

Analytical Methods

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3 Determination of Cr(VI) in cosmetic products using ion chromatography with
4 dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-
5 ICP-MS.
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8 Francesco Petrucci and Oreste Senofonte
9 Istituto Superiore di Sanità, Department of the Environment and Primary Prevention
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Introduction

Chromium oxide (Cr_2O_3) and hydroxide ($\text{Cr}_2\text{O}(\text{OH})_4$) are the only chromium-based dyes allowed by the Regulation of the European Community (EC/ 1223/2009 (Annex IV) for the preparation of cosmetic products. These substances may contain Cr (VI) which can cause chronic toxicity and has been classified as carcinogenic to humans (IARC, Monogr. Eval. Carcinog. Risks Hum.1990). In addition, Cr (VI) is a potent allergen causing skin allergies through dermal adsorption (1, 2). Contact allergies caused by Cr (VI) are generally found in occupational settings as in cement and leather processing, but the hexavalent form can also be found in soaps and detergents (3). Usually the levels of hexavalent chromium in cosmetics are very low and should not lead to skin sensitization. However, if a consumer has been previously sensitized to Cr (VI) from other sources, the low concentration permitted in cosmetics could arise allergic reactions (4). In this regard, eye shadow, which can contain up to 70% of Cr (III) green pigments, is the product causing the highest risk of allergy. The German Institute *Informationsverbund Dermatologischer Kliniken und zur Erfassung wissenschaftlichen Auswertung von Kontaktallergien* which collects and evaluates clinical data for the severe contact allergies, estimates that 0.3% of the German population is sensitive to hexavalent chromium.. According to the EC/1223/2009 (art. 17), the unintentional and technically unavoidable presence of a small quantity of a prohibited substance stemming from: *i*), impurities of natural or synthetic ingredients; *ii*), manufacturing process; *iii*), storage; and, *iv*), migration from packaging, is allowed provided that such presence is in accordance with art. 3 on the safety of cosmetic products.

In the past, no analytical method was suitable and available for the control of Cr (VI) to the levels mg/kg and less. Therefore, a threshold for these 'technically unavoidable' amounts has not yet been established due also to the discrepancies on toxicological evaluations. As an example, the *German Federal Institute for Risk Assessment* (BfR) considers that the concentration of 1 mg/kg of Cr (VI) in cosmetic products can cause contact dermatitis (4,5). On the contrary, Basketter et al. (6) estimates that a level of Cr (VI) of less than 5 mg/kg in consumer products would be considered safe.

There have been a variety of methods reported for the determination of Cr (VI) in waters and soils, including the traditional diphenylcarbazide complexation method followed by colorimetric determination of the Cr (VI) species (7, 8), separation *via* ion chromatography (IC) with either inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) detection (9-14) and ion pair chromatography with ICP-MS detection (15-16).

The speciation analysis of Cr, however, is a challenging task, since the stability of different Cr species is easily affected by conditions during sample collection and treatment. For example, low pH values may lead to the degradation of Cr (VI) to Cr (III) due to the increased redox potential, while high pH values may lead to the precipitation of Cr (III) as $\text{Cr}(\text{OH})_3$.

The stability becomes a crucial issue when an extraction of solid samples has to be carried out. In fact, to quantify Cr (VI) in a solid matrix must satisfy three criteria: *i*), the extraction solution has to solubilize all forms of Cr (VI); *ii*), the conditions of the extraction must not induce the reduction of Cr (VI) to Cr (III); and *iii*), the whole procedure should not cause the oxidation to Cr (VI) of the Cr (III) occurring in the sample. Among various methods of extraction the 3060A US Environmental Protection Agency (US EPA 3060A) meets these criteria for a broad spectrum of solid matrices. This method is certainly one of the most widely used and is based on a procedure for alkaline digestion designed to extract Cr (VI) from soils, sludge, sediments and similar wastes (18).

An additional difficulty in the accurate quantification of Cr by ICP-MS are the numerous spectral interferences (e.g. $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$ or $^{40}\text{Ar}^{12}\text{C}^+$) on the most abundant Cr isotope, ^{52}Cr . In order to overcome these interferences high resolution-sector field SF-ICP-MS (14) or dynamic reaction cell

(DRC) ICP-MS can be used. The use of a DRC system with ammonia as a reaction gas can dramatically reduce the interference effects while obtaining signals intensity as those obtained using a SF-ICP-MS system (17).

