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Research Paper

The quality of Spanish cosmetic-pharmaceutical talcum powders

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ABSTRACT

Seven cosmetic-pharmaceutical talcum powders from different commercial brands, currently for sale in Spanish pharmacies, have been studied in order to determine their mineral and pharmacopoeia quality. Four samples met the required conditions to be classified both of “cosmetic quality” and “pharmacopoeia quality”. These conditions are: absence of potentially carcinogenic minerals, talc purity of more than 90%, low levels of toxic elements and suitable compositional levels of Al, Mg and Ca. The remaining three samples were classified as of “industrial quality”. Although these are free from fibrous minerals, the high carbonate content, specifically dolomite (close to 40%) and calcite (about 10%), impacts on the purity in talc by significantly reducing its quantity to the point that the material no longer satisfies many of the compositional tests of the European Pharmacopoeia. The detailed microanalysis with SEM-EDX and size measurements of elongated particles present in the samples showed them to be harmless as their mineral composition is talc and they appear in very low proportions. The SEM-EDX study highlighted the properties for which talcum powder has classically been employed for topical cutaneous use. The comparison of the current results with those of the Spanish market of talcum powder sold in pharmacies in the decade of the 1980s resulted in three principal findings. First, the fibrous minerals have disappeared. In the past, a significant number of samples showed evidence of amphiboles. Second, the purity in talc in samples of cosmetic quality has improved from 94% to 96%. Finally, in the 1980s there were no samples in the Spanish market with talc purity as low as today (60%). Dolomite is currently present in excessive quantities in some talcum powders.

1. Introduction

The phyllosilicate talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) is the main component of talcum powder. This mineral is associated with metamorphic rocks deposits where it appears as a fine-grained compact, foliated, fibrous (radiated) or massive material (Klein and Dutrow, 2017). The talc raw material frequently contains accompanying mineral species such as other phyllosilicates (chlorites -clinochlore-, interstratified talc-chlorite, micas -phlogopite, muscovite-, kaolin, pyrophyllite), fibrous silicates (amphiboles -tremolite, anthophyllite, actinolite-, serpentine -chrysotile-), carbonates (dolomite, calcite, magnesite), tectosilicates (quartz, feldspars), and oxides (rutile) (Röhl et al., 1976; Soriano et al., 1996).

The structure of the mineral talc is formed of sheets stacked and joined by weak residual bonds. Their crystallographic and physical properties (perfect cleavage {001}, low hardness -H = 1-, greasy feel, sectile, flexible -but not elastic-, pearly to greasy luster, white or

gray colour) constitute a large part of the basis for the pharmaceutical and cosmetic use of talc, although there are few specific studies on this topic (Soriano et al., 1998; Gámiz et al., 2002). Chemically, talc is an acid-insoluble compound that contains very small amounts of Al, Ti, Fe^{2+} and Fe^{3+} (Deer et al., 1992). Therefore, talc has high chemical inertia and does not absorb onto the skin (Galán et al., 1985). This is important for pharmaceutical and cosmetic use, although the presence of accompanying minerals may significantly change the chemical composition of talcum powder.

“Talc” (name given to industrial powdered raw material rich in talc) have been used mainly in the paper industry, ceramic, paints and coatings, agro-food industries, cosmetics, pharmacy and medicine (Poirier et al., 2019). In 2011 the world leaders in talc production were in Asia (China, South Korea, India, Japan), together with United States, Finland, France, and Brazil (King, 2019). Nowadays, United States produces 615,000 metric tons per year, of which 7% are dedi-

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cated to pharmaceutical/cosmetic use (U.S. Geological Survey, 2019).

The pharmaceutical and cosmetic usefulness of talcs were widely addressed (Galán et al., 1985; López-Galindo et al., 2007; Viseras et al., 2007; Carretero and Pozo, 2009, 2010): dermatological and antipruritic protector; lubricant; excipient; diluent and binder; emulsifier, thickener and anticaking agent; flavor corrector; carrier-releaser of active principles; filling, protection or adsorbent agent in creams and pastes; ability to adsorb oils and fats; etc. In this sense, the quality of talcum powder for use in pharmacy and cosmetics is regulated by pharmacopoeias.

The European Pharmacopoeia is in force in the European countries, with different versions, the most recent being from 2014 (8th edition) and 2016 (9th edition). All these versions contain a specific monograph for talc, taking into account some issues such as the presence of asbestos (since 2001, X-ray diffraction is included as a diagnostic tool for their detection), or the compositional limits for Al, Mg, Fe, etc. Materials that meet Pharmacopoeia standards are denominated "European Pharmacopoeia quality". The Royal Spanish Pharmacopoeia (1st edition, 1997) is harmonized with the European Pharmacopoeia (3rd edition of 1997), being an integral version of the latter (Valverde et al., 1996). Before 1997, the Spanish Official Pharmacopoeia (1954) was in force with a specific monograph for talc.

The pharmaceutical and cosmetic use of talcs (with adequate quality) as a disease inducer has also been discussed in previous studies (Carretero et al., 2013). For example, the presence of fibrous minerals has been banned by the European Pharmacopoeia since 1997 (European Pharmacopoeia, 1997), due to the relationship between cancers and fibres (Gordon et al., 2014). However, not only does the asbestos mineral types (amphiboles and serpentines) content induces harm, but so also does the particle morphology measured by the ratio of the dimensions length/width (ANSES, 2012). CIRC (2010) considers inhaled talcum powder that does not contain asbestos as unclassifiable in terms of its carcinogenicity in humans, although it is not recommended for genital use.

In view of the above, it is clear that the assessment of the mineral quality of talcum powder is of paramount importance for their use in body care and human health.

However, there are few studies on the mineral composition of talcum powders sold in pharmacies and specialized shops or of powdered talcs used as a raw material in such formulations (Roth et al., 1976; Paoletti et al., 1984; Delgado et al., 1985; Soriano et al., 1996; Hu et al., 2014; Fitzgerald et al., 2019; FDA, 2019) but no studies at all have been found on the application of pharmacopoeia standards to such materials.

The main objective was to study the compositional and quality properties of talcum powders for cosmetic-pharmaceutical use, currently for sale in Spanish pharmacies. The second objective was to compare the quality of talcum powders in the current Spanish market (2019) with that of those studied by our research group in the 1980s (Delgado et al., 1985). We could thus analyze the talcum powder quality before and after the harmonization (in 1997) of the Span-

ish pharmacopoeia with the European pharmacopoeia and the inclusion of XRD analysis and the presence of fibres in the talc monograph.

2. Material and methods

Seven samples of talcum powder for cosmetic/pharmaceutical use, currently available in Spanish pharmacies (Table 1) and purchased in the final months of 2018 were studied. According to the labelling, two samples are intended for use in babies and children (T1 and T2) and three in adults (T3, T4 and T5). Only two indicated the presence of inorganic pharmaceutical additives: T3 with zinc oxide and T6 with calamine. T1, T3 and T7 included the mineralogical composition on the label. All are cosmetic-pharmaceutical preparations perfumed with fragrances and have different pharmaceutical additives of organic nature.

2.1. Colour measurement

The coordinates for lightness L^* (0–100), red-green a^* and yellow-blue b^* parameters were measured with a Minolta CM-2600d spectrophotometer (Minolta, Tokio, Japan) for an area of 50 mm² of the surface of talcum samples in shallow cylindrical containers of 15 mm diameter and 5 mm depth.

2.2. Mineralogical composition

The mineralogical composition was determined from mineralogical analysis by X-Ray Diffraction (XRD), Inductively Coupled Plasma Mass Spectrometry (ICPMS) (Zn-bearing phases: Zincite, Hidrozinclite) and volumetric analysis of carbonates (dolomite, calcite) in the Bernard Calcimeter (MAPA, 1994). XRD was performed with a powder diffractometer BRUKER D8 ADVANCE with automated control and data collection using STAD14 and XSCANS software packages. Metallic Si was used as an internal standard. A lateral charge sample holder was used to ensure disorientation of particles. The computerized files allowed the use of various software packages for the identification of mineral species (X Powder 12.1 by Martín-Ramos, 2012). The semiquantitative analysis was carried out according to Delgado et al. (1985) using the reflective powers technique. Before the volumetric analysis (Bernard Calcimeter), an acid attack to the sample and a XRD analysis of the insoluble residue was made showing that dolomite was completely removed from the sample (disappear in the XRD spectra), demonstrating that dolomite is completely soluble with the cold HCl used in the volumetric analysis.

