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## Research Article

# Use of carboxylic group functionalized magnetic nanoparticles for the preconcentration of metals in juice samples prior to the determination by capillary electrophoresis

Nowadays food industry demands reliable and precise methods to resolve problems related to quality and security control. The pretreatment steps, prior to sample analysis, are necessary to extract the target analytes because of the complexities of the food samples matrices. In this work, we have studied, for the first time, the potential of carboxylic group functionalized magnetic nanoparticles to preconcentrate metals from liquid samples before CE analysis. For the extraction of metals, 10 mL of an aqueous sample containing the metal mixture was added to 2 mg carboxylic group functionalized magnetic nanoparticles. Metals retained in the nanoparticles were re-extracted with 200  $\mu$ L solution consisting of 0.8 mM 1,10-phenanthroline and 0.04% hydroxylamine chloride at pH 2. The electrophoretic buffer used in this work to separate different metals (Co, Cu, Zn, Ni, and Cd) consisted of 30 mM hydroxylamine chloride, 0.30 mM 1,10-phenanthroline, 80 mM urea, 15 mM ammonium chloride, and 0.1% methanol at pH 3.6. Finally, measurements were made at 270 nm. Under the optimized conditions, detection limits for Co, Zn, Cu, Ni, and Cd were 0.004, 0.003, 0.004, 0.008, and 0.009 mg L<sup>-1</sup>, respectively.

### Keywords:

Capillary electrophoresis / Carboxylic group functionalized magnetic nanoparticles / Metals / 1,10-Phenanthroline  
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## 1 Introduction

Recently, nanoparticles with novel optical, electrical, and magnetic properties have become more prevalent in diverse fields, such as biosensor [1], nanomedicine [2], and separation science [3] among others. Typical advantages of nanoparticles are that they can be used to improve selectivity, sensitivity, rapidity, miniaturization, or portability of the analytical system. Consequently, nanoparticles can be used for purposes such as sample treatment, instrumental separation of analytes, or even detection.

Among various nanostructured materials, magnetic nanoparticles—such as magnetite, magemite, nickel, and cobalt—show super paramagnetism, high field irreversibility, and high saturation field. There is growing interest in magnetic nanostructured materials because of their unique properties and potential applications in various fields, especially in biomedicine and bioengineering such as magnet-

ically assisted drug delivery [4], cell isolation [5], magnetic resonance imaging with contrast agents [6], and biomacromolecule purification [7].

Magnetic nanoparticles possess three properties: (i) they have a large surface, (ii) their surface can also be functionalized with various chemical groups to increase their affinity toward analytes, and (iii) the magnetic nanoparticles with adsorbed analyte can be easily collected by using an external magnet, which makes sampling and collection easier and faster. Moreover, the magnetic nanoparticles can be reused or recycled. For these reasons, magnetic nanoparticles are attractive sorbents compared with traditional solid-phase extraction. Among the wide variety of existing commercial magnetic nanoparticles, in this work, we have selected one type that is functionalized with carboxylic groups because of their affinity with cationic metals. The potential of these nanoparticles has already been demonstrated in the mRNA isolation and extraction of supercoiled plasmid DNA [8].

In CE, different magnetic nanoparticles have been used in the electrophoretic system [9–11], in the pretreatment of the sample [12–14], and also CE has been used to separate magnetic nanoparticles [15]. As it is well known, CE suffers from poor concentration sensitivity for absorbance detection

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due to the low injected sample volumes and the narrow inner capillary diameter being the optical path length. Preconcentration with magnetic nanoparticles in the sample treatment is a new alternative to improve the sensitivity of this technique.

In this project, the potential of carboxylic group functionalized magnetic nanoparticles in CE has been proved by concentration metals in liquid samples. The determination of metals is important for routine quality control of beverage products, among other fields, due to their essential or toxic action; there are studies that indicate that some metals act as catalysts in the oxidative reactions of biological macromolecules [16]. The U.S. Food and Nutrition Board of the Institute of Medicine have carried out risk assessments dealing with the toxicity by establishing the tolerable upper intake level for trace elements. The value calculated for Zn and Co is 40 mg/day and 10 mg/day [17], respectively. Although the trace metal content in food is important, in juices only the content of Pb and Sn is legislated by the European Union according to Directive 2001/112/EC, being the maximum permissible concentration (0.05 mg/Kg and 100 mg/Kg, respectively).

