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Determination of aluminum in moisturizing body lotions using graphite furnace atomic absorption spectrometry

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Abstract

A method has been developed for the determination of Al in commercial moisturizing body lotions using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS). The most sensitive absorption line at 309.271 nm has been used for all determinations. The samples were prepared via a suspension with 0.3 mol L^{-1} nitric acid. Comparisons were made with pyrolysis and atomization curves using ruthenium and zirconium as permanent modifiers, and without a modifier to reduce the interaction of Al with the graphite surface and to improve the atomization efficiency of Al. 400 µg Zr was finally chosen as the best permanent modifier. The limits of detection and quantification were 30 ng g^{-1} and 95 ng g^{-1} Al, respectively. The proposed method was applied for 15 commercial moisturizing body lotions with results ranging between 0.17 ± 0.05 µg g^{-1} and 11.8 ± 0.43 µg g^{-1}. Analyte addition tests have been used to evaluate the accuracy of the method and the recovery ranged between 103 and 110%, indicating that there was no serious matrix effect.

Keywords: Aluminum; Graphite furnace atomization; High-resolution continuum source atomic absorption spectrometry; Moisturizing body lotions; Cosmetics.

1. Introduction

Aluminum is an abundant metallic element in the Earth's crust and does not have any known function in the human metabolism. Low concentrations (below 5 μg L^{-1}) are associated with many diseases, such as kidney failure, pulmonary fibrosis, encephalopathy, anemia and others. People with Alzheimer's disease have high concentrations of Al in their brains.[1,2] Some studies suggest that Al can be accumulated in the brain *via* different routes (drinking water, eating food, using medications and others) and it affects the activity of our nervous system.[3-5] In the last years, the interest in studying the toxicity of Al has increased;[6] hence, the determination of low levels of Al is very important.

According to the National Health Surveillance Agency, Brazil (Agência Nacional de Vigilância Sanitária, ANVISA), cosmetics, toiletries and perfumes have both natural and synthetic substances and are used externally on many parts of our body. The only objective of them is to clean our body, remove a bad odor or to keep it in a good shape. ANVISA also says that body moisturizers are a cosmetic.[7] Although there is regulation for a lot of elements, and Al is present in antiperspirants, there is no regulation for Al in body moisturizers.

There are no reported studies about metallic elements in body moisturizers either. However, with the antiperspirants, a study published by Flarend *et al.*[8] used radioactive aluminum to evaluate the presence of the element in our skin. The study concluded that a simple application of an antiperspirant does not increase the Al in our body. However, the authors made clear that more detailed studies are needed to elude the absorption of Al in our body.

Pereira *et al.*[9] optimized the pyrolysis and atomization conditions for aluminum in drinking water with different modifiers. The results obtained using zirconium as a permanent modifier were better than with others modifiers, such as Ru, Rh or Ir. The optimum temperatures for pyrolysis and atomization were 1000 °C and 2500 °C, respectively. With Zr as a permanent modifier, the peak shape was found to be very symmetrical and to return to the baseline in 2 s.[9]

In order to reduce the interaction of Al with the graphite surface and hence improve the atomization efficiency of Al, Quadros *et al.*[10] tested different modifiers: $Mg(NO_3)_2$ only, a mixture of $Pd(NO_3)_2$ and $Mg(NO_3)_2$ in solution, and Zr as a permanent modifier. According to the authors, the repeatability of successive measurements was significantly improved in the presence of the modifiers, especially when Zr was used. The best sensitivity was also obtained for the Zr-treated tube, when compared to the modifier in solution, indicating that the Zr layer probably inhibits the direct interaction of Al with the graphite surface and hence improves the atomization efficiency of Al.[10]

Borges *et al.*[11] tested different modifiers, among them Ru and Zr, for the determination of Al in beer. They observed that the zirconium modifier provided a good analytical signal, which returned to the baseline within 6 s without any noticeable sensitivity problems or memory effect.[11]

The objective of this work was to develop a method for the determination of Al in moisturizing body lotions. Graphite furnace atomic absorption spectrometry (GF AAS) is a consolidated technique and very common for the determination of trace elements in complex matrices, using direct solid sample or suspension analysis.[12-15] For both techniques, however, there might be problems with a high background absorption, calibration difficulties, and the non-homogeneity of the samples.[14-18] At least the background correction problems could be solved much more efficiently using high-resolution continuum source GF AAS (HR-CS GF AAS). The analysis of suspensions has been used in this work, although the only automatic slurry sampling system is not available anymore.[19]