2.3. Chemical composition

The major chemical elements were measured with X-Ray Fluorescence (XRF) using a compact Panaalytical-model Zetium spectrometer, elemental range F to Uranium. The minor chemical elements were determined by ICPMS with a NEXION-model 300D equipment, plasma torch ionization source and quadruple ion filter; samples were digested in a capped Teflon beaker using HNO₃, HF, and HClO₄.

Table 1
Talcum powder samples available in Spanish pharmacies. Information contained in the labelling and colour parameters.

Sample	Made in	Trade name	Recommended use	Mineral composition shows on the label	L^*	a^*	b^*
T1	Spain	Talcum powder	Baby	Talc, dolomite, chlorite, calcite	92.22	-0.07	0.54
T2	Spain	Scented talcum powder	Children	Talc	94.14	-0.16	2.12
T3	Spain	Talc	Adults. Talcum powder for feet	Talc, zinc oxide, calcium carbonate, silica	89.43	3.88	1.37
T4	Mexico	Scented talc	Adults. Skin	Talc	95.41	0.12	1.15
T5	Spain	Cutaneous powder	Adults. Analgesic, anti-inflammatory, antipruritic	Talc, 99,23%	89.26	0.14	5.98
T6	Spain	Talc	Sensitive or irritated skin	Talc, calamine	87.01	9.57	6.80
T7	Spain	Talc	Skin	Talc, magnesium carbonate	94.68	-0.24	1.83

2.4. Morphological and microelemental analysis of particles

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectrometry (EDX) were used for the morphological and microelemental analysis of particles. The samples were sprinkled on double-sided carbon adhesive tape attached to an aluminum sample stub-holder. They were metallized with carbon with a Polaron CC7650 metallizer. The equipment was a High Resolution Field Emission SEM (FESEM), model LEO 1500, GEMINI, CARL ZEISS, equipped with an EDX Spectrometer with Inca Energy software from Oxford Instruments. The particles present in the powders were photographed and analyzed and the particle size (projected maximum diameter) measured in a minimum of 50 particles following the method described in Gámiz et al. (1989b). In addition, the fibrous character (length, L; width, W and L/W ratio) of elongated particles was evaluated on particles with $L \geq 5 \mu\text{m}$ and $L/W \geq 5/1$ (Gordon et al., 2014), analyzing fields with at least 500 particles. Each elongated particle was analyzed with EDX. Although European Pharmacopoeia (2014) proposes the use of optical microscopy to study the presence of fibres, it has been preferred to use SEM-EDX because it provides three-dimensional vision with depth of field, allowing the collection of morphological data in detail. These data are essential to distinguish between serpentine and talc, both containing the same elements (Si, Mg, O and H) but each with a very different morphological appearance. SEM was also employed to explain why talc is used for topical use on the skin.

2.5. Quality control according to European Pharmacopoeia

The cosmetic-pharmaceutical quality of the talcum powder based on the limits marked in the talc monograph (Talcum) [14807-96-6] (p. 3361) (European Pharmacopoeia, 2014) was evaluated. The 2014 version was chosen for being available to talc producers and cosmetic laboratories at the time the samples were manufactured. Some Pharmacopoeia methods have been replaced by equivalent alternatives, which are expressly authorized without preventing the quality classification of the material within the Pharmacopoeia rules (see: 1.1 General Statements, p. 3, paragraph 8). This was the case of the presence of fibres (SEM-EDX, as explained above in section 2.4) and the contents of Al, Ca, Mg (XRF) and Pb (ICPMS). It was not possible to apply the limit of Pharmacopoeia for "Loss of ignition" because our samples, cosmetic-pharmaceutical preparations (talcum powders) rather than talcs (raw materials), included organic compounds such as perfumes. For the same reason, the Fe test extracted with HCl did not provide secure values.

3. Results and discussion

3.1. Mineralogical composition

The most abundant mineral phase was talc (Table 2) but other minerals also appeared in minor quantities: dolomite, chlorite, quartz, calcite and magnesite, as well as pharmaceutical cosmetic additives such as zincite and hydrozincite. These additives gave the material a more coloured appearance (higher a^* , Table 1). The XRD diagrams (Fig. 1) show this composition with the main reflections of talc at 0.933, 0.467, 0.311, and 0.248 nm. In no case were reflections corresponding to amphiboles and/or serpentines detected in the angular sector between 10 and 12 degrees 2θ (European Pharmacopoeia, 2014).

The talc percentages (Table 2, once the amounts of Zn additives were discounted) ranged between 99% in T4 and 55% in T2. Four samples had talc percentages > 90%: T1, T4, T5, and T6. The amount of talc was close to 88% in T3 but significantly dropped in T2 and T7, up to a minimum of 60%. Dolomite was the main accompanying min-

Table 2
Mineralogical analysis of talcum powder samples (%).

Mineral	T1	T2	T3	T4	T5	T6	T7
Talc ^a	95	55	82 ^d	99	95	79 ^e	61
Chlorite ^a	3	<1	4	<1	4	1	tr
Calcite ^b	-	-	8	-	-	-	tr
Dolomite ^b	2	41	-	1	1	5	39
Magnesite ^a	-	-	-	<1	-	tr	-
Quartz ^a	-	4	-	tr	-	-	4
Sum acc. min.	5	45	12	1	5	6	39
Additives ^f							
Zincite ^c	-	-	6	-	-	-	-
Hydrozincite ^c	-	-	-	-	-	15	-

tr, traces (diagnostic reflections of the mineral are identified, but its small peak area makes it difficult to quantify); Sum acc. min., Sum of accompanying minerals (different from talc and no additives). Mineral formula: Talc, $\text{Si}_4\text{O}_{10}\text{Mg}_3(\text{OH})_2$; Chlorite (penninite clinoclone), $(\text{Si}_{6.3}\text{Al}_{1.7})(\text{Al}_{1.3}\text{Mg}_{10.5}\text{Fe}_{0.2})(\text{O}_{20}(\text{OH})_{16})$; Calcite, CaCO_3 ; $\text{CaMg}(\text{CO}_3)_2$; Magnesite, MgCO_3 ; Quartz, SiO_2 ; Zincite, ZnO ; Hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$.

^a Quantified by XRD.

^b Quantified by volumetry.

^c Quantified by ICPMS (Table 4).

^d 88% without Zn additives.

^e 94% without Zn additives.

^f inorganic additives in pharmaceutical/cosmetic formulation (Zn bearing minerals).

eral, present in all samples except in T4 (high purity in talc), reaching maximum levels in T2 and T7 with 41% and 39%, respectively. This is evident in the XRD diagram (Fig. 1), shown by a relevant reflection at 0.289 nm. As the second most abundant mineral component in samples was dolomite, there was statistically significant negative correlation between the quantity of this mineral and that of talc ($r = -0.977$; $P < .001$). Chlorite was also detected in all talcum samples, having contents < 5%. Quartz, also <5%, was only detected in the two dolomite-rich samples (T2 and T7), while calcite was only found in a single sample (T3), although in a significant quantity (8%). Finally, very small quantities of magnesite were found in samples T4 and T6, its presence in XRD being identified by the reflection at 0.274 nm.

The mineralogy permits discussion of the degree of quality of the raw material and the deposit type. Those samples with high talc content (paradigm T4) corresponded to mineral deposits selected for their purity, and within these, to high grade batches (Rolh et al., 1976). Commercial talcs (raw materials) of high purity have also been reported by Verdel et al. (1985) and Gámiz et al. (1989a). The opposite occurred in the two dolomite-rich samples (T2 and T7), which could not be classified as high grade. Raw materials with these high quantities of impurities can be found on the market (Verdel et al., 1985). For more details, see section 4.

On the other hand, the presence of dolomite, calcite, and magnesite in samples indicates that they have not undergone an acid purification treatment, which would have completely eliminated these carbonates (Li et al., 2013). Even in the T4 sample, with only <1% magnesite, this purification procedure can be discounted since the morphology of the sheets observed by SEM (Fig. 2) does not show the typical delamination produced by an acid attack (Castillo et al., 2011). The high talc purities seem to be due, as suggested previously, to the choice of deposit and batch.

There were some discrepancies between the mineralogical composition according to sample analysis (Table 2) and the mineral information provided by the manufacturer on the label (Table 1). For example, in T2, the label only mentioned talc and omitted a significant percentage of dolomite while in T7, the manufacturer apparently confused dolomite with magnesite, because the latter was not present in the sample. Other samples also omitted the accompanying mineral phases (T2, T4, T5, T6) from the labelling. The label of T5 claimed a talc purity of 99.23%, when analytically it was 95%.

