

Potentially Toxic Elements in Commercial Soap and Powder Detergent Samples

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Dry decomposition, wet digestion, and dissolution in aqueous medium for direct analysis were evaluated for the preparation of eight samples of liquid and bar soap and one powder detergent for later determination of Cd, Mg, Pb, and Zn by inductively coupled plasma optical emission spectroscopy (ICP OES). The evaluation of the best conditions for digestion of the samples were chosen from a set of tests where conventional heating using 1 mol L⁻¹ HNO₃ with addition of 30% H₂O₂ proved to be the most efficient method. The average hydrodynamic diameter of 525 nm was determined using dynamic light scattering measurements. The concentrations found were: Cd and Pb (< limit of detection (LOD)), Mg (50.89 to 1119 µg g⁻¹), and Zn (280.25 to 537.54 µg g⁻¹). After evaluating the sample preparation methods, the accuracy of the methodology was verified through recovery tests of analytes, obtaining values between 83 and 119% and a relative standard deviation (RSD) ≤ 4.30% (n = 6; 4 mg L⁻¹). The LOD ranged from 0.015 to 0.5 µg g⁻¹ and the limits of quantification (LOQ) from 0.045 to 2 µg g⁻¹. The soaps and powder detergent samples studied here may be used without any harm to health as the contents were within the limits established by the legislation.

Keywords: sample preparation, ICP OES, dynamic light scattering, dissolved organic carbon, elements determination

Introduction

Soaps are long-chain salts of carboxylic acids of plant or animal origin, formed by a saponification reaction. Saponification consists of a hot reaction between an alkaline compound (NaOH or KOH) and higher fatty acids. The long molecules formed have a nonpolar chain and a polar end. These characteristics facilitate the interaction of soap with polar and nonpolar environments through the formation of micelles, which favors cleaning.¹⁻³ Currently, there are a wide variety of soaps and powder detergents for various uses: hydration, antiseptic, medicinal, deodorant, and cleaning, among others.

Among the main constituents of soaps or powder detergents are fatty acids (vegetable or animal oils), alkali, additives, antioxidants, petroleum derivatives,^{4,5} potentiating and bleaching agents and chelators.⁶ In many cases, metals such as Hg and Cd are used for skin whitening.⁷ In the manufacture of detergents, surfactants and builders (e.g., phosphates, silicates, zeolites, among

others) are used, as well as additives to improve the quality of the product, such as softeners, enzymes, optical brighteners and thickening agents.⁸

Considering that soaps are products that are in continuous contact with the skin, it is vital to know whether they contain potentially toxic compounds or elements that are harmful to human health. These could trigger health issues; in milder cases, these can be irritations, dermatitis, and inflammation. When absorbed by the human body these can cause intoxication, substitution of essential trace elements, and neuronal problems, among others. It should be noted that both national^{9,10} and international^{11,12} laws limit or prohibit the use of elements such as As, Cd, Ni, and Pb in cosmetics or in personal care products. This means that users must identify the elemental chemical composition of the soaps and powder detergents they use.

Before the determination of elemental composition, an essential step consists of submitting the samples to an appropriate treatment for later determination of the analytes.¹³⁻¹⁵ Among the different sample preparation strategies, there are conventional heating,¹⁶ heating in a muffle furnace^{17,18} and the use of microwave radiation.^{19,20}

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Wet decomposition consists of decomposing organic and inorganic compounds into their constituent elements by means of oxidizing minerals and heating, destroying the matrix to release the analytes. The oxidizing minerals used are usually concentrated, with one or a mixture of acids; in some cases, hydrogen peroxide is added.^{16,19,21,22} The decomposition reaction can take place in open or closed flasks, but, in the case of open systems, the process is limited to the boiling temperature of the acid used; this requires more execution time or more reagents. Closed systems, however, are favored by high pressure and temperature inside a container, increasing the efficiency of the process.^{13,16,23} Dry decomposition, on the other hand, is probably one of the simplest methods of decomposition and corresponds to melting and combustion.^{16,24,25} The long wait for the oxidation of the matrix (between 5 and 8 h), a high energy expenditure, difficulty in dissolving some incinerated materials, and the possibility of contamination and losses of analyte by volatilization, however, are some of the disadvantages of this process.²⁵

Most procedures, even though they are efficient, involve complex methods and the use of highly concentrated acids. Direct analysis of aqueous samples, where only dilution is performed, is a simple method that significantly reduces pre-treatment time, in addition to contributing to the principles of green chemistry. Moreover, it is easy to handle and highly efficient, with less risk of sample contamination, generates less residue, and presents less danger because it needs neither toxic or corrosive reagents nor heating, preventing the volatilization of analytes, and allowing greater precision in the determination of elements.^{13,19,25-27} Among the different analytical techniques for determination of the elements, we can highlight inductively coupled plasma optical emission spectrometry (ICP OES) which is a safe and relatively interference-free technique, which has a satisfactory analytical performance. It is used for the determination of macro and micronutrients and trace elements, at concentration levels of $\mu\text{g L}^{-1}$ or even lower in different matrices, using argon plasma as a source of excitation.²⁸⁻³⁰

There are not many reports of methods in the literature for the determination of metals or potentially toxic elements in bar and liquid soaps, and powder detergents or washing powder. This work aimed to evaluate the decomposition of soaps and detergent powder by different methods: a dry method using a muffle furnace, wet decomposition, by conventional heating and microwave radiation, as well as by dissolution in an aqueous medium and direct analysis. After the comparison, the best condition for decomposition was selected for later determination of the elements Cd, Mg, Pb, and Zn by ICP OES.

