Mikrochim. Acta 132, 95–100 (1999)

Mikrochimica Acta

Printed in Austria

Direct Analysis of Coffee and Tea for Aluminium Determination by Electrothermal Atomic Absorption Spectrometry

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Abstract. A method for direct analysis of tea and coffee samples by using electrothermal atomic absorption spectrometry is described. Coffee and tea from different sources were analyzed without digestion step. For slurry analyses the samples were ground, sieved at 105 μm and then suspended in 0.2% v/v HNO_3 and 10% v/v Triton X-100 medium. For liquid phase aluminium determination the samples were prepared in the same way and only the liquid is introduced directly into the graphite furnace. Calibration was performed by aqueous standards for both cases and the determinations were carried out in the linear range between 50 and 250 μg L^{-1}. The characteristic mass of aluminium and the detection limit were 45 pg and 2 μg L^{-1}, respectively. Using a typical 0.1% m/v coffee slurry sample, the relative standard deviation of measurements (n = 15) for repeatability was about 8.2%.

Key words: Slurry atomization; aluminium; tea and coffee; ETAAS.

The knowledge of the role of trace elements in human health has been widely growing in recent years. Aluminium is one of the most common elements on earth and the interest its potential biological function has become of great importance, since this element intoxication appears to be linked with a variety of neurological and behavioral disorders [1, 2] such as Alzheimer senile and pre-senile dementia, amyotrophic lateral sclerosis, Parkinson dementia of Guam and in the dialysis encephalopathy [2].

Daily intakes of aluminium present in food have been estimated as 2–6 mg for children and 9–14 mg for adults [3]. Foodstuffs such as coffee and tea accumulate naturally high levels of aluminium (up to 450 μg^{-1}) [2], and, in addition, these levels can be increased as a result of contamination during processing, packing and from the use of permitted additives such as aluminium phosphates, aluminosilicates and aluminum colorants [3].

Koch et al. [4] observed an increase in the urinary aluminium levels in human volunteers, following the consumption of relatively large amounts of tea.

Because of wide aluminum range concentration reported in foods [5], a great demand for its determination in these kinds of samples is noted, particularly in countries where the people use to drink many times per day.

For this purpose, several methods have been applied to the determination of aluminium in foods and beverages including neutron activation analysis [6], chromatography [7], spectrophotometry [8], atomic emission [5, 9, 10] and absorption [5, 9, 11–23] spectrometry. The best results have been attained using electrothermal atomic absorption spectrometry (ETAAS) due to the combination of sensitivity, simplicity and relatively low cost obtained by this technique [9]. However, in any method, the dissolution of solid samples requires the use of high-purity reagents and uses procedures which are sometimes hazardous and commonly laborious [2, 10]. Besides, there is still a risk of analyte losses by either volatilization or adsorption in the walls of the digestion vessels [24]. Otherwise, with direct analysis, the use of special tools

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or equipments are minimized and the samples can be prepared by using few amounts of the original samples and can be diluted, if necessary [25–27].

In this way, this work describes the direct analysis of tea and coffee for aluminium determination in slurry and liquid phases by using electrothermal atomization. The calibration was performed by means of aqueous standards.

Experimental

Apparatus

A Perkin-Elmer 4100ZL atomic absorption spectrometer equipped with a longitudinal Zeeman-effect background correction system furnished with standard THGA and integrated platform was employed. The spectral bandwidth was set at 0.7 nm. The analytical measurements were made at 309.3 nm by using a Perkin-Elmer aluminium hollow cathode lamp. Sample and modifier aliquots of 20 µL and 10 µL, respectively, were sampled from polypropylene cups and delivered into the tube by means of an AS-71 autosampler from the same manufacturer. Argon was used as purge gas and the heating programme is shown in Table 1. All measurements were made with at least three replicates and based on integrated absorbance.

An ultrasonic bath (Thornton, São Paulo, Brazil) was employed to provide a better homogenization of the slurries prior to its introduction into the graphite furnace.

Reagents, Solutions and Samples

All solutions were prepared employing analytical-grade reagent unless otherwise specified. High purity deionized water (18-MΩ) purified by a Milli-Q Water Purification System (Millipore, Bedford, USA) was used throughout. Nitric acid (Grade reagent Merck, Darmstadt, Germany) was further purified by distillation in quartz sub-boiling stills (Küner, Germany).