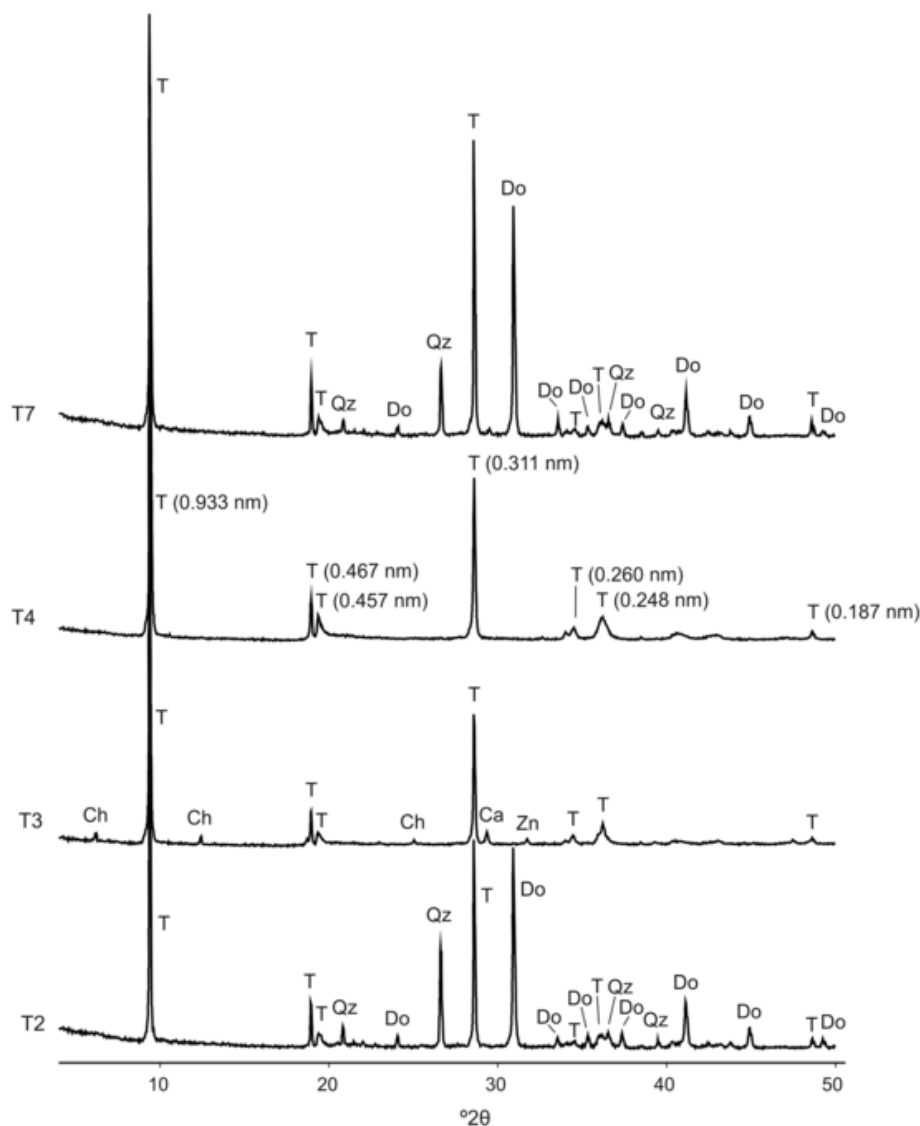


Fig. 1. Four examples of XRD diagrams. In all samples, talc is the most abundant mineral phase; almost exclusively in T4. T2 and T7 show a notable presence of dolomite and, to a lesser extent, quartz. T3 shows the presence of chlorite, calcite and zincite. Abbreviations: T-talc, Chl-chlorite, Qz-quartz, Do-dolomite, Ca-calcite, Zn-zincite.

There are few previous studies on this subject, making it difficult to assess the significance of the results of this study. However, it can be asserted that talcum samples of this study lack amphibole (Fig. 1), which was common in other cosmetic-pharmaceutical talcums from Europe and USA (Rolh et al., 1976; Paoletti et al., 1984; Soriano et al., 1996; ANSES, 2012). Regarding the talc content of many of samples from this study (>90%), Soriano et al. (1996) reported an average purity of talc in the European market of around 80%, although Germany exceeded 90%, and talcum powders from North America were 91%. These are talcums consumed and/or produced in developed countries, but when examining these materials from other parts of the world, such as those from Pakistani cosmetic stores and supermarkets (Alam et al., 2018), local brands did not reach 50% in talc purity and contained chlorite, dolomite, chrysotile, quartz, and chromite. These powders are clearly unsuitable for human use.

3.2. SEM and EDX analysis of particles

The mineralogical composition determined by XRD analysis (Table 2) was confirmed by SEM-EDX analysis (Figs. 2 and 3). The talc mineral species was dominant (Fig. 2a, b, c, d, e, 3a, b, c, d, f, g and

h), accompanied by dolomite (Fig. 2g), quartz (Fig. 2h) and chlorite (Figs. 2f and 3e).

All samples appeared as particulate material (Fig. 2a), a consequence of the grinding process, since the natural talc is massive (Klein and Dutrow, 2017). Most particles were smaller than 50 μm in size. Section 4.3 provides more particle-size data.

Different shapes were encountered in the talc particles, including laminar (Fig. 2d and e), pseudo-ellipsoidal-sub-rounded (Fig. 2b and c), and, rarely, elongated with several patterns (Fig. 3). Elongated particles are discussed in depth in Section 3.4.

The perfect cleavage of talc according to $\{001\}$ is the most obvious physical property (Figs. 2d, e, and 3e). The pseudo-hexagonal or pseudorhombic parting is also evident according to planes (110), (010), and $(hk0)$ (reminiscent of pinacoid and prism outlines) (Figs. 2e and 3e). The flexibility of the talc sheets is also observable in the microphotographs. The sheets curve, bend (Figs. 2b, c, g, 3f, g and h) and even adapt easily to the shape of other particles (Fig. 2g). Flexibility should not be confused with elasticity, a property which talc does not possess (Klein and Dutrow, 2017).

The laminar habit of many of the particles is mainly due to talc being a phyllosilicate, with a crystalline lattice formed by flat layers

