cosmetics

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Study Design on the Presence of Metals in Moisturisers, and Compliance with Regulation (EC) No. 1223/2009 of the European Parliament and of the Council of the European Union, on Cosmetic Products

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Abstract: Metals are present in cosmetics due to deliberate addition by the manufacturers, contamination of raw materials, and/or contamination during their manufacture or storage. The objective of this work was to explore the metal content in the most-consumed moisturising creams on the Spanish market, to verify their degree of compliance with Regulation (EC) No. 1223/2009 of the European Parliament and of the Council of the European Union, regarding the presence of metals in cosmetics. The moisturisers were digested (microwave-assisted acid digestion) and analysed by inductively coupled plasma-mass spectrometry (ICP-MS), for metal assessment. The ICP-MS measurements were successfully validated (RSDs lower than 5% and analytical recoveries within the 91–110% range). Metals banned in cosmetics were found at very low concentrations in some of the moisturisers, as inevitable traces of pollutants. This was the case with beryllium (found in only two samples, at concentrations lower than 0.10 μg g^{-1}), cadmium (found at 0.075 μg g^{-1} in one sample), mercury (found in four samples at concentrations within the 0.10–0.18 μg g^{-1} range), and lead (also found in four samples at concentrations from 0.03 to 0.44 μg g^{-1}). Furthermore, nickel (0.16–0.56 μg g^{-1}, six samples), chromium (0.09–0.30 μg g^{-1}, three samples), and cobalt (lower than 0.13 μg g^{-1}, two samples) were also found in the analysed creams.

Keywords: moisturisers; metals; regulation (EC) No. 1223/2009; microwave-assisted acid digestion; inductively coupled plasma-mass spectrometry

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Citation: Rujido-Santos, I.; Herbello-Hermelo, P.; Barciela-Alonso, M.C.; Bermejo-Barrera, P.; Moreda-Piñeiro, A. Study Design on the Presence of Metals in Moisturisers, and Compliance with Regulation (EC) No. 1223/2009 of the European Parliament and of the Council of the European Union, on Cosmetic Products. *Cosmetics* **2022**, *9*, 82. https://doi.org/10.3390/cosmetics9040082

Academic Editors: Helena Ribeiro, Joana Marques Marto and Antonio Vassallo

Received: 6 June 2022
Accepted: 31 July 2022
Published: 4 August 2022

1. Introduction

The colouration of cosmetics can be achieved by the addition of compounds based on metals such as antimony, cadmium, and chromium [1]. Whitening colours, which are preferable in moisturising creams, are obtained by adding aluminium, silver, zinc oxide, and titanium dioxide powders, among others [2]. Moreover, metals modify the surface appearance of cosmetics, providing colour (zinc oxide, titanium dioxide, and aluminium oxide), metal brightness (copper, brass, silver, gold, and aluminium powders), pearled glitter (bismuth oxychloride and mica) or dullness (titanium dioxide) [3]. In addition, zinc oxide, titanium dioxide, and aluminium oxide can act as agents to cover imperfections of the skin. Inorganic mercury species, like ammoniated mercury, are added to skin lightening creams, due to their ability to inhibit the formation of melanin by competing with copper in the enzyme tyrosinase. On the other hand, organic mercury species (phenyl and thiomersal mercury salts) are used to preserve cosmetics [1].

Table 1 summarises the properties provided by metal-based compounds to moisturising creams. This table is an adaptation from the European Commission's inventory of ingredients in cosmetics [4]; it was prepared on the basis of the metal compounds allowed by Regulation (EC) No. 1223/2009 on cosmetic products [5], and the type of matrix under study (moisturisers).

Table 1. Functions of the studied metals in formulations of moisturising creams (adaptation from the European Commission's inventory of ingredients in cosmetic products [4], considering the metal compounds allowed by Regulation (EC) No. 1223/2009 on cosmetic products [5]).