Aluminium analytical reference solutions in 0.2% v/v HNO_3 containing 0, 50, 100, 150, 200 and 250 µg L^{-1} Al were prepared daily by serial dilutions from a Titrisol concentrate containing 1000 mg L^{-1} Al (Merck, Darmstadt, Germany).

The 0.06 to 1.0% m/v $Mg(NO_3)_2$ were prepared by dilution from $Mg(NO_3)_2$ solution (Merck, Darmstadt, Germany). These solutions were used to investigate the effect of the chemical modifier concentration.

Table 1. THGA heating programme

Step	Temp./°C	Ramp/s	Hold/s	Argon flow rate/mL min^{-1}
1	140	1	10	250
2	150	1	20	250
3	180	3	30	250
4	600	5	10	250
5	1700	10	20	250
6	2300	0	5	0
7	2500	1	3	250

Programme time 119s; injection temperature: 20 °C.

Triton X-100 (Amershaw/Searle, Arlington Heights, USA) solution was added to all slurry samples and standards involved in the determination of aluminium in order to obtain a final 10% v/v concentration.

The effect of the concomitants was investigated with solutions containing up to 1000 mg L^{-1} Na^+ (NaCl, Johnson Matthey, Royston, UK), 1000 mg L^{-1} K^+ (KCl, Johnson Matthey), 1000 mg L^{-1} K^+ (KCl, Johnson Matthey), 1000 mg L^{-1} Ca^{2+} ($CaCO_3$, Johnson Matthey), 1000 mg L^{-1} Cl^- (HCl, Merck), 1000 mg L^{-1} PO_4^{3-} ($NH_4H_2PO_4$, Suprapur Merck) and 1000 mg L^{-1} SO_4^{2-} (H_2SO_4, Suprapur Merck). All solutions were prepared in HNO_3 0.2% v/v.

Coffee and tea samples from different commercial brands were purchased at local markets.

Storage and Cleaning Materials

All solutions were stored in polypropylene bottles (Nalgene). Plastic bottles, autosampler cups and glassware materials were cleaned by soaking in 20% v/v HNO_3 for 24 h, rinsing 5 times with Milli-Q water and keeping to dryness in a Class 100 laminar flow hood.

Extraction and Preparation of Slurry

Samples were ground using an agate pestle and mortar for 15 min and then sieved at 105 µm. The sample were accurately weighted (30–50 mg) and dispensed into a 50 mL beaker. Next, 20 mL of 0.2% v/v HNO_3 were placed in the beaker. Soon afterwards, the sample was heated at 80–90 °C on a hot plate for 15 min so that the aluminium extraction to the aqueous phase can be enhanced. The slurry was cooled at room temperature and quantitatively transferred to a 50-mL volumetric flask. After setting of solids the supernatant liquid was analyzed for ''extracted aluminium''. For preparation of the slurry a volume of 20 mL of 25% v/v Triton X-100 was added and the slurry was diluted up to 50 mL with water. The formed slurry was then placed in a Thronton ultrasonic bath for 10 min to ensure complete homogenization of the solid particles. When the sonication is over, an aliquot of the slurry is transferred to the autosampler cup and analyzed immediately. In all instances, a reagent blank was identically prepared in parallel. Both aliquots of 20 µL slurry sample and 10 µL of 1% m/v magnesium nitrate solution as chemical modifier were sequentially introduced into the THGA tube and the calibration was performed by aqueous standard solutions. For the analysis of the liquid phase, the slurry is allowed to settle completely. After, an aliquot of the liquid phase is collected by means of a micropipette to be delivered to the autosampler cup and analyzed identically. The heating programme is shown in Table 1.

Wet Digestion

For comparison purposes, the samples were also analyzed in the following way: three replicates of each sample were run and in masses varying from 60 to 100 mg were weighed and quantitatively transferred to a 50 mL digestion tube. Then 10 mL conc. HNO_3 was added and the mixture heated at 105 °C during four hours in a digestor block, almost to dryness; five drops of hydrogen peroxide were then added, and after heating (ca. 105 °C) the solution was evaporated (almost to dryness) and diluted with water in order to decrease the acidity. The sample was cooled at room temperature and quantitatively transferred to a 100 mL volumetric flask and the volume completed with water. Reagent blanks were also carried out through the entire procedure. The same heating programme mentioned as above was used and calibration was also

attained by means of aqueous standard solutions under identical experimental conditions.

Results and Discussion

All studies involving slurries were carried out with roasted coffee samples purchased at local markets.