However, the direct final quantification of Cr by means of MS (both SF-ICP or DRC-ICP) systems avoids the use of reaction post-columns to derivatize Cr with 1,5-diphenyl carbazide (DPC) for the spectrophotometric determination. Such reactions are, in fact, very much influenced by the pH value, as the high pH values in the alkaline extraction solution cause inhibition of the Cr (PDCA)₂ – complex formation.

The purpose of this study is to optimize and apply a simple, fast, sensitive, accurate and reproducible analytical procedure - based on a alkaline extraction, chromatographic separation and final direct determination by ICP-MS - for the determination of Cr (VI) in cosmetics; two type of powder-based products widely used are tested, namely face powder and eye shadow. Usually, face powder is a mixture of fine perfumed powders with colloidal substances such as starch, giving the adhesiveness, pigments (zinc carbonate, barium sulfate, etc.) to ensure the covering power, and the presence of talc and starch for the necessary absorbing power. Eye shadow, in its turn, is a mixture of mica, magnesium stearate, talc, oil, jojoba oil, lanolin, squalene, and pigments, usually oxides. The lipid content (essentially, oils) of the latter type of products allowed the analytical procedure to face both potential matrices occurring in cosmetic products, i.e., powder (minerals) and lipids.

Experimental

Apparatus

Chromatographic separations were carried out using a Dionex ion chromatography system ICS-5000⁺ Thermo Fisher Scientific Inc. (Waltham, MA USA). Due to its completely metal-free solvent pathway, this system is perfectly suitable for elemental speciation studies at the trace levels required by this application. For the separation of the two Cr species, the AG-7 (2 x 50mm) and AS-7 (2 x 250mm) anion exchange columns (both from Thermo Fisher Scientific Dionex) were used throughout this study.

As detector an ICP-MS PerkinElmer SCIEX ELANs DRC II (Concord, ON, Canada) was used. The ICP-MS was equipped with a one-piece quartz injector, a quartz cyclonic spray chamber and a quartz concentric nebulizer. Ammonia (Matheson, Newark, CA, USA) at 99.999% purity was used as reaction gas. The dynamic reaction cell (DRC) conditions were optimized for Cr using a solution containing the IC mobile phase as blank and the same solution spiked with 1 ppb Cr (III) as optimization standard. Using a flow rate of 1.0 mL/min on the peristaltic pump, the system was optimized for the lowest background equivalent concentration (BEC) while maintaining suitable sensitivity for Cr.

The settings used for the IC and DRC ICP-MS operations are reported in Table 1. A fully automated operation of the IC was achieved using the Chromelion software (Thermo Fisher Scientific, version 7.1) in conjunction with the standard ELAN Operating Software (version 3.3) provided by Perkin Elmer SCIEX for ICP-MS systems. All calculations, including background subtraction, peak area integration and calibrations were performed with the Chromera (version 1.2) software.

Reagents

The solution for the extraction of Cr (VI) from the powder is obtained by dissolution of Na₂CO₃ and NaOH (Fluka, Buch Switzerland). The mobile phase used in the chromatographic separation is a buffer solution of NH₄(SO₄), 0.25 M, (Panreac Química, Castellar del Vallès, Spain) and 0.1 M NH₄OH (Fluka). Standard solutions of 1000 mg/L (HPS, Charleston, SC, USA) was used for Cr (III) whilst K₂Cr₂O₇ (Schiaparelli, Torino, Italy) was dissolved in deionized H₂O (Easy Pure, PBI

International, Milan, Italy) for preparing Cr (VI) standard. For recovery test a certified reference material NIST SRM 2701 (Gaithersburg, MD, USA) with a certified content of Cr (VI) in contaminated soils was used.