Experimental

Instrumentation

For decomposition by incineration, a muffle-type oven was used (EDG, model 3P-S-3000, São Carlos, SP, Brazil). For decomposition by conventional heating, in an open system, a heating plate (model Fisatom, 14 cm, 1800 rpm, São Paulo, SP, Brazil) was used. Finally, digestion was carried out in a microwave oven (Milestone, model Start D, Sorisole, BG, Italy) with space for 10 Teflon® flasks, with volumes between 8 to 12 mL.

For the determination of Cd, Mg, Pb and Zn in the commercial bar and liquid soap and powder detergent samples, an inductively coupled plasma optical emission spectrometer (ICP OES) model Optima 7000 DV (PerkinElmer, Waltham-Massachusetts, USA) was used. The equipment consisted of a charge coupled device (CCD) solid state detector system; argon purged optics; Echelle optics, concentric nebulizer coupled to a Scott type nebulizer chamber and cross-flow nebulizer. Argon was the gas used, with a purity of 99.999%. Table 1 shows the instrumental parameters of the equipment.

Table 1. Instrumental conditions and operational parameters for the ICP OES

Parameter	
RF power / kW	1.3
Nebulizer gas flow / (L min ⁻¹)	0.8
Auxiliary gas flow / (L min ⁻¹)	0.2
Plasma gas flow / (L min ⁻¹)	15
Sample aspiration rate / (mL min ⁻¹)	1.0
Replicates	3
Nebulizer	cross flow
Nebulization chamber	Scott
Plasma observation view	axial
Element and wavelength / nm	C (I) 193.030
	Cd (I) 228.802
	Mg (I) 285.213
	Pb (II) 220.353
	Zn (II) 206.200

(I) and (II): atomic and ionic emission lines, respectively. RF: radio frequency.

Particle size measurement by dynamic light scattering (DLS) was performed on a liquid soap sample. The methodology was adapted from da Costa *et al.*²⁵ The sample was submitted to an ultrasonic bath (Elmasonic Easy 20 H, Singen, Germany) for the homogenization of the samples. Subsequently, the particle size distribution was determined by a Zetasizer Nano ZS90 particle analyzer (model ZEN3690, Worcestershire, United

Kingdom) in combination with the Zetasizer Nano software V3.30.

Samples, reagents, and standards

The reagents used in all experiments were of analytical grade. Purified distilled water was obtained using a distiller (Quimis brand, model Pilsen-Q341, São Paulo, SP, Brazil).

The standard solutions for Cd, Mg, and Pb were prepared from the dilution of stock solutions of 1000 mg L⁻¹ (Inorganic Ventures, Christiansburg, VA, USA) and for Zn from a mono-elemental solution of 1000 mg L⁻¹ (Fluka Analytical, Buchs, Switzerland). A stock solution of 50000 mg L⁻¹ carbon (equivalent to 5% carbon) was prepared using anhydrous D-glucose (dextrose) (C₆H₁₂O₆ brand Synth, São Paulo, SP, Brazil). For the calibration curves, the standards were prepared by dilution of the respective stock solutions with concentrations varying between 0.01 and 8.00 mg L⁻¹ for Cd, Mg, Pb and Zn and 10 to 4000 mg L⁻¹ for carbon. For the decomposition procedures of the soap samples, the following reagents were used: HNO₃ P.A. 68-70% (Alphatec, São Paulo, SP, Brazil) and H₂O₂ (Anidrol).

The cleaning process for both the sample storage bottles and the material used for weighing, decomposition, and sample preparation was carried out by immersion in a 10% (v v⁻¹) HNO₃ solution for at least 24 h. After the immersion period in the bath, they were washed with tap water and then with distilled water and placed to dry at room temperature. One sample of commercial powder detergent (J1) and eight samples of soap (four liquid soaps-J2, J5, J6, and J9 and four solid soaps-J3, J4, J7, and J8) were used in this study. All samples analyzed were purchased in the metropolitan region of Recife (PE, Brazil).

