Microchemical Journal 127 (2016) 1–6

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Determination of Cr and Mn in moisturizing creams by graphite furnace atomic absorption spectrometry through direct introduction of the samples in the form of emulsions

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ARTICLE INFO

Article history:
Received 5 November 2015
Received in revised form 10 January 2016
Accepted 25 January 2016
Available online 3 February 2016

Keywords:
Trace elements
Moisturizing creams
GF AAS
Emulsions

ABSTRACT

This paper reports the development of a novel method for the determination of Cr and Mn in moisturizing creams by graphite furnace atomic absorption spectrometry (GF AAS) through direct introduction of the samples in the form of emulsion. The method was optimized by evaluating the influence of several variables such as the sonication time, concentration of acid and mass of sample employed in the procedure and emulsion stability. The curves of pyrolysis and atomization were constructed for both analytes in order to evaluate their thermal behavior in the presence of the matrix and to investigate the possible use of different chemical modifiers. The optimized conditions of both Cr and Mn were achieved when 1000 mg of the samples was mixed with 0.5 mol L^{-1} HCl solution sufficient to complete 5 mL. Then, the mixture was sonicated for 20 min, using an ultrasonic probe. The emulsions prepared in this way remained stable for 60 min, at least. The developed method was successfully applied in the determination of Cr and Mn in five samples of commercially available moisturizing creams. Recovery tests were performed, yielding recovery percentages in the range of 93%–108% and 87%–104% for Mn and Cr, respectively.

1. Introduction

The European directive number 76/768 defines a cosmetic as "a substance or mixture of substances manufactured for use in cleaning, improvement or alteration in skin, hair, lips, nails or teeth" [1]. An infinity of new cosmetic products is launched every year and represents a growing market that moves billions of dollars a year worldwide.

For a while, it was believed that cosmetic products had only action on the surface of the skin. In the 80s decade, studies have shown that some substances applied to the skin can have systemic absorption, raising concern about the safety of these products [2]. This information proved the need for studies and regulations to ensure product quality and safety use. Currently, there are few regulations governing the tests to be performed for the determination of metals in cosmetic products, as well as a few studies reported in the literature. This fact shows that, despite being a sector of the industry booming, there is a shortage in the control of impurities, such as metals, in Brazil and worldwide.

The European Union prepared, in 2012, a list of some substances that cannot be part of the composition of cosmetic products, because they are considered unsafe. Among these substances some metals, such as antimony, arsenic, cadmium, chromium, cobalt, mercury, nickel and lead are listed [3].

The Brazilian regulation agency (ANVISA), considering the need to update the rules and procedures for the registration of cosmetic products, published the Resolution No. 79, on 28th August 2000, establishing limits for the use of dyes, which must comply with the specifications established by the international reference. For formulations containing organic dyes the limits are 500 mg L^{-1} for barium, 3 mg L^{-1} for arsenic, 20 mg L^{-1} for lead and the sum of the concentrations of other metals should not exceed 100 mg L^{-1}. In the cases of thimerosal and phenylmercuric substances, which are used in cosmetic formulations for eyes and lips, the limit for mercury concentration is 0.7 mg L^{-1} [4]. Also, in 2007, ANVISA has developed the Quality Cosmetic Control Guide indicating qualitative and quantitative assays of substances in cosmetic products. In this guide, methods are listed for the determination of soluble lead, aluminum and zirconium in formulations of antiperspirants. Different techniques are recommended for the detection of the different metals. However, in all cases, the analytical procedure requires that the sample is decomposed with nitric acid under heating, for 5 min [5].

None of the cited regulation laws establish specific limits for the concentrations of Mn and Cr in cosmetic products. Although these elements are essential micronutrients, they can become toxic when humans are exposed to elevated concentrations. It has been reported that chronic exposure to excessive doses of Mn can cause neurologic disorders,

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http://dx.doi.org/10.1016/j.microc.2016.01.017
0026-265X/

resulting in lethargy, disorientation, speech disturbances, memory loss and acute anxiety [6,7,8]. In the case of Cr, it is well known that its toxicity depends on the chemical form. Hexavalent chromium is carcinogenic, whereas both Cr(III) and Cr(VI) are potential contact allergy agents [9]. It is important to know that dermal absorption has been considered an important pathway of chromium uptake by humans [10–12].

Cosmetic products are not a simple matrix, as in their composition is present a lot of substances. Different procedures have been adopted for their conversion into liquid form prior to analysis, which is a suitable form for introduction in the most of instruments. The acid digestion either by conventional heating [13–22], or using microwave radiation [23–26] is the most popular of the dissolution methods of solid samples. The problem is that these procedures, besides laborious, are slow (especially when the conventional heating is used) and require the handling of toxic and corrosive reagents.

In the last years, the development of methods based on the direct introduction of cosmetic samples into the instruments is a tendency [27–29]. Several advantages can be observed when this strategy is used: (i) no (or minimum) dilution of the samples, which allow that excellent limits of quantification can be achieved; (ii) minimum manipulation of the samples, which minimize their contamination and the loss of the analytes during the analytical process; and (iii) increase of productivity, since the time-consuming step of sample preparation is eliminated.