Samples processing

The extraction procedure for Cr (VI) from samples of face powder and eye shadow was conducted according to the modified method US EPA 3060A. As the actual amounts of cosmetics available for analysis are usually smaller than those of soil/waste samples, i.e., *ca.* 0.5 g, against 2.5 g foreseen for the basic method, some changes and optimizations were required to increase to efficiency of extraction. Furthermore, MgCl₂ and phosphate buffer were eliminated from the extraction procedure. Although these reagents, in fact, act to suppress oxidation of Cr (III) and to eliminate, by precipitation, elements that may give concurrent processes of reduction of the Cr (VI), on the other hand they can reduce recoveries by inclusion of part of the Cr (VI) forms in the precipitate (18).

Before alkaline extraction, samples containing lipidic substances, as eye shadows, were subjected to a step of defatting with a 10 ml of ethanol-hexane (1:1, v/v) solution in 15-ml polypropylene centrifuge tubes. The mixtures were sonicated for 15 min, followed by centrifugation for 20 min at 450 rpm. After the solution was removed, this process was repeated 3 times and all the solutions were collected and analyzed to assess the possible presence of Cr (III) and Cr (VI). The solid sample was dried at 60 °C for 12 h, then it was subjected to the extraction procedure.

Previously defatted samples of about 0.5 g were transferred into glass flasks of 250 ml and after adding an aliquot of 50 ml of an alkaline extraction solution (AES) (0.28 M Na₂CO₃ + 0.5 M NaOH, pH = 13.5), were weighed. Subsequently, the solutions were heated, under stirring, at 90-95 ° C for 60 mins. After the extraction process, the sample was cooled and weighed again, and in the case of a weight loss, this was corrected by adding the AES solution. At a later stage, the content was centrifuged at 4000 rpm for 20 mins. The supernatant solution was filtered on a PVDF membrane filter (0.45 mm) and analyzed. The same procedure was also performed on samples used for recovery test, i.e. the mixture of sample with the addition of certified reference material.

Analytical method

For the chromatographic separation of the species of Cr (III) and Cr (VI) and their quantization through mass spectrometry the operating conditions reported in Table 1 have been used.

The setup of the analytical conditions for the separation of the two species of chromium was carried out using Cr (III) and Cr (VI) standards dissolved in water and in AES - this last used for samples extraction. Figures 1A and 1B show the separation of Cr (III) and Cr (VI) in water with the following retention times (RT), 1.046 mins and 6.327 mins, respectively. Figures 2A and 2B show, instead, the same separation in AES; the absence of Cr (III) in AES confirms the fact that in the presence of a strongly alkaline solution Cr (III) precipitates as hydroxide (18,19).

Table 1. IC and ICP-MS operating conditions

| Instrument | Ion Chromatography DIONEX ICS 5000 ⁺ |
|------------------|--|
| Column | Dionex IonPac AS7 (2x250 mm), AG7(4x50 mm), |
| Eluent | NH ₄ (SO ₄) (0.25 M) + NH ₄ OH (0.1 M) |
| Injection volume | 25 µl |
| Eluent flow | 0.5 ml/min |

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|------------------------|---|
| Detector | ICP-MS |
| Instrument | ICP-MS Elan DRC II, Perkin Elmer |
| Flow gas | Plasma, 15 l/min; aerosol 1.05 l/min; auxiliary 1.2 l/min |
| Power RF | 1400 w |
| Reaction gas | NH ₃ |
| Reaction gas flow | 0.65 l/min |
| RPq | 0.75 |
| Analytic Mass | ⁵² Cr |
| Dwell time | 250 ms |
| Readings | 1.3–1.9 s |
| Total acquisition time | 15 min |

