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Cloud point extraction and spectrofluorimetric determination of aluminium and zinc in foodstuffs and water samples

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Abstract

Cloud point methodology was successfully used for the extraction of trace amounts of aluminium and zinc as a prior step to their determination by spectrofluorimetry. Aluminium and zinc react with 8-hydroxyquinoline in a surfactant solution yielding a hydrophobic complex, which then is entrapped in surfactant micelles. Optimization was performed of the variables affecting complexation and phase separation. Under the experimental conditions used, preconcentration of 25 ml of sample in the presence of 0.12% (v/v) Triton X-114 permitted the detection of 0.79 $\mu g\,l^{-1}$ of aluminium and 1.2 $\mu g\,l^{-1}$ of zinc, respectively. The relative standard deviation for five replicate determinations of aluminium and zinc at 40 and 100 $\mu g\,l^{-1}$ concentration level, were 2.72 and 2.1%, respectively. Good recoveries in the range of 95–104% were obtained for spiked samples. The proposed method was applied to the determination of aluminium and zinc in different samples.

Keywords: Cloud point extraction; Aluminium; Zinc; Spectrofluorimetry; Foodstuffs

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1. Introduction

Aluminium (Al) is a non-essential, toxic metal to which humans are frequently exposed. It is present in food, water and pharmaceutical compounds. This element has been involved as a causative factor in several clinical and neuropathological diseases, particularly in patients with chronic renal failure. Elevated levels of Al have been implicated in the aetiology of Alzheimer's disease, Parkinson's disease, Parkinson-Guam disease, amyotrophic lateral sclerosis, diabetes and cancer (Lévesque, Mizzen, McLachlan, & Fraser, 2000; Polizzi et al., 2002; Roberts, Clough, Bellia, & Kim, 1998). Several epidemiological studies investigate the correlation between the uptake of Al from drinking waters and the Alzheimer's disease (Flaten, 2001).

Normally Al is found at low levels ($\mu g\,l^{-1}$) in most drinking waters because Al is still used as a flocculating agent in potable water treatment units. The maximum permissible content of Al in drinking water is 0.2 mg l^{-1} (Erdemoğlu, Pyrzyniska, & Güçer, 2000). Therefore, there is a strong need for Al monitoring in water samples (Huang & Shiu, 1996) and also other samples.

Zinc (Zn) is an essential trace element of great importance for humans, plants and animals. A remarkable mention is made of superoxide dismutase, as it has a principle function in the protection of the organism against activated oxygen species (Terrés-Martos et al., 2002). However, if it is in excess, this metal can also play an important role in the progression of several damages to human body, including disturbances in energy metabolism or increasing in oxidative stress. The wide range of functions that Zn plays in the organism may be due to its role as a cofactor of over 200 enzymes and to its structural role in a large number of Zn finger proteins (Salgueiro et al., 2000). Growth retardation, altered immune response, prematurity pregnancy, weight loss, anorexia and ets. are some of the Zn deficiency consequences. The most important and common causes in

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Zn deficiency are related to the nutritional causes, thus, identifying the Zn content in different samples is very important.

At the moment, the widely used analytical techniques for the detection of the Al are the graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Bocca et al., 2004; Polizzi et al., 2002; Popińska et al., 1999; Roberts et al., 1998; Sanz-Medel, Soldado Cabezuelo, Milačič, & Bantan Polak, 2002). However, both of these methods are relatively expensive and are not accurately reliable for the determination of trace amounts of Al (Beniz Gündüz, Küçükkolbaşý, Atakol, & Kýlýç, 2005). In the case of Zn, the widely used analytical techniques are GF-AAS and flame-AAS (FAAS) (Acar, 2004; Bağ, Türker, Cośkun, Saçak, & Yiğitoğlu, 2000; Lemos, Lopes dos Santos, Santos, & de Carvalho, 2003; Terrés-Martos et al., 2002). On the other hand, due to matrix effects and low concentrations of Al and Zn in different samples, using separation and preconcentration steps are still necessary and coupling of them with simple and less expensive determination techniques such as spectrofluorimetry is very attractive.

