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ON THE HEAVY METALS CONTENT IN COSMETIC FORMULATIONS: AN ATOMIC ABSORPTION SPECTROSCOPY INVESTIGATION

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Synopsis

The levels of four heavy metals (Pb, Cd, Hg and Cr), have been measured by means of an atomic absorption spectroscopy (AAS) method in 18 different cosmetic formulations, (8 body creams, 3 of them being purchased from herbal shops; 6 hands creams, 2 intime hygiene soaps, 1 face cream, 1 foam bath soap), periodically sampled over a total period of time of 10 months.

The levels of heavy metals have been shown to be in the great majority of samples extremely reduced and in some instances below the detection limits of the applied technique. More precisely, levels of Hg were below the detection limit of the AAS technique in all samples, while mean levels of Pb, Cd and Cr never exceeded 0.184 ppm, 0.035 ppm and 0.270 ppm respectively. However, since the frequency of administration of cosmetic products is very high and it is generally protracted for prolonged periods of time, the toxicologic significance of the present results should be further evaluated, also in the light of a more exhaustive study, carried out on the basis of a more interdisciplinar approach.

Riassunto

Questo articolo riporta i risultati di uno studio spettrofotometrico per assorbimento atomico (AAS) riguardante la determinazione della concentrazione di metalli pesanti in formulazioni cosmetiche. L'indagine, condotta in seguito ad un periodo di campionamento di 10 mesi, ha considerato quattro specifici metalli pesanti (piombo, cadmio, cromo e mercurio) ed é stata condotta su 18 differenti campioni di formulazioni cosmetiche: 8 creme per il corpo, 3 delle quali di erboristeria; 6 creme per le mani, 2 saponi per l'igiene intima, 1 crema per il viso, 1 bagno schiuma. Nella maggioranza dei campioni analizzati la concentrazione di metalli pesanti é risultata estremamente bassa, ed in alcuni casi inferiore al limite di rilevabilità della tecnica AAS impiegata. Più precisamente, i livelli di Hg sono stati sempre al di sotto del limite di rilevabilità in tutti i campioni considerati, mentre i livelli medi di Pb, Cd e Cr non hanno mai superato i valori di 0.184 ppm, 0.035 ppm e 0.270 ppm rispettivamente.

Poiché la frequenza di somministrazione di un prodotto cosmetico é generalmente molto alta, oltre che protratta per lunghi periodi di tempo, il significato tossicologico dei risultati presentati in questo lavoro dovrebbe comunque essere ulteriormente approfondito, preferibilmente alla luce di studi più interdisciplinari.

Introduction

Cosmetic formulations are a class of products whose peculiar features can be considered, from a biochemical and toxicological point of view, as intermediate between foods and drugs.
For indeed, the frequency of administration of cosmetic formulations is generally scheduled on a daily basis, and in some instances several cosmetic products, like, for example, a lipstick or a hand cream, can be applied to the body twice or more times a day. At the same time, the techniques that are generally used to produce a great variety of cosmetic formulations are directly derived from the experience of pharmaceutics.
It is therefore self evident that any activity devoted to the definition of the possible risks for the consumer due to the presence of toxic substances in a cosmetic formulation is to be strongly supported. In this light, the Italian Law (Legge 713/86) states the procedures to be followed for the commercialization of cosmetic products. More specifically, the supplement II ("Allegato II") of the same law lists a broad group of chemicals whose cannot be employed for the production of any cosmetic formulation.
The limited amount of information, available both from a normative and from a technical point of view, concerning the presence of heavy metals in the cosmetic products and the possible effects of this elements by transcutaneous absorption following topical administration, has suggested to us to plan an experimental study, whose aim was to quantitatively evaluate the levels of some representative heavy metals in various cosmetic formulations.
The assayed samples have been obtained from different suppliers (mainly department stores) located in the East area of Rome, within the inner city limits. Samples of 18 different cosmetic formulations, (8 body creams, 3 of them being purchased from herbal shops; 6 hands creams, 2 intime hygiene soaps, 1 face cream, 1 foam bath soap) were collected, in triplicate, every two months for ten months, so that a total of 270 samples (18x3x5) were assayed by AAS. The obtained results were compared in order to assess the variability over the period of sampling of the single heavy metals concentrations in each cosmetic formulation.
Results of this preliminary investigation are presented and discussed taking in the due account the indications given by the Italian Law concerning the presence of heavy metals in cosmetic formulations.
In the light of the results obtained in the present work, the need for a more precise definition of heavy metals toxicity, i.e. by considering also the possible presence in the cosmetic formulations of other components, which could, in turn, either reduce or enhance the toxicity of heavy metals, is also stressed.

