Novel spectrophotometric method for the determination of aluminum in soda drinks packed in cans and plastic bottles

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ABSTRACT

In the present work, a new spectrophotometric method was developed for the determination of aluminum in soda drinks packed in different materials. Reaction among Al(III), phenylfluorone (PF) and cetylpyridinium chloride (CPC) in slightly alkaline medium was explored for this purpose. The method was optimized regarding to its chemical parameters in order to establish better conditions in terms of sensitivity and selectivity. The results obtained showed that the concentration of CPC presented remarkable influence on the sensitivity and acted as a sensitizer for the studied system. The possible interferences of some metallic cations were evaluated and the cations Cu(II), Mn(II), and Zn(II) presented noticed interference on the Al(III) signal. So, their interference was eliminated by using EDTA with minimum loss of sensitivity. The results obtained in the determination of total aluminum in soda drinks by the developed methodology were not statistically different from those obtained by electrothermal atomic absorption spectrometry. In the optimized conditions the method presented a linear range of 5–100 μg L^{-1}. The limits of detection and quantification were 0.81 and 2.7 μg L^{-1}, respectively. The methodology was successfully applied in the determination of aluminum in 10 samples of soda drinks packed in cans and plastic bottles.

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1. Introduction

The aluminum is the third most abundant element on the Earth crust after oxygen and silicon. It does not appear in the nature in a pure form, being always associated to other elements forming oxides, phosphates, sulfates, etc. These naturally occurring forms are stable and do not play relevant role in the animal or human biological processes [1]. Nevertheless, the excessive ingestion of aluminum can influence negatively the human organism disturbing calcium and phosphate metabolisms and thus damaging the bone system. Moreover, the accumulation of high amounts of aluminum in the brain is associated to Alzheimer disease, senescence symptoms and amnesia of young people [2].

Human beings are exposed to aluminum from several sources such as atmospheric air, cosmetics, foods, drinking water and medicines. According to Soni et al. [1], food can be considered the most important source of human aluminum intake, once it could be naturally present in several kinds of foodstuffs or found in the composition of additives like coloring agents, preservatives or leavening agents. Also, aluminum can be unintentionally added to foods during cooking, packing or handling. In these cases, the contact of acidic foods with metallic aluminum containers can convert the metal into other chemical forms and even into ionic aluminum (Al(III)) [1]. In front of this scenario, the development of methods for low-level aluminum determination has become an important task in the food science.

Several analytical techniques devoted to low-level metals determination like electrothermal atomic absorption [3–5], ICP OES [6], ICP-MS [7–9] and adsorptive cathodic stripping voltammetry [10–12] have been employed for the Al determination in different kinds of samples. Although the sensitivity of the above mentioned techniques is high, some problems are verified in their application. ETAAS, ICP OES and ICP-MS techniques present very high acquisition and operational costs, being inaccessible for the most of routine laboratories. On the other hand, voltammetry is a cheaper technique but with complex operation and maintenance.

Spectrophotometry is a well-established analytical technique widely used in the analytical laboratories especially due to its low cost, simplicity and wide range of applications. Spectrophotometric methods are precise and accurate but, in many cases, they do not present suitable sensitivity and selectivity, being necessary the use of preconcentration and/or separation procedures to achieve satisfactory results [13,14].

Many traditional chromogenic reagents were already proposed for aluminum determination by spectrophotometry in the visible spectral range [15–18]. Even so, in the last few years, methodologies based on new organic reagents have been developed for the spectrophotometric determination of aluminum in different kinds

Table 1
Operational conditions employed in the determination of aluminum by ETAAS.

Parameter	Set value
Lamp current	10 mA
Wavelength	396.2 nm
Spectral bandwidth	0.5 nm
Purge gas	Ar
Background correction mode	Polarized Zeeman-effect
Graphite furnace	Pyrolytical-coated tube

Table 2
Temperature program used in the determination of Al in soft drinks by ETAAS.

Step	Temperature (°C)	Ramp (s)	Hold (s)	Gas flow rate (mL min^{-1})
Drying	85	5	0	300
	95	40	0	300
	120	10	5	300
Pyrolysis	1000	5	3	300
Atomization	2500	0.8	2	0
Cleaning	2600	1	2	300

of samples [19–22]. However, most of these methods have low sensitivity and/or selectivity, being necessary the application of complicated and time-consuming extraction procedures to separate interferent ions and/or preconcentrate the analytes. All these operations are very difficult to implement in a routine procedure.