2. Experimental

2.1. Instrumentation

All measurements were carried out using a contrAA 600 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with a transversely heated graphite tube atomizer. The instrument is equipped with a 300W xenon short-arc lamp, operating in a hot-spot mode, as continuous radiation source for the wavelength range from 189-900 nm; a high-resolution double monochromator, consisting of a prism pre-monochromator and an echelle grating monochromator, providing a spectral bandwidth per pixel of about 1.6 pm at 200 nm; and a linear charge coupled device (CCD) array detector with 588 pixels, 200 of which are used for analytical purposes, displaying the vicinity of the analytical line at high resolution. The most sensitive absorption line at 309.271 nm was used for the determination of Al. All measurements were made with 300 scans per reading and an integration time of 10 ms each.

The graphite furnace technique was used exclusively for all measurements. Pyrolytically coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025) and an MPE 60 autosampler were used for the measurement of the aqueous standard solutions. The integrated absorbance of three pixels has been added (peak volume selected absorbance, PVSA, $A_{\Sigma3,\mathrm{int}}$),[20] as this resulted in the best signal-to-noise ratio. Argon 99.996% (Air Liquid, Florianópolis, Brazil) was used as purge and protective gas. The temperature program used for the determination of Al is shown in Table 1.

An ultrasound bath Model Unique-Torthon USC-2850 (Torthon, São Paulo, Brazil) was used to prepare the suspensions in 15-mL polypropylene flasks.

2.2. Reagents and standard solutions

All reagents used in this work were at least of analytical grade. Nitric acid (Merck, Darmstadt, Germany) was further purified by double sub-boiling distillation in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). Distilled and deionized water obtained from a Model Mega ROUP purification system (Equisul, Pelotas, Brazil) with a specific resistivity of 18 MΩ cm was used throughout for preparation of calibration solutions and slurry preparation. All bottles were decontaminated with 30% v/v nitric acid for 24 h and then rinsed with deionized water three times before use.

The standard solutions were prepared by serial dilution of a 1000 mg L^{-1} Al stock solution (Fluka, Buchs, Switzerland) with water. For the determination of aluminum, Zr has been used as a permanent modifier. A stock solution containing 1000 mg L^{-1} Zr (SPEX, Edison, NJ, USA) has been used as provided for coating of the platform. Ten repetitive injections of 40 μL of the stock solution, each one followed by a four-step temperature program with previously optimized ramp and hold times, have been used for coating the platform with a total of 400 μg Zr as a permanent modifier.[21] The same procedure was followed with the alternate modifier Ru (Fluka, Buchs, Switzerland).

2.3. Samples and sample preparation

15 samples of moisturizing body lotion were analyzed. All samples were weighed directly into 15-mL flasks with the mass ranging between about 0.05 and 0.57 g. To these samples HNO_3 was added in order to obtain a final concentration of 0.3 mol L^{-1} and then completed to 10 mL with deionized water. The samples in suspension were taken to an ultrasonic bath where they remained for 30 min. An automatic sampler was used to provide 20 µL from the suspended samples into the graphite furnace. Before every injection, the samples were homogenized manually using a micropipette. The Al solutions used for calibration contained 0.1 mol L^{-1} HNO_3.

No attempt has been made to correlate the concentration of aluminum found in the samples with a possible level of toxicity for the human skin.

3. Results and discussion

3.1. Pyrolysis and atomization curves

The pyrolysis and atomization curves for aluminum, using an aqueous standard solution and the permanent modifiers Ru and Zr are shown in Figure 1. Pyrolysis and atomization curves for the suspension of a moisturizing body lotion with the flavor of açaí berry are shown in Figure 2. It can be seen that the sensitivity is better when using Zr as a permanent modifier than with Ru, but the optimum pyrolysis temperature is basically the same in both cases.

In the determinations without a modifier, the precision was low (RSD > 20%), probably because of the formation of refractory carbides of the graphite platform with the analyte.[13] The repeatability of the method was better in the presence of modifiers, especially in the case of Zr (RSD ≤ 4 %), particularly in an aqueous solution, suggesting that the layer of Zr inhibits the direct interaction of Al with the graphite surface and, consequently, providing a better efficiency of the Al atomization.