Compound	Function
ALUMINIUM	
Aluminium capryloyl hydrolysed collagen	Skin conditioning
Aluminium undecylenoyl collagen amino acids	Skin conditioning
Alumina	Opacifying/viscosity controlling
Aluminium behenate	Opacifying/viscosity controlling
Aluminium silicate	Opacifying/absorbent
Aluminium caprylate	Emulsion stabilising/opacifying/viscosity controlling
Aluminium dilinoleate	Emulsion stabilising/opacifying/viscosity controlling
Aluminium dimyristate	Emulsion stabilising/opacifying/viscosity controlling
Aluminium distearate and aluminium tristearate	Emulsion stabilising/opacifying/viscosity controlling/emollient
Aluminium isostearate	Emulsion stabilising/opacifying/viscosity controlling
Aluminium isostearates/laurates/palmitates	Emulsion stabilising/opacifying/viscosity controlling
Aluminium isostearates/myristates	Emulsion stabilising/opacifying/viscosity controlling
Aluminium isostearates/palmitates	Emulsion stabilising/opacifying/viscosity controlling
Aluminium isostearates/stearates	Emulsion stabilising/opacifying/viscosity controlling
Aluminium myristates/palmitates	Emulsion stabilising/opacifying/viscosity controlling
Aluminium methionate	Viscosity controlling
Aluminium starch octenylsuccinate	Viscosity controlling/absorbent
Aluminium hydroxide	Viscosity controlling/emollient/humectant
Aluminium butoxide	Emulsion stabilising
Aluminium myristate	Emulsion stabilising
Aluminium dicetyl phosphate	Emulsion stabilising
Aluminium/magnesium hydroxide stearate	Emulsion stabilising
Aluminium lanolate	Emulsifying/surfactant
Aluminium hydrogenated tallow glutamate	Surfactant
Aluminium acetate	Antimicrobial
Aluminium benzoate	Antimicrobial
Aluminium diacetate	Antimicrobial
Aluminium formate	Antimicrobial
Aluminium phenolsulphonate	Antimicrobial
Aluminium glycinate	Buffering
Aluminium lactate	Buffering/astringent
Aluminium PCA	Astringent
Aluminium bromohydrate	Astringent
Aluminium chloride	Astringent
Aluminium chlorohydrate	Astringent
Aluminium chlorohydrex PEG	Astringent
Aluminium chlorohydrex PG	Astringent
Aluminium dichlorohydrate	Astringent
Aluminium dichlorohydrex PEG	Astringent
Aluminium dichlorohydrex PG	Astringent
Aluminium sesquichlorohydrate	Astringent
Aluminium sesquichlorohydrex PEG	Astringent
Aluminium sesquichlorohydrex PG	Astringent
Aluminium citrate	Astringent
Aluminium	Colourant (CI 77000, E 173, white)
Aluminium hydroxide sulphate	Colourant (CI 77002, white)
Natural hydrated aluminium silicate, ($Al_2O_3.2SiO_2.2H_2O$)	Colourant (CI 77004, white)
Aluminium stearate	Colourant (white)

Table 1. *Cont.*

Compound	Function
BARIUM	
Barium sulphate	Opacifying, colourant (CI 77120, white)
COBALT	
Cobalt titanium oxide	Skin conditioning
COPPER	
Alanine/histidine/lysine polypeptide copper HCl	Skin conditioning
Copper sulphate	Skin conditioning
Cupric acetate	Skin conditioning
Saccharomyces/copper ferment	Skin conditioning
Copper acetylmethionate	Skin conditioning/moisturising
Copper aspartate	Skin conditioning/skin protecting
Copper gluconate	Skin conditioning/skin protecting
Copper acetyl tyrosinate methylsilanol	Humectant
Copper PCA	Humectant
Copper PCA methylsilanol	Humectant
Copper usnate	Antimicrobial
Disodium cupric citrate	Stabilising
Disodium EDTA-copper	Chelating/astringent
IRON	
Ferric citrate	Skin conditioning
Ferrous aspartate	Skin conditioning
Ferrous glucoheptonate	Skin conditioning
Saccharomyces/iron ferment	Skin conditioning
Ferric chloride	Astringent
Ferric glycerophosphate	Astringent
Ferrous sulphate	Astringent
Iron hydroxide	Stabilising
LITHIUM	
Lithium gluconate	Skin conditioning
Dilithium oxalate	Chelating
Lithium magnesium silicate	Binding/viscosity controlling/bulking
Lithium magnesium sodium silicate	Viscosity controlling/bulking
Lithium oxidised polyethylene	Film forming/viscosity controlling
Lithium stearate	Opacifying/viscosity controlling/binding
NICKEL	
Nickel gluconate	Humectant
MANGANESE	
Manganese acetylmethionate	Skin conditioning
Manganese aspartate	Skin conditioning
Manganese chloride	Skin conditioning
Manganese gluconate	Skin conditioning
Saccharomyces/manganese ferment	Skin conditioning
Manganese glycerophosphate	Astringent
Manganese PCA	Humectant/skin conditioning/moisturising
MOLYBDENUM	
Molybdenum aspartate	Skin conditioning
SILVER	
Silver chloride	Antimicrobial
Silver acetylmethionate	Antimicrobial
Silver borosilicate	Antimicrobial
Silver sulphate	Antimicrobial
Silver magnesium aluminium phosphate	Bulking
Silver	Colourant (CI 77820, E174, white)