The main goal of the present work was to develop a new simple methodology for the spectrophotometric determination of aluminum in soda drink samples only employing reagents regularly found in analytical laboratories. The method, based on the complexation of Al(III) ion with phenylfluorone (PF) in the presence of cetylpyridinium chloride (CPC) as sensitizer and EDTA as masking agent, showed good sensitive and selective, being able to determine the analyte in the μg L^{-1} range free of interferences. Also, samples packed in different containers (cans and plastic bottles) were analyzed and the difference between aluminum found was evaluated.

2. Experimental

2.1. Apparatus

All absorbance measurements were performed with a Femto spectrophotometer (São Paulo, Brazil), model 800 XI, and standard quartz cells of 10-mm path length furnished by Hellma (Plainview, USA).

ETAAS measurements were carried out with a Varian AA240Z equipped with a Varian GTA 120 graphite furnace and a Varian PSD 120 autosampler (Mulgrave, Australia). Background correction was performed with a polarized Zeeman-effect corrector already installed in the instrument. Aluminum hollow cathode lamp, furnished by Varian, was used as radiation source. The instrumental conditions (Table 1) and the temperature program (Table 2) were adapted from those suggested by the manufacturer of the equipment and allowed the determination of aluminum in the range of 5–20 μg L^{-1}. Atomization was carried out on the wall of graphite tubes made of electrolytic graphite coated with pyrolytic graphite, also furnished by Varian.

All pH measurements were carried out with a Digimed potenciometer (São Paulo, Brazil), model DM-22, equipped with a standard combined glass electrode also provided by Digimed.

2.2. Reagents and solutions

All solutions used in the present work were prepared from analytical grade reagents used without further purification. Ultra-

pure water, obtained in a Direct-Q 3 system from Millipore (Saint Quentin Yvelines, France), was used in the preparation of all solutions.

A commercially available aluminum standard solution (1000 mg L^{-1}) provided by Vetec (Rio de Janeiro, Brazil) was used through all the experimental work. Working standard solutions with different concentrations were prepared by adequate dilution of the stock solution.

A 1.0×10^{-4} mol L^{-1} phenylfluorone stock solution was prepared by dissolving 16.0 mg of the reagent, furnished by Acros Organics (Saint Louis, USA), in a mixture of 1 mL of concentrated HCl (Tedia, Rio de Janeiro, Brazil) and 50 mL of absolute ethanol (Tedia, Rio de Janeiro, Brazil). After total dissolution of the solid, the obtained solution was transferred to a 500 mL volumetric flask and the volume was completed to the mark with absolute ethanol. This solution was stable for 2 weeks, at least. During the experimental work, more diluted PF solutions were prepared, just before use, by adequate dilution of the stock solution with ultrapure water.

A 0.10 mol L^{-1} cetylpyridinium chloride stock solution was prepared by dissolving 1.79 g of the reagent (Acros Organics, Saint Loius, USA) in water enough to complete a final volume of exactly 500 mL.

A phosphate buffer solution with total concentration of 0.10 mol L^{-1} was prepared by dissolving 1.40 g of Na$_2$HPO$_4$ (Vetec, Rio de Janeiro, Brazil) in approximately 85 mL of water. Afterwards, the pH of the solution was adjusted to 7.5 by using 2 mol L^{-1} HCl solution and the volume was completed to 100 mL in a volumetric flask.

An EDTA solution (1.00×10^{-1}) was prepared by dissolving 18.612 g of the reagent in ultrapure water enough to make a final volume of 500 mL in volumetric flask.

2.3. Material decontamination

In order to avoid contamination in the experiments, all glassware and plastic flasks used in this work were decontaminated by washing with purified water followed by soaking in a 10% (v/v) HCl solution for 24 h. Afterwards, they were rinsed several times with purified water, dried at ambient temperature and stored in a clean place.