One problem in the determination of metal ions by CE is that most of the transition metals have almost the same mobility due to their similar size and identical charge. An alternative to resolve this problem is to use a chromogenic chelating reagent capable of strong complex formation and conversion of metal ions into positively charged chelates with different electrophoretic mobilities. Many chelating reagents such as porphyrins [18], 4-(2-pyridylazo)resorcinol [19], several aminopolycarboxylic acids [20], 1,10-phenanthroline [21], etc have been employed for the direct absorbance-based detection of alkaline earth, transition, and lanthanide metals ions. In this work, the potential of a new material to increase the sensitivity in CE with UV-VIS detection for the determination of Co, Cu, Zn, Mg, Ni, and Cd has been studied. The results shown in this paper could be used to extend the application of these magnetic nanoparticles to preconcentrate other analytes. We combine the advantages of carboxylic group functionalized magnetic nanoparticles and the formation of complexes with 1,10-phenanthroline to carry out the extraction and preconcentration of metals present in juice samples prior to analysis by CE.

## 2 Materials and methods

### 2.1 Reagents

Nitrate salts of Cd(II), Mg(II), Cu(II), Co(II), Zn(II), and Ni(II) were obtained from Sigma (St. Louis, MO, USA). They were used for preparing stock solutions of 1000 mg L<sup>-1</sup> at pH 2 adjusted with HCl. The working solutions of the metals were prepared by appropriately diluting the stock solutions with distilled water and adjusting the pH to 8 with NaOH to carry out the extraction and preconcentration of metals with the carboxylic group functionalized magnetic nanoparticles. Reagents used for preparing the buffer solu-

tion and re-extraction solution (hydroxylamine chloride, 1,10-phenanthroline, urea, ammonium chloride) were supplied by Sigma, except methanol that was obtained from Panreac (Barcelona, Spain). The water used was purified by passing it through a Milli-Q apparatus from Millipore (Bedford, MA, USA). Carboxylic group functionalized magnetic nanoparticles were provided from MagnaMedics (Geleen, The Netherlands). Juice samples were purchased from local commercial stores.

### 2.2 Apparatus and operating conditions

The measurements of pH solutions were realized in a Micro-pH 2000 pH meter from Crison (Barcelona, Spain). The magnetic field was applied with a combination of three magnets with following characteristics: (i) magnets with a coating of Ni-Cu-Ni, (ii) axial pull force of 4.8 kg, (iii) inner diameter of 6 mm and external diameter of 15 mm, and (iv) thickness of 5 ± 0.1 mm. Analytes were separated and quantified on a P/ACE MDQ Capillary Electrophoresis System from Beckman (Palo Alto, CA, USA) equipped with a DAD and using a fused silica capillary (Beckman Coulter) of 50 µm inner diameter, 50.2 cm total length, and 40 cm effective separation length.

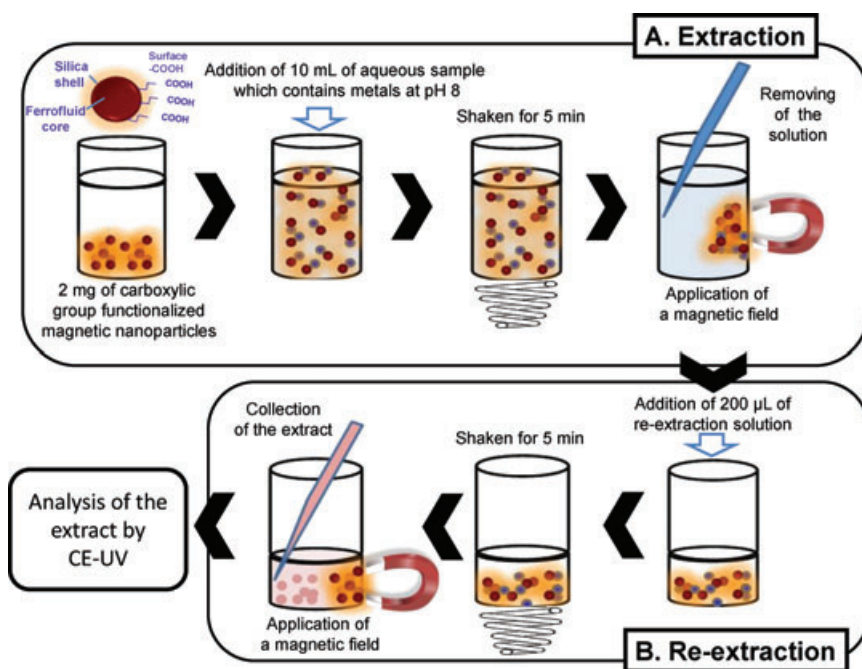
The running buffer was composed of 30 mM hydroxylamine chloride, 0.30 mM 1,10-phenanthroline, 80 mM urea, 15 mM ammonium chloride, and 0.1% methanol at pH 3.6. The applied voltage was 20 kV and the working temperature 25°C. The samples were injected into the capillary by hydrodynamic injection during 30 s at 0.5 psi. Electropherograms were recorded at a wavelength of 270 nm, using normal polarity. All buffer solutions were filtered through a Nylon membrane of 0.45 µm pore size before analysis.