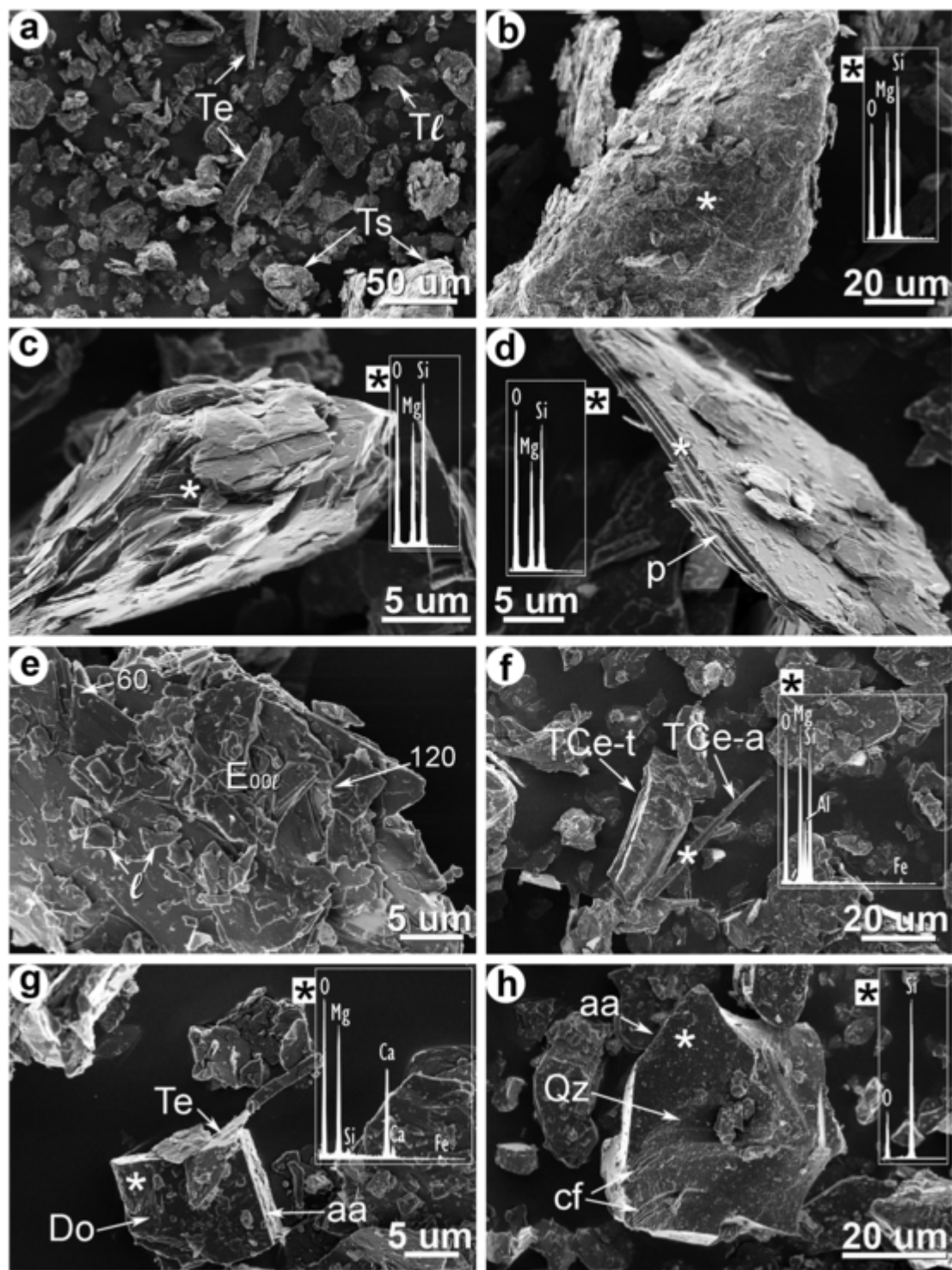


Fig. 2. SEM-EDX analysis of mineral talc and accompanying minerals. a) Talc 4. General appearance of talcum powder. Particle field, mainly of talc mineral. Different morphologies: Ts, pseudoellipsoidal-subrounded. Te, elongated. Tl, laminar. b) Talc 4. Detail of Fig. 2a, corner S-E. Talc particle of pseudospherical-subrounded morphology. Small stacked sheets, which, being flexible, adapt and cover the surface giving it a smooth and shiny appearance. Characteristic talc EDX spectrum (Si and Mg peaks). c) Talc 1. Talc particle of pseudospherical-subrounded morphology. The ellipsoid-like morphology is defined internally by stacked curved sheets, and externally by the sheet covering. EDX spectra characteristic of talc (peaks of Si and Mg). It demonstrates the cleavage and flexibility of talc. d) Talc 1. Talc particle with highly laminar morphology. Thickness close to 2 μm . Perfect cleavage according to (001), in packs (p) with thickness between 1 μm and 500–200 nm. Characteristic talc EDX spectrum (Si and Mg peaks). e) Talc 1. Talc particle surface of laminar morphology. Perfect cleavage according to 001 (E001). Small sheets of diameter between 1 and 20 μm (approx.) and thickness of tenths of micras are easily individualized; they often have straight edges and angles of around 60 and 120 degrees. f) Talc 1. Two particles of talc-chlorite mineralogy. Characteristic talc EDX spectrum, with peaks of Si and Mg; with an evident peak of Al and a small peak of Fe, attributable to chlorite. Elongated particle in slat (TlCe-t). More rigid and massive appearance than pure talc. Acicular elongated particle (TlCe-a) (Length/width approx. 15). g) Pseudopolyhedral crystal (near-rhombohedral) of dolomite (Do), about 20 μm in diameter. EDX spectrum characteristic of dolomite (peaks of O, Ca and Mg) with a peak of Fe. Note the sharp edges (aa), which a priori demonstrate less aptitude for topical cutaneous use. Elongated talc particle (Te), showing great flexibility; it easily bends and adapts to the surface of dolomite crystal and the sample holder. h) Talc 7. Xenomorph quartz particle (Qz), about 50 μm . Characteristic EDX spectrum (unique peaks of Si and O). Note the sharp edges (aa) and the conchoid fractures (cf). Its greater relative size and its sharp edges a priori demonstrate its lower aptitude for topical cutaneous use.