2.4. Spectrophotometric Al(III) determination

In order to build up analytical curves, reagents and standard solutions containing known amounts of Al(III) were added to different 25 mL volumetric flasks. To each flask, 2.0 mL of the phenylfluorone stock solution, a known volume of a 1 mg L^{-1} Al(III) solution, 1.0 mL of the buffer solution, 1.5 mL of the CPC stock solution and 0.25 mL of the EDTA solution were added, in this sequence. After this, the obtained mixture was shaken in order to promote reaction and the volume was completed to the mark with purified water. The absorbance of the final solution was measured at 567 nm against a blank solution containing only the reagents.

All the samples received the same treatment of the standard solutions. However, before the application of the methodology, they were degassed by sonication in an ultrasonic bath for 60 min in order to remove CO$_2$.

2.5. Determination of aluminum by ETAAS

A volume of 20 μL of the sample (50-fold diluted) or standard solution was injected into a pyrolytical-coated graphite furnace. Then, the temperature program was run and integrated atomic absorbance was measured under the conditions shown in Table 1. The temperature program used is listed in
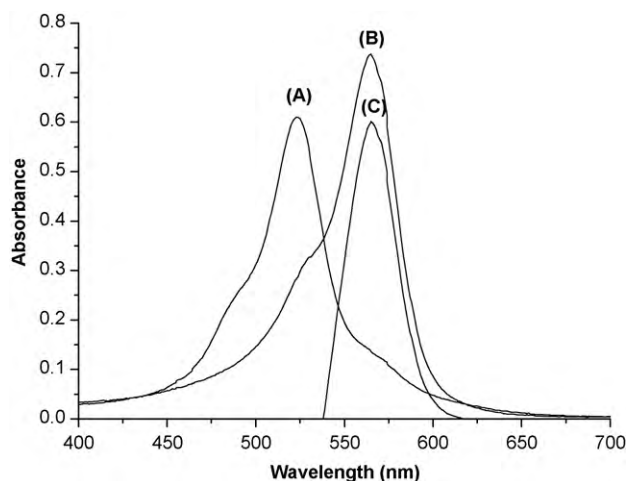
Fig. 1. Absorption spectra of solutions containing the reagents (A), the reagents plus Al(III) 200 μg L^{-1} against water (B) and the reagents plus Al(III) against the reagents (C).
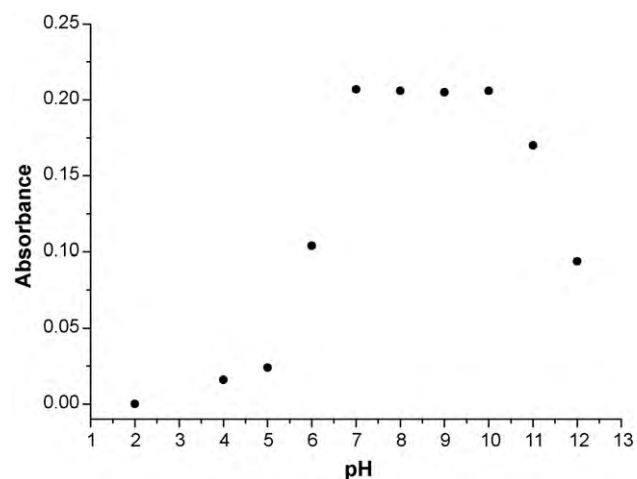

Fig. 2. Effect of the pH on the absorbance of the Al(III) solutions plus reagents against reagents.

Table 2. No chemical modifier was employed in this determination.

3. Results and discussion

The study and development of the methodology for Al(III) determination in soft drinks, exploring its complexation with phenylfluorone and posterior formation of the ionic-pair with CPC, was performed through optimization of the experimental conditions by univariate approach. Optimization process comprised the evaluation of the pH, buffer solution concentration, phenylfluorone concentration and CPC concentration effects. Afterwards, the influence of possible interferents was tested (and eliminated, when necessary) and the method was applied in the determination of Al(III) in real samples of soft drinks packed in aluminum cans.

3.1. Initial evaluation of the reaction between Al(III) and PF in the presence of CPC and Triton X-100

The reaction of some metallic cations such as Cu(II) and Mn(II) with phenylfluorone in the presence of CPC and Triton X-100 as sensitizer was already explored for analytical purposes [23,24]. The authors of these works stated that a quaternary complex was formed involving metallic cations, PF, CPC and Triton X-100. However, no experimental evidences of this fact are shown in these papers. It is important to mention that this reaction was never explored before this work for Al(III) determination.