Sample preparation

Dry decomposition of the samples from the bar and liquid soaps and the powder detergent using a muffle furnace

Initially, approximately 3 g of each sample was placed directly into a porcelain crucible. To obtain the optimal conditions for the incineration of the samples, the following program was used: (i) heating step: 30 min at 90 °C; (ii) decomposition step: 60 min at 500 °C. Then, the ash was solubilized using HNO₃ in three different concentrations (1, 2 and 5 mol L⁻¹) in the absence and presence of 30% H₂O₂. Initially, a total of six experiments were conducted, each involving 2 mL of HNO₃ at three different concentrations: 1, 2, and 5 mol L⁻¹. In the first experiment, 2 mL of HNO₃ at concentrations of 1, 2, and 5 mol L⁻¹ were each mixed with

2 mL of water. In the second experiment, 2 mL of HNO₃ at concentrations of 1, 2, and 5 mol L⁻¹ were each mixed with 2 mL of 30% H₂O₂. After filtration, the solutions were transferred to 25 mL volumetric flasks and topped up with ultrapure water. These conditions were selected and adapted according to the procedure developed by Salvador *et al.*²⁶

Decomposition of soap and the detergent samples by conventional heating in an open bottle

For the decomposition in an acidic medium using the conventional method in an open system, approximately 0.5 g of each sample was directly weighed in a beaker. Subsequently, 20 mL of HNO₃ at different concentrations (1, 2, and 5 mol L⁻¹) were added, along with 2 mL of ultrapure H₂O (which was substituted by 2 mL of H₂O₂ in the second experiment). The final solutions were transferred to 25 mL volumetric flasks and topped up with ultrapure water, for a total of 6 experiments. The decomposition procedures for all samples were stabilized at 80 °C and remained for 1 h after reaching this temperature. An external thermometer was used to check the temperature of the solution when in contact with the hot plate. The conditions were selected and adapted according to the procedure of Bielemann *et al.*¹⁸

Decomposition of soap and the powder detergent samples assisted by microwave radiation

Microwave-assisted wet decomposition proposed by Milestone Note HPR-CH-12 methodology suggests the use of 6 mL of 65% HNO₃, 2 mL of 96% H₂SO₄, 1 mL of water, and 0.5 g of soap sample. The program consists of: (i) 15 min ramp up to 1200 W; (ii) maintained to 1200 W and 200 °C, 45 bar for 15 min; (iii) 0 W for 15 min (cooling step). The methodology proposed in this work is a modification of the previous one, evaluating HNO₃ in three different concentrations (1, 2 and 5 mol L⁻¹) in the absence (first experiment) and presence (second experiment) of 30% H₂O₂ as the digesting solution. Approximately 0.5 g of the sample was weighed directly in its reaction flask, to which 8 mL of HNO₃ (1, 2 and 5 mol L⁻¹) and 2 mL of H₂O had been added in the first experiment; and 8 mL of HNO₃ (1, 2 and 5 mol L⁻¹) and 2 mL of 30% H₂O₂ in the second experiment, for a total of 7 experiments. Then, the flasks were stoppered, fixed to the rotor of the microwave, and submitted to the following microwave radiation program: (i) 15 min ramp up to 500 W; (ii) maintained at 500 W and 200 °C, 45 bar for 15 min; (iii); 0 W for 20 min (cooling step). At the end of the heating, decomposition and cooling steps, the solutions obtained were transferred to 25 mL volumetric flasks and topped up with ultrapure water.

Direct analysis

Approximately 0.5 g of each sample was weighed and diluted in 5 mL of HNO_3 in the three different concentrations evaluated (1, 2 and 5 mol L^{-1}). The samples were submitted to an ultrasonic bath for 20 min, before measuring the particle size by DLS, for the homogenization of the samples.²⁵ All experiments were performed in triplicate.

Evaluation of digestion efficiency

The acidity was determined according to that reported by Guida *et al.*³¹ by means of an acid-base titration of the digests. The titration was made with a standardized solution of sodium hydroxide (0.102 mol L^{-1}) and 1.0% (m/v) phenolphthalein in ethanol as a visual indicator. Dissolved organic carbon was evaluated by ICP OES using an emission line (I) 193.030 nm, expressed in mg L^{-1} .

Recovery tests

Considering the lack of certified reference material (CRM) suitable for these types of samples, the accuracy of the method was determined using soap and the powder detergent samples spiked at four different concentration levels: 1.0 and 6.0 mg L^{-1} for the analytes Mg and Zn, 0.1 and 0.5 mg L^{-1} for the analytes Cd and Pb. The spiking was performed before the digestion of the samples. These experiments were performed to verify that there was no matrix effect.

Statistical analysis

Two-way analysis of variance (ANOVA) was used to determine whether the sample preparation method varied significantly. To calculate this difference, the concentrations of dissolved organic carbon and the acidity found in the object sample were used. The statistical calculations were performed with OriginPro 9.0.³²

Results and Discussion

Evaluation of the sample preparation method

Microwave-assisted wet decomposition was used as a reference methodology for comparative purposes with respect to the methodologies proposed in this study, which aimed to implement the use of diluted acid. The acidity ranged from 2.9 to 5.3 mol L^{-1} , with acidity percentages > 20%, considering the acidity of concentrated HNO_3 (14.4 mol L^{-1}) as 100%. Dissolved carbon ranged from 858 to 2342 mg L^{-1} .