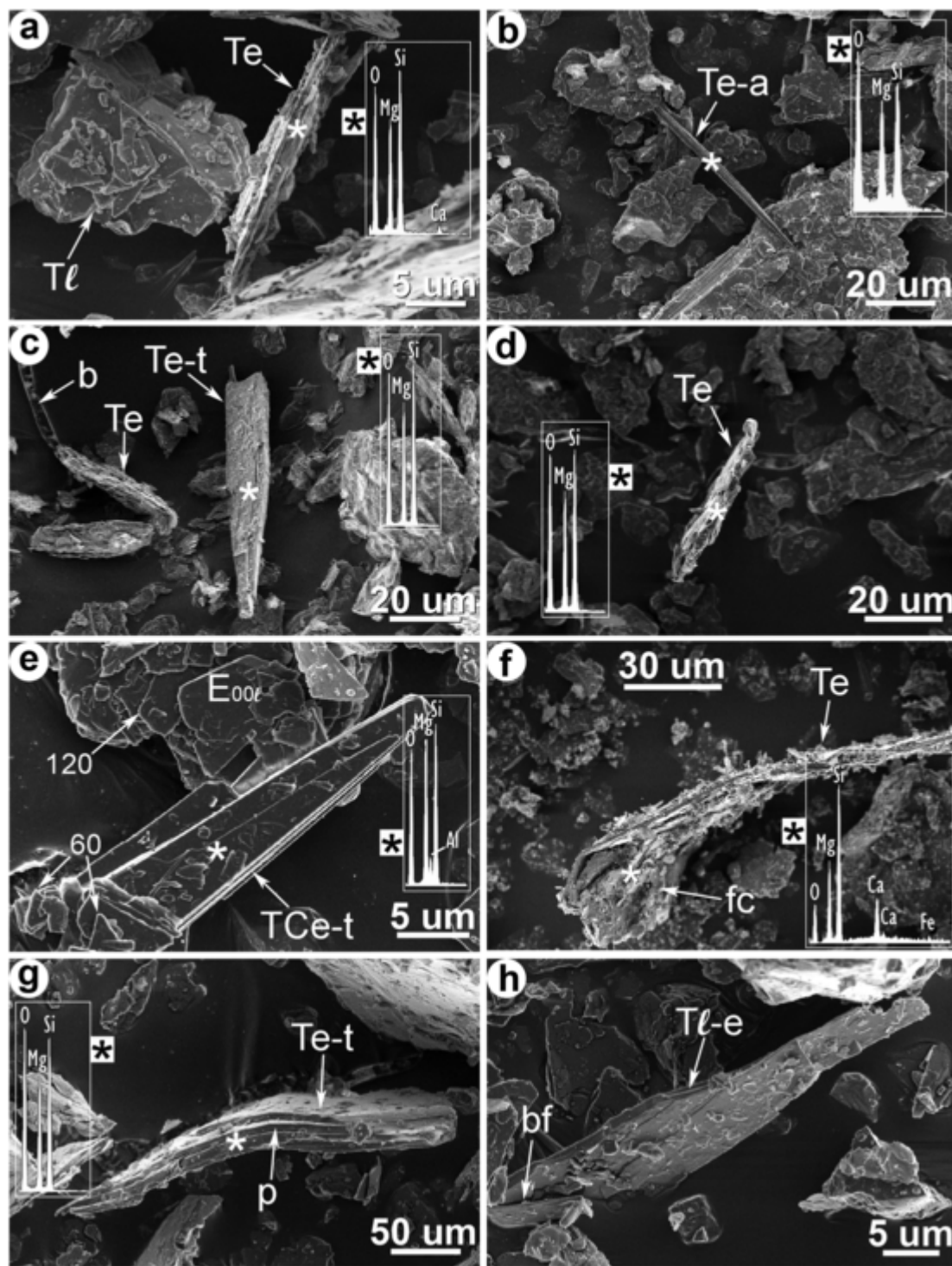


Fig. 3. SEM-EDX analysis of the elongated particles of the talcs. a) Talc 2. Elongated particle (Te), infrequent. Length (L), 30 μm ; Length/width (L/W) approx. 8. Formed by bundles of acicular particles joined together by small sheets. EDX spectrum characteristic of talc (Si and Mg peaks). Laminar particle of talc (Tl), with manifest cleavage {001} and edges with angles at 60 and 120 degrees. b) Talc 1. Acicular elongated particle (Te-a), infrequent. L, 75 μm ; L/A approx. 25. Characteristic talc EDX spectrum (Si and Mg peaks). c) Talc 4. Detail of Fig. 2a, north of the photograph. Two elongated talc particles. The center particle, elongated-slat morphology (Te-t), is generated by the perfect cleavage {001} and the parting (*hk*0). L, 75 μm , L/W approx. 6. The particle on the left (Te) is segmented into three parts; it has been generated by grinding, clearly forming a bag (or sheath) with particles inside it in its narrowest upper part (b). Ltotal, more than 100 μm , variable L/W, between 6 and 12. EDX spectra characteristic of talc (Si and Mg peaks). d) Talc 5. Elongated particle (Te) formed by sheets that curl and wrap around the major axis of the particle. It has its origin in the cleavage and flexibility of talc sheets. L, 50 μm ; L/A, 7. Characteristic talc EDX spectrum (Si and Mg peaks). e) Talc 5. Elongated-slat particle of talc-chlorite mineralogy (TCe-t). EDX spectrum characteristic of talc-chlorite, peaks of Si and Mg, with a peak of Al. Generated by parting according to the (*hk*0) planes and cleavage, of few sheets, in packs according to {001}. L, 30 μm ; L/A approx. 6. Talc laminar particle (Tl), which demonstrates the cleavage according to {001} (E00l) and the pseudohexagonal (or pseudotrigonal) symmetry of the talc, with edges at 60 and 120 degrees. f) Talc 3. Elongated particle of talc (Te) that could be qualified as "hair", even with its follicle (fc). By zones, bundles of talc sheets appear, bent and curved, together with others that are bags filled with particles some of non-laminar appearance, probably calcite (Ca); latter feature very evident in the follicle (fc). EDX of talc, peaks of Si and Mg; with a peak of Ca. L minimum, 150 μm ; L/W in the hair zone 11–12. g) Talc 7. Elongated-slat particle of talc (Te-t). L, 300 μm ; thickness, 30 μm . Formed by packs of sheets (p) of an individual thickness of about 10 μm . The soft folds are evident. EDX spectrum characteris-

tic of talc (Si and Mg peaks). The particle genesis is related to the {001} cleavage and the (*hk*0) parting planes (perpendicular to the plane of the photo). Flexibility facilitates the soft folds. h) Lamellar-elongated particle of talc (T1-e). L, 46 µm; thickness, 2 µm. It demonstrates the cleavage of talc, which generates particles that reach a large relative dimensions according to (001) planes. In the south-west corner of the photo several folds (bf) are shown, which demonstrate the great flexibility of the talc, since the particle bends on itself but does not break.

and easy cleavage. The lamellar particles may have very small thicknesses (a few microns) (Fig. 2d). The particulate nature of the samples is generated during mechanical stresses and the consequent crushing of the material induced by grinding. The lamellar particles can be separated, without too much effort, from the larger morphological units. The generation of lamellar talc particles of low hardness ($H = 1$) and quite flexible also justifies the other shapes previously described for talc particles. The lamellar particles can be rounded and curved in their continuous rotation derived from grinding. In addition, they can form stacks with other lamellar particles, which would be coupled by folding and coating them. This results in pseudospherical-sub-rounded shapes, with an internal fabric very close to onion layers, and a surface that appears to be soft (Fig. 2b and c), as also described by Gámiz et al. (2002). Sometimes, the grinding process even folds and twist the sheets on themselves, with such intensity that they generate elongated shapes (Fig. 3d). A group of sheets can even generate a bag, also elongated, that houses smaller sheets or other particles (Fig. 3c and f). Finally, the partition of the talc sheets during grinding plays an important role in the generation of elongated particles (Figs. 2f, 3b, c, e, g and h). See more in section 3.4.

The SEM observations allow understanding clearly, in a graphical way, why ground talcum has been used since ancient times for topical use (cosmetic/pharmaceutical). When the powder is applied to the skin, as a result of the perfect cleavage {001}, the particles can be divided, leaving small lamellae attached and adapted to the skin due to their flexibility. In the rubbing of the skin resulting from body movements, talc cleavage again plays an important role, as the sheets may absorb the energy when separated, avoiding erosion of the skin. Talc particles are not physically aggressive - they do not scratch - due to their low hardness ($H = 1$), less than that of the skin ($H = 1.5$). The lamellar shapes seem to favor cutaneous use, in the same way as spheroids, since they move and fit easily on the skin. The elongated shapes, apparently less favourable, were only present in very low proportions (Table 5).

Along with the above, it must be taken into account the chemical composition of talc, poor in toxic elements and highly insoluble, which makes it inert. In addition, the residual charges of the sheet (in the planes of oxygen) could adsorb the sweat (with exudates, toxins, etc.) and release additives (refreshing, conditioning, etc.) previously fixed. This would take place preferentially on the surface (001). The small sheets of talc do not cover sweat and sebaceous pores (Viseras et al., 2007), thus contributing to a lubricating/cooling effect. Galán et

al. (1985) emphasized the lubricating power of talc. On the other hand, grinding may favor the adsorbent power of talc sheets by increasing their specific surface area (Dellisanti et al., 2009).

The particles of other minerals accompanying talc were characterized and identified by SEM-EDX according to their habits, microanalysis, and particle sizes. Dolomite appeared as pseudopolyhedral crystals, with recognizable crystal faces, straight and sharp edges, sometimes reaching 20 µm, and an EDX spectrum with Ca and Mg (Fig. 2g). Quartz was identified by its EDX spectrum (Si and O) and xenomorphic grains -fragments of other larger grains-, also with sharp edges and a particle size that stands out from the rest, between 30 and 100 µm. The observation of the microphotographs (Fig. 2g and h) is sufficient to suggest a different topical behaviour on the skin of dolomite and quartz. Compared to talc, dolomite and quartz have sharp edges, always equidimensional shapes, hardness of 3.5 and 7, respectively, and even larger grains, especially in the quartz.

Finally, the SEM-EDX observations suggest that chlorite is not a mineral phase independent of talc, but forming mixed-layers with it, with an EDX spectrum typical of talc (Si and Mg peaks) besides the presence of a prominent peak of Al and, in many cases, also Fe (Figs. 2f and 3e). According to Gámiz et al. (1989a), chlorite may be penninite-clinochlore type. The talc-chlorite association in cosmetic talcums was proposed by Soriano (1994) using observations of electron microscopy, and Shau and Peacor (1992), who analyzed petrological data. Talc-chlorite particles did not differ much from those of talc, except, perhaps, that with SEM they showed a more consistent appearance, less cleavage, and with fewer curves and bends than those of pure talc. This is due to the hardness of chlorite being between 2 and 3 (Deer et al., 1992).

3.3. Chemical composition

Si and Mg were the most abundant major elements measured by XRF (Table 3), in agreement with a material whose majority phase is talc ($Mg_3Si_4O_{10}(OH)_2$). This is why sample T4, with 99% talc (Table 2), had a chemical composition close to that of the ideal talc (Table 3). Similar values were reported in other commercial talcums (Verdel et al., 1985; Gámiz et al., 1989a) with purities >95% in mineral talc.

The small amounts of Al, Fe and Ca in T4 could be attributed to the presence of chlorite and dolomite. In the same way, the maximum contents of Al appeared in samples with more chlorite (T1, T3, and T5) and those of Ca when there was more dolomite (T2 and T7) or cal-

Table 3
Major element composition (XRF) of talcum powder samples (% oxides).

	T1	T2	T3	T4	T5	T6	T7	Mean
SiO ₂	58,05	36,76	51,87	61,81	56,27	51,31	42,17	51,18
Al ₂ O ₃	2,44	0,40	1,02	0,20	2,71	0,86	0,14	1,11
Fe ₂ O ₃	0,80	1,71	0,83	0,16	0,77	0,95	1,69	0,99
MnO	0,01	0,05	<LLD	<LLD	<LLD	<LLD	0,04	0,03
MgO	31,21	22,51	26,54	31,37	30,57	26,09	23,26	27,36
CaO	0,66	14,51	4,46	0,39	0,47	0,36	12,10	4,71
Na ₂ O	<LLD	<LLD	0,91	<LLD	<LLD	1,73	0,28	0,97
K ₂ O	<LLD	0,01	<LLD	<LLD	<LLD	<LLD	0,01	0,01
TiO ₂	0,08	0,06	0,04	0,04	0,10	0,21	0,08	0,09
P ₂ O ₅	0,07	0,04	0,04	0,06	0,08	0,05	0,04	0,05
LOI	6,44	24,00	8,37	5,93	9,29	7,52	20,29	11,69
Sum	99,76	100,05	94,08 ^a	99,96	100,26	89,08 ^a	100,10	97,61

LLD, lower limit of detection; LOI, loss of ignition (1000 °C). Chemical composition of talc (theoretical composition): SiO₂, 63,50%; MgO, 31,70%; LOI, 4,80%.