Table 1. *Cont.*

Compound	Function
TIN	
Sodium stannate	Viscosity controlling/stabilising
Tin oxide	Viscosity controlling/opacifying
Stannous chloride	Reducing
ZINC	
Zinc oxide	UV filter, colourant (CI 77947, white)
Zinc oxide (nanoparticulate)	UV filter
Zinc stearate	Colourant (white)
Lactobacillus/zinc ferment	Skin protecting
Porphyridium/zinc ferment	Skin protecting
Saccharomyces/zinc ferment	Skin conditioning
Zinc acetylmethionate	Skin conditioning
Zinc aspartate	Skin conditioning
Zinc DNA	Skin conditioning
Zinc glucoheptonate	Skin conditioning
Zinc gluconate	Skin conditioning
Zinc glutamate	Skin conditioning
Zinc hydrolysed collagen	Skin conditioning
Zinc yeast derivative	Skin conditioning
Zinc pentadecene tricarboxylate	Skin conditioning/surfactant
Zinc PCA	Skin conditioning/humectant
Zinc laurate	Opacifying/viscosity controlling
Zinc myristate	Opacifying/viscosity controlling
Zinc neodecanoate	Opacifying/viscosity controlling
Zinc acetate	Antimicrobial
Zinc sulphate	Antimicrobial
Zinc undecylenate	Antimicrobial/opacifying
Zinc dibutyldithiocarbamate	Antimicrobial/antioxidant
Zinc phenolsulphonate	Antimicrobial/astringent
Zinc borosilicate	Bulking
Zinc carbonate	Opacifying
Zinc ricinoleate	Opacifying
Zinc rosinate	Opacifying/viscosity controlling
Zinc formaldehyde sulphoxylate	Reducing

Nevertheless, metals in cosmetics can penetrate the skin, reaching its deepest layers or even the bloodstream [6]. Thus, metals can be distributed throughout the body and accumulate in several organs and tissues. This risk is enhanced by daily use and prolonged exposure to cosmetic products.

Several studies have demonstrated metal percutaneous penetration and skin lesions caused by metals. Long-term exposure to arsenic has been reported to produce skin lesions such as hyperpigmentation, hyperkeratosis, and basal and squamous cell carcinomas [7,8]. Beryllium salts cause dermal hypersensitivity, resulting in dermatitis or even ulcers [9,10], and gold salts are skin allergens [11]. Nickel, cobalt, and chromium also cause contact skin allergies, and in vitro experiments have shown that these chemicals can penetrate the skin [12,13].

Thallium salts, typically used in depilatory products in the 1920s, are now forbidden in cosmetic formulations, as these salts cause alopecia, in addition to poisoning symptoms like gastrointestinal disorders, nervous system damage, cardiac diseases, hallucinations, and delirium [14]. Chronic topical exposure to mercury salts leads to bluish/blackish pigmentation of the skin, contact dermatitis, erythroderma, purpura, gingivostomatitis, and acrodynia (the latter disease is common in children) [15]. Zirconium salts can be used in antiperspirants, but their use has been demonstrated to cause granulomas [16]. Compounds of lead and barium can penetrate the skin [17,18], and cadmium causes oxidative stress and DNA damage in the HaCaT cell line (immortalised non-tumoral human keratinocytes) [19].

Bluish–black skin discolouration, scaling and itching of the skin, and inhibition of sweat secretion can be induced by tellurium exposure [20]. Studies on the dermal toxicity of vanadium in humans are not available, but pentavalent vanadium (the most toxic vanadium form) has been shown to accumulate in the lungs, and can be distributed throughout the body, causing diseases, or even poisoning human organs [21].

Because of these possible hazardous effects, the presence of metals in cosmetic products is regulated by Regulation (EC) No. 1223/2009 in Europe [5]. This regulation bans antimony, arsenic, beryllium, cadmium, lead, tellurium, thallium, zirconium, mercury, and their compounds in cosmetic products. In addition, the use of barium salts, gold salts, various strontium compounds (lactate, nitrate, and polycarboxylate), chromium, divanadium pentaoxide, indium phosphide, nickel and a lot of nickel compounds, and several compounds of potassium, sodium, cobalt, molybdenum, and tin are not allowed. There are several exceptions to the aforementioned prohibitions: barium sulphides (depilatories, 6% as sulphur), barium colourants listed in the Annex IV, phenylmercuric salts (as preservatives in eye products up to 0.007% Hg), aluminium zirconium chloride hydroxide complexes (antiperspirants products and 5.4% of zirconium as maximum concentration), and gold (colouring purposes, code: E175; purity: 90% or higher [5,22]) can be added to cosmetics. Metal compounds allowed in cosmetic products are listed in Annexes III, IV, V, and VI of Regulation (EC) No. 1223/2009 ("list of substances which cosmetic products must not contain except subject to the restrictions laid down", "list of colourants allowed in cosmetic products", "list of preservatives allowed in cosmetic products", and "list of UV filters allowed in cosmetic products", respectively) [5].

