

The **REACH regulation** and the European cosmetics legislation on cosmetics (EU 1223/2009/EC) prohibit the use of known toxic heavy metals (Cr, Ni, Pb) and suspected toxic heavy metal (Al) in finished products. At the same time, the regulation tolerates their presence in traces provided that it is technically unavoidable. Exception are allowed, as like mineral pigments (Cr₂O₃).

OBJECTIVES:

- Metals evaluation on a large sample population, with special attention to creams detergents and oils, considering REACH regulation and ISS advice.
- Cosmetics have a variety of different matrixes so that it is fundamental to use different approaches.
- Three methods of sample preparation were used, with different reagents.
 - 1) Wet digestion
 - 2) Dry-ashing
 - 3) Closed vessel microwave digestion

Investigated metals

Al
Great quantities are found in deodorants and antiperspirants, also used as pigment

Ni
Nickel free (<1ppm)
Could cause allergic reactions and consequent dermatitis.

Cd
Forbidden in any case, it is found in ppb.

Pb
Kajal (PbS).
Forbidden in any case.

Ag
Pigment max 4% (AgNO₃), antibacterial.

Cr
Used as pigment in make up products.

Zn
Zn could always be found in cosmetics: firstly as a process pollution, secondly as an ingredient (matting agent ZnO)

Normative references

REACH

- Annex II: forbidden substances.
- Annex III: allowed substances (concentrations limits).
- Annex IV: list of allowed pigments and colorants in cosmetic products

Istituto Superiore di Sanità (ISS) Advice

Metals	German limits	Canadian limits	Italian limits
As	5	3	1
Cd	5	3	5
Co	-	-	5
Cr(III)	-	-	5
Cr(VI)	-	-	1
Hg	1	3	1
Ni	-	0	10
Pb	20	10	20
Sb	10	5	10

Products categories



Table: Cosmetics divided into categories

Cosmetic Products	Ag 328.068 mg/kg	Al 396.153 mg/kg	Cd 228.802 mg/kg	Cr 267.716 mg/kg	Ni 231.604 mg/kg	Pb 220.353 mg/kg	Zn 206.200 mg/kg
Eye pencil Blue	4.74	5509	0.06	3.41	2.46	n.d.	8
Eye pencil Green	n.d.	2935	n.d.	5.42	n.d.	n.d.	33
Leap pencil Green	4	1690	n.d.	1.93	4.66	n.d.	16
Ca(OH) ₂ based shaving mineral powder	n.d.	3077	0.04	0.46	0.16	n.d.	4.5
Ca(OH) ₂ based shaving mineral powder	n.d.	1811	0.07	0.44	n.d.	0.354	4.7
Ca(OH) ₂ based shaving mineral powder	n.d.	1450	0.07	0.42	0.24	3.215	3.7
Brush shaving foam	n.d.	n.d.	0.03	0.078	n.d.	n.d.	1.2
Brush shaving foam	n.d.	33.3	0.02	n.d.	n.d.	n.d.	n.d.
Brush shaving foam	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	0.91
Anti-cellulite oil	n.d.	1.0	0.02	n.d.	n.d.	n.d.	15.5
Anti-cellulite oil	n.d.	n.d.	0.01	0.06	n.d.	n.d.	15.4
Anti-cellulite oil	n.d.	2.4	0.01	n.d.	0.268	n.d.	19
Mix of 10 oils	6.0	6.2	0.1	1.5	1.0	0.7	5.3
Mix of 3 oils for hair care	5.3	8.0	0.1	1.3	0.1	0.7	6.6
Hemp oil (cosmetic formula)	n.d.	n.d.	0.6	n.d.	0.9	n.d.	0.8
Linen oil (cosmetic formula)	n.d.	2.7	0.6	n.d.	0.8	0.06	10
Sun-screan oil	n.d.	1.0	0.04	0.6	n.d.	n.d.	3.9
After shave cream	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.
After shave gel	n.d.	n.d.	0.04	0.03	n.d.	1.99	2.7
Nutrient Body cream	n.d.	n.d.	0.43	n.d.	1.2	n.d.	1.9
Face cream based on borage oil	n.d.	1.6	0.01	0.05	0.13	0.74	2.4
Face cream based on She-ass milk	n.d.	0.4	0.02	0.03	n.d.	n.d.	0.5
Face cream based on She-ass milk	n.d.	1.7	0.04	0.01	n.d.	n.d.	0.7
Face cream based on She-ass milk	n.d.	n.d.	0.03	0.02	n.d.	n.d.	1.6
Deodorant cream	n.d.	19325	0.44	n.d.	1.3	n.d.	2.8
Water based deodorant	n.d.	8138	0.02	0.07	n.d.	n.d.	4.0
Shampoo	n.d.	0.4	0.03	n.d.	n.d.	n.d.	n.d.
Shampoo	n.d.	0.15	0.03	0.03	n.d.	n.d.	1.6
Face detergent gel	n.d.	n.d.	0.05	0.4	n.d.	0.3	n.d.
Bubble bath	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.
Bubble bath	n.d.	0.8	0.04	n.d.	n.d.	n.d.	n.d.
Intimate detergent	n.d.	n.d.	0.02	0.05	n.d.	n.d.	1.8
Aleppo Soap - 5%	n.d.	n.d.	n.d.	0.27	0.4	n.d.	4.1
Aleppo Soap - 16%	n.d.	6.0	0.3	n.d.	1.6	n.d.	12

Methods



HNO₃ was used to mineralized the samples. Few drops of HCl were added to complex metals as reduced their volatility.

Oil and Soaps

Dry-ashing

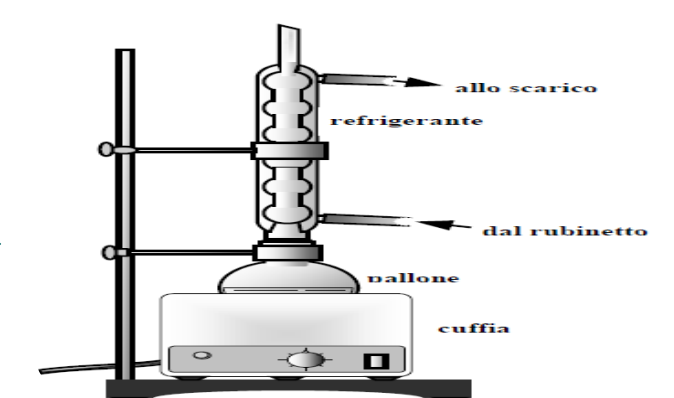


Oils

Ash recovery → Aq. REGIA

Cream and Powders

Wet digestion



Powders

Main organic matrix → Aq. REGIA

Main mineral matrix → Inverted Aq. REGIA (3:1)

Oil Soaps Creams Powders

Micro-wave digestion



ICP-OES



CONCLUSIONS

- The method comparison showed, in any case, that microwave assisted allows a better and easier sample preparation.
- DRY and WET digestion are extremely subjected to environment pollution because of broad use of reagents.
- The categorization on the main metal, and on matrix type, helps to set the best sample preparation method.