Materials and methods

Instrumentation

The AAS system is constituted by a Perkin Elmer mod. 1100B atomic absorption spectrometer, equipped with an HGA-700 graphite furnace, a deuterium-arc background correction, and a computer-driven Perkin Elmer Model AS-70 autosampler, (Perkin Elmer Italia SpA, Monza, Italy); the results have been recorded by an Epson EX-850 dot-matrix printer (Epson Italia S.p.A., Milano, Italy).
The detection of mercury, by the cold vapor technique, has been carried out by a Varian Techtron mod. AA-475 atomic absorption spectrometer (Varian Italia, Milano).

Materials

Samples of cosmetic formulations.

The AAS study was carried out on eighteen samples of cosmetic formulations **(#1-18)**, indicated as follows:
5 body creams **(#1-5)**;
3 body creams, purchased by herbal shops **(#6-8)**;
6 hands creams **(#9-14)**;
2 intime hygiene soaps **(#15-16)**;
1 face cream **(#17)**;
1 foam bath **(#18)**.

All samples were purchased by different commercial suppliers located in the East area of Rome; more precisely, sampling was repeated five times, once every two months, so that the assayed samples cover a total interval of time of ten months, precisely in the period january-october 1995. It follows that for each one of the 18 cosmetic formulations 15 samples were collected. Each specific sample was always purchased by the same dealer.

The levels of the four representative heavy metals (Pb, Cd, Cr and Hg) have been determinated on all the above mentioned samples, according to a procedure recently described (Conti et al., 1996).

The determination of Pb, Cd and Cr was carried out following mineralization of samples, according to the dry mineralization procedure, carried out in order to fully destroy the organic matter More in details, the mineralization procedure was carried out according to the following stages:

1 weight calibration of quartz weighting bottles;
2 transfer of samples in the quartz weighting bottles and determination of the humid weight;
3 dessication of the sample in oven (T = 105 °C; time of treatment: 12 hours);
4 slow thermal treatment ($\Delta T/\Delta t$ = 50 °C/hour); then
5 calcination at T = 450 °C ± 10 °C in a special oven with the internal walls covered by a layer of quartz;
6 collection of white ashes, or, alternatively, repetition of the last passage;
7 dissolution of the ashes in 1 mL nitric acid at T=40 °C;
8 transfer of final solutions in 50 mL volumetric flasks and dilution to volume with deionized water.

The determination of Hg was carried out following a wet mineralization procedure, according to the following stages:

1 transfer of samples in 25.0 mL volumetric flasks;
2 addition of 5.0 mL of concentrated HNO_3/H_2SO_4 (1:1);
3 boiling to reflux until a clear solution is obtained;
4 cooling of the solution;
5 concentration of the solution on heating plate;
6 transfer of the solution into 50.0 mL volumetric flasks and dilution to volume with bidistilled/deionized water.

Laboratory glassware, reagents and standards of heavy metals.

All the glassware used for the preparation of stock and standard solutions was decontaminated from the possible presence of heavy metals by overnight treatment with metal-free, concentrated HNO_3 (Merck, Darmstadt, Germany).

All reagents were analytical grade. Cadmium, chromium, lead and mercury standards were prepared by dilution with 2% HNO_3 from stock standard solutions of their respective nitric salts (1000 ± 2 ppm in 0.5 M HNO_3), supplied by Merck (Darmstadt, Germany); water ultrapure grade by Milli-Q from Millipore (Millipore Corporation U.S.A.) was used for the preparation of all solutions.