Separation and preconcentration based on cloud point extraction (CPE) is becoming an important and practical application in the use of surfactants in analytical chemistry (Rubio & Pérez-Bendito, 2003; Sanz-Medel, Fernandez de la Campa, Gonzalez, & Fernandez-Sanchez, 1999; Stalikas, 2002). The principle, advantages and applications of CPE have been well-established and identified in recent years. The use of preconcentration steps based on CPE offers a conventional alternative to more traditional extraction systems and permits the design of extraction schemes that are simple, cheap, of high efficiency and of lower toxicity than extractions that use organic solvents. To date, CPE has been used for the extraction and preconcentration of metal ions after the formation of sparingly water-soluble complexes, then the complex in the surfactant-rich phase is determined by different spectrometric methods (Gallindo Borges, Mesquita Silva da Veiga, Azzolin Frescura, Welz, & Jose Curtius, 2003; Kulichenko, Doroschuk, & Lelyushok, 2003; Manzoori & Bavili-Tabrizi, 2002a, 2002b, 2003; Nascentes & Arruda, 2003; Ortega, Gomez, Olsina, Silva, & Martinez, 2002; Paleologos, Vlessidis, Karayannis, & Evmiridis, 2003; Wuilloud et al., 2002).

In the present work, we report on the results obtained from applying the CPE for the extraction of Al and Zn from waters and foodstuffs and their determination by spectrofluorimetry. Several experimental variables affecting the method sensitivity and stability were investigated in detail. Applying the CPE before spectrofluorimetric determination makes the method more advantageous when compared with expensive and labour intensive methods, such as GF-AAS or ICP-AES. The simplicity, high efficiency and low-cost of performance are the other features of the proposed method.

2. Materials and methods

2.1. Apparatus

All fluorescence measurements were made on a Shimadzu RF-5301 PC spectrofluorophotometer equipped with a 150 W Xenon lamp and using 1.00 cm quartz cells. Instrument excitation and emission slits both were adjusted to 5 nm. A thermostated bath (636 Friedberg/Hessen, Germany), was used for CPE experiments. A Segurita centrifuge (BHG 1100 type) with 25 ml calibrated centrifuge tubes was used to accelerate the phase separation process. A Corning M120 pH-meter was used for pH measurements.

2.2. Reagents

The non-ionic surfactant Triton X-114 (Sigma, St. Louis, MO, USA) was used without further purification. Stock standard solution of Al and Zn at a concentration of 1000 $\mu g\ ml^{-1}$ was prepared from pure aluminium and zinc nitrate (E-Merck), respectively. Working standard solutions were obtained by appropriate dilution of these stock standard solutions. A $2.76 \times 10^{-3}\ mol\ l^{-1}$ solution of 8-hydroxyquinoline (8-HQ) (E. Merck) was prepared by dissolving appropriate amount of this reagent in 5 ml ethanol (E. Merck) and diluting to 25 ml with double distilled water and was kept in refrigerator (4 °C) for one week.

A stock standard buffer solution, sodium acetate 3-hydrate (1.0 $mol\ l^{-1}$) (Riedel-de Haen) and sodium tetraborate 10-hydrate and acid boric (0.05 + 0.5 $mol\ l^{-1}$, respectively) (E. Merck) were prepared by dissolving appropriate amounts of these compounds in double distilled water and adjusting to pH 6.2 and 9, respectively, by adding diluted HCl or NaOH solution.

All other reagents were of analytical-reagent grade (E. Merck) and all solutions were prepared in double distilled water. The pipettes and vessels used for trace analysis were kept in dilute nitric acid at least over night and subsequently washed three times with distilled water.

2.3. Procedure

For Al extraction and preconcentration, aliquots of 25 ml solution containing the Al (in the range of 2–200 $\mu g\ l^{-1}$), 0.6 ml 8-HQ solution ($2.76 \times 10^{-3}\ mol\ l^{-1}$), 2 ml buffer solution (sodium acetate, pH 6.2) and 1.5 ml Triton X-114 (2% v/v) and for Zn determination, aliquots of 25 ml solution containing the Zn (in the range of 5–250 $\mu g\ l^{-1}$), 0.6 ml 8-HQ solution ($2.76 \times 10^{-3}\ mol\ l^{-1}$), 2 ml buffer solution (sodium tetra borate and acid boric, pH 9) and 1.5 ml Triton X-114 (2% v/v) were subjected to CPE. The tubes were kept in a thermostated bath at 45 °C for 10 min. Separation of the two phases was achieved by centrifuging for 7 min at 3500 rpm. After cooling in an ice bath for 5 min, the surfactant-rich phase became viscous, and the supernatant aqueous phase was separated with a syringe. The surfactant-rich phase was treated with 2.5 ml ethanol and the fluorescence intensity was measured at 512 and 500 nm with the excitation wavelength set at 375 and 385 nm for Al and Zn determination, respectively.

