diffraction for Natural Clay Material

Preliminary work on the presence of minerals in the natural clay material was evaluated using XRD. Amongst the other applications of XRD is to study the mineralogical composition of the raw material components.²⁰ XRD results presented in Fig. 2 indicated the presence of kaolinite, goethite and quartz as three major minerals in the natural clay material. The peaks were assigned by following the data available in literature for minerals.^{21–23}

3.2.4. Functional Group Analysis of Clay and Cosmetic Products

The contents of natural clay material were further analyzed using FTIR (Fig. 3). The infrared spectrum for raw natural clay

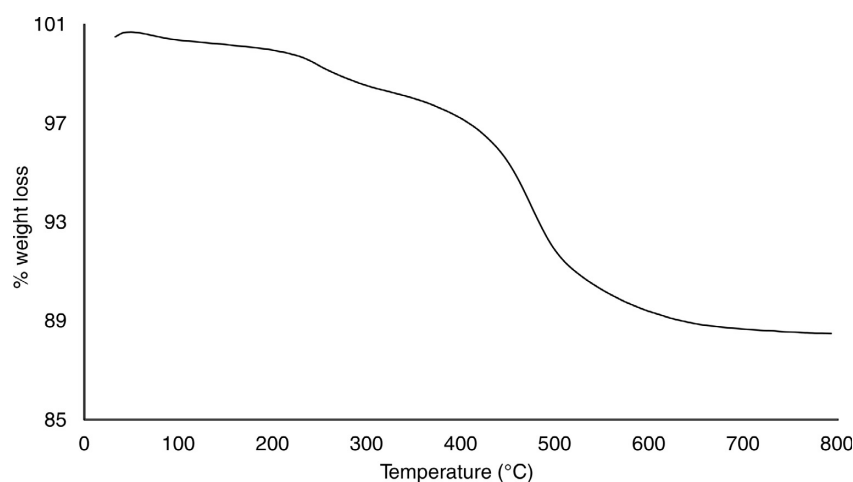
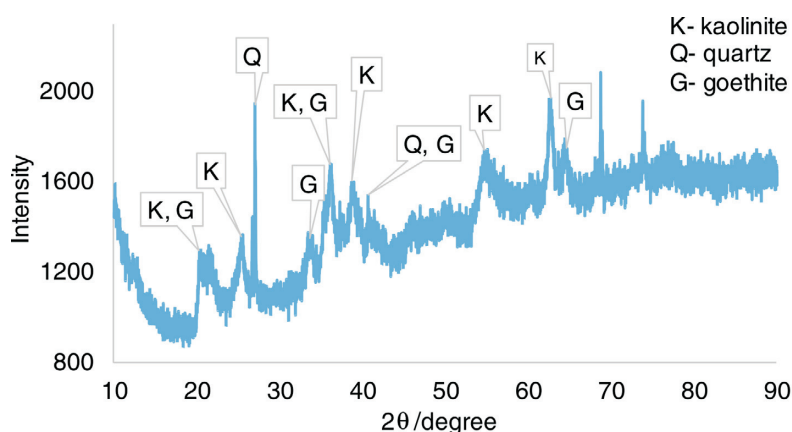
**Figure 1** Thermogravimetric analysis of clay material.

Table 3 Physicochemical properties of clay and cosmetic products.

Parameter	Sample					
	Clay	Face mask	Foundation	Scrub	Face cream	Control
pH	4.929	6.974	6.851	4.942	5.043	7.03
EC ($\mu\text{S cm}^{-1}$)	315	97.6	199.2	63.7	87.3	143.6
Salinity (psu)	0.17	0.05	0.10	0.04	0.05	0.07
DO (mg L^{-1})	5.63	4.39	5.82	3.83	4.23	4.72
TDS (mg L^{-1})	81.3	49.5	100.2	32.0	43.3	72.5