The parameters selected to establish the decomposition methodology of the samples were dissolved organic carbon and residual acidity. A comparison of the results obtained for residual acidity and dissolved organic carbon in the methodologies is shown in Figure 1. Two-way ANOVA ($p < 0.05$) was used to evaluate the methods at each concentration. The results for organic carbon showed that the mean concentrations were significantly different in all cases. At the same time, there was no significant difference in the acidity concentrations found in the three different decomposition methodologies and HNO_3 concentrations used.

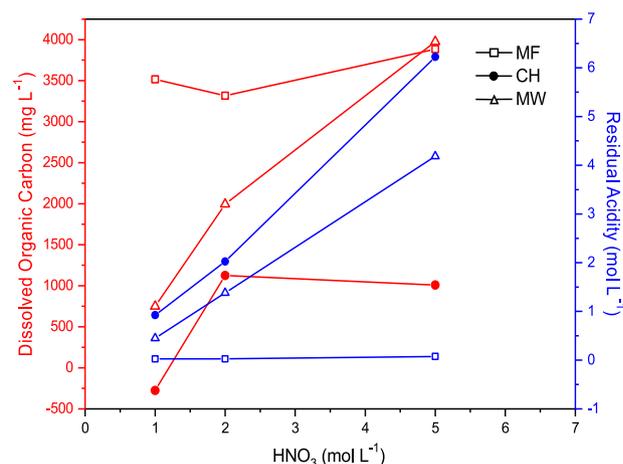


Figure 1. (a) Effect of diluted HNO_3 concentration and volume on residual acidity and dissolved organic carbon in soap digests. For a 0.5 g sample, digestion was conducted with 1, 2 and 5 mol L^{-1} . The decomposition methodologies were: muffle (MF), conventional heating (CH), microwave radiation (MW).

A high residual acidity negatively affects the nebulizer devices and causes physical interference during measurements, in addition, it should be noted that a high acidity does not comply with the principles of green chemistry.^{19,33} The acidity concentrations found by the decomposition methods evaluated varied from 0.025 to 6.2 mol L^{-1} , however, two-way ANOVA showed that the concentrations are statistically equal. Carbon content is decisive in the decomposition of the sample since it provides information on the efficiency of the oxidation of organic matter. A high residual organic carbon content from undecomposed organic matter can cause instability in the plasma, system obstruction, background enhancement, and affect the accuracy of the results. Therefore, dissolved solids below 0.1% (m/v) are recommended.^{19,33} The concentrations obtained by the decomposition methods evaluated varied from -276.4 to 3884 mg L^{-1} . The digests that showed the best results were conventional heating with a carbon dissolved organic (< 189 mg L^{-1}) and acidity (0.95 mol L^{-1}) employing 1 mol L^{-1} concentration of HNO_3 and 30% H_2O_2 . Most of

the solutions obtained after the use of the first methodology that had not included 30% H_2O_2 were inadequate and incompatible for the determination of the elements by ICP OES. The solutions presented residues at the bottom of the flasks, brown and yellow in color, a layer of fat on the surface and a high content of dissolved organic carbon.

The results obtained in the second methodology which included 30% H_2O_2 in the decomposition had a clearer appearance after decomposition. Decomposition by conventional heating using $1 \text{ mol L}^{-1} \text{ HNO}_3$ and 2 mL of 30% H_2O_2 presented a clear, clean solution, free of staining and residues, with low concentrations of dissolved organic carbon and residual acidity, and suitable for analysis by ICP OES, as can be seen in Figure 2.

Particle size measurement: DLS

Direct analysis of the granulometric distribution in the samples is an important step. It is known that a very large particle size (for example, 5000 nm) impairs the efficiency of the ICP OES so that the samples cannot be properly nebulized when introduced into the argon plasma; their movement will be much slower compared to smaller particles.^{19,26,34}

Granulometric distribution analysis was carried out with a problem sample whose solution had a very marked colloidal appearance, with foam on the surface of the solution and high

turbidity. Considering the characteristics of the solution, this was chosen as the reference for the other samples.

The sample was dissolved in the HNO_3 (1 , 2 and 5 mol L^{-1}) and submitted to DLS analysis. The solution of the sample in 1 mol L^{-1} nitric acid (Figure 3a) showed two peaks where the highest represented 93.9% of the particles with an average size of 524.9 nm; 6.1% of the particles were larger than 5000 nm. In Figure 3b, using sample solutions in $2 \text{ mol L}^{-1} \text{ HNO}_3$, 90.8% of the particles had an average size of 544.8 nm; 9.2% of them had a size of 5381 nm. Figure 2c shows a single peak with an average particle size of 454.6 nm for the sample solution dissolved in 5 mol L^{-1} nitric acid. According to the results, the solution using $5 \text{ mol L}^{-1} \text{ HNO}_3$ would be ideal for a later determination by ICP OES, due to the particle size indicating solution homogeneity and better nebulization. Given that this process was evaluated only for liquid soap samples, this represents a limitation. Both solid and powder samples with a lower concentration of HNO_3 (1 mol L^{-1}) in the presence of 30% H_2O_2 , have already proved to be adequate for the decomposition of the analyzed samples, generating less toxic waste.