Prior to first use, the capillary was conditioned by rinsing with 1 M HCl for 5 min, 0.1 M NaOH for 10 min, and water for 5 min using a pressure of 20 psi in all cases. The capillary was prepared for daily use by rinsing with 0.1 M NaOH for 5 min, water for 5 min and separation buffer for 15 min, with a pressure of 20 psi. Between individual analysis, the capillary was conditioned with water for 5 min and separation buffer for 5 min prior to injection.

### 2.3 Sample treatment

#### 2.3.1 Mineralization of juice samples

Fifteen milliliters of juice sample was added in a crucible with 0.5 mL of concentrated nitric acid and the mixture was taken to dryness in a sand bath, keeping the temperature less than 100°C. After that, the sample was carbonized with a Bunsen burner. Then the sample was incinerated at 400°C approximately for 16 h in an oven until the ashes were almost white. In the case that ashes were not clear enough, an additional five drops of concentrated nitric acid was added and both dryness and incineration processes were repeated. Next, 5 mL of 1 M nitric acid were added to the final residue in the crucible, and it was taken to almost dryness in a sand bath. Finally, the



**Figure 1.** Scheme of the method to extract and preconcentrate metals from aqueous samples using carboxylic group functionalized magnetic nanoparticles.

residue was dissolved in 10 mL of water (if it is necessary this solution can be filtered) and the pH was adjusted to pH 8 in order to preparing the mineralized juice sample for the extraction and preconcentration method with carboxylic group functionalized magnetic nanoparticles.

### 2.3.2 Extraction and preconcentration method using carboxylic group functionalized magnetic nanoparticles

The carboxylic group functionalized magnetic beads used in this work are composed of a ferrofluid encapsulated in a matrix of silica. This ferrofluid is composed of magnetic nanoparticles of diameter less than 10 nm containing iron oxides (magnetite,  $\gamma\text{-Fe}_2\text{O}_3$ , and magnetite,  $\text{Fe}_3\text{O}_4$ ). The mean size of the magnetic beads is 1.2  $\mu\text{m}$ . By controlling the pH in the magnetic nanoparticles, the surface can be charged positively or negatively and the nanoparticles can be applied to separate different molecules.

Commercial magnetic nanoparticles must be preconditioned prior to using (see Fig. 1). For this purpose, in a vial, 2 mg of nanoparticles were shaken in a vortex during 5 min with 10 mL of water solution at pH 8. Then magnetic nanoparticles were aggregated by an external magnet, and the solution was removed using a pipette. After, magnetic nanoparticles were resuspended in 200  $\mu\text{L}$  of re-extraction solution of metals (0.8 mM 1,10-phenanthroline and 0.04% hydroxylamine chloride at pH 2) and were shaken in the vortex for 5 min. Following this, nanoparticles were separated from solution with an external magnet and the solution was removed. This cycle of washing must be repeated four times.

Once the magnetic nanoparticles are washed, 10 mL of aqueous sample containing the metal mixture at pH 8 were

added. The solution was shaken in the vortex for 5 min. Then nanoparticles retaining metals were separated from solution using a magnet and removed from the solution with a pipette. A total of 200  $\mu\text{L}$  of re-extraction solution (0.8 mM 1,10-phenanthroline and 0.04% hydroxylamine chloride at pH 2) were added to the nanoparticles retaining metals. The solution was shaken in the vortex for 5 min. Finally, magnetic nanoparticles retaining metals were separated from solution with an external magnet and the extract was analyzed by CE. Figure 1 shows the steps followed to extract and preconcentrate the metals from the aqueous samples.

Magnetic nanoparticles were reused after a cleaning process. After each extraction the nanoparticles were washed twice with 200  $\mu\text{L}$  of re-extraction solution (0.8 mM 1,10-phenanthroline and 0.04% hydroxylamine chloride at pH 2) and then with 5 mL of water solution at pH 8.