The stabilization of the analyte clearly occurs because of the presence of Zr. This effect makes possible the use of higher temperatures for pyrolysis and atomization, 1500 ºC and 2600 ºC, respectively, which were chosen as the optimum. All the following measurements were carried out using the temperature program shown in Table 1.

3.2. Spectrum analysis

Figures 3A and 3B show the time-resolved absorbance spectra of aluminum in an açaí berry moisturizing body lotion obtained via HR-CS GF AAS. The spectrum in Fig. 3A is without a chemical modifier and shows a pronounced double peak, indicating a strong interaction between Al and the carbon of the graphite tube or platform, as was extensively discussed in the literature in the 1980s and early 1990s.[13] The spectrum in Fig. 3B shows the same measurement, but with Zr as a permanent modifier. The chemical modifier, besides providing a higher sensitivity, also improves the profile of the absorption signal and eliminates completely the double peak.

3.3 Figures of merit

After all the analytical conditions have been optimized, a calibration curve has been established and the analytical figures of merit have been determined. The linear regression equation, the coefficient of correlation (R), the characteristic mass (m_0), limit of detection (LOD) and quantification (LOQ) for Al are shown in Table 2. The characteristic mass is the mass of an analyte required to generate an integrated absorbance of 0.0044 s.

The LOD and LOQ have been calculated as 3 and 10 σ/S (n = 10), respectively, where σ is the standard deviation of a blank, and S is the slope of the calibration curve.

3.4 Analysis of moisturizing body lotions

The results obtained for aluminum in different moisturizing body lotions, using HR-CS GF AAS and the direct analysis of suspensions, are shown in Table 3. The results are based on a Student t-test on a 95% confidence interval.[22]

The origin of the aluminum found in these samples is unknown. It is possible that it is a contamination from the raw material itself or even from the preservatives used in the process of making the moisturizing body lotion.

The açaí berry and buriti palm samples showed higher and very similar values (11.8 and 11.1 μg g^{-1}, respectively). Those samples probably have the same production line. It is the same case for jasmine & orchid and flowers & fruits samples. It is also worth mentioning that samples with a higher viscosity and lower aluminum concentration showed a higher value of RSD (10 to 15%), whereas the two samples with a high Al content showed an RSD of 0.7% and 1.5%, respectively. It might therefore be more meaningful to consider the SD instead of the RSD values, which are, with two exceptions, all close to or below 0.2 μg g^{-1}.

3.4 Recovery tests

The recovery (or recovery factor) is the quantity of an added component that can be extracted and quantified from the sample material.[23] Recovery tests were carried out to evaluate the accuracy of the method, as no certified reference material with a composition comparable to body lotions is available in the market; and the results for two body lotions are shown in Table 4; the results are satisfactory for the samples, since the accepted value is between 80 and 120%.[23]

4. Conclusion

A procedure for the determination of aluminum in moisturizing body lotions has been developed using graphite furnace atomic absorption spectrometry. The method requires essentially no toxic or corrosive acid and produces no harmful discharge to the environment. In addition, it is fast and requires little sample preparation. The calibration can be performed with aqueous standard solutions, which further simplifies the procedure. The method could probably be applied for the determination of other elements in this matrix after optimization of the analytical parameters, and certainly for the determination of Al in many other cosmetic products of similar composition.

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Table 1. Temperature program for the determination of Al in slurries of moisturizing body lotion; argon gas flow rate 2.0 L min^{-1} in all stages except during atomization, where the gas flow was interrupted.

Stage	Temperature / °C	Ramp / °C s^{-1}	Hold Time / s
Drying	90	6	20
Drying	110	5	10
Pyrolysis	1500	300	10
Atomization	2600	1500	3
Cleaning	2700	500	4

Table 2. Figures of merit for the determination of Al by GF AAS.