Method validation

The limits of detection (LOD) and quantification (LOQ) were calculated according to Association of Official

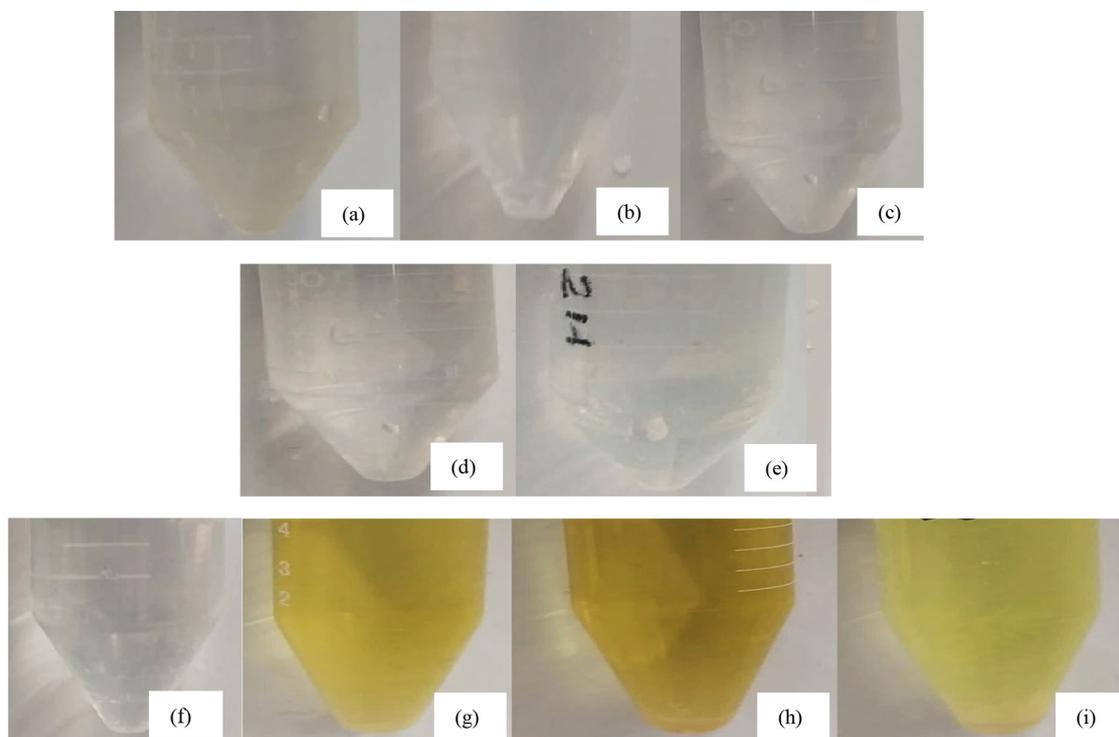


Figure 2. Aspects of the solutions obtained after decomposition using the dry method, diluting the ash in (a) $1 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 ; (b) $2 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 ; (c) $5 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 ; (d) solutions after decomposition by conventional heating using $1 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 ; (e) $2 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 ; (f) $5 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 ; (g) solutions after decomposition by microwave radiation using $1 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 ; (h) $2 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 ; (i) $5 \text{ mol L}^{-1} \text{ HNO}_3$, 30% H_2O_2 .

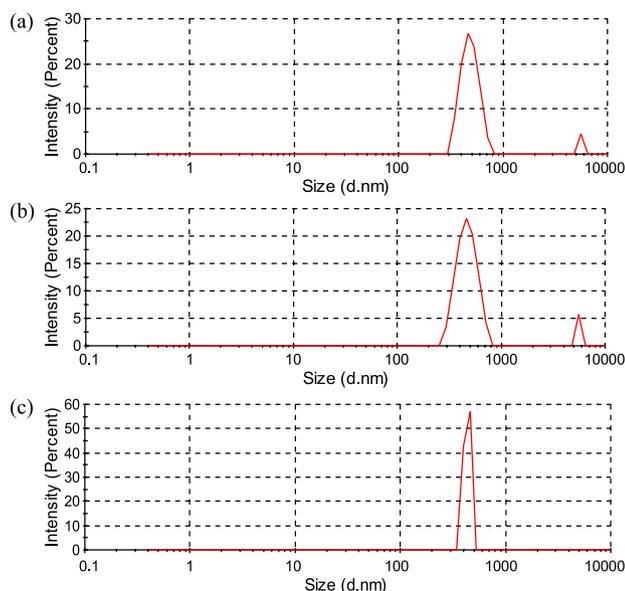


Figure 3. Size distribution in particle intensity obtained by DLS for sample J2 in solution with HNO_3 , (a) 1 mol L^{-1} , (b) 2 mol L^{-1} and (c) 5 mol L^{-1} .