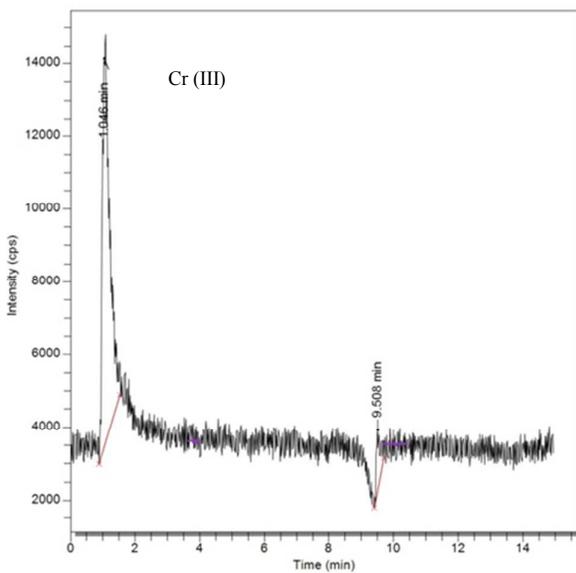


Figure 1A. 10 µg/l Cr (III) in water

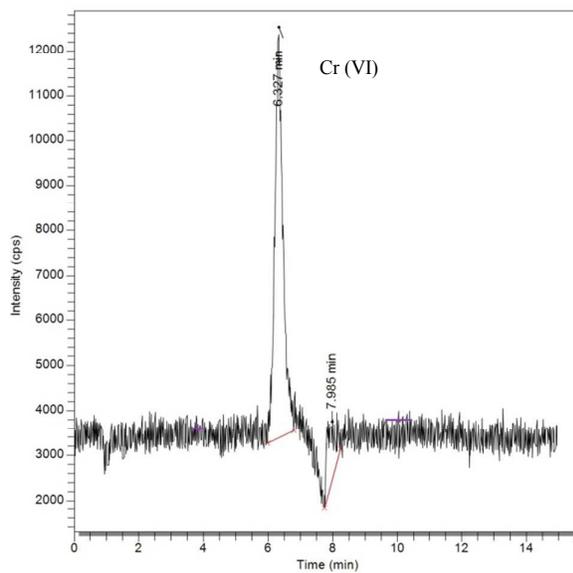


Figure 1B. 10 µg/l Cr (VI) in water

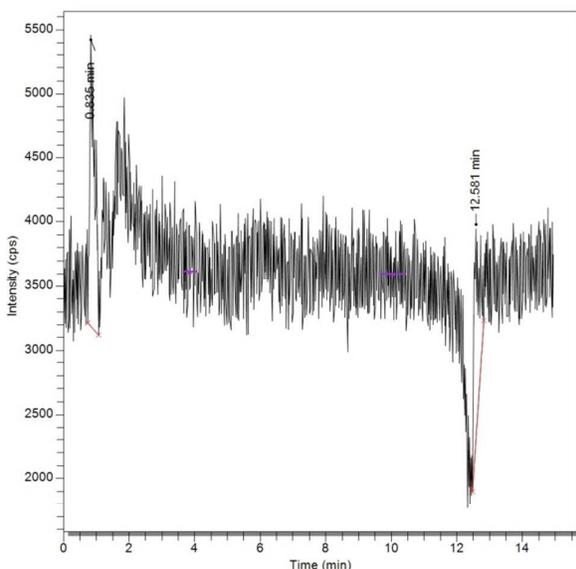


Figure 2A. 10 µg/l Cr III in AES

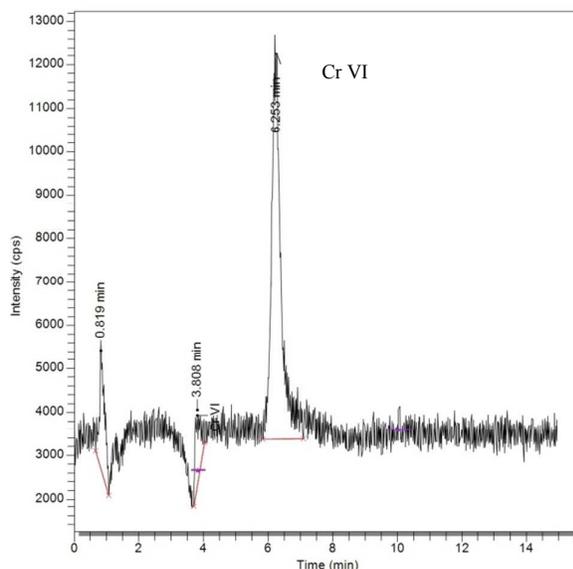


Figure 2B. 10 µg/l Cr VI in AES

Performances of the method

Due to the lack of certified reference materials (CRM) for the content of Cr (VI) in matrices like the samples under study, the tests for the accuracy of the method have been performed through recovery tests on samples obtained by adding a solid certified material to the face powder and eye shadow so as to allow an easy and homogeneous mixture. The solid material NIST SRM 2701, a soil with certified content of Cr (VI) ($551.2 \pm 34.5 \text{ mg kg}^{-1}$) was chosen for similarity of physical state. Since the very high concentration of Cr (VI), as well as of Cr (III), in the CRM, this was diluted with the face powder in the ratio 1:50. The preparation of the mixture was performed through subsequent dilutions and homogenizations in a ball mill of tungsten carbide Vibratory Micro Mill Pulverisette (Fritsch, Idar-Oberstein, Germany). The final blend of face powder + NIST had an expected content of 11.94 µg/g of Cr (VI). To assess the homogeneity of the mixture the test of accuracy was repeated 4 times on 4 different aliquots of the final mixture.

For the accuracy test on the eye shadow matrix a mixture of different eye shadow colors was defatted, then it was mixed and homogenized with the CRM, similarly to what done for face powder, to obtain a final expected concentration of Cr (VI) 11.94 µg/g .

The linearity of the method was evaluated with 0, 5, 10, 20, 50, 100 ng/ml of Cr (VI) in AES.

The analytical precision was determined by the repeatability and within-laboratory reproducibility. The repeatability is the precision under repeatability conditions, that are the conditions where independent test results are obtained with the same method on the same sample in the same laboratory by the same operator using the same equipment in a short interval of time. While, the within-laboratory reproducibility is the precision obtained in the same laboratory under predetermined conditions over long time intervals. The intra-day repeatability and within-laboratory reproducibility were calculated as coefficient of variation in percent (CV %) of ten samples containing about 10 ng/ml of Cr (VI) analyzed in one simple run and three independent sets of ten samples containing about 10 ng/ml of Cr (VI) analyzed in three different days, respectively.

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3 The LoQ, the lowest concentration quantifiable with acceptable precision, was calculated following