According to the literature, most trace metal analyses in cosmetic matrices focus on coloured make-up products, as a lot of pigments contain metal compounds. However, studies on the presence of metals in daily-use personal care items, like moisturising creams, are scarce [23–30]. Therefore, the scope of this study was the description of a validated methodology based on microwave-assisted acid digestion as a sample pre-treatment, and inductively coupled plasma-mass spectrometry (ICP-MS) as a multi-element analytical tool for assessing metals as minor components and as trace pollutants in common moisturisers found in the Spanish market.

2. Materials and Methods

2.1. Instrumentation

An analytical balance ML 204T (Mettler Toledo, Colombus, OH, USA) was used for weighing reagents and samples. An ETHOS PLUS microwave lab-station (Milestone, Sorisole, Italy) was used for microwave-assisted acid digestion of moisturisers. Quantification of metals was carried out using a NexION® 300X ICP-MS (Perkin Elmer, Waltham, MA, USA) equipped with a SeaFastSC2 DX autosampler (Elemental Scientific, Omaha, NB, USA). Nebulisation was carried out by a Meinhard® nebuliser and a cyclonic spray chamber thermostated by a Peltier refrigerator.

2.2. Reagents

Nitric acid (Hiperpur, 69%) and 33% hydrogen peroxide were from Panreac (Barcelona, Spain). Memory Test 1 Solution (1000 mg L^{-1} Al, Ca, Fe, K, Mg, Na and 20 mg L^{-1}Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl, V, Zn), NexIon Setup Solution (10 µg L^{-1} of U, Pb, Mg, Li, In, Fe, Ce, Be), and individual standards of Sn, Ge, Rh, and In (1000 mg L^{-1} each) were supplied by Perkin Elmer. Standards of 1000 mg L^{-1} B, Li, Mo, and Sb were purchased from Merck (Darmstadt, Germany). Y and Hg (1000 mg L^{-1} each) were from Panreac and Scharlau (Barcelona, Spain), respectively. Ultrapure water (18 MΩcm) was collected from a Milli-Q® water purification system (Millipore, Bedford, MA, USA).

2.3. Samples

The composition of the analysed moisturisers is shown in Supplementary Table S1. The cosmetic samples were purchased from online stores (creams coded as C1, C2, C4, and

C5) and from local shops in Santiago de Compostela, Spain (moisturiser C3 was bought in a pharmacy, and coded creams from C6 to C14 in cosmetic shops). Before sampling, the upper part of the creams was removed (due to their possible oxidation), and they were homogenised with a plastic spatula. The samples were sealed and kept at 4 °C.

2.4. Microwave-Assisted Acid Digestion

The samples were subjected to microwave irradiation (800 W) in a four-stage temperature program consisting of: (1) a first ramp by increasing the temperature from room temperature to 90 °C in 2.0 min; (2) a second step by increasing the temperature from 90 °C to 140 °C in 5.0 min; (3) a third temperature ramp from 140 °C to 200 °C in 5.0 min; (4) a final stage by keeping the temperature at 200 °C for 5.0 min.

Moisturisers were digested in triplicate, and one blank was carried out for each set of digestions. Once digestion was completed, the samples and blanks were made up to 25 mL with ultrapure water.

2.5. Quantification of Metals by ICP-MS

A solution containing 1 μg L^{-1} of Be, Ce, Fe, ln, Li, Mg, Pb, and U was used for daily adjustment of the ICP-MS parameters (torch position, nebulisation flow, and quadrupole voltages), to enhance the sensitivity.

The acid digests were ten-fold diluted with ultrapure water, prior to ICP-MS analyses, except for the samples coded as C1 and C2, which were five thousand times diluted for zinc assessment, and twenty times for the remaining metals.

Table 2 shows the ICP-MS parameters used for metal determination, where a longer dwell time (200 ms instead 50 ms) was used for arsenic assessment, due to its low sensitivity.

Table 2. ICP-MS parameters for metal determination in moisturisers.

Operating Parameters	
Radiofrequency power (W)	1600
Plasma gas flow (L min^{-1})	16
Auxiliary gas flow (L min^{-1})	1.2
Nebulisation gas flow (L min^{-1})	0.9–1.1
Collision cell gas	He
Acquisition parameters	
Replicates	3
Sweeps/Reading	20
Dwell time per amu (ms)	50 (200 for As)
Integration time (ms)	1000 (4000 for As)
Monitored ions (*m*/*z*)	
1.0 mL min^{-1} He	^{7}Li, ^{9}Be, ^{55}Mn, ^{63}Cu, ^{98}Mo, ^{107}Ag, ^{111}Cd, ^{138}Ba, ^{202}Hg, ^{208}Pb
4.0 mL min^{-1} He	^{27}Al, ^{51}V, ^{53}Cr, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{66}Zn, ^{75}As, ^{118}Sn, ^{121}Sb
Internal standards	^{74}Ge, ^{89}Y, ^{103}Rh, ^{115}In

Standard addition calibration was performed to avoid matrix effects. The calibration covered the linear range of 0–100 μg L^{-1}, except for aluminium and iron (0–5000 μg L^{-1}). Polyatomic interferences were minimised using helium as a collision cell gas (variable helium flow rates were used depending on the analyte, Table 2).