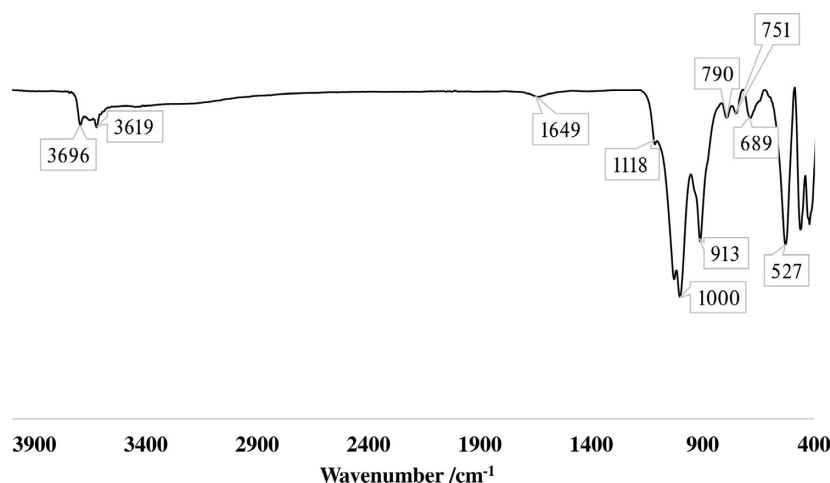
**Figure 2** X-ray diffractogram of clay ($\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV, 40 mA in a 2θ range of 10° to 70°).

was similar to that obtained for the study of clay reported in Nigeria.²² The characteristic peaks of kaolinite were observed at 3696 , 3619 , 1000 and 913 cm^{-1} , which are in relation with the data obtained from XRD. The OH bands were observed at 3696 and 3619 cm^{-1} , whereas there was Al-O bending at 913 cm^{-1} which could be linked to the presence of aluminosilicate mineral.²¹ It has been reported that pure kaolinite exhibits two peaks at 797 and 750 cm^{-1} and a well crystallized kaolinite exhibits two sharp peaks at 3690 and 3620 cm^{-1} .²² Furthermore, FTIR spectra obtained for cosmetic products (Fig. 4 and Table 4) showed the existence of new peaks at 3287 , 2918 , 2849 and 1465 cm^{-1} that were due to the additives used in cosmetic formulations. Examples of such additives are stearic acid and glycerine.

3.2.5. Scanning Electron Microscopy and Elemental Composition of Raw Clay

Results for SEM coupled with EDS are presented in Fig. 5. Based on elemental composition, a ratio of 1:1 for silicon/alu-

minium composition was observed which could be translated to the presence of kaolinite which correlates with FTIR and XRD data. Kaolinite is an important soil mineral, as it has important uses in pharmaceutical preparations that include being a diluent and binder, emulsifying, thickening and anticaking agent, flavour corrector and carrier-releaser of active principles.²⁵ High amount of oxygen (58.8%) was observed, as reported for the clay samples that were collected in northern Cameroon.²⁴ Other elements found in clay were carbon (C), magnesium (Mg), aluminium (Al), silicon (Si) and iron (Fe). The same elements were found in cosmetic products using ICP analysis, where the concentration (mg kg^{-1}) ranges for magnesium, aluminium, silicon and iron were 176 – 2660 , 10129 – 69844 , 873 – 1364 and 9838 – 54529 , respectively. These elemental concentrations are comparable with those found in clay soils elsewhere.²⁶ For example, the concentration of iron obtained in soil samples from Tanzania ranged from 13567 to $160850 \mu\text{g g}^{-1}$.²⁶ A better distribution map of these elements can be seen in the SEM EDS maps