Parameter	Value
LOD (n = 10)	30 ng g^{-1}
LOQ (n = 10)	95 ng g^{-1}
m_0	17 pg
Sensitivity (B)	0.2504 s^{-1} ng^{-1}
R	0.99904

Table 3. Results obtained for the determination of Al in moisturizing body lotions; all values are average ± standard deviation of n = 5 determinations

Sample	Concentration found / µg g^{-1}	RSD / %
Buriti palm	11.1 ± 0.19	0.7
Vanilla	0.89 ± 0.17	7.7
Flowers & fruits	0.35 ± 0.14	15
Oatmeal	1.76 ± 0.31	7.1
Fennel	0.45 ± 0.09	8.0
Jasmine & orchid	0.35 ± 0.14	15
Violet & Lychee	0.17 ± 0.05	11
Chamomile & mauve	0.47 ± 0.03	2.6
Luscious	1.68 ± 0.12	2.9
Açaí berry	11.8 ± 0.43	1.5
Brazilian cherry	2.60 ± 0.23	3.6
Cotton flower	0.41 ± 0.15	14
Red fruits	0.49 ± 0.15	12
Carambole	0.68 ± 0.17	10
Organic	0.66 ± 0.03	1.8

Table 4. Results obtained for the determination of Al in moisturizing body lotions after a dilution in standard solution of known Al concentrations (n = 3 determinations).

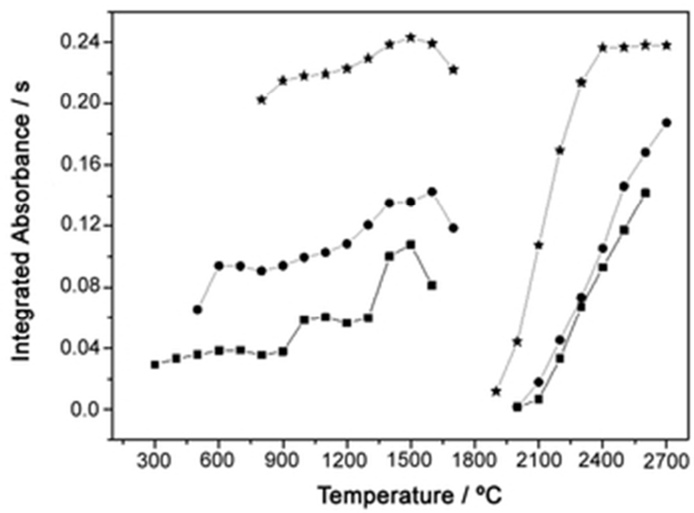
Açaí berry			**Organic**		
Added / $\mu g\ g^{-1}$	Found / $\mu g\ g^{-1}$	Recovered / %	Added / $\mu g\ g^{-1}$	Found / $\mu g\ g^{-1}$	Recovered / %
0	10.71 ± 0.24	-	0	0.66 ± 0.02	-
0.2	12.87 ± 0.12	108	0.2	0.85 ± 0.01	110
0.4	15.32 ± 0.25	103	0.4	1.01 ± 0.02	107

Figure captions.

Figure 1. Pyrolysis and atomization curves obtained by HR-CS GF AAS for Al in a standard solution of aluminum with 400 µg Ru (-■-) or Zr (-★-) as permanent modifiers and without a modifier (-●-). The atomization temperature for the pyrolysis curves was 2500 °C and the pyrolysis temperature for the atomization curves was 1500 °C.

Figure 2. Pyrolysis and atomization curves obtained by HR-CS GF AAS for Al in a moisturizing body lotion of açai berry with 400 µg Zr (-★-) as a permanent modifier and without a modifier (-●-). The atomization temperature for the pyrolysis curves was 2600 °C and the pyrolysis temperature for the atomization curves was 1500 °C.

Figure 3. Time-resolved absorbance spectrum for an açaí berry moisturizing body lotion sample in the vicinity of the aluminum line at 309.271 nm; T_{pyr} = 1500 ºC; T_{at} = 2600 ºC. (A) Without a chemical modifier; (B) with 400µg Zr as a permanent chemical modifier.



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38x23mm (300 x 300 DPI)