Germanium, yttrium, rhodium, and indium were used as internal standards (10 μg L^{-1} in 1% HNO_3). Internal standards were added to the standards and samples, using a T-shaped plastic connector before their introduction into the nebuliser.

2.6. Validation

Limit of detection (LOD) and limit of quantification (LOQ) were calculated in terms of 3σ/m and 10σ/m criteria, respectively—σ being the standard deviation of eleven measurements of a blank (1% nitric acid) by ICP-MS, while m is the slope of the standard addition calibration. The LODs and LOQs for the studied metals are listed in Table 3. The lowest

LOQ was obtained for beryllium (0.00770 μg g^{-1}), and the highest was for aluminium (3.37 μg g^{-1}).

Table 3. Methodology validation.

			Analytical Recoveries		
	LOD_{method} (μg g^{-1})	LOQ_{method} (μg g^{-1})	μg L^{-1} Added	Mean Value (%)	RSD (%)
Li	0.00932	0.0311	0.25, 0.50, 1.0	107 ± 3	3
Be	0.00231	0.00770	0.25, 0.50, 1.0	106 ± 4	1
Al	1.01	3.37	12.5, 25.0, 50.0	100 ± 6	3
V	0.00602	0.0201	0.25, 0.50, 1.0	105 ± 4	3
Cr	0.0266	0.0887	0.25, 0.50, 1.0	110 ± 5	3
Mn	0.00623	0.0208	0.25, 0.50, 1.0	106 ± 5	1
Fe	0.171	0.571	12.5, 25.0, 50.0	105 ± 4	3
Co	0.00249	0.00829	0.25, 0.50, 1.0	106 ± 3	2
Ni	0.0323	0.108	0.50, 1.0	91 ± 3	3
Cu	0.0220	0.0734	0.50, 1.0	105 ± 4	1
Zn	0.0594	0.198	25.0, 50.0	109 ± 4	2
As	0.0235	0.0785	0.25, 0.50, 1.0	104 ± 4	3
Mo	0.00271	0.00905	0.25, 0.50, 1.0	108 ± 6	1
Ag	0.0102	0.0339	0.25, 0.50, 1.0	96 ± 2	2
Cd	0.00663	0.0221	0.25, 0.50, 1.0	99 ± 4	2
Sn	0.00757	0.0252	0.25, 0.50, 1.0	102 ± 6	2
Sb	0.0230	0.0765	0.25, 0.50, 1.0	93 ± 5	4
Ba	0.0152	0.0505	0.25, 0.50, 1.0	104 ± 5	1
Hg	0.0265	0.0885	1.0, 5.0, 10	102 ± 2	3
Pb	0.00866	0.0289	0.25, 0.50, 1.0	105 ± 4	2

The precision of the ICP-MS determinations was assessed by the relative standard deviation (RSD) of eleven measurements of an acid digest, prepared by mixing acid digests from several moisturiser creams, and spiked at 1.0 μg L^{-1} for all elements except for Al, Fe and Zn (spiked at 25 μg L^{-1}). The calculated RSDs values were in the range of 1–4% (Table 3), which demonstrated the high precision of the ICP-MS assessments.

Due to the lack of certified reference materials, the accuracy of the ICP-MS analyses was evaluated by analytical recovery assays, after spiking aliquots of an acid digest mixture at three concentration levels (0.25, 0.50, and 1.0 μg L^{-1} for trace elements, and 12.5, 25, and 50 μg L^{-1} for Al, Fe, and Zn) (Table 3). Analytical recoveries at each spiked concentration level were calculated for all analytes after eleven ICP-MS measurements, and the obtained values (91–110%) verified the accuracy of the ICP-MS quantification.

3. Results and Discussion

Table 4 shows the concentrations of metals found in the analysed moisturisers. These samples represented the most commercialised moisturising creams in Spain. In this way, the results obtained could not be extrapolated to the rest of the products found in the Spanish and European markets. As mentioned above, compounds or salts of arsenic, antimony, beryllium, cadmium, lead, and mercury are not allowed in cosmetic samples in the European Union [5]. Nevertheless, quantifiable amounts of some of these forbidden metals were found in some of the moisturising creams. Beryllium was present in the samples coded as C1 and C2 (0.00809 ± 0.000838 and 0.0825 ± 0.00455 μg g^{-1}, respectively). Cream C2 was the only sample which contained cadmium (0.0745 ± 0.00958 μg g^{-1}). Lead was quantified in four of the moisturisers (C1, C2, C6, and C7), and the concentrations found (0.0342–0.437 μg g^{-1}) were higher than those reported by Bocca, et al. [23]. In addition, moisturising creams coded as C2, C3, C4, and C10 were found to contain mercury (within the range of 0.0990–0.180 μg g^{-1}). On the other hand, arsenic and antimony were not detected in any studied cosmetic sample.