**Figure 3** Fourier transform infrared spectrum of clay.

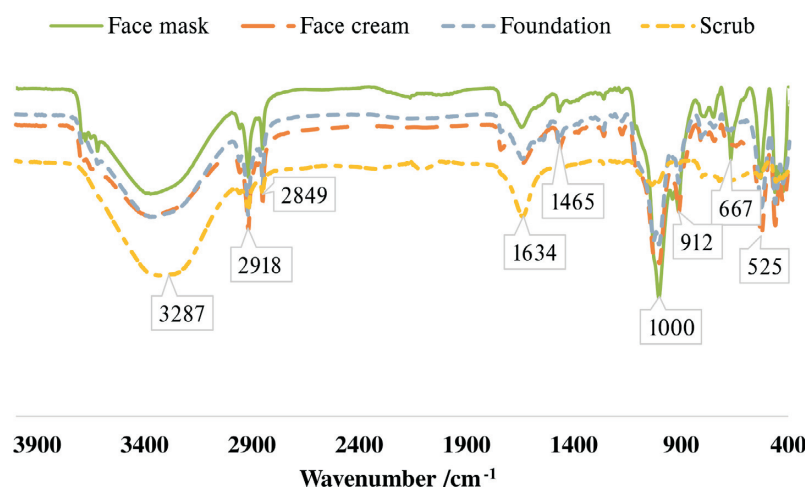


Figure 4 Fourier transform infrared spectrum of cosmetic products manufactured from clay material.

Table 4 Major FTIR bends recorded for natural clay material and cosmetic products sample.

Wavenumber (cm ⁻¹)	Sample	Proposed signal	References
3619–3696	Clay	O-H stretch usually observed in kaolinite-based clay	24, 15
3287, 2918, 2849, 1465 and 525–527	Cosmetics	Peaks due to additives used in cosmetic formulation	
1634–1649	Clay and all tested cosmetics	O-H bending of water	24, 15
1000–1118	Clay and all tested cosmetics	Si-O-Si vibrations, these may also be due to sulfates and phosphates	15
912–913	Clay and all tested cosmetics	Al-O bend usually observed in aluminosilicate minerals	24
667–689	All samples	Si-O and Si-O-Fe stretch	20

which were inserted in Fig. 5. These elements are highly important in cosmetic products because of their role on the skin. Such roles include, the use of Fe as an antiseptic and as cell renewal catalyst, Si as providing reconstruction of skin tissues, hydration

and soothing effect, while Mg is invigorating.¹⁶ In addition, ICP results indicated the presence of trace amounts of lead and arsenic in cosmetic products, while mercury and cadmium were not detected (Table 5). Some toxic elements such as mercury and

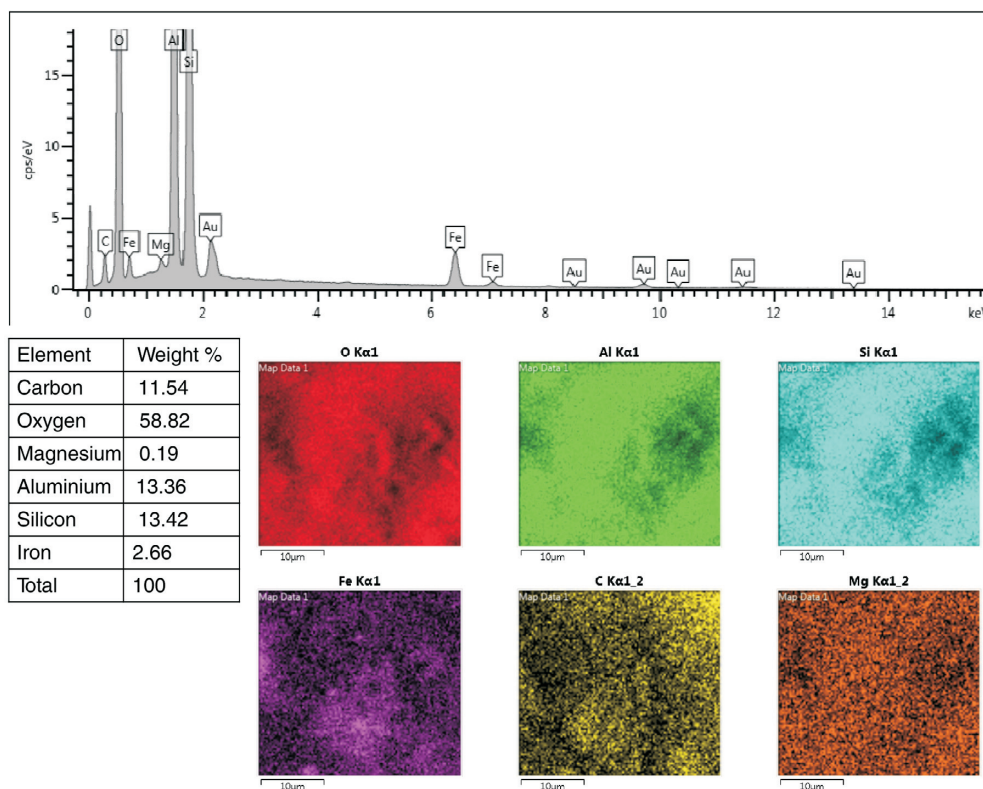


Figure 5 Results for SEM of clay coupled with EDS spectrum.