In this context, the main goal of this study was to develop an analytical method for Cr and Mn determination in moisturizing creams by graphite furnace atomic absorption spectrometry (GF AAS) through direct introduction of the samples in the form of emulsion.

2. Experimental

2.1. Apparatus

All experiments were performed with a graphite furnace atomic absorption spectrometer from Varian (Mulgrave, Australia), model AA240Z, equipped with an automatic sampler Varian PSD 120, an atomization unit Varian GTA 120 and Zeeman-effect background correction system. The atomization was performed from the graphite tube walls (pyrolytic graphite), also supplied by Varian.

Individual hollow cathode lamps of Cr and Mn were used as radiation sources, operating at 7.0 and 5.0 mA, respectively. The measurement of the signals was made using the following instrumental parameters: slit width of 0.2 nm and wavelength of 357.9 nm for Cr; and slit width of 0.2 nm and wavelength of 279.5 nm for Mn. All measurements were based on values of integrated absorbance and the protective gas used was argon (99.99% purity), supplied by Linde Gases (Macaé, Brazil).

An ultrasonic processor from Sonics (Newtown, CT, USA), model VCX 750W, equipped with a 13-mm diameter probe was employed in this work in order to ensure the homogenization of the emulsions.

2.2. Reagents and solutions

All solutions were prepared using ultrapure water produced in a Direct-Q 3 System, provided by Millipore (Milford, USA). The water employed throughout the experimental work always had a resistivity of 18.2 MΩ cm or higher.

The chromium and manganese analytical solutions used in the study were prepared in volumetric flasks of 5 mL from the appropriate dilution of the stock solutions of 1000 mg L^{-1}, provided by Tedia (Fairfield, OH, USA).

During the development of the method, we used standard stock solutions of palladium 10,000 mg L^{-1} (Merck, Darmstadt, Germany), iridium 10,000 mg L^{-1} (Merck, Darmstadt, Germany) and magnesium nitrate 10,000 mg L^{-1} (Merck, Darmstadt, Germany) as chemical modifiers.

2.3. Sample preparation and analysis

For sample preparation, 1.0 g of each sample was weighed directly into a 15 mL capped polyethylene flask. Afterward, we added 0.5 mol L^{-1} HCl solution sufficient to complete 5 mL. Then, the mixture was sonicated for 20 min, in continuous mode, using an ultrasonic probe operated at 50% amplitude. The ultrasonic probe was not introduced into the flask containing the mixture, but it was immersed together with the polyethylene flask in a beaker with distilled water. The emulsion formed inside the polyethylene flask was transferred to the vial of the instrument and directly introduced into the GF AAS (20 μL) for the measurement of Cr and Mn signals, using the optimized temperature program. Throughout the development of the method and for the determination of the analytes in the samples, the results were expressed as the average of three independent replicates. All optimization experiments were carried out with sample S_1.

2.4. Decontamination of the materials

All glassware and plastic flasks used in this work were washed with water and immersed in a 10% (*v*/*v*) HNO_3 solution for 24 h. Afterward, the materials were carefully washed with ultrapure water and dried in an oven at 40 °C (except volumetric flasks), avoiding any contact with metallic materials. Then, they were stored in a closed and dust-free environment until their use.

3. Results and discussion

3.1. Effect of the sample mass used in the emulsion preparation

An emulsion is defined as a mixture of two immiscible liquids in which one (the dispersed phase) is in the form of small droplets within another liquid (continuous phase) [30]. In most cases, for the formation of an emulsion, the presence of a third phase is needed, the surfactant. The moisturizing creams evaluated in the present work were typical oil-in-water emulsions (o/w), in which small droplets of oil are dispersed within an aqueous phase. Despite that water-in-oil emulsions (w/o) have a high moisturizing power, the most cosmetic formulations are formed by (o/w) emulsions because of the ease of removal with water and "soft touch" provided during application [31].

As the continuous phase of the samples is aqueous, the studied (o/w) emulsions could be easily diluted with water or other aqueous solution without losing stability. Thus, the first part of this study was to determine the amount of sample that could be employed in the emulsion preparation. The obtained emulsion should be stable and with a suitable viscosity, in order to ensure the repeatability of the sample introduction procedure into the graphite tube. The influence of the sample mass used in the emulsion preparation was assessed varying this parameter from 50 to 2000 mg of the sample dispersed in purified water sufficient to complete 5 mL. The obtained emulsion was sonicated for 10 min.

As can be seen in Fig. 1, the repeatability of the measurements was lower in the extremes of the studied range. The elevated variability of the signals observed in the beginning of the range can be explained by the instability of the emulsions formed under this condition, which led to the injection of a non-homogeneous "solution" into the instrument. On the other hand, the problem observed when high masses of the sample were used was the elevated viscosity of the resulting emulsions. In this condition, the automatic micro-syringe used to introduce the samples into the spectrometer was not able to take reproducible volumes of the sample, impairing significantly the precision of the measurements. Therefore, the best condition was found when 500 or 1000 mg of the sample was employed. In order to work in conditions of higher sensitivity, we used the dilution of 1000 mg of the sample to 5 mL in all further experiments.