Table 1

OPERATIVE CONDITIONS IN THE SPECTROMETRIC ASSAYS

Element	Wavelenght (nm)	Slit width (nm)	Matrix modifier	Graphite tubes
Pb	283.3	0.7	0.2 mg/10 µl $NH_4H_2PO_4$	pyrolytic/wall
Cd	228.8	0.7	0.2 mg/10 µl $NH_4H_2PO_4$	pyrolytic/wall
Cr	357.9	0.7	0.05 mg/10 µl $NH_4H_2PO_4$	pyrolytic/wall
Hg	253.7	0.5	-----	-----

Operative conditions in the spectrometric assays.

The quantitative determination of each analyte was carried out by applying the method of the linear regression to the calibration plot following the addition of different aliquots of known standards to the samples under investigation.

The determination of cadmium, chromium and lead has been carried out with the graphite furnace, while the determination of mercury has been carried out according to the cold vapor technique.

The instrumental specification of the method are given in table 1,while the description of the thermal programs followed for the determination of each single metal are reported in tables 2-4. Results of the recovery tests and of the precision tests are given in tables 5 and 6 respectively.

Results

Tables 5-6 show that the analytical procedures followed in the present work allow to obtain reliable results, as indicated by both the values of the recovery assays (Table 5) and of the precision study (Table 6).

All results of the present study are reported in table

Table 2

FURNACE PROGRAM FOR THE DETERMINATION OF Pb
(atomization occurs at step 6; volume of sample injected = 20 µl)

Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow (ml/min)
1	80	20	40	300
2	100	20	40	300
3	120	20	60	300
4	300	30	30	300
5	750	30	45	300
6	2000	0	4	0
7	2650	1	5	300
8	20	1	10	300

Table 3

FURNACE PROGRAM FOR THE DETERMINATION OF Cd
(atomization occurs at step 4; volume of sample injected = 10 µl)

Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow (ml/min)
1	120	20	10	300
2	350	10	10	300
3	600	10	10	300
4	2100	0	3	0
5	2650	1	5	300
6	20	1	10	300

Table 4

FURNACE PROGRAM FOR THE DETERMINATION OF Cr
(atomization occurs at step 5; volume of sample injected = 15 µl)

Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow (ml/min)
1	120	20	10	300
2	300	10	20	300
3	450	10	20	300
4	1650	10	20	300
5	2500	0	5	0
6	2700	1	3	300
7	20	5	5	300

Table 5

RECOVERY TESTS

Element	N. of tests	Concentration added (µg/L)	Recovery (mean ± SD)
Pb	11	10	96.8 ± 4
Cd	10	1	93.7 ± 2
Cr	11	5	96.0 ± 3
Hg	9	2	94.8 ± 5

Table 6

PRECISION TESTS

Element	N. of tests	Concentration (µg/L)	Variation coefficient (%)
Pb	10	4.2	6.1
Cd	10	1.0	3.6
Cr	10	8.2	4.7
Hg	8	1.5	8.4

7. All data are expressed as µg of heavy metal/100.0g of cosmetic formulation. The analytical results are here discussed for each one of the considered analytes.

Lead

Nine out of eighteen samples of cosmetic formulations have shown levels of lead that lie below the detection limit of the instrumental technique. In the other nine samples the values varied from a minimum of 14.2 ppb to a maximum of 184.4 ppb. As it can be seen by the values of the standard deviations, levels of lead show a very narrow variability over the period of time of sampling (10 months),

Table 7

CONCENTRATION OF HEAVY METALS
ON SAMPLES OF COSMETIC FORMULATIONS.
RESULTS (MEAN OF FIVE INDEPENDENT SAMPLE PREPARATIONS ±SD)
ARE EXPRESSED IN µg/100 g OF SAMPLE.