^a Sum values approach 100% if ZnO content (from Table 4) is added: T3, 99,78%; T6, 100,21%.

cite (T3). This relationship between chemical and mineralogical composition was supported by the significant correlations: SiO₂ vs. Talc ($r = 0.987$; $P < .001$), MgO vs. Talc ($r = 0.969$; $P < .001$), Al₂O₃ vs. Chlorite ($r = 0.819$; $P < .01$), and CaO vs. Dolomite ($r = 0.951$; $P < .001$). The maximum values of Fe occurred in the samples with more dolomite (T2, T7), thus being associated with this component (Fe₂O₃ vs. dolomite: $r = 0.880$; $P < .01$). In many of the EDX spectra of dolomite (Fig. 2g) a Fe peak was recorded.

The remaining elements measured with XRF (Mn, Na, K, Ti, P) were present in smaller amounts.

The samples with Zn additives, such as zincite and hydrozincite (T3, T6), showed an analysis of major elements that did not total 100% until corrected by adding the content of Zn (Table 4). The colour was a useful indicator of the Zn content and other elements such as Na, Ti and Cd, seemingly associated with these inorganic additives (Tables 2, 3 and 4), all significantly correlated ($r = 0.8$ to 0.9) with the colour parameter a* (Table 1).

The LOI values (Table 3) were difficult to interpret as the samples were cosmetic preparations containing additives of diverse organic nature (oils, perfumes and others) that distort the data. Only the result of T4 could be clearly interpreted, with 99% talc and a LOI of 5.93%; 1% more than the theoretical talc (4.80%).

The content of minor ICPMS elements (Table 4) showed great variability, both between different elements and between samples. The greatest contents, by far, corresponded to Zn added in the additives. The Cr (5.95–1.31 mg/kg, average 3.29 mg/kg) and Ni (3.57–8.99 mg/kg, average 7.20 mg/kg) also stood out. Six elements oscillated around 1 mg/kg (Sc, Co, Y, Sn, Th and U) whereas eleven were below 1 mg/kg (Be, Cu, As, Mo, Cd, In, Sb, Ba, Tl, Pb, Bi).

Although it is not the objective of this study, the data for minor elements permitted interpretation of the geological relationship between samples and to formulate hypotheses regarding the mineral origin. It is worth noting, for example, the pair of samples T2-T7, with almost equal amounts of elements (e.g. Zr, 9.30–9.00 mg/kg, respectively). Something similar occurred with T1-T5. In addition, the mineralogy of these sample pairs is similar (Table 2). Each pair seems to be the

same commercial product, probably from the same deposit and sample batches of similar quality. On the other hand, it does not seem that any of the deposits originated in the metasomatism of ultramafic rocks, since the contents of Co, Cr, and Ni were below those reported by Rolh et al. (1976) for these materials (p. 274, Table 6).

3.4. Particle size (SEM)

The particle size of our talcum powder (Table 5) was around 10 μm (from 9.1 μm in T3 to 13.9 μm in T7), with a mean of 12 μm . This size corresponds to a micronized material, suitable for cosmetic use (Gámiz et al., 1989b). However, this material is not homogeneous in size but shows great dispersion, especially in T7 with a range from 321.5 to 0.9 μm . The role played by large powder particles (>30, 50, 100 μm , etc.) in topical use should be discussed together with their mineral composition and their relative quantity (percentage), also bearing in mind that the skin cells measure tens of μm . If the large particles are of talc mineral (i.e., Fig. 2b), they should not cause problems, since, as they exfoliate easily, their size is drastically reduced almost instantaneously when applied to the skin. This is not the case with other minerals such as quartz, not easily crumbled, hard ($H = 7$) and about 100 μm in size in the registered cases (Fig. 2h). Its effect can be abrasive and defoliant on the skin and, if present in very large amounts, it would preclude topical application. Nevertheless, in our talcum samples (Table 2), quartz never exceeded 4%. Another case is dolomite, with H between 3.5 and 4, and sometimes with a particle diameter reaching 20 μm (Fig. 2f) or more. The percentage of dolomite was high in T2 and T7 (around 40%). These talcum powders would thus not be suitable for topical cutaneous use due to particle size, combined with the hardness of the mineral and its percentage in the commercial product.

3.5. SEM and EDX analysis of elongated particles

The mineralogical analysis (Table 2, Fig. 1) showed the absence of asbestos belonging to serpentine or amphibole mineral groups,

Table 4
Minor element composition (ICPMS) of talcum powder samples (mg/kg).

	T1	T2	T3	T4	T5	T6	T7	Mean
Zr	14,70	9,30	7,70	6,50	16,30	6,50	9,00	10,00
Be	0,63	0,16	0,32	0,04	0,76	0,28	0,16	0,34
Sc	1,91	0,63	1,80	0,93	1,62	1,16	0,97	1,29
V	5,87	2,48	4,48	3,99	6,96	3,03	2,44	4,18
Cr	5,19	1,63	2,81	1,31	5,95	3,93	2,23	3,29
Mn	23,56	387,84	21,83	8,24	21,98	24,35	322,21	115,72
Co	1,08	3,74	1,57	0,49	1,20	2,14	4,29	2,07
Ni	8,92	6,97	8,05	3,57	8,99	7,95	5,96	7,20
Cu	0,30	0,34	0,43	0,48	0,48	0,45	0,03	0,36
Zn	32,91	7,44	46681,17	41,46	4,91	89489,84	96,53	19479,18
As	0,10	0,07	0,11	0,01	<LLD	<LLD	0,11	0,08
Y	0,95	2,03	0,92	0,55	0,88	1,35	1,61	1,18
Mo	0,26	0,05	0,11	0,84	0,17	0,25	0,01	0,24
Cd	<LLD	0,07	0,04	0,02	<LLD	0,16	0,02	0,06
In	0,01	0,03	0,01	0,01	0,01	0,01	0,02	0,01
Sn	3,90	0,03	1,32	<LLD	4,41	0,72	0,19	1,76
Sb	<LLD	0,21	0,11	0,05	<LLD	0,16	0,06	0,12
Ba	<LLD	0,55	<LLD	<LLD	<LLD	<LLD	<LLD	0,55
Tl	0,02	0,02	0,32	0,02	0,02	0,10	0,01	0,07
Pb	<LLD	0,54	0,11	<LLD	<LLD	0,78	0,24	0,42
Bi	0,07	0,05	0,04	0,03	0,04	0,01	0,02	0,04
Th	1,86	0,24	0,46	0,17	1,05	0,27	0,13	0,60
U	2,58	0,50	1,48	2,37	3,38	2,19	0,56	1,87

LLD, lower limit of detection.

Table 5
Morphological parameters measured with SEM of talcum powder sample particles.

Granulometry ^a			Elongated mineral particles (L ≥ 5 μm) ^b								
	Mean size (±SD) (μm)	Range (min–max) (μm)	Number of particles ^c		Length (L) (±SD) (μm)	Range (min–max) (μm)	Width (W) (±SD) (μm)	Range (min–max) (μm)	L/W (±SD)	Range (min–max) (μm)	
			Particles with L/W ≥ 5	Particles with L/W ≥ 20							
T1	13,5 ± 15	1,8–88,9	9	1,8	22,9 ± 20,9	4,5–75,0	2,7 ± 1,8	0,9–6,4	8,3 ± 6,2	5,0–25,0	
T2	11,2 ± 12,8	0,3–68,2	11	2,2	18,1 ± 7,3	9,1–31,8	2,9 ± 1,6	0,9–6,4	6,9 ± 2,2	4,3–11,0	
T3	9,1 ± 13,5	0,9–133,3	11	2,2	18,4 ± 16,7	8,2–59,1	2,2 ± 1,9	0,7–6,4	8,9 ± 2,6	5,0–12,7	
T4	11,4 ± 14,7	1,8–150	18	3,6	21,7 ± 18,7	5,5–72,7 ^d	3,8 ± 4,4	0,5–17,3	8,2 ± 4,3	4,0–17,0	
T5	12,5 ± 11,3	2,6–94,5	13	2,6	26,6 ± 13,1	11,8–56,4	4,9 ± 3,1	2,0–12,7	5,9 ± 1,9	4,1–9,5	
T6	12,7 ± 10,4	3,6–81,8	8	1,6	22,8 ± 16,4	7,3–57,3	4,3 ± 3,0	1,4–10,0	5,5 ± 1,0	4,0–6,9	
T7	13,9 ± 31,6	0,9–321,46	9	1,8	11,3 ± 2,9	8,2–16,4	2,3 ± 0,9	1,4–4,1	5,4 ± 1,7	3,6–9,0	
Mean talc	12,0 ± 15,6	1,7–134,0	11	2,3	20,3 ± 13,7	7,8–52,7	3,3 ± 2,4	1,1–9,0	7,0 ± 2,8	4,3–13,0	

^a Maximum projected diameter.