Table 4. Concentration (μg g^{-1}) of the studied metals in commercial moisturising creams.

Sample Code	Li	Be	Al	V	Cr	Mn
C1	<LOD	0.00809 ± 0.000838	<LOQ	<LOQ	<LOQ	0.0522 ± 0.00439
C2	8.35 ± 0.904	0.0825 ± 0.00455	2176 ± 257.7	0.173 ± 0.0173	0.303 ± 0.0191	10.7 ± 0.959
C3	<LOD	<LOD	<LOD	<LOD	0.0934 ± 0.00320	0.0595 ± 0.0101
C4	<LOD	<LOD	<LOQ	<LOD	<LOQ	<LOQ
C5	<LOD	<LOD	<LOD	<LOD	<LOQ	0.0412 ± 0.00496
C6	<LOD	<LOD	<LOQ	<LOD	<LOD	0.0353 ± 0.000876
C7	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOQ
C8	<LOD	<LOD	31.3 ± 1.72	<LOD	<LOD	0.0636 ± 0.00143
C9	<LOD	<LOD	<LOQ	<LOD	<LOQ	0.0325 ± 0.00288
C10	<LOQ	<LOD	<LOD	<LOD	0.213 ± 0.00462	0.0836 ± 0.0131
C11	<LOQ	<LOD	<LOQ	<LOD	<LOQ	0.0245 ± 0.00205
C12	1.07 ± 0.0275	<LOQ	<LOQ	<LOD	<LOQ	0.0277 ± 0.00481
C13	<LOD	<LOD	5.10 ± 0.0212	<LOD	<LOQ	0.0418 ± 0.00506
C14	0.0445 ± 0.00493	<LOD	7.47 ± 0.162	<LOD	<LOQ	0.0379 ± 0.00281

Sample Code	Fe	Co	Ni	Cu	Zn	Mo
C1	<LOQ	<LOQ	<LOQ	5.00 ± 0.694	73479 ± 3017.4	<LOQ
C2	4933 ± 292.2	0.134 ± 0.000803	0.559 ± 0.0490	2.55 ± 0.256	25455 ± 1600.8	<LOQ
C3	1.44 ± 0.268	0.0178 ± 0.00131	<LOQ	0.283 ± 0.00102	2.22 ± 0.333	0.0162 ± 0.00244
C4	<LOQ	<LOD	0.257 ± 0.0414	<LOD	<LOD	<LOQ
C5	<LOD	<LOD	0.164 ± 0.0184	0.145 ± 0.0217	2.96 ± 0.338	<LOQ
C6	<LOQ	<LOD	0.425 ± 0.0261	<LOD	<LOD	<LOD
C7	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ
C8	<LOD	<LOD	<LOD	0.171 ± 0.00868	2.23 ± 0.305	<LOD
C9	<LOD	<LOD	<LOD	0.192 ± 0.0267	41.2 ± 1.36	<LOD
C10	1.01 ± 0.0774	<LOQ	<LOQ	0.102 ± 0.00192	4.07 ± 0.0785	<LOQ
C11	1.62 ± 0.112	<LOD	0.501 ± 0.0800	0.512 ± 0.0815	8.58 ± 0.871	0.191 ± 0.00957
C12	<LOQ	<LOD	0.216 ± 0.0347	0.318 ± 0.0303	1.83 ± 0.0884	<LOQ
C13	1.49 ± 0.205	<LOD	<LOD	0.243 ± 0.0360	<LOD	<LOD
C14	0.699 ± 0.133	<LOD	<LOD	0.251 ± 0.0350	<LOD	<LOD

Sample Code	Ag	Cd	Sn	Ba	Hg	Pb
C1	0.380 ± 0.00959	<LOD	<LOQ	0.0601 ± 0.00299	<LOD	0.0509 ± 0.00354
C2	0.0859 ± 0.00888	0.0745 ± 0.00958	0.483 ± 0.0147	4.84 ± 0.384	0.0990 ± 0.00633	0.437 ± 0.0383
C3	2329 ± 262.0	<LOQ	0.0388 ± 0.00427	0.180 ± 0.0140	0.180 ± 0.0281	<LOD
C4	1.18 ± 0.0710	<LOQ	<LOD	<LOD	0.107 ± 0.0119	<LOD
C5	31.1 ± 3.81	<LOQ	<LOD	<LOQ	<LOD	<LOQ
C6	<LOD	<LOD	<LOQ	<LOD	<LOD	0.0342 ± 0.000183
C7	<LOD	<LOD	<LOD	<LOD	<LOD	0.0987 ± 0.0124
C8	<LOD	<LOD	0.108 ± 0.00121	<LOQ	<LOD	<LOD
C9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
C10	<LOD	<LOQ	<LOD	0.440 ± 0.0138	0.150 ± 0.0272	<LOD
C11	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD
C12	0.0408 ± 0.00471	<LOD	0.425 ± 0.0434	0.680 ± 0.0114	<LOD	<LOD
C13	<LOD	<LOD	0.130 ± 0.00610	<LOD	<LOD	<LOD
C14	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

<LOD: below LOD; <LOQ: below LOQ.