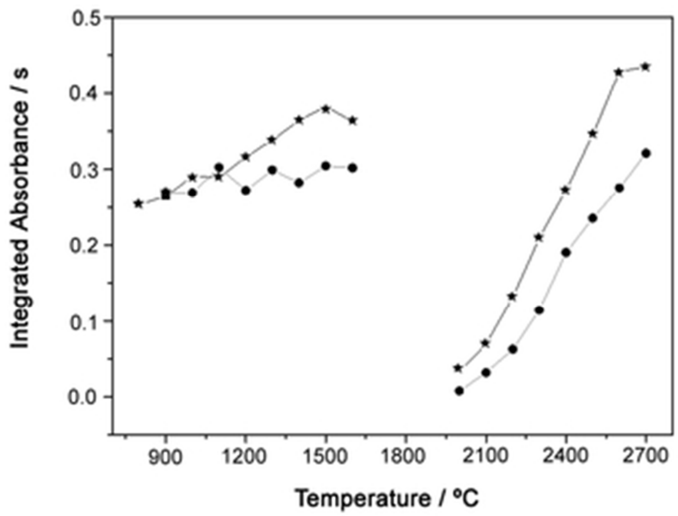
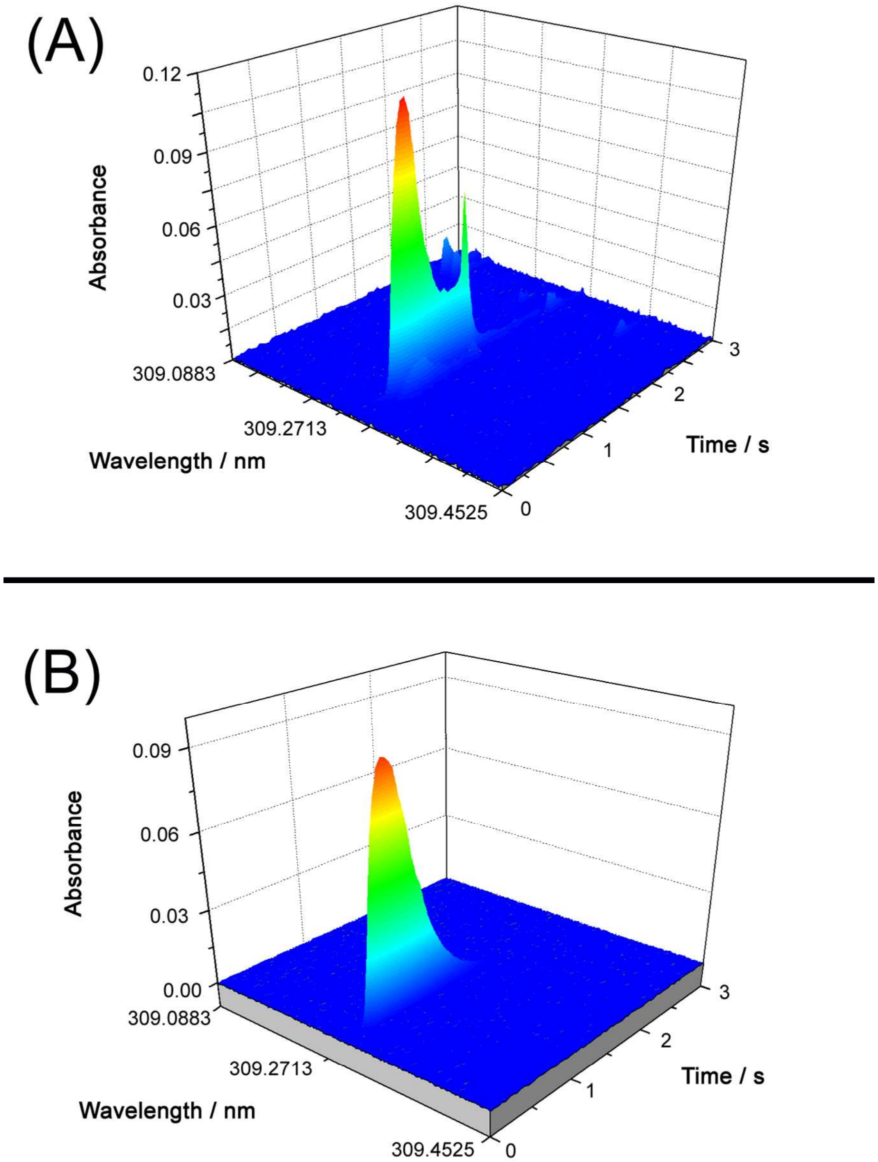


Figure 2. Pyrolysis and atomization curves obtained by HR-CS GF AAS for Al in a moisturizing body lotion of açai berry with 400 µg Zr (-★-) as a permanent modifier and without a modifier (-●-). The atomization temperature for the pyrolysis curves was 2600 °C and the pyrolysis temperature for the atomization curves was 1500 °C.
38x23mm (300 x 300 DPI)



122x169mm (300 x 300 DPI)

Aluminum has been determined in body lotions after mixing with dilute nitric acid using graphite furnace AAS and Zr as a permanent modifier.
23x7mm (300 x 300 DPI)