4 the criterion of the 10 *sigma*, analyzing 10 samples of ASE (blank) and 10 samples of ASE with
5 addition of 10 ng/ml of Cr (VI).
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7 Finally, to test the potential inter-conversion between Cr (III) and Cr (VI) species a sample of green
8 eye shadow was analysed for the content of Cr (VI) after spiking 10 ng/ml of Cr (III) and subjected
9 to alkaline extraction procedure.
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11 **Results**

12 In order to assess the accuracy of the method by recovery test of Cr VI contained in a mixture of
13 two completely different matrices such as soil, in the case of NIST, and face powder a test to verify
14 that the prepared mixture is homogeneous is required. To calculate homogeneity, four aliquots were
15 withdrawn from the mixture and analyzed following the whole method.
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18 The results reported in Table 2 show a precision of 6.2 % in the analysis of Cr VI content in
19 different aliquots. The mixture of two different solid matrices, then, can be considered
20 homogeneous. On the other hand, an average recovery of 106 % shows that the Cr VI is stable
21 during the extraction and analytical phases. So, the analyzed sample can also be used for the
22 recovery tests on samples of eye shadow. The recovery data obtained for the Eye shadow specimen
23 was 99.6 % as reported in Table 2.
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26 The linearity of the method was evaluated with 0, 5, 10, 20, 50, 100 ng/ml of Cr (VI) in AES. The
27 calibration curve for Cr (VI), between 0 and 100 ng/ml, shows an excellent linearity with a
28 correlation coefficient being 0.9996 (Fig. 3).
29

30 The precision of the method was calculated as 9.2 % in the repeatability and 14.5% in within-
31 laboratory reproducibility.

32 Using injections of 25 μ l, the method has a LoQ for Cr (VI) of 0.11 mg/Kg, which is sufficient for
33 the determination of safe cosmetic products. This values are 10 to 50 lower than the safety limit for
34 the Cr VI in cosmetic products.
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Table 2. Recovery data obtained in four aliquots withdrawn from the mixture of face powder+NIST and from mixture Eye shadow + face powder + NIST

| Matrix | Found Concentration (µg/g) | Expected concentration (µg/g) | Recovery (%) |
|---------------------------------------|----------------------------|-------------------------------|--------------|
| Face powder + NIST | | | |
| Aliquot 1 | 13.8 | 11.94 | 115 |
| Aliquot 2 | 11.8 | | 98.8 |
| Aliquot 3 | 12.2 | | 102 |
| Aliquot 4 | 12.1 | | 101 |
| Average | 12.47 | | 106 |
| Standard Deviation | 0.78 | | 7.8 |
| SD % | 6.24 | | 7.4 |
| Eyeshadow + Face Powder + NIST | | | |
| Aliquot 1 | 11.89 | 11.94 | 99.6 |