In order to evaluate the possibility of exploring the foremost cited reaction for Al(III) determination, an initial test was performed involving the reaction of Al(III) with PF in the presence of CPC. This experiment was also used to identify the wavelength where the absorbing specie presented maximum absorbance. The experimental conditions in this test (pH = 8.0 with phosphate buffer, [PF] = 2.0×10^{-5} mol L^{-1}, [CPC] = 6.0×10^{-4} mol L^{-1} and [TX-100] = 2.0×10^{-3} mol L^{-1}) were chosen taken other study as reference [23]. As it can be seen in Fig. 1, the appearance of a intense band at 567 nm was observed in the presence of Al(III), probably due to the formation of a new compound containing Al(III) and the reagents added to the solution. Although the reagents mixture presented some absorbance at this wavelength, it was chosen for all further experiments, since maximum difference between solutions with and without Al(III) was observed at this point.

3.2. Effect of the pH

The first parameter investigated was the pH of the reaction medium. This parameter was chosen because it plays important role in the complexation reaction of Al(III) by PF, since this substance behaves as a weak acid (H$_3$L) in aqueous solution. The PF capacity to form complex ions depends on the ionized form found in solution, which is strictly related with the pH. In order to evaluate the influence of the pH on the sensitivity of Al(III) determination, 100 μg L^{-1} Al(III) solutions were prepared and the pH values were adjusted ranging from 2.0 to 12.0. The results obtained in this experiment are shown in Fig. 2.

As it can be seen, at low pH values (2.0–5.0) the absorbance verified was negligible because, in this range, the PF is fully protonated (H$_3$L form) being not able to complex Al(III) ions. An increase in the absorbance of the solutions was verified in higher pH values, probably due to the formation of unprotonated species of PF, which are capable to react with Al(III) forming a complex. Maximum absorbance values were obtained in the range of 7.0–10.0, due to the predominance of the phenylfluorone specie that reacts preferentially with Al(III) ions. In pH values higher than 10.0, the absorbance decreases again probably due to the formation of a PF specie totally unprotonated, which does not present high affinity by Al(III). Also, it is important to remark that the formation of the ionic-pair between Al(III)–PF complex and CPC depends on the charge of the formed complex and this process seems to be favored in the pH range of 7.0–10. A pH value of 8.0 was chosen for the method and a phosphate buffer system was employed to adjust the pH of the solutions.

Also in order to obtain maximum sensitivity, the effect of the total concentration of the buffer system added in the preparation of solutions was examined. Solutions with total phosphate buffer concentration between 2.0×10^{-3} and 2.0×10^{-2} mol L^{-1} were tested. The final concentration of Al(III) in the solutions was always maintained at 100 μg L^{-1}. The absorbance observed did not varied significantly in the whole range tested. Therefore, a total phosphate buffer concentration of 2.0×10^{-3} mol L^{-1} was employed in all further experiments in order to save reagent and avoid excessive residues generation.

3.3. Evaluation of the influence of PF concentration

The concentration of the chromogenic reagent is an important parameter to be studied in the development of any spectrophotometric methodology. In these cases, the reagent concentration
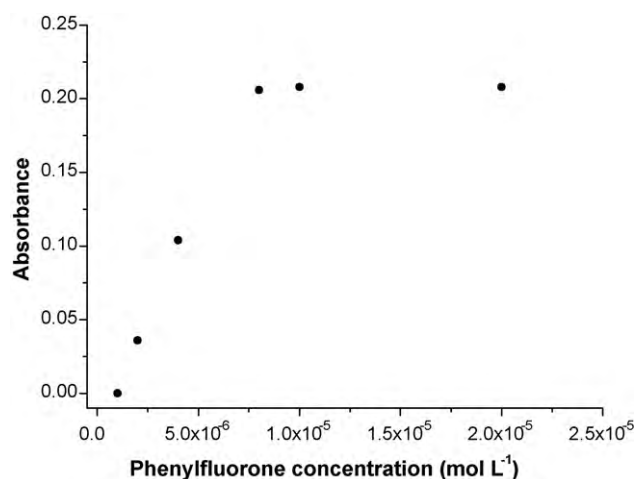
Fig. 3. Effect of the phenylfluorone concentration on the absorbance of a 100 $\mu g \, L^{-1}$ Al(III) solution.