Stability of the Slurries

Most of papers related to food or biological materials to date have dealt with electrothermal atomization of slurries [19–22, 25–32, 34, 35] because particle size is less critical in this technique. Regarding this point, it was found that relative standard deviations were very similar (ca. 10%) for particle sizes up to 105 µm. Thus, it was decided to work with this particle size.

Another parameter, in this context, is the use of a stabilizing agent which is almost always required to disperse solid particles that might otherwise tend to float on the top of the liquid [26]. Several workers [27, 29, 36] reported that some stabilizing agents such as glycerol and Viscalex cause serious problems with the reproducibility of the volumes deposited by the autosampler, because the sample solution adheres to the outside of the autosampler capillary impairing the precision. Also, it seems that using Triton X-100 the stability of the suspensions is maintained for longer time [25, 37]. For these reasons, it is one of the most useful stabilizing agents [10, 25, 27, 28, 36] and was selected as the most suitable agent in this work. Several different concentrations were evaluated to establish the most convenient within-run precision and the best sensitivity (Fig. 1). A poor relative standard deviation was observed when working at concentrations lower than 10% v/v Triton X-100. This is not surprising since there is an insufficient amount of Triton X-100 to stabilize the slurry. On the other hand, when Triton X-100 concentration was 10% v/v or higher, better relative standard deviations were achieved. However, a large depression of the analytical signal was noted when the concentration was higher than 10% v/v. This is probably due to excessive amount of Triton X-100 which often causes the fluid to run off the platform and the production of a carbonaceous residue in the graphite, as well. According to Stephen et al. [30] this carbonaceous residue eventually affect the sensitivity of the analysis and may partially block the optical beam. Thus, 10% v/v was chosen as the optimum concentration of

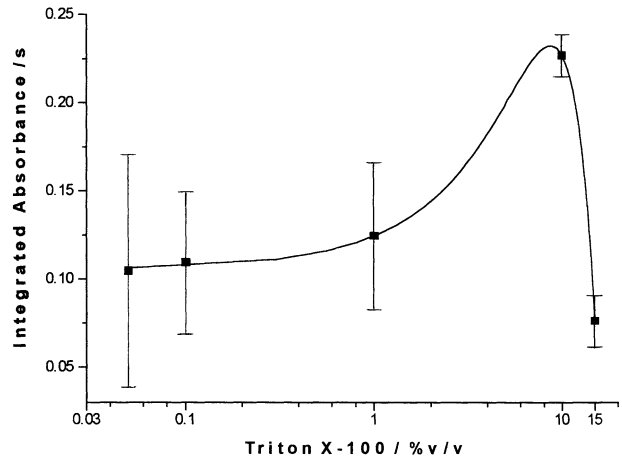

Fig. 1. Effect of Triton X-100 on the slurry stabilization of 119.3 µg L^{-1} Al coffee sample in presence of 1% (m/v) $Mg(NO_3)_2$ as chemical modifier. Volumes injected: 20 µl of sample/standard + 10 µl of chemical modifier. Furnace conditions as in Table 1. Bars indicate the absolute standard deviation of the measurements (n = 9)

Triton X-100 and a previous pyrolysis step of 600 °C during 10 s was added in the heating programme with the purpose of aiding the elimination of the Triton X-100 for analysis of the slurry samples.

Acidity

In the preliminary studies concerning aluminium quantification in different samples and reference material, Viñas et al. [20] observed that using just water as suspending medium led to standard addition with no reproducible slopes. Also, the use of HNO_3 solution in the slurry analysis is well-known as diluent, which performs the extraction of the analyte into the liquid phase of the slurry [31] and apparently plays an important role in reproducibility [38]. For these reasons, the addition of HNO_3 to the suspension medium is widely recommended [19–23, 25, 27, 28, 31, 32]. However, it is noteworthy that with higher acidity, the tube lifetime is decreased. Thus, it was very satisfactory to adopt 0.2% v/v HNO_3 as optimum acidic medium concentration since it reaches reasonable sensitivity and relative standard deviation.

Furnace Conditions Optimization

After defining the suitable conditions for slurry stabilization and acidity, the furnace programme (Table 1) was evaluated.

Taking into account the high content of organic compounds (including Triton X-100) in the slurry medium, poor results were obtained when fast programme methodology [33] was adopted due to high background signal, which had an appearance time very similar to the atomic signal. Consequently, this methodology was discarded and then a conventional programme using platform atomization was improved by experiments involving slurry coffee samples and aqueous standard solutions to determine the optimum temperatures and times for the drying, ashing and atomization steps. The updated programme included three temperature ramps to guarantee a mild and complete drying and prevent sputtering of the sample.