2.4. Preparation of real samples

Bottled mineral water samples were obtained from local sources. Fifteen millilitre of each water sample was subjected to the CPE as described in the previous section. Proper amounts of other samples (1 g) were dried to constant weight at 150 °C, dry-ashed in a muffle furnace at 450 °C and dissolved in dilute hydrochloric acid (Müller, Anke, & Illing-Günther, 1998) and diluted to 25–100 ml in volumetric flask depending on their Al or Zn content. Five millilitre of each diluted sample was subjected to the CPE as mentioned above.

3. Results and discussion

Al and Zn react with 8-HQ in a micellar medium and form a hydrophobic complex (AlQ_3 or ZnQ_2), which is subsequently trapped in the surfactant micelles and separated from the aqueous phase. These complexes have broad excitation and emission bands, with excitation at 375 ± 3 and 385 ± 3 nm and emission at 512 ± 3 and 500 ± 3 nm in the case of Al and Zn, respectively. The fluorescence excitation and emission spectra of AlQ_3 are shown in Fig. 1. The fluorescence excitation and emission spectra of ZnQ_2 are approximately similar to Al. CPE conditions were studied and suitably adjusted as follows.

3.1. Effect of pH

Extraction yield depends on the pH at which complex formation is carried out. CPE of Al and Zn were performed in different pH buffer solutions. Fig. 2 shows the effect of pH on the spectrofluorimetric responses. As can be seen the pH range of 5.6–7.1 and 8–10 are optimum for CPE of Al and Zn, respectively. Hence, pH 6.2 (acetate buffer) and 9.0 (sodium tetraborate + acid boric buffer) were chosen for CPE of Al and Zn, respectively. Since the optimum pH ranges for two elements do not overlap, simultaneous extraction is not feasible. Although, selective extraction of each cation is possible by performing the extraction at two different pHs.

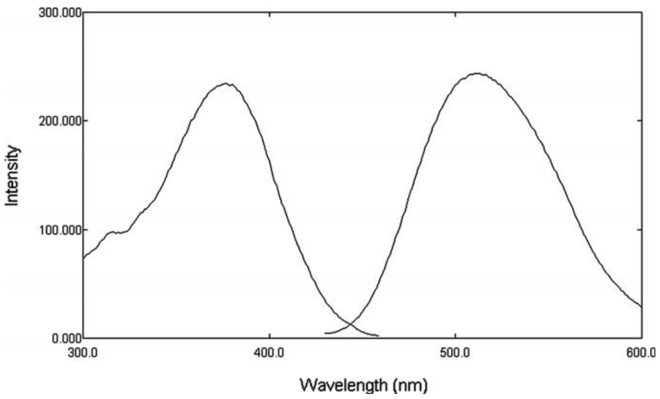

Fig. 1. Excitation and emission spectra for AlQ_3: 50 $\mu g\,l^{-1}$ Al, 6.62×10^{-5} mol l^{-1} 8-HQ, 0.12% (v/v) Triton X-114, pH 6.2.

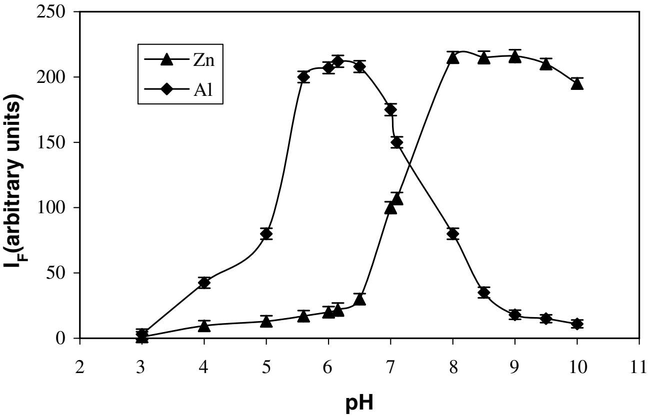

Fig. 2. Effect of pH on the spectrofluorimetric responses: 50 $\mu g\,l^{-1}$ Al or 80 $\mu g\,l^{-1}$ Zn, 6.62×10^{-5} mol l^{-1} 8-HQ, 0.15% (v/v) Triton X-114.