Table 5 Element analysis in cosmetic products.

Element	Concentration (mg kg ⁻¹)			
	Face mask	Face cream	Foundation	Scrub
Lead	2.14	0.72	1.48	1.07
Mercury	nd	nd	nd	nd
Arsenic	0.69	nd	0.60	0.49
Cadmium	nd	nd	nd	nd

nd = not detected.

Detection limits: lead and mercury = 0.042 mg kg⁻¹; arsenic and cadmium = 0.083 mg kg⁻¹.

cadmium were not detected in any cosmetic products. Both lead and arsenic have been detected in cosmetic products. Such elements can be allocated in the structure of clay minerals or their accompanying accessory phases, or adsorbed on clay particles.²⁷ The presence of carbon in clay could be an indication of organic contamination which correlate with the results obtained with CHN analyzer and TGA.

3.2.6. Chemical Composition of the Raw Clay

The main oxides detected in clay using XRF were Al₂O₃ (27.75 %), SiO₂ (37.83 %) and Fe₂O₃ (19.01 %) (Table 6). The iron content is evidence for the presence of iron based minerals such as goethite or hematite and this was confirmed in both TGA and XRD. These are the same oxides that were detected in the clay materials from the north of Cameroon.²⁸ The presence of Al₂O₃, Fe₂O₃ and SiO₂ confirmed the occurrence of kaolinite, goethite and quartz (indicated in XRD data), respectively. The amount of TiO₂ found in the clay was 1.44 %, which could play a significant role as a physical UV filter due to its ability for reflection of UV light and blocking out of sunlight. Overall, the oxides detected in this study were also detected in other clay samples originating from other African countries such as Tunisia, Nigeria, Ivory Coast, Guinea and Senegal.^{29–31} In addition, the loss of ignition (12.55 %) is in agreement with the results reported elsewhere for clay deposits sampled from KwaZulu-Natal and Limpopo provinces of South Africa.³² The loss of ignition is attributed to organic matter and the value obtained in this study is coherent with kaolinite rich clay, for which 13–14 % loss of ignition is known as a mean value.^{33,34}

4. Conclusions

The calculated SPF values of both commercial products were in close agreement with the labelled SPF values, and were used to validate all SPF calculations which are reported herein. Cosmetic products manufactured from natural clay material have high SPF values, and they can be used for cleansing the skin, emulsification, beautification, adsorption and detoxification. The natural clay itself has been used over the years for traditional purposes in the Eastern Cape Province of South Africa. The natural clay had a low SPF value, thus, this indicated that it can provide very low UV protection. The low UV protection of the raw clay justified the presence of other reagents such as TiO₂ to increase the SPF value. The newly formulated products are affordable to the local citizens and made from the natural material that is not hazardous on the human skin. The characterization of natural clay material using XRD, XRF, FTIR and SEM indicated the presence of kaolinite, goethite and quartz as major minerals in the sample. Elements detected in raw clay using EDS were carbon, oxygen, magnesium, aluminium, silicon and iron; which were further confirmed with ICP. Physicochemical characterization results such as pH, conductivity and salinity agreed well with the data in literature.

Table 6 Chemical composition of clay.

Oxide	Content %
Al ₂ O ₃	27.75
CaO	0.03
Cr ₂ O ₃	0.01
Fe ₂ O ₃	19.01
K ₂ O	0.11
MgO	0.18
MnO	0.05
Na ₂ O	0.02
P ₂ O ₅	0.07
SiO ₂	37.83
TiO ₂	1.44
Loss of ignition	12.55
Total	99.05

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