## 3 Results and discussions

The potential of carboxylic functionalized magnetic nanoparticles has been studied to preconcentrate metals in aqueous food samples (such as juices, tea, etc.) by using electrophoretic buffer containing a strong complexing agent, 0.30 mM 1,10-phenanthroline for direct UV detection, 30 mM hydroxylamine chloride, 80 mM urea, 15 mM ammonium chloride, and 0.1% methanol at pH 3.6. The urea acts as a weak complexing agent with its lone pair of electrons on the nitrogen atom interacting with the complexes. This decreases the charge density of the complexes and its migration times are changed [22]. The metal chelates formed showed different electrophoretic mobilities and solved the comigration problem for CE separation of free metal ions.

To obtain stable metal-phenanthroline chelates during the CE run, both precapillary and on-capillary complexation are required and threefold excess of phenanthroline over metal ions is added to the sample. In the literature, among the varied electrophoretic methods to determine metals in CE a re-optimized electrophoretic method reported by other authors [22,23] has been used in order to achieve better electrophoretic resolution between analytes.

### 3.1 Optimization of extraction and preconcentration method

In order to optimize the best method for extraction and preconcentration of metals from aqueous samples, the following variables were studied: the effect of extraction time; the effect of pH of the solution-containing the metal mixture; the effect of re-extraction time; and the effect of pH, concentration of 1,10-phenanthroline, and concentration of hydroxylamine chloride in the re-extraction solution; and finally, the effect of the amount of magnetic nanoparticles in the extraction method was also studied.

A mixture solution containing  $0.1 \text{ mg L}^{-1}$  of each metal (Co, Cu, Zn, Mg, Ni, and Cd) was used in the optimization experiments. The optimization process was done based on the peak area of the mixture of analytes.

#### 3.1.1 Optimization of extraction conditions

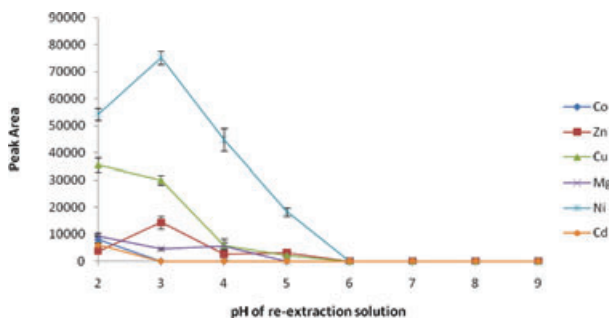
The effect of extraction time and effect of the pH of the aqueous solution containing the mixture of analytes were studied for the extraction of metals (see Fig. 1A) from the aqueous solution into carboxylic group functionalized magnetic nanoparticles.

In order to determine the optimal extraction time required for quantitative adsorption, 10 mL of a metal mixture at  $0.1 \text{ mg L}^{-1}$  were mixed with 2 mg of magnetic nanoparticles and the extraction times studied were 1, 3, 5, 7, 10, and 20 min. The electrophoretic signal of metals was constant after 5 min, therefore this value was chosen as the optimum extraction time. In these conditions, the sorption of metals onto magnetic nanoparticles reached the equilibrium.

The effect of the pH in the solution of metals was also checked. The studied range of pH was between 2 and 10. Improvement in signals for metals was obtained while increasing pH. A pH of 8 was selected as the optimum value. At this pH, the carboxylic groups at the surface of nanoparticles are negatively charged and attract the positive charge of metals. When pH decreases, adsorption also decreases.

#### 3.1.2 Optimization of re-extraction conditions

For the re-extraction of metals (see Fig. 1B) from the carboxylic group functionalized magnetic nanoparticles to re-extraction solution, the effect of re-extraction time has been studied; and the effect of pH of re-extraction solution, concen-



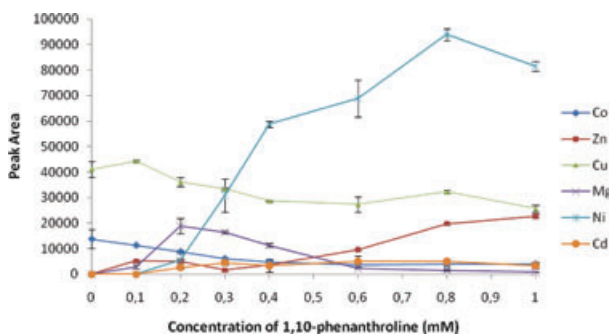
**Figure 2.** Effect of the pH of the re-extraction solution. Buffer consisting of 30 mM hydroxylamine chloride, 0.30 mM 1,10-phenanthroline, 80 mM urea, 15 mM ammonium chloride, and 0.1% methanol at pH 3.6; hydrodynamic injection during 30 s at 0.5 psi; voltage applied, 20 kV; UV detection at 270 nm.

tration of 1,10-phenanthroline, and concentration of hydroxylamine chloride were also studied.