Nickel (and a vast number of nickel compounds), chromium, and several cobalt compounds are also not allowed in cosmetic samples in the European Union, due to their allergenic potential. However, chromium was quantified in three of the creams (codes C2, C3, and C10), cobalt in two (codes C2 and C3), and nickel in six samples (codes C2, C4, C5, C6, C11, and C12); the concentration ranges were 0.0934–0.303 μg g^{-1}, 0.0178–0.134 μg g^{-1}, and 0.164–0.559 μg g^{-1} for Cr, Co, and Ni, respectively. Bocca, et al. [23], reported similar concentrations of chromium and cobalt in moisturising creams, while the nickel concentrations were lower (0.0175–0.153 μg g^{-1}) than those found in our study.

Aluminium and aluminium compounds provide whitening colours, and functions like skin conditioning, emulsion stabilising, opacifying, and viscosity controlling, as is indicated in Table 1. Creams C13 and C14 were found to contain relatively similar aluminium content (5.10 ± 0.0212 and 7.47 ± 0.162 μg g^{-1}, respectively), while it was quantified at higher levels in samples C2 (2176 ± 257.7 μg g^{-1}) and C8 (31.3 ± 1.72 μg g^{-1}).

The European Commission allows the use of zinc oxide and zinc stearate as whitening colourants, as well as zinc oxide (bulk and nanoparticulate forms) as a UV filter. The maximum concentration of zinc oxide is 25% (*w/w*), which applies also in cases of combined bulk and nano form [5]. Furthermore, a high number of zinc compounds are used to achieve properties such as skin protecting, skin conditioning, antimicrobial, and opacifying, among others (Table 1); however, the maximum concentration of several of these zinc compounds is regulated, as in the case of zinc peroxide (4.0% of H_2O_2, present or released, in skin products) and several water-soluble zinc salts (acetate, chloride, gluconate, and glutamate not exceeding 1% zinc) [5].

Of the 14 studied samples, 9 contained zinc, and samples C1 and C2 were found to contain very high zinc concentrations (73,479 ± 3017 and 25,455 ± 1601 µg g^{-1}, respectively). Zinc concentrations in the remaining moisturisers varied from 1.83 to 41.2 µg g^{-1}.

Several manganese compounds are added to cosmetics to obtain skin conditioning and moisturising properties (Table 1). Our results showed that 12 moisturisers contained manganese in their formulations within the range of 0.0245–0.0836 µg g^{-1} (similar manganese content was reported by de Paula, et al. [25]), except for cream C2, which showed a higher concentration (10.7 ± 0.959 µg g^{-1}).

Several lithium compounds (lithium nickel dioxide, cobalt lithium nickel oxide, and lithium perfluorooctane sulfonate) are banned in the European Union [5]. Creams coded as C2, C12, and C14 contained lithium in their formulations. In particular, the concentration of lithium in the moisturiser C2 (8.35 ± 0.904 µg g^{-1}) was much higher than in the other two samples.

Divanadium pentaoxide and nickel divanadium hexaoxide were the only banned vanadium species [5], and vanadium was solely quantified in the moisturising cream C2 (0.173 ± 0.0173 µg g^{-1}).

Copper was quantified in 11 samples, and its concentration was below 1.00 µg g^{-1}, except for creams C1 and C2 (5.00 ± 0.694 and 2.55 ± 0.256 µg g^{-1}, respectively). Copper concentrations found in the studied moisturising creams—mainly in samples C1 and C2—were higher than those shown in the study performed by Bocca, et al. [23], (0.00327–0.0512 µg g^{-1}). As shown in Supplementary Table S1, zinc oxide is an ingredient listed in the formulation of moisturisers C1 and C2 (9.0 and 2.96%, respectively). The high number of moisturisers with copper can be attributed to the use of copper compounds that provide properties such as skin conditioners, skin protectors, and humectants (Table 1).

Iron was found in six samples (C2, C3, C10, C11, C13, and C14), and its concentration varied between 0.699 and 1.62 µg g^{-1}, excluding sample C2, which contained the highest concentration (4933 ± 292.2 µg g^{-1}).