3.2. Effect of 8-HQ concentration

The effect of concentration of the chelating agent on the analytical responses was examined and the results are shown in Fig. 3. Major improvement on the responses was obtained as the chelating agent concentration increased up to certain values, which are sufficient for total complexation and the extraction. A concentration of 6.62×10^{-5} mol l^{-1} (0.6 ml from 2.76×10^{-3} mol l^{-1} solution) was chosen as the optimum concentration of the chelating agent for CPE of Al and Zn. The concentrations above this value have no significant effect on the perfor-

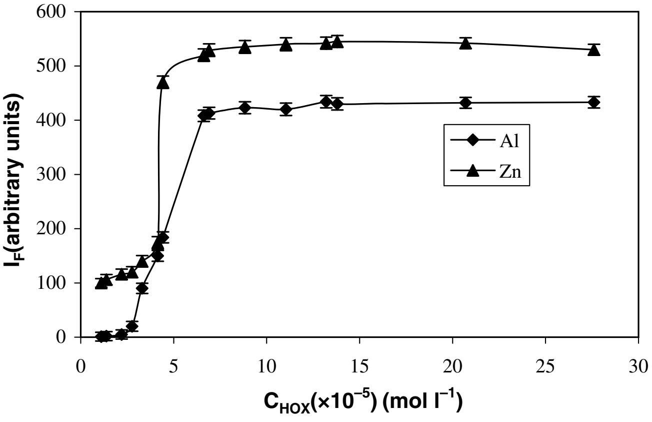

Fig. 3. Effect of 8-HQ concentration on the spectrofluorimetric responses: 100 $\mu g\,l^{-1}$ Al, 0.15% (v/v) Triton X-114, pH 6.2; 200 $\mu g\,l^{-1}$ Zn, 0.15% (v/v) Triton X-114, pH 9.

mance of the system. The slight difference in the behaviour of 8-HQ with Al and Zn is probably due to different chelate formation constants.

3.3. Effect of Triton X-114 concentration

Several non-ionic surfactant including Triton X-114, Triton X-100 and PONPE 7.5 were tested for performing of CPE. Among them Triton X-114 was chosen because of its higher extraction efficiency as well as its appropriate cloud point temperature as compared with other tested surfactants. Fig. 4 shows the variation of the analytical signal as a function of Triton X-114 concentration. In the case of Al, signal increases with increasing the concentration of the surfactant and reaches a maximum in the concentration range of 0.1–0.2% v/v from Triton X-114 due to enhanced extraction, then remains almost constant over this range. But, in the case of Zn major improvement on the responses was obtained as the Triton X-114 concentration increased up to 0.05% v/v. The increase of concentration of Triton X-114 above this value, has not any significant effect on the analytical signals. A concentration of 0.12% v/v from Triton X-114 was chosen for performing of CPE of these two ions.

3.4. Diluting agent for the surfactant-rich phase

The effect of various solvents on the fluorescence behaviour of metal quinolinates has already been tested (Popovych & Rogers, 1960), but these effects have not been studied in the presence of surfactants. Though ether (Et_2O), dimethylformamide (DMF) and chloroform ($CHCl_3$) are strongly recommended by several researchers as greatly enhancing the inherent fluorescence intensity, but they cannot be used in this work due to low solubility of chelates in DMF and immiscibility of Et_2O and $CHCl_3$ with surfactant-rich phase. Among the other water-soluble solvents, i.e. methanol, ethanol and *i*-propanol, ethanol was chosen because of better solubility of chelates and producing higher analytical signals in this solvent. The amount of residual water in the surfactant-rich phase is very small compared to the added ethanol (2.5 ml) and therefore it has no significant effect on the reproducibility of the signals.

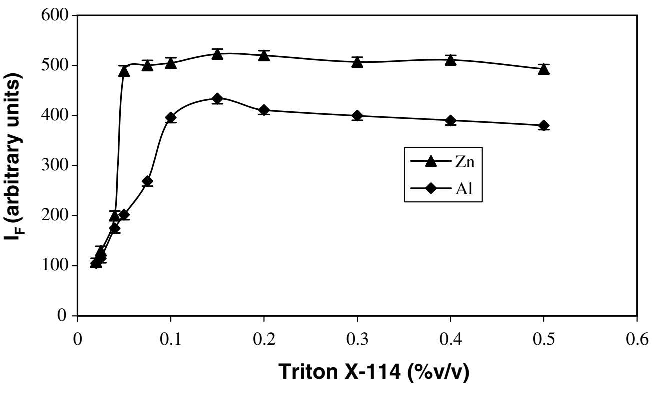

Fig. 4. Effect of Triton X-114 concentration on the spectrofluorimetric responses: 100 μg l^{-1} Al or 200 μg l^{-1} Zn, 6.62×10^{-5} mol l^{-1} 8-HQ, 0.15% (v/v) Triton X-114.