Concerning chemical modifiers, some workers [21–23, 39, 40] have proposed several ones at different concentrations and magnesium nitrate seems the best for the purpose. Thus, it was adopted as chemical modifier and experiments were carried out to select its most suitable concentration. Modifier concentrations up to 1% m/v for injected volumes of 10 µL were investigated. Although no differences in the signal profile were observed and always low background signals obtained (ca. 0.005 A.s) concentrations below 1% m/v exhibited higher relative standard deviation (ca. 22%) compared to 1% m/v. For this reason, 1% m/v was chosen as the optimum magnesium nitrate concentration.

In order to destroy the excess of Triton X-100, an additional pyrolysis step was added as suggested in some works [34, 35]. The best result was achieved when the sample was heated at 600 °C for 10 s. The charring temperature was optimized, always trying to reach the highest temperature possible without premature analyte losses, in the 1200–2200 °C range, and 1700 °C for 20 s was found as the best charring condition since higher temperatures (up to 1900 °C) produced unacceptable relative standard deviations (>14%). These experiments were carried out in the presence or absence of magnesium nitrate solution (1% m/v) as chemical modifier by using either aluminium analytical reference solution (100 μg^{-1}) or coffee slurry sample (0.1% m/v). The atomization temperature was investigated in the 2000–2500 °C range. The maximum signal was reached at 2300 °C for both coffee slurry and aluminium analytical reference solution. It should be pointed out that under established furnace conditions no significant build up of carbonaceous residues inside the tube was observed. The results are summarized in Fig. 2 where

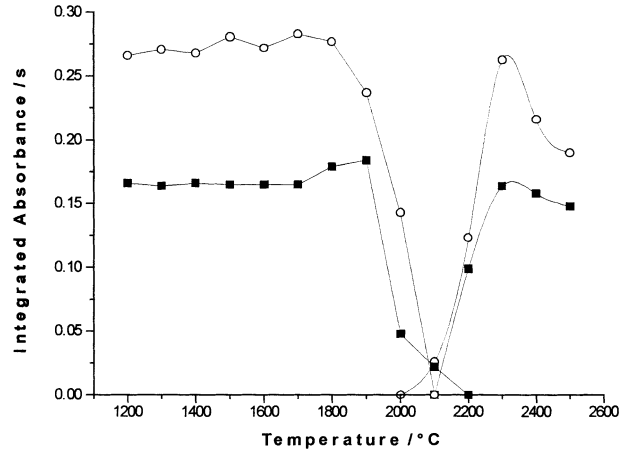

Fig. 2. Pyrolysis and atomization temperature curves of (■) 100.0 µg L^{-1} Al standard solution and (○) 119.3 µg L^{-1} Al coffee sample in presence of 1% (m/v) $Mg(NO_3)_2$ as chemical modifier. Volumes injected: 20 µl of sample/standard + 10 µl of chemical modifier. Furnace conditions as in Table 1

the pyrolysis and atomization curves are depicted using magnesium nitrate as chemical modifier.

Selectivity

To ensure the absence of matrix effect a detailed study was carried out. The main concomitants, which can be found in coffee and tea (0.1–1.1% m/m) are calcium, chloride, potassium, sodium, phosphate and sulphate [2]. So, 10 µL of aluminium analytical reference solution (100 µg L^{-1}) +10 µL of chemical modifier were injected into the graphite furnace. Thereafter, 10 µL more of each species at different concentrations (100 to 1000 mg L^{-1}) were also injected into the furnace. The results are presented as percentage of interference (Fig. 3). Some interferences from calcium and sulfate in the aluminium signal were observed by using concentrations higher than 250 mg L^{-1}. Interferences due to sodium and chloride only appear above 500 mg L^{-1}. The others did not cause variations (±10%) up to 500 mg L^{-1}. These results indicate good selectivity for aluminium determination. It is interesting to note that working at 0.1% m/v slurry, the concentration of concomitants are in the 1–11 mg L^{-1} range.