^b Most particles were talc (with EDX), and few were talc-chlorite (Fig. 3).

^c In a count of ~500 particles.

^d A single case with L > 100 μm (exceptionally sized) has been found, in a segmented particle (Fig. 3c).

which could generate fine carcinogenic particles of great length. However, the specific microscopic analysis of the elongated particles, as proposed by European Pharmacopoeia (2014), is an interesting topic, performed with SEM-EDX based on the morphological description and microchemical analysis (Figs. 3 and 2), together with dimension measurements (Table 5).

The elongated particles ≥5 μm found in our talcum powders belonged to at least five morphological types. Type 1 were acicular-shaped particles (Figs. 2f and 3b). Type 2 resembles a ribbon (pseudo-prismatic) or a slat, of variable thickness (Figs. 2f, 3c and e). These types are the most frequent and are seemingly generated by cleavage {001} and partition along planes (hk0). Other elongated particles are formed due to the flexibility of the sheets, such as type 3, which curl up on themselves (Fig. 3d). Type 4, elongated bags of laminae (Fig. 3c and f), owe their genesis to flexibility and also to cleavage, since the exfoliated sheets also fold and bend, enveloping other particles in the manner of a bag. Type 5 are bundles of acicles joined by laminae (Fig. 3a).

The EDX spectra indicate that the majority of the elongated particles are mineral talc and some talc-chlorite, the latter being flatter and with less folding and curvature (Figs. 2f and 3e) due to the greater hardness of chlorite. Elongated particles can even be associated with carbonate particles in type 4 (Fig. 3f).

The presence of talc particles morphologically similar to other fibrous minerals in talcum powder was also noted by several authors (Paoletti et al., 1984; ANSES, 2012). It is suggested that these elongated particles in the talcum samples are a result of the mechanical forces of grinding causing cleavage and parting. Grinding, in turn, folds and curls the small sheets that form. It should also be remembered that some rupture orientations may be inherited from geological material. Alignments of preferential fractures might also favor elongated particles during the grinding process (types 1, 2, 5). It should not be forgotten that many talcs are of metamorphic in origin.

Nevertheless, the elongated particles from our samples T1-T7 did not have the SEM characteristics described by European Pharmacopoeia (2014), page 1999) for harmful fibres: “parallel fibres occur-

ring in bundles; fibre bundles displaying frayed ends; fibre in the form of thin needles; matted masses of individual fibres and/or fibres showing curvature”.

The dimensions of the elongated particles (Table 5) again showed relative variability. On average, length (L) ranged from 11.3 μm (T7) to 26.6 μm (T5), with a mean for all samples of 20.3 μm. They were thus larger than the mean of all the particles (12 μm). However, the L/W ratio is even more diagnostic than L, with values between 5.4 (T7) and 8.9 (T3), far below the harmful limit (L/W > 20) established by European Pharmacopoeia (2014).

In addition, a parameter that Pharmacopoeia does not consider was calculated, as it is not especially precise in its proposal for microscopic study of potential fibres. We decided it would be useful to consider the number of elongated particles per 100 particles. This percentage for all talcums was close to 2%, taking into account particles with L/W > 5 (Table 5), and below 0.4% (2 cases out of the 500 evaluated in T1) when considering particles with L/W > 20. These percentages confirm the null or irrelevant harmfulness of these elongated particles.

Therefore, the mineral nature (talc), morphology (aspect and ratio L/W) and percentage of elongated particles in our talcum powders did not represent any risk for health. Although some of these particles have a fibrous or acicular appearance (Type 1, Figs. 2b and 3b), their composition of talc and sometimes talc-chlorite suggests that once in contact with the skin they will immediately crumble and exfoliate to form harmless small sheets.

4. Talcum suitability for cosmetic-pharmaceutical use

First it will be evaluated what has denominated “mineral quality” and then “European Pharmacopoeia quality (2014)” (Table 6).

Mineral quality is derived directly from criterion 1: mineralogical composition, including 1–1) talc content compared to other minerals and 1–2) absence/presence of asbestos; and criterion 2: chemical composition in toxic trace elements.

According to 1–1 and 1–2, talcums with talc mineral content ≥ 90% and absence of asbestos can be referred to as cosmetic grade talcum and the rest as industrial grade talcum (Rolh et al., 1976;

Table 6

Assessment of the suitability of talcum powder samples available in Spanish pharmacies for cosmetic/pharmaceutical use. Mineral and European Pharmacopoeia (2014) qualities.

Mineral quality parameters ^a							Pharmacopoeia quality parameters ^b				
Talc content (%)	Presence of fibrous minerals	Cd + Cr + Pb ^c (ppm)	Pb ^d (ppm)	As ^d (ppm)	Cd ^d (ppm)	Mineral quality	Al (%)	Ca (%)	Mg (%)	Pharmacopoeia quality	
T1	95	No	5,25	<LLD	0,10	<LLD	Cosmetic	1,29	0,47	18,73	Suitable
T2	55	No	2,24	0,54	0,07	0,07	Industrial	0,13	10,30	13,51	Non suitable
T3	88	No	2,95	0,11	0,11	0,04	Industrial	0,53	3,17	16,89 ^e	Non suitable
T4	99	No	8,26	<LLD	0,01	0,02	Cosmetic	0,12	0,28	18,82	Suitable
T5	95	No	5,95	<LLD	<LLD	<LLD	Cosmetic	1,44	0,33	18,34	Suitable
T6	94	No	4,86	0,78	<LLD	0,16	Cosmetic	0,46	0,26	16,95 ^e	Suitable
T7	61	No	2,94	0,24	0,11	0,02	Industrial	0,07	8,59	13,96	Non suitable

LLD, lower limit of detection.

^a For cosmetic mineral quality the talcum powder sample must contain: >90% of talc (T3 and T6 talc content was calculated without Zn additives); no fibrous minerals; Cd + Cr + Pb < 100 ppm; Pb < 0,5 ppm; As < 0,2 ppm; Cd < 0,3 ppm.^b For "suitable" European Pharmacopoeia (2014) quality the talcum powder sample must contain: Al < 2%; Ca < 0,9%; 19.5% ≥ Mg ≥ 17% (Tables 3 and 4).^c Limits on packaging constituent materials (European Parliament and Council Directive 94/62/EC).^d Limits for continued talc inhalation (ICH, 2019).^e Samples T3 and T6 without Zn additives.

Blount and Vassiliou, 1983; Burns et al., 2019). Industrial talcums would not be suitable for human use as talcum powder.

The limit of 90% talc guarantees the properties for topical use of the material: physical properties (cleavage, hardness, flexibility, etc.), adsorptive properties and chemical inertia (absence of toxicity and insolubility in the skin). T1, T4, T5 and T6, which fully meet the requirement (>90% talc), would be of cosmetic quality while T3 is approaching (87% talc) whereas T2 and T7 have surprisingly low talc contents (60%) for cosmetic-pharmaceutical use. T3, T2 and T7 have an important presence of carbonates (Table 2), reducing the talc content to the point where they are classified as industrial quality.

The seven talcum samples, according to the criterion 1–2 (fibres), would all be of good mineral quality, since the XRD diagrams (Fig. 1) and the microscopic and microanalytical analysis of the elongated particles (Sections 4–5) did not reveal asbestos.

The assessment of mineral quality according to the content of toxic trace elements (criterion 2 of mineral quality) is more uncertain as the harmful limits for cosmetic materials have not yet been specifically established. Then it will be considered the limits for other uses adapted to our study, particularly the limits for packaging (European Parliament and Council, 1994) evaluating the sum Cd + Cr + Pb (Table 6). None of our samples exceeded 100 ppm. The limits of metals for medicines (ICH, 2019) were also tested, considering three of the elements classified as class 1 (maximum toxicity). Among them, we selected inhaled drugs, as the only relevant case here, supposing that talcum powder could be inhaled accidentally and continuously. The results (Table 6) indicate that two of the talcums, T2 and T6, slightly exceeded the Pb limit (0.5 ppm). This is consistent in T2 with its rating as industrial talcum, not suitable for human use. The manufacturer should control the Pb content of the mineral raw material and the rest of components, since the Pb measured by ICPMS came from the total talcum powder: minerals + additives.