Analytical Chemists (AOAC).^{35,36} Table 2 shows the results of analytical performance parameters, all calibration curves were linear, with correlation coefficients (r) greater than 0.9991 (Cd) and relative standard deviations equal to or less than 4.30% ($n = 6$; 4 mg L^{-1}). These results are in accordance with the US EPA.¹¹

The LODs ($\mu\text{g g}^{-1}$) ranged from 0.015 (Cd) to 0.5 (Pb), and the LOQs ($\mu\text{g g}^{-1}$) ranged from 0.045 (Cd) to 2.0 (Pb). However, the literature does not report limits of detection

for the determination of metals in soaps by ICP OES technique, but rather by atomic absorption spectroscopy (AAS). It can be seen that the Cd has a LOD comparable to similar studies (Table 3). In the case of Pb, this work presented a higher LOD, as shown in Table 3.

To evaluate the accuracy of the method proposed in this work, recovery tests were performed using four concentration levels 1.0 and 6.0 mg L^{-1} for Mg and Zn, related to low and high concentration values of the analytical curve, and 0.1 and 0.5 mg L^{-1} for Cd and Pb, related to low concentration values of the analytical curve, since these metals presented concentration values below the LOD. The recovery results can be seen in Table 4. The measurements were made in triplicate and the recovery results ranged from 83.0 to 112%; the relative standard deviation was obtained for point of the curve (medium concentration, 4 mg L^{-1}), the highest RSD being 3.47% ($n = 6$). The values found are in accordance with the US EPA¹¹ acceptance criteria for the ICP OES technique.

Comparison results

The suitability of the proposed method for decomposition was also evaluated. The decomposition was applied in one sample of powder detergent (J1), two samples of solid soaps (J3 and J4), and one sample of liquid soap (J6) to check the feasibility of the method. The results obtained by the proposed method of decomposition and the reference method (Milestone Note HPR-CH-12)³⁹ were compared as

Table 2. Analytical performance results using the developed method in this study

Element	Calibration curve	Linearity (r)	LOD / ($\mu\text{g g}^{-1}$)	LOQ / ($\mu\text{g g}^{-1}$)	RSD / %
Cd	$y = 154023x + 11407$	0.9991	0.015	0.045	4.3
Mg	$y = 395879x + 9212.3$	0.9997	0.25	1.0	2.5
Pb	$y = 6850.9x + 466.04$	0.9993	0.5	2.0	3.5
Zn	$y = 23778x - 569.77$	0.9997	0.05	0.2	0.78

y : analytical; x : concentration; r : correlation coefficient; LOD: limit of detection; LOQ: limit of quantification; RSD: relative standard deviation.

Table 3. LOD values in soap samples by the developed method chosen for this work and comparison with their values reported in the literature

Sample	Sample weight / g	Acid		H_2O_2 / mL	Final volume / mL	Instrument	LOD / ($\mu\text{g g}^{-1}$)	Reference
		(mol L^{-1})	mL					
Soap	0.5	HNO_3 (1, 2, 5)	2, 20, 8	2	25	ICP OES	Cd (0.015), Mg (0.25), Pb (0.5), Zn (0.05)	this work
Soap	0.5	HNO_3 (65%) + HClO_4 (70%) + HF (40%)	5 + 1 + 1	–	25	AAS	Cd (0.01), Pb (0.013), Zn (0.005)	Oyekunle <i>et al.</i> ⁷
Soap	N/R	HNO_3 (65%)	15	5	50	AAS	Pb (0.242 ppm)	Endah and Surantaatmadja ³⁷
Soap	0.5	HNO_3 (65%) + HClO_4 (70%) + HCl	15 (3:1:1)	–	25	AAS	Cd (0.02), Pb (0.03), Zn (0.04)	Iwegbue <i>et al.</i> ³⁸

N/R: not reported; LOD: limit of detection; ICP OES: inductively coupled plasma optical emission spectrometry; AAS: atomic absorption spectrometry.