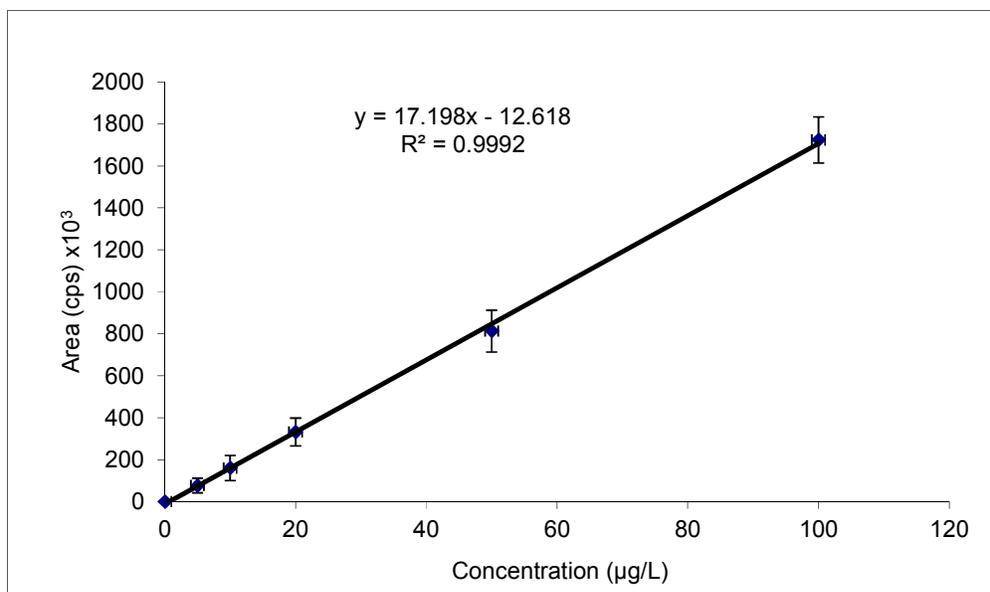


Figure 3. The calibration curve for Cr (VI) detection. The calibration curve was obtained by least-square linear regression with the coefficient of correlation (r^2) being 0.9992.

The reliability of the whole method with regard to the stability of the Cr VI species and the non-oxidation of Cr III to Cr VI was tested by analyzing two samples of eye shadow. Figure 4 shows the chromatogram of specimen without (A) and with (B) a solution of 10 ng/ml of Cr III added to the matrix.

As it can be seen from the figure, the peak corresponding to Cr (VI) has not increased in the B chromatogram compared with A. Therefore Cr III, added to the specimen before the method application, was not oxidized during the extraction phase and during the chromatographic run.