3.5. Effects of other experimental factors

The incubation time and equilibration temperature above the cloud point were thoroughly optimized. It is desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of the phases. The dependence of extraction efficiency on equilibration temperature and time were studied within a range of 30–60 °C and 10–50 min, respectively. The results showed that an equilibration temperature of 45 °C and an equilibration time of 10 min are adequate to obtain quantitative extraction of two ions. The effect of the centrifugation time on the extraction efficiency was also studied within a range of 5–25 min. A centrifugation time of 7 min at 3500 rpm was selected for the entire procedure, since analyte extraction in this time is almost quantitative.

3.6. Characteristics of the method

Calibration graphs were obtained by preconcentrating of 25 ml of standard solutions containing known amounts of the analyte in the presence of 0.12% v/v Triton X-114 and under the experimental conditions specified in the procedure. The surfactant-rich phase was diluted with 2.5 ml ethanol and the fluorescence intensity of the chelate was measured. In all cases, linear relationships between the fluorescence measured and the concentration of the Al or Zn in the solution were obtained. Table 1 gives the parameters of calibration graphs. The relative standard deviations (RSDs) were obtained for five sampled subjected to the complete procedure, and the limit of detection (LOD) calculated as three times the standard deviation of the blank signals. The obtained LODs were sufficiently low as to be valuable for detecting both cations in different samples and by considering the preconcentration factor (C_F) achieved in this work (≈10), are comparable with those obtained in other CPE methods used for extraction and preconcantration of Al (Sombra, Luconi, Silva, Olsina, & Fernandez, 2001; Sombra et al., 2003) or Zn (Cerrato Oliveros, Jimenez de Blas, Pérez Pavón, & Moreno Cordero, 1998). It is obvious that this C_F and hence LOD can be improved by using larger volume of initial

Table 1
Analytical characteristics of the method

Element	Concentration range (μg l^{-1})	Slope	Intercept	R	RSD%[a] ($n = 5$)	LOD[b] (μg l^{-1})
Al	2–200	4.31	5.151	0.998	2.72(40)	0.79
Zn	5–250	4.11	4.282	0.997	2.1(100)	1.2

[a] Values in parentheses are the analyte concentrations (as μg l^{-1}) for which the RSD was obtained.

[b] Determined as three times the standard deviation of the blank signals.

solution or small-volume cells and diluting the surfactant-rich phase by small amounts of ethanol.

3.7. Interferences

The interferences studied were those relating to the preconcentration step, i.e. cations that may react with 8-HQ or species that may react with Al or Zn and decrease the extraction efficiency. To perform this study, 25 ml solution containing 100 μg l^{-1} of Al or Zn and interfering ion in different interferent-to-analyte ratios were subjected to the complete procedure. Al and Zn recoveries are almost quantitative in the presence of other species with tolerance limits (error <5%) indicated in Table 2. As can be seen in Table 2, some metal ions including Fe^{3+}, Zn^{2+}, Cd^{2+} and Cu^{2+} can interfere with the determination of Al. The interference from these ions can be eliminated by using ascorbic acid (5×10^{-2} mol l^{-1}) and 1,10-phenanthroline (5×10^{-3} mol l^{-1}) as masking agent, that form strong hydrophilic complexes with these ions. In the case of Zn the major interferences are Fe^{3+}, Al^{3+}, and Cu^{2+}. Using sodium thiosulphate (2×10^{-2} mol l^{-1}) and sodium pyrophosphate (5×10^{-4} mol l^{-1}) as masking agents can eliminate these interferences.

3.8. The validation and application of the method

Proposed method was applied to the determination of Al and Zn in different samples. Fifteen millilitre of water samples and 5 ml of other samples were subjected to the complete CPE procedure. Recovery experiments were conducted as well for some samples and recoveries ranged from 95% to 104% (Table 3). As shown in Table 4, the concentrations of Al and Zn in different samples determined by the present method were in good agreement with those determined by an independent ET-AAS method for Al (López, Cabrera, Lorenzo, & López, 2002) and Zn (Acar, 2004) determination with some modifications. A comparison using *t*-test at 95% confidence interval demonstrates, that there is not significant difference among the achieved results using the proposed method and the ET-AAS method.