Table 4. Recovery values and standard deviation on soap and the powder detergent samples for Cd, Mg, Pb, and Zn by ICP OES

Analyte	Added / (mg L ⁻¹)	Recovery ± standard deviation / %			
		J1	J3	J4	J6
Cd	0.1	93.2 ± 0.9	94.1 ± 0.3	94.8 ± 0.8	105.9 ± 13.6
	0.5	84.5 ± 2.1	83.2 ± 2.0	84.8 ± 3.9	83.7 ± 2.8
Mg	1.0	91.6 ± 16.2	94.4 ± 1.8	91.5 ± 4.7	112 ± 5
	6.0	100 ± 6	111 ± 4	85.2 ± 7.4	97.6 ± 4.9
Pb	0.1	106 ± 10.2	96.4 ± 9.4	103 ± 6.8	110 ± 6.8
	0.5	98.6 ± 7.4	82.3 ± 3.9	94.8 ± 1.5	101 ± 1.6
Zn	1.0	83.0 ± 14.1	94.6 ± 2.5	92.0 ± 6.5	90.1 ± 4.5
	6.0	102 ± 4	101 ± 1	95.9 ± 0.8	86.4 ± 0.3

shown in Table 5. The paired Student's *t*-test, at a confidence level of 95%, was employed to verify the accuracy of the results. The calculated *t*-values for Mg (0.85) and Zn (0.37) are lower than the theoretical *t*-value of 3.18, indicating that there was no statistically significant difference between the response of two decomposition methods. For the metals Cd and Pb, which are all below the LOD paired Student's *t*-test was not realized. In conclusion, there is no statistically significant difference between the results obtained from the proposed method in this study and the reference method for any of the studied metals.

Elemental analysis in soap and powder detergent samples

The results obtained for the Pb and Cd elements were below the LOD for all samples analyzed: the powder detergent, bar and liquid soap samples. According to Abdullah and Ibrahim,⁴⁰ who studied two types of soaps (beauty and black African), the average content of Pb was 0.403 and 0.481 μg g⁻¹, respectively. Endah and Surantaatmadja,³⁷ also studied lead content in cosmetic soap by AAS. The results showed that only one sample exceeded lead levels and 9 samples met the requirements. In other studies, Ayenimo *et al.*⁴¹ analyzed samples of medicated and unmedicated soap and found average concentrations of Cd of 0.252 and 0.024 mg L⁻¹, respectively. However,

Cd is prohibited in any amount in cosmetics and hygiene products.

According to the Brazilian Agência Nacional de Vigilância Sanitária (ANVISA), Resolution RDC No. 44,¹⁰ the maximum amount of minerals in artificial organic dyes used during the manufacturing of soaps is regulated. In the case of the element Pb, a concentration of 20 mg L⁻¹ is allowed; for other potentially toxic metals, up to 100 mg L⁻¹ except arsenic (expressed as As₂O₃) and soluble barium (expressed as barium chloride) with permitted limits of 3 and 500 mg L⁻¹, respectively. The values expressed in Table 6 indicate that these elements did not represent a danger in the personal hygiene materials analyzed.

Figure 4 shows the concentrations of both Mg and Zn. The metals Cd and Pb could not be plotted, because their concentrations were below the limit of detection.

Regarding Zn, the concentrations ranged from 280.25 to 537.54 μg g⁻¹. The highest concentration of this element corresponds to sample J4, bar soap, specific for mixed skin with imperfections. Samples J2 and J4, which are exclusively used for the face, show levels that are relatively different. The Zn contents that are closest to the J4 sample are present in the J1 (powder detergent) and J8 (antibacterial soap) samples. Iwegbue *et al.*³⁸ analyzed different types of soaps: medicated whitening, moisturizing, and shower gel; the Zn content ranged from 25.5 to 1000 μg g⁻¹. According

Table 5. Comparison of the results obtained in the determination of Cd, Mg, Pb, and Zn in soap and powder detergent samples by the proposed and reference methods of sample decomposition (n = 3)

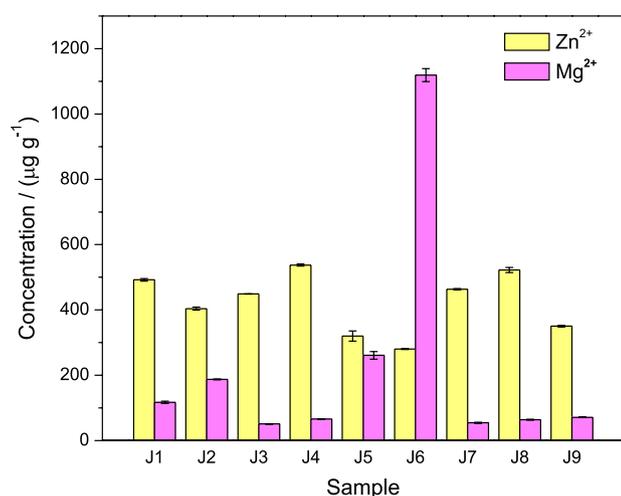
Sample	Proposed method / (μg g ⁻¹)				Reference method / (μg g ⁻¹)			
	Cd	Mg	Pb	Zn	Cd	Mg	Pb	Zn
J1	< LOD	117.0 ± 3.6	< LOD	492.3 ± 3.9	< LOD	128.3 ± 16.0	< LOD	463.5 ± 3.7
J3	< LOD	50.9 ± 0.9	< LOD	448.9 ± 0.6	< LOD	46.3 ± 0.1	< LOD	452.2 ± 1.4
J4	< LOD	66.1 ± 0.8	< LOD	537.5 ± 2.9	< LOD	64.0 ± 0.4	< LOD	553.5 ± 2.7
J6	< LOD	1119 ± 20	< LOD	280.3 ± 1.6	< LOD	1070 ± 10	< LOD	275.7 ± 5.5

LOD: limit of detection.