Silver can be used as a whitening colourant, antimicrobial agent, preservative, and bulking material (Table 1). The use of silver chloride as a preservative in cosmetics is restricted, and the maximum allowed concentration is 0.004% (as AgCl) or 20% AgCl (*w/w*) if it is deposited on titanium dioxide [5]. Silver content in the studied creams varied between 0.0408 and 1.18 µg g^{-1}, except for samples C3 (2329 ± 262.0 µg g^{-1}) and C5 (31.1 ± 3.81 µg g^{-1}). In previous studies, it was demonstrated that moisturising creams C3, C4, and C5 contained silver nanoparticles (AgNPs) [31]. In spite of Regulation (EC) No. 1223/2009, stating that cosmetic products containing nanomaterials must be notified to the European Commission, and that they must be clearly indicated in the list of ingredients (names of such ingredients followed by the word 'nano' in brackets) [5], there was no indication about the presence of AgNPs in the lists of ingredients for moisturisers C3, C4, and C5.

Moisturising creams C3 and C11 were the only creams with molybdenum (0.0162 ± 0.00244 and 0.191 ± 0.00957 µg g^{-1}, respectively). The unique molybdenum compound listed in the inventory of ingredients of cosmetic products elaborated by the European Commission is molybdenum aspartate, which has skin conditioning properties [4].

Several stannous compounds are banned by the European Commission, namely dibutyltin hydrogen borate, nickel stannate, dibutyltin dichloride (DBTC), dimethyltin dichloride, tributyltin compounds, and dibutyltin dilaurate [5]. Creams coded as C2, C3, C8, C12, and C13 were found to contain tin, and the maximum concentration was 0.483 ± 0.0147 µg g^{-1} (sample C2).

Barium species allowed in cosmetics are barium sulphate (whitening colourant, CI 77120) and other coloured barium pigments (CI 10316, CI 12085, CI 15510, CI 15580, CI 15630, CI 15850, CI 15865, CI 15985, CI 16255, CI 17200, CI 19140, CI 42051, CI 45370, CI 45380, CI 45410, and CI 45430) [5]. Barium was quantified in five samples (C1, C2, C3, C10, and C12), and its concentrations were lower than 0.700 µg g^{-1}, except for moisturiser C2, which contained 4.84 ± 0.384 µg g^{-1} of barium.

4. Conclusions

All studied metals, except molybdenum, antimony, and arsenic were found at low concentrations (inevitable traces of pollutants) in moisturising cream C2 (sample purchased from an online store). Furthermore, cream C2 showed quantifiable contents of nickel, cobalt, and chromium, which are also banned, owing to their allergenic effect on the skin. Similarly, moisturisers C1, C3, C4, C6, C7, and C10 did not comply with Regulation (EC) No. 1223/2009, due to the presence of lead (C6 and C7), beryllium and lead (C1), chromium and mercury (C10), and mercury (C3 and C4). Moisturisers C5, C11, and C12 probably did not comply with Regulation (EC) No. 1223/2009, as nickel and many nickel salts (potential allergens) are banned in cosmetic products. Regarding barium, its allowed species (barium sulphate [CI 77120] and other barium pigments) were not listed in the ingredients of creams C1, C2, C3, C10, and C12, therefore the presence of barium in these samples was neither justified nor allowed. The moisturising creams labelled as C3, C4, and C5 contained Ag (as AgNPs according to published studies) but the presence of AgNPs was not indicated in the list of ingredients, in breach of the Regulation (EC) No. 1223/2009.

To conclude, moisturising creams coded as C1, C2, C3, C4, C5, C6, C7, C10, C11, and C12 did not comply with Regulation (EC) No. 1223/2009 on cosmetic products, and the only moisturiser that fulfilled the stated regulation was the sample coded as C9. Furthermore, speciation studies were necessary in the cases of samples C8 and C13 (tin speciation) and C14 (lithium speciation), to ensure compliance with Regulation (EC) No. 1223/2009 (several lithium and stannous compounds are banned by the European Commission).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cosmetics9040082/s1, Table S1: Ingredients of analysed moisturising creams.

Author Contributions: Conceptualisation and supervision, A.M.-P. and M.C.B.-A.; software and resources, P.H.-H.; project administration and funding acquisition, A.M.-P. and P.B.-B.; formal analysis and writing—original draft preparation, I.R.-S.; writing—review and editing, I.R.-S. and A.M.-P. All authors have read and agreed to the published version of the manuscript.

Funding: The authors wish to acknowledge the financial support of the Ministerio de Economía y Competitividad (projects INNOVANANO, reference RT2018-099222-B-100), and the Xunta de Galicia (Grupo de Referencia Competitiva, grant number ED431C2018/19).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All the results obtained are shown in this article.

Acknowledgments: I. Rujido-Santos thanks the Xunta de Galicia and the European Social Fund (FSE) for a pre-doctoral grant (ref. ED481A-2018/127).

Conflicts of Interest: The authors declare no conflict of interest.

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