Sample	Lead	Cadmium	Chromium	Mercury
1	n. d.	n. d.	2.38 ± 0.82	n. d.
2	1.42 ± 0.40	n. d.	24.70 ± 5.20	n. d.
3	n. d.	n. d.	1.21 ± 0.60	n. d.
4	4.06 ± 1.12	0.08 ± 1.25	0.44 ± 1.35	n. d.
5	1.86 ± 0.76	n. d.	0.84 ± 0.47	n. d.
6	n. d.	0.34 ± 1.80	0.69 ± 2.13	n. d.
7	n. d.	1.17 ± 1.20	4.70 ± 0.95	n. d.
8	n. d.	3.50 ± 0.70	9.50 ± 2.43	n. d.
9	2.47 ± 2.11	0.07 ± 0.65	0.56 ± 0.35	n. d.
10	18.44 ± 0.60	0.09 ± 0.40	0.39 ± 0.25	n. d.
11	n. d.	0.09 ± 1.35	0.38 ± 0.40	n. d.
12	18.43 ± 1.23	n. d.	0.69 ± 0.15	n. d.
13	9.06 ± 0.22	0.19 ± 0.58	1.15 ± 0.22	n. d.
14	1.96 ± 0.35	n. d.	3.74 ± 1.70	n. d.
15	10.95 ± 1.40	1.40 ± 0.46	1.40 ± 2.20	n. d.
16	n. d.	n. d.	12.06 ± 3.50	n. d.
17	n. d.	n. d.	5.60 ± 4.12	n. d.
18	n. d.	0.67 ± 0.24	27.07 ± 6.15	n. d.

n.d.: not detectable ([Pb] < 5 µg/L; [Cd] < 0.1 µg/L; [Cr] < 4 µg/L; [Hg] < 1 µg/L in the measuring solution).

thus indicating that the concentration of Pb is virtually independent of seasonal events.

Cadmium

Eight out of eighteen samples of cosmetic formulations have shown levels of cadmium that lie below the detection limit of the instrumental technique. In the other ten samples the values varied from a minimum of 0.7 ppb to a maximum of 35.0 ppb. As it can be seen by the values of the standard deviations, unlike the case of lead, levels of cadmium show a broad variability over the period of time of sampling.

Chromium

Levels of chromium in the eighteen assayed samples varied from a minimum of 3.8 ppb to a maximum of 270.7ppb. Also in this case there is a marked variability of the values along the time.

Mercury

In all the eighteen samples the levels of mercury lied below the sensitivity limits of the instrumental technique.

Discussion

The complete set of experimental results obtained on the 18 different cosmetic formulations and summarized by data reported in table 7 allows to draw the following conclusions:

- the concentration of mercury has been found to lie below the detection limits of the experimental technique in all the 18 assayed samples;
- the presence of chromium was detected in all the 18 assayed samples;
- apart from lead, all the assayed elements showed a marked variability of the concentration values over the time, thus indicating that the differences in the concentration values could be due to environmental factors;
- in four samples (**#1**, **3**, **16**, and **17**, that is 2 out of 5 body creams, 1 out of 2 soaps for the intime hygiene and the only assayed body cream) chromium was the only element to be detected;

The overall picture deriving from the experimental results seems to indicate that no ultimate conclusions can be driven by a simple determination of the concentration of heavy metals in cosmetic formulations, since there is a very broad variability of the results as a function of the sampling period and, at the same time, a non uniform distribution of the single heavy metals in the different samples. The average value are however low enough to ensure the safety of use, provided the cosmetic is applied in the most correct way and, obviously, only on intact skin.

Moreover, the intrinsic toxicity of each heavy metal is a necessary but not a sufficient information in order to quantitatively assess the risk for the cousumer, since the bioavailability of a heavy metal can be markedly affected by the presence in the cosmetic formulation of other compounds (e.g. EDTA), which could act as carriers of the metal cation.

Finally, it seems worthwhile to us to highlight that, as of now, no indication is given by the Italian Law concerning the accidental presence of heavy metals in a cosmetic formulation, the only statement being that heavy metals are included in the list of chemicals that cannot be present in any ingredients of a cosmetic product.

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