Fig. 4. Effect of the cetylpyridinium chloride on the absorbance of a 100 $\mu g \, L^{-1}$ Al(III) solution.

must be as high as possible to convert all analyte into its respective complex, avoiding lost of sensitivity. However, on the other hand, a high excess of the reagent should be prevented in order to avoid the observation of high absorbance in the blank solutions, a phenomenon especially intense when there is an overlapping between reagents and product bands, which is the present case.

The concentration of PF was evaluated in the range of 1.0×10^{-6} to 2.0×10^{-5} mol L^{-1}. The pH was adjusted to 8.0 with a phosphate buffer solution with final concentration of 2.0×10^{-3} mol L^{-1} and the Al(III) concentration was 100 $\mu g \, L^{-1}$, as in the previous experiments. The results obtained are shown in Fig. 3. As it can be seen, the absorbance (against a blank solution with the same PF concentration) has a strong increase in PF solutions in concentration up to 8.0×10^{-6} mol L^{-1} and remains constant in higher concentrations. So, concentration of 8.0×10^{-6} mol L^{-1} PF was established for the method.

3.4. Evaluation of the influence of CPC concentration

The spectrophotometric method studied in the present work was based on the formation of an ionic-pair between Al(III)–PF complex and CPC, as previously stated. Therefore, the study of the suitable concentration of CPC added to the medium was important to guarantee the formation of the absorbing specie. In this experiment, the CPC concentration in the solution was varied between 0×10^{-2} mol L^{-1} (no CPC added) and 1.2×10^{-2} mol L^{-1} and the experimental conditions previously optimized were maintained. The results obtained in this experiment showed that the concentration of CPC influences significantly the sensitivity of the methodology (Fig. 4). In the absence of CPC, the intensity of the absorbance signal was only around 25% of that observed when 2.0×10^{-3} mol L^{-1} CPC was added. No noticeable variation in the sensitivity was verified between this value and 8.0×10^{-3} mol L^{-1} of CPC. In order to ensure maximum sensitivity and robustness for the method, a CPC concentration of 6.0×10^{-3} mol L^{-1} was used in all further experiments.

3.5. Effect of the addition of Triton X-100

In two works, Winkler et al. [23,24] report that the Cu(II) and Mn(II) ions react with PF, CPC and Triton X-100 to form a quaternary complex. Therefore, in the present work, the effect of the concentration of Triton X-100 added to the reaction medium was evaluated. The Triton X-100 concentration was varied between 0 mol L^{-1} (no Triton X-100 added) and 8.0×10^{-3} mol L^{-1}. No remarkable varia-
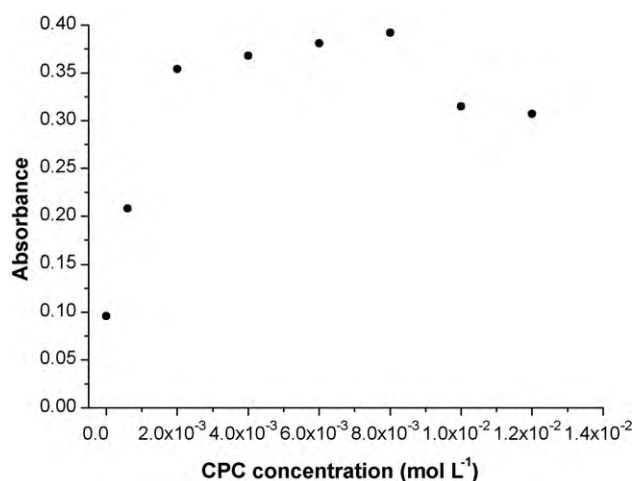
tion in the absorbance signal was verified over the entire studied range, proving that Triton X-100 does not participate significantly in the reaction of Al(III) with PF and CPC. So, Triton X-100 was not added to the solution for the Al(III) measurement by the proposed methodology.

3.6. Evaluation of the order of addition of reagents

The sequence of the reagents addition has a significant influence on the signal obtained in some spectrophotometric methods [25–27], affecting the complex formation and influencing the sensitivity of the methodology. In the present work, 16 experiments were performed covering all possible sequences of addition of reagents. The obtained results indicated that there is significant effect of this parameter on the method sensitivity. In a general way, the highest absorbances were verified when PF was added before Al(III), indicating that the Al(III)–PF complex formation can be affected by the others reagents added to the solutions.