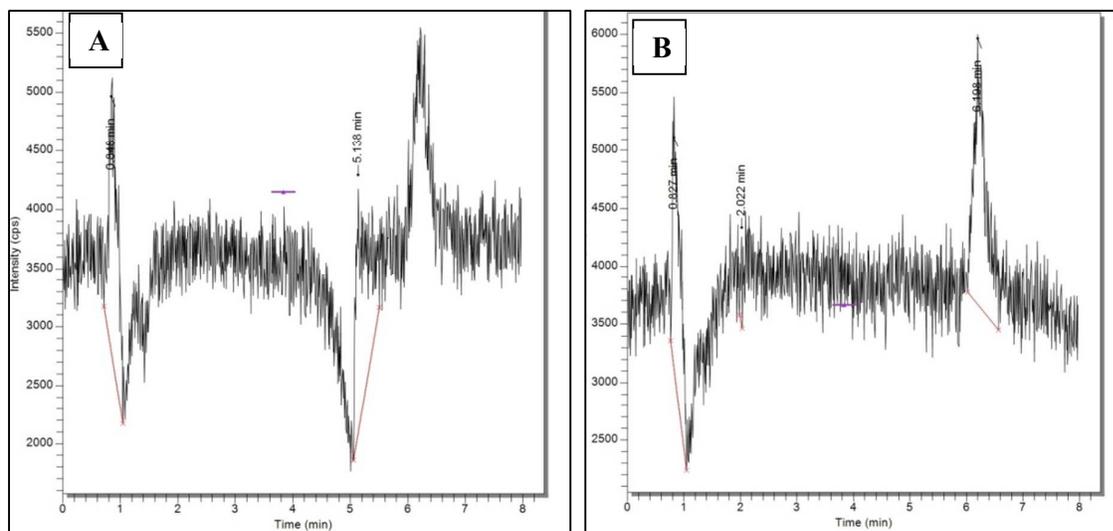


Figure 4. Chromatographic pattern of a sample of eye shadow: A) without Cr III spiked and B) with 10 ng/ml of Cr III.

Analysis of real sample

The described extraction methods could be used for the quantification of chromium (VI) in real samples. For this reason some cosmetic products such as one sample of face powder and four samples of eye shadow were purchased in Rome in 2013. The concentrations of the total chromium in the products are summarized in Table 3.

A defatting step was needed prior to performing the alkaline extraction step and measuring the chromium(VI) content of eye shadow. No presence of Cr VI was found in the defatting solution collected. The calibration plot was prepared in AES matrix with 0, 5, 10 and 20 ng/ml of Cr VI. The calibration curve was obtained by least-square linear regression with the coefficient of correlation being 0.9998.

In Table 3 the concentration of Cr VI, found in different samples, is also showed. Cr VI was not detected in the face powder sample analyzed. Two samples of eye shadow did not present detectable values of Cr VI. On the other hand, in the green eye shadow Cr VI is present at a concentration of 0.7 mg/Kg, below the safety range. Whilst, in the bronze color the concentration of Cr VI at 9.8 mg/Kg is about 25 % of the total element and represents a value higher than the safety threshold for contact dermatitis.

Table 3. Total Chromium and Cr VI concentration in face powder and eye shadow samples

| Product type | Product name | Total Chromium (mg/Kg) | Chromium VI (mg/Kg) |
|--------------|--------------|------------------------|---------------------|
| Face powder | | 4.05 | n.d. |
| Eye shadow | White cream | 10.6 | n.d. |
| Eye shadow | Green | 2.87 | n.d. |
| Eye shadow | Yellow gold | 14.5 | 0.7 |
| Eye shadow | Bronze | 39.7 | 9.8 |

Conclusion

A pre-treatment and analysis method for Cr (VI) in cosmetic products was applied in order to avoid Cr (III) to be changed into Cr (VI) through redox reactions during the pre-treatment process. Critical points of the method were the removing of the matrix including fat and powder-coating materials, and the minimization of oxidation of Cr (III) to Cr (VI).

Throughout the whole method, we confirmed that Cr (III) was not exchanged to Cr (VI). Moreover, we optimized and validated the method in terms of linearity, recovery, precision and LOQ through IC combined with DRC-ICP-MS. The direct determination of Cr by means of mass spectrometry has avoided the use of postcolumn reactions of derivatization with 1,5-diphenyl carbazide (DPC) for the spectrophotometric determination of Cr. Such reactions are in fact very much influenced by the pH value. The pH values of the sample and eluent systems are critical to the efficiency of the separation. The high pH values cause inhibition of the Cr (PDCA)₂ – complex formation, and low pH values cause a marked conversion of chromate ion to dichromate ion, which can be harmful to the column. Moreover, the fast flow of postcolumn reagent causes noise that decreases sensitivity of detection. The too-slow flow of postcolumn reagent causes ineffective formation of Cr (VI)-DPC complex that causes decreasing sensitivity of Cr(VI) detection.

We applied the optimized method to analyze 4 eye shadows and 1 face powder. Despite the fact that the regulations relating to cosmetic products do not permit Cr(VI) in cosmetic products sold in the

1
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3 EU, the Cr(VI) in one out of 4 of the products contained more than 5 mg l⁻¹. 5 mg l⁻¹ is the lowest
4 level for safety on skin. With this threshold for allergic reactivity to Cr(VI) 15% of positive allergic
5 responses were appeared (20).
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