Table 2
Tolerance limits of interfering species in the determination of 100 μg l^{-1} of Al or Zn

Interferent-to-analyte ratio	Al	Zn
1000:1	As^{3+}, Ni^{2+}, Sn^{2+}, Bi^{3+}, Li^{+}, Na^{+}, K^{+}, I^{-}, Cl^{-}, ClO_4^{-}, CO_3^{2-}, SO_4^{2-}, NO_3^{-}, tartrate	As^{3+}, Ni^{2+}, Sn^{2+}, Bi^{3+}, Li^{+}, Na^{+}, K^{+}, I^{-}, Cl^{-}, ClO_4^{-}, CO_3^{2-}, SO_4^{2-}, Pb^{2+}, NO_3^{-}, F^{-}, thiourea, urea, citrate, tartrate
500:1	Pb^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Cr^{3+}, glycine, thiourea, urea	Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Cr^{3+}, glycine
100:1	Oxalate, F^{-}, PO_4^{3-}	Oxalate, Cd^{2+}
50:1	Zn^{2+}, Cd^{2+}, Cu^{2+}	Al^{3+}, Cu^{2+}, PO_4^{3-}
1:1	Fe^{3+}, EDTA, citrate	Fe^{3+}, EDTA

Table 3
Determination of Al and Zn in some spiked samples

Analyte	Sample	Spiked	Found[a]	Recovery (%)
Al	Mineral water[b]	10	9.50 ± 0.25	95
		20	20.6 ± 0.50	103
	Apple[c]	1.0	1.02 ± 0.03	102
		2.0	1.96 ± 0.05	98
	Bread[c]	2.0	1.92 ± 0.05	96
		4.0	3.90 ± 0.11	97.5
Zn	Mineral water[b]	10	9.80 ± 0.22	98
		20	19.0 ± 0.42	95
	Apple[c]	1.0	1.04 ± 0.02	104
		2.0	1.94 ± 0.04	97
	Bread[c]	2.0	2.06 ± 0.04	103
		4.0	3.84 ± 0.08	96

[a] Average of three determinations ± standard deviation.
[b] Spiked and found as μg l^{-1}.
[c] Spiked and found as μg g^{-1}.

Table 4
Determination of Al and Zn in different samples

Sample	Al[a] (μg l^{-1})		Zn[a] (μg l^{-1})	
	Proposed method	ET-AAS method	Proposed method	ET-AAS method
Tap water	25.3 ± 0.68	24.8 ± 0.56	12.3 ± 0.26	12.6 ± 0.24
Mineral water 1	n.d.[b]	–	8.5 ± 0.18	8.8 ± 0.20
Mineral water 2	15.2 ± 0.39	15.7 ± 0.37	5.8 ± 0.12	6.0 ± 0.14
Mineral water 3	13.5 ± 0.36	13.1 ± 0.31	7.2 ± 0.15	7.0 ± 0.16
Apple[c]	1.9 ± 0.05	1.8 ± 0.05	5.8 ± 0.12	5.6 ± 0.13
Tomato[c]	1.8 ± 0.05	1.8 ± 0.04	14.0 ± 0.30	14.4 ± 0.32
Carrots[c]	2.9 ± 0.08	3.0 ± 0.07	9.8 ± 0.22	10.1 ± 0.25
Potato[c]	4.8 ± 0.13	4.6 ± 0.12	8.8 ± 0.19	8.5 ± 0.21
Yoghurt[c]	1.3 ± 0.03	1.3 ± 0.03	4.1 ± 0.09	4.0 ± 0.11
Bread[c]	5.9 ± 0.16	5.7 ± 0.14	10.5 ± 0.24	10.9 ± 0.27
Wheat flour[c]	6.2 ± 0.17	6.4 ± 0.15	28.4 ± 0.60	29.3 ± 0.68
Sausage[c]	3.5 ± 0.10	3.6 ± 0.08	32.8 ± 0.67	31.9 ± 0.71

[a] Average of three determinations ± standard deviation.
[b] Not detected.
[c] Al and Zn reported as μg g^{-1} fresh matter.

4. Conclusions

The results demonstrate the usefulness of this CPE method to quantitative extraction of Al and Zn in different samples. The proposed method allowed Al and Zn determination at μg l^{-1} levels, thus represents a promising approach in the monitoring of Al and Zn in different samples with low cost, simplicity, efficiency, versatility and non-polluting respect. The proposed CPE method gives low LOD, good RSD and solvent-free extraction of the Al and Zn from its initial matrix without previous treatment. Due to versatility, it can be applied to the monitoring of Al and Zn in various samples of environmental, toxicological and medical analysis.

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