Table 6. Potentially toxic elements of soap and powder detergent samples analyzed by ICP OES, after decomposition by conventional heating using 1 mol L⁻¹ nitric acid and 30% H₂O₂

Sample	Analyte / (μg g ⁻¹)			
	Cd	Mg	Pb	Zn
J1	< LOD	117.0 ± 3.6	< LOD	492.3 ± 3.9
J2	< LOD	187.3 ± 1.4	< LOD	403.9 ± 4.6
J3	< LOD	50.9 ± 0.9	< LOD	448.9 ± 0.6
J4	< LOD	66.1 ± 0.8	< LOD	537.5 ± 2.9
J5	< LOD	261.0 ± 11.8	< LOD	320.0 ± 15.9
J6	< LOD	1119 ± 20	< LOD	280.3 ± 1.6
J7	< LOD	54.5 ± 1.7	< LOD	463.2 ± 2.0
J8	< LOD	63.8 ± 1.3	< LOD	522.5 ± 7.9
J9	< LOD	71.0 ± 0.6	< LOD	350.4 ± 2.4

LOD: limit of detection.

**Figure 4.** Concentration of Mg and Zn, in μg g⁻¹, determined in nine soap samples after decomposition by conventional heating at 80 °C with 1 mol L⁻¹ HNO₃ and 2 mL of 30% H₂O₂. Error bars show the standard deviation (n = 3).

to Oyekunle *et al.*⁷ the Zn content in cocoa soaps and palm bunches, made in Nigeria, showed maximum levels of 50.82 and 119.21 μg g⁻¹, respectively. Rehan *et al.*⁴² analyzed soaps made with Neem leaves and the maximum Zn content was 14 mg L⁻¹.

The Zn contents reported in the literature have values relatively similar to the contents found in the soaps and powder detergent analyzed in this work. It should be noted that zinc poisoning is rare, but concentrations above 40 mg L⁻¹ in water can induce toxicity.⁴³ According to the International Nomenclature Cosmetic Ingredient (INCI) in Regulation (EC) No. 1223/2009,⁴⁴ products for brief contact with the skin and hair, which use preservatives based on zinc pyritonate, are limited to a maximum concentration of 0.5% (5 mg L⁻¹). In European legislation, Annex VI Last update 2021,⁴⁵ the list of UV filters used in cosmetic

products limited the maximum concentration of zinc oxide in nano and non-nano UV filters to 25% (EU). Zn is added to soap in the form of ZnO and protects the skin against ultraviolet radiation. Excessive exposure to Zn, however, can cause neurological disorders and other consequences.³⁸ In conclusion, Zn or nanoparticles de ZnO pose a threat to the ecosystem and to human beings.⁴⁶

The highest content of Mg was found in sample J6, a product used as a body moisturizer, thus justifying the greater amount of this element in the product. According to dermatological studies,⁴⁷⁻⁴⁹ the presence of minerals such as magnesium, zinc and iodine in bath products helps to improve the skin barrier function, hydrates and reduces inflammation in atopic dry skin thanks to the protection provided by free radicals and bacteria that afflict atopic dermatitis lesions. In addition, magnesium ions have shown in both *in vivo* and *in vitro* studies their ability to inhibit the production of antigens by Langerhans cells, promoting efficacy in the inflammatory processes of skin diseases. In biological processes, they collaborate with cell renewal in cases of acute dermatitis and with anticarcinogenic effect.⁵⁰

Therefore, it is worth noting that none of the analyzed samples presented levels above those established in the legislation. However, the toxicity of metals is not only due to their physical characteristics, but also to the concentrations used in a product, and, more importantly, the type of compound or metabolite they form.

Conclusions

The results showed that the wet decomposition using conventional heating in an open system produced the best results, when the proposed method was compared to the reference one, the results did not show statistically significant differences in the quantified concentrations. In addition, the proposed method did not require the use of concentrated HNO₃. The best conditions for the decomposition of the samples included the use of 1 mol L⁻¹ HNO₃ together with 30% H₂O₂. This condition presented the lowest content of dissolved organic carbon (< 189 mg L⁻¹) and residual acidity (0.95 mg L⁻¹). The concentrations of Cd (< LOD), Mg (50.89 to 1119 μg g⁻¹), Pb (< LOD), and Zn (280.25 to 537.54 μg g⁻¹) were determined in samples of commercial soaps and powder detergent. All samples were below the levels established in legislation, both Brazilian and international. Therefore, the analytes determined in the samples were seen not to represent risks to the consumer. In the evaluation of recovery, the results varied from 79.0 to 118.6%, and relative standard deviations equal to or less than 4.30% (n = 6) were obtained. These results are within acceptable values by the US EPA.

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