The European Pharmacopoeia (2014) quality and the fulfillment of what is included in its Talc monograph suggest an additional comment to the valuation made in Table 6. Our talcums meet the conditions established for production, as a mineral deposit without asbestos was selected. With regard to the element content tests, the seven samples conformed to the standard in Al (<2%) and in Pb (<10 ppm). However, Ca and Mg again showed unsuitable values in T2, T3 and T7, exceeding the permitted limit for Ca (0.9%) and not reaching the minimum threshold in Mg (17%). The presence of calcite (source of Ca) in T3 and dolomite (source of Ca and Mg) in T2 and T7 (Table 2) would explain this. Dolomite has 13.2% Mg content, lower than that of

the talc mineral (19.3%). Consequently, on replacing talc in the mixture it dilutes the Mg content such that it does not reach the Pharmacopoeia threshold (17%). T6 has a percentage of Mg (16.95%) just within the limit (17%), but the LOI of this talcum powder (Table 3) is 7.52%, probably due to organic cosmetic additives other than hydrozincite. In the case of not having additives, 17.97% of Mg should be expected with 94% of talc. It is then classified as suitable.

To summarize this section and Table 6, it can be stated that mineral quality and pharmacopoeia quality have coincided in their results and diagnosis of suitability. In other words, the samples with cosmetic quality also have pharmacopoeia quality due to their mineral quality, unlike the industrial samples.

5. Evolution of the mineral quality of talcum powder for sale in Spanish pharmacies over the last thirty years

The evolution of quality has been determined by comparing the results of the present study and those obtained by our team in the 1980s using XRD (DeIgado et al., 1985) (Table 7). In the past, 12 samples were studied whereas in the present study there were only 7, reflecting the decrease in the number of brands available in Spanish pharmacies.

Previously, there were 6 talcum powders with cosmetic quality for their talc content (>90%), without asbestos, and another 6 industrial talcums (50%). The proportion of cosmetic talcums has slightly increased today, to 57% (4 vs. 3 samples). This is clearly not a substantial improvement. However, the percentage of talc has increased slightly in cosmetic talcum powders: 96% today compared to 94% in the 1980s. There are no appreciable differences in calcite and quartz. The chlorite content has increased very slightly, from <1 to 2%, and the amounts of dolomite have remained constant.

With respect to the talcum powder of industrial quality, currently available in pharmacies, its talc content (on average 67%) is lower today than in the 1980s (87%), resulting in a decrease in the overall average quality of the talcum powder at 82% vs. 90% (Table 7). This is due to the fact that in the current market there are preparations with high amounts of calcimagnesian carbonates (dolomite).

However, while, previously, signs of the presence of amphiboles (small reflections in $10.5 \pm 0.1^{\circ}2\theta$) were detected in 4 samples, none of the 7 samples currently studied contained traces of amphibole. This is a significant improvement.

This comparative study can also be approached from the point of view of the talcum quality norms at different times. The talcum powder currently on the market in Spain must have been regulated in its production by the 5th Edition of the Real Farmacopea Española

Table 7

Evolution of the mineral contents (%) of talcum powder samples available in Spanish pharmacies in the last 30 years (all data are mean values).

	Talc	Chlorite	Calcite	Dolomite	Quartz	Amphibole
In the 1980s (twentieth century) ^a						
Cosmetic talcum powder ^c	94	<1	3	2	1	–
Industrial talcum powder ^d	87	5	4	2	<1	2 ^f
Mean talcum powder ^e	90	3	3	2	1	1
In the 2010s (current century) ^b						
Cosmetic talcum powder ^c	96	2	–	2	–	–
Industrial talcum powder ^d	67	1	3	27	2	–
Mean talcum powder ^e	82	2	1	14	1	–

^a 12 samples (6 cosmetic talcum powders and 6 industrial talcum powders) analyzed by XRD (Delgado et al., 1985).

^b 7 samples (4 cosmetic talcum powders and 3 industrial talcum powders) analyzed by XRD, ICPMS and carbonates volumetry (Table 2).

^c Cosmetic talcum powder must contain >90% talc without amphibole.

^d Industrial talcum powder can contain <90% talc with/without amphibole.

^e Mean talcum powder weighted to number of cosmetic/industrial samples.

^f 4 samples contained amphibole.

ola (2015), whose talc monograph is identical to that of the European Pharmacopoeia of 2014 (used in section 4). In the 1980s, talcum powder was regulated by the Spanish Official Pharmacopoeia (1954), in which the compositional tests were eminently qualitative and did not use XRD or consider fibres. Nonetheless, the talcum of cosmetic mineral quality in the 1980s had a composition similar to the present, possibly guaranteed by the industrial producer, who would reserve the best batches for pharmaceutical use.

However, industrial quality talcum previously contained more chlorite and frequently amphibole than its current counterpart, since the content of Al and fibres was not regulated by the current pharmacopoeia.

Finally, taking into account the pharmacopoeias, it is difficult to explain the drastic increase in the dolomite content in industrial talcum powders (Table 7), on average from 2% to 27%, suggesting an error in the quality control system.

6. Final considerations and conclusions

The microscopic morphological observation (SEM) of talc particles ($Mg_3Si_4O_{10}OH_2$) revealed the physical, physicochemical and chemical reasons why talc is a natural material suitable for topical use on human skin. The perfect cleavage {001} facilitates the supply of small laminar talc particles onto the skin. These slide and adapt to the skin surface due to their flexibility. Talc, as a result of its low hardness, also protects and absorbs energy from friction and does not scratch the skin. In addition, the residual charges of the talc sheets adsorb exudates, toxins and help it to retain perfumes and other refreshing additives, skin conditioners, etc. This takes place in an environment of chemical inertia and zero toxicity, being insoluble at skin level and composed of innocu-

ous elements (Si, Mg, O and H). Moreover, due to its inorganic nature, talcum is unlikely to be contaminated by microorganisms. Consequently, talcum powder is considered a protective material with lubricating and refreshing characteristics for cutaneous use.

However, talc mineral may be accompanied by varying amounts of other mineral phases due to its natural origin. In order to ensure the absence of undesirable minerals, it has been suggested that talc be synthesized, which is expensive, or be replaced with corn starch powder, which does not have the surface properties mentioned previously and would probably be more susceptible to microbial contamination. Further studies on this are required.

For the use of talcum powder in Pharmacy and Cosmetics it is vital to guarantee its mineral composition. A purity in talc of at least 90% is desirable, without potentially carcinogenic asbestos. Over the last two decades the European Pharmacopoeia has been updated with several compositional, mineralogical and morphological tests in order to ensure the quality of talcum powder for pharmaceutical use. Choosing mineral deposits and batches of high quality material, without fibres and with high talc purity, should be an essential task for the producers. This is relatively feasible today in view of current geological and mineralogical knowledge.

In seven talcum powders currently sold in Spanish pharmacies, the following was found: 1) Four met the required mineral quality and European Pharmacopoeia quality. They had a purity in talc >90% without potentially carcinogenic fibrous minerals and low toxic metal content. 2) The remaining three samples, although not containing fibres, failed other compositional and mineralogical tests due to impermissible quantities of dolomite (40%) and calcite (10%). Consequently, these materials should be for industrial use only and not for human cosmetic-pharmaceutical use. 3) Some samples contained elongated particles. However, exhaustive and detailed analysis by SEM-EDX revealed they were composed of talc and were only present in low quantities. Consequently, they pose no danger to health. 4) Their comparison with talcum powders for sale in pharmacies during the 1980s revealed the following: i) fibrous minerals have disappeared from the talc currently available in Spain, whereas four of the twelve samples from the 1980s showed signs of amphiboles; ii) purity in talc has increased by two percentage points, from 94 to 96% when compared with the six good quality samples from the 1980s (>90 in talc and without fibrous phases); and iii) in the 1980s samples with such a low purity in talc as currently (around 60%, due to the presence of the contaminant dolomite) were not available.

The quality control of pharmaceutical and cosmetic raw materials is still an important scientific challenge today. The strength of the single European (and global) market lies in complying with the purity standards of its products, especially those for cosmetic and sanitary use.

Dedication of Competing Interest

To Professor Emilio Galán Huertos, pioneer of Applied Mineralogy in Spain, meticulous scientist and humanist.

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

Uncited references

European Pharmacopoeia, 1997

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