3.7. Interference study

Several interferent cations, especially the ones that form stable complexes with phenylfluorone and could be present in the samples, were evaluated as possible interferents for the methodology. So, Cu(II), Mn(II), Fe(III), Co(II), Ni(II), Pb(II), Zn(II), Cd(II) and Mg(II) were tested in concentrations 10 times higher than the concentrations of Al(III). Significant positive interference was only noted due to the presence of Cu(II), Mn(II) and Zn(II) in the medium even when they were present in the concentration of $40 \, \mu g \, L^{-1}$ (the same concentration of Al(III)). These interferences can be explained by analyzing Fig. 5. The reaction of Al(III) with the reagents forms a substance with maximum absorbance at 567 nm (as previously stated), while the chromogenic substances formed with all other metallic cations presented maximum absorbance at wavelengths higher than 575 nm (except for Cd(II)). However, the most prominent overlapping was observed among the bands of Al(III) with Mn(II), Cu(II) and Zn(II) products, explaining the interference caused by these ions. It is also important to notice that the most intense band was observed for Al(III).

In order to overcome the interferences due to Mn(II), Cu(II) and Zn(II), EDTA was tested as masking agent, being added to the solutions in concentrations between 1.0×10^{-5} and 1.0×10^{-2} mol L^{-1}. Better results were observed when EDTA was added at a concentration of 1.0×10^{-3} mol L^{-1}, although some lost of sensitivity (around 10%) for Al(III) determination was verified in this condition. Using

Table 3
Results obtained in the determination of Al in the samples by the proposed methodology and ETAAS. All results are expressed as mean ± standard deviation of three independent determinations.

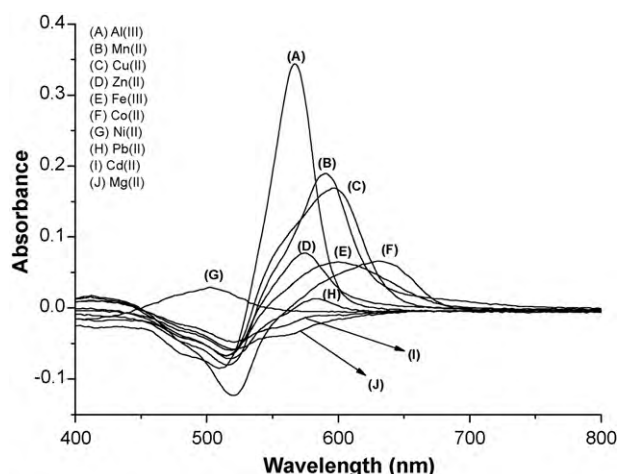| Sample	Package	Al(III) proposed methodology (mg L^{-1})	Al(III) ETAAS methodology (mg L^{-1})
I	Al can	1.5 ± 0.1	1.6 ± 0.1
II	Al can	1.4 ± 0.1	1.5 ± 0.1
III	Al can	0.92 ± 0.02	1.1 ± 0.2
IV	Al can	0.93 ± 0.17	1.1 ± 0,2
V	Al can	0.75 ± 0.08	0.69 ± 0.08
VI	PET bottle	0.53 ± 0.12	0.55 ± 0.12
VII	PET bottle	0.45 ± 0.07	0.45 ± 0.18
VIII	PET bottle	0.47 ± 0.05	0.49 ± 0.05
IX	PET bottle	0.64 ± 0.02	0.62 ± 0.02
X	PET bottle	0.34 ± 0.03	0.41 ± 0.12

Fig. 5. Spectra of Al(III) and the interferents tested at optimized conditions. The concentrations of all species were 100 μg L^{-1}.

1.0×10^{-3} mol L^{-1} of EDTA, Hg(II), Cu(II) and Zn(II) were tolerated in concentrations up to 400 μg L^{-1} (maximum tested).