In this way, the standard additions method was properly used as a complementary study to selectivity. Under recommended experimental conditions, a calibration graph obtained using aqueous standards of aluminium gave a slope of 0.0909±0.0034 L s^{-1}

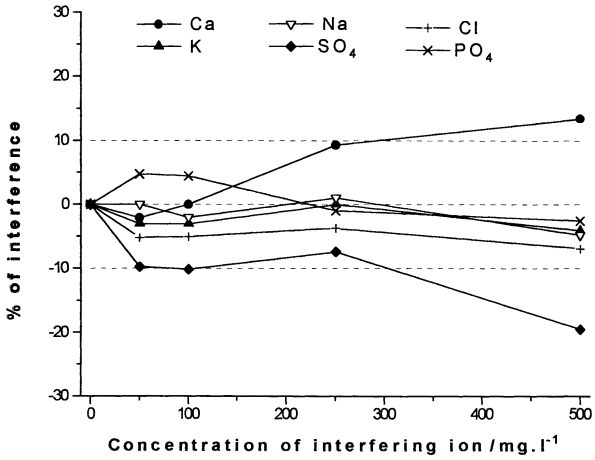

Fig. 3. Effect on the selectivity in presence (50–500 mgL^{-1}) and absense of concomitants. Al concentration, 100 μL^{-1}; chemical modifier 1% (m/v) $Mg(NO_3)_2$. Furnace conditions as in Table 1

μg^{-1}. Each graph was constructed from eight points and each point was measured three times. The standard additions method gave a slope of 0.0950± 0.0051 L s^{-1} μg^{-1}. As can be noted, these slopes were similar, indicating that the effect of chemical interferences due to matrix was negligible and suggests the simplest calibration with aqueous standards is a valid alternative within the context of this comparison.

Analytical Characteristics

A linear range ($r > 0.998$; $n = 6$) up to 250 µg L^{-1} Al was obtained using the furnace programme as shown in Table 1. The characteristic mass of 45 pg was calculated using a 100 µg L^{-1} Al standard solution. The detection and quantification limits of 2 and 7 µg L^{-1} Al, respectively were calculated according to IUPAC recommendation [41]. The precision was estimated by using a typical 0.1% m/v coffee slurry sample achieving a repeatability of 8.2% ($n = 15$) and 9.8% for reproducibility ($n = 5$)

Analysis of Coffee and Tea Samples

Various coffee and tea samples were analyzed with a minimum preparation (as described in slurry analysis section). In this way, the slurry samples were analyzed in order to compare the results obtained with the slurries and those obtained with wet digestion. Applying the t-test the results were found to be similar at the 95% confidence interval.

Table 2. Aluminium contents in coffee and tea samples and in aqueous phase determined by slurry and wet digestion ETAAS ($n = 5$)

Sample	Aqueous phase % Al extracted	Slurry $\mu g\,g^{-1}$±SD	Wet digestion $\mu g\,g^{-1}$±SD
Coffee 1	22.5	64.8±7.7	62.7±3.6
Coffee 2	54.3	63.0±6.5	70.3±3.9
Coffee 3	31.6	143.8±17.6	141.2±3.0
Coffee 4	45.2	63.5±8.0	62.9±1.0
Coffee 5	41.6	119.3±8.4	113.8±1.8
Coffee 6*‡	–	4.7±0.5	4.5±0.1
Tea 1*	–	176.5±5.0	171.3±4.4
Tea	63.6	207.6±21.0	212.8±10.5

* Soluble beverage.
† Slurry preparation: 500 mg/50 mL.

The results for Al determination in coffee and tea by slurry-ETAAS, expressed in $\mu g\,g^{-1}$ are shown in Table 2, which also exhibits the extracted aluminium in the aqueous phase. There is no relation between total aluminium and extracted aluminium. As can be seen in Table 2, the values ranged between 22.5 and 41.6% of extracted aluminium in the aqueous phase when compared to results obtained with slurry analyses. Since these coffees are originating from different regions of Brazil, this large variation of extracted aluminium can be attributed to differences in soil pH which gives rise to several forms of aluminium (free or complexed) in those soils, or else the presence of adulterants in the final product.

Conclusions

Aluminium can be determined in the coffee and tea slurries by using ETAAS as detection technique, with a minimum manipulation and analytical precision and accuracy are acceptable. Detection limits, relative standard deviations and sensitivity are suitable for the aluminium concentrations range encountered and are compatible with other authors [10, 19–22, 27]. Based on the results, this method provides a good alternative for routine purposes.

Acknowledgements. The authors are grateful to Uelintion Guaita (CENA-USP) for his helpful assistance in the technical support. We also thank the Prof. C. Collins and Prof. C. Pasquini for language assistance, to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, S. Paulo, Brasil) grant numbers 95/5782-7 and 96/6845-5 and to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brasília, Brasil) for fellowships of C.E.C.M.; F. J. K and M.A.Z.A.

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Received December 27, 1998. Revision March 18, 1999.