4. Analytical features of the method

At the optimized conditions, the methodology was able to produce linear analytical fits in the concentrations ranging from 5 to 100 μg L^{-1} Al(III). This fit could be well represented by the following equation: $A = 0.0037$ [Al(III) (μg L^{-1})] $+ 0.002$, $r^2 = 0.9992$. The limit of detection, estimated from three times the standard deviation of 10 measurements of the blank, was 0.81 μg L^{-1} while the limit of quantification, estimated from 10 times the standard deviation, was 2.7 μg L^{-1}. The RSD, calculated by taking 10 measurements of the 5 μg L^{-1} Al(III) standard solution was 4.9%. The molar absorptivity of the absorbing specie in the optimized conditions was 1.02×10^5 L mol^{-1} cm^{-1}.

The robustness of the method was also evaluated. In this case, the slopes of 10 analytical curves, built up in 10 consecutive days, were compared. The average slope obtained was 0.00368 with a standard deviation of 0.00023, which represents a coefficient of variation of only 6.2%, indicating that there is no important variation of the sensitivity by varying measuring conditions.

5. Application

The spectrophotometric methodology was applied in the determination of Al(III) in soft drinks packed in cans and plastic bottles. In order to test the accuracy of the developed procedure, the obtained results were compared with those obtained by ETAAS methodology. However, before the analysis of the samples, a study was performed to establish the correct calibration approach for the

methodology. For all samples, a strong matrix interference was noted, since the slopes of the analytical curves were higher than the slopes of the standard addition curves even when samples were diluted 25 times before determination. This effect can be attributed to the presence of high concentrations of sugar in the samples, altering their physical characteristics such as refractory index and affecting the spectrophotometric measurement. Therefore, the standard addition method was always employed in the quantification of aluminum in the samples.

As it can be seen in Table 3, there was no significant statistical difference among the results obtained by the two methodologies (developed spectrophotometric method and ETAAS method) when a paired-t-test was applied with a 95% confidence level [28]. In this case, the value calculated for t was 1.94 and the critical value for nine degrees of freedom is 2.36. Another test applied to verify the difference between the developed methodology and ETAAS was the correlation test. In this test, the following equation was obtained: Al-ETAAS = 1.05 Al-PM + 0.005, $r^2 = 0.9712$, where Al-PM and Al-ETAAS are the concentrations of total aluminum found by the proposed spectrophotometric method and the ETAAS method, respectively. Both slope and intercept of the equation were not statistically different of 1 and 0, respectively (at 95% confidence level), evidencing that there is no systematic errors associated to the determination of aluminum by the spectrophotometric procedure. The molar absorptivity of the absorbing specie was 1.02×10^5 L mol^{-1} cm^{-1}.

Analyzing the results obtained in the determination of aluminum in the samples, it was possible to realize that there is a significant difference between the values of total aluminum found in the samples packed in the Al cans and in the ones found in the plastic bottles. The average value of total aluminum found in the samples packed in the Al cans was 1.1 ± 0.3, while in the samples packed in the plastic bottles was 0.49 ± 0.11. These values were statistically different at a 95% confidence level when a Student's t-test was applied, indicating that some Al could be leached out of the package in the samples stored in the cans. This hypothesis is reinforced by the fact that all samples presented very strong acidity (pH between 2.67 and 3.47), creating a medium very favorable to the leaching of small quantities of Al from the own can used for packing.

6. Conclusions

The spectrophotometric method proposed in the present study can be considered an excellent alternative for low-level aluminum determination, since it presents high sensitivity, being compared to the electrothermal atomic absorption spectrometry in this point. Also, suitable selectivity can be achieved by simple addition of EDTA to the solutions in order to eliminate the positive interference of Mn(II), Cu(II) and Zn(II), which are the most important interferents for the method.

The developed method is simple and fast and does not require the use of hazardous organic solvents for extraction aiming the separation or preconcentration of the analyte. Under the optimized conditions, the method presented a detection limit of $0.81\,\mu g\,L^{-1}$ and a quantification limit of $2.7\,\mu g\,L^{-1}$. The Lambert–Beer law was obeyed in the range of 5–$100\,\mu g\,L^{-1}$ and a molar absorptivity of $1.02 \times 10^5\,L\,mol^{-1}\,cm^{-1}$ was derived for the absorbing specie.

The results obtained in the application of the methodology to the determination of total Al in soda drinks showed that the concentrations found in the samples packed in Al cans is higher than those found in the plastic bottles, indicating that the acidic soda drinks are able to promote the leaching of Al out of the package.

Acknowledgments

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