The re-extraction time was 1, 3, 5, 7, 10, and 20 min. Practically constant signals were observed from 3 to 7 min. Therefore, 5 min was selected as optimum re-extraction time.

The influence of pH of re-extraction solution was studied in the range of 2–9. The results are shown in Fig. 2. For this variable, pH 2 was selected as optimum value in order to obtain a signal in less-sensitive elements such as Cd, Co, Mg, and Zn. However, the manufacturers of the magnetic nanoparticles recommend working at pH values between 3 and 13, in order to avoid Fe leaching at pH below 3. For this reason, after four cycles of use, it was observed that there was a formation of a layer of brown particles without magnetic properties. This was attributed to the deterioration of the silica matrix causing the leaching of the iron oxides into the solution. Taking into account these recommendations, pH 2 was selected since protonation of carboxylic acid groups is favored making that metals unattracted to the magnetic nanoparticles and with the presence of 1,10-phenanthroline in the acid medium it favors the formation of metal-1,10-phenanthroline complexes.

The 1,10-phenanthroline was used to extract complex metals from magnetic nanoparticles. The concentration range studied was between 0 and 1 mM. The results are shown in the Fig. 3. From the data shown in this figure, it



**Figure 3.** Effect of concentration of 1,10-phenanthroline (mM) in the re-extraction solution. Others conditions are same as in Fig. 2.

can be seen that Co and Cu are able to be re-extracted even in the absence of 1,10-phenanthroline only by the change of pH. It was observed that the signal of these metals was decreasing with the increase of phenanthroline concentration, especially for Co. As we expected in the case of Zn, Ni, and Cd, the signal increases with the increase of the concentration of 1,10-phenanthroline, while the Mg has a maximum at 0.2 mM. In order to have an excess of phenanthroline for metal complexation, 0.8 mM was selected as the optimum value.

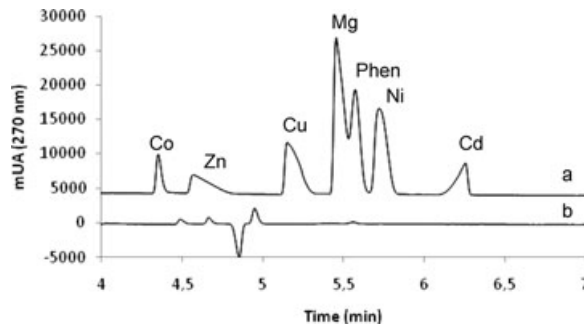
Finally, hydroxylamine chloride was used to change the ionic strength and to improve the resolution of the analytes in the electropherogram, and to avoid oxidation of metals with valence +2 to +3 (Co and Ni), and thus, to favor the complexation of metals with the 1,10-phenanthroline. In this study, the concentration of hydroxylamine hydrochloride varied from 0 to 0.07%, while the 1,10-phenanthroline concentration was kept at 0.8 mM. The best resolution was at 0.04%, therefore it was chosen as optimum concentration.

### 3.1.3 Effect of amount of magnetic nanoparticles in the extraction method

The amount of magnetic nanoparticles was also evaluated, over the range of 1–3 mg of magnetic nanoparticles. Using 1 mg and 10 mL of 0.1 mg L<sup>-1</sup> metals mixture solution (solution A), the extraction was not completed. This was checked by analyzing the re-extraction solution once it was separated from magnetic nanoparticles in which metal were retained. Traces of signals of the metals were obtained in the electropherograms.

With 3 mg of magnetic nanoparticles a more difficult separation of the nanoparticles from the solution A using the magnets available was observed, causing this process to be slower. The disadvantage of using this amount of nanoparticles is that in each cycle of use a little amount of magnetic nanoparticles was lost, thus the extraction efficiency of the process is changing and therefore the process will not have repeatability. It is also possible that these suspended nanoparticles can enter into the capillary and clog it. For all of these reasons, it was decided to use 2 mg of magnetic nanoparticles for the separation process.

Once the variables of the extraction and preconcentration method were optimized, a metal mixture at a concentration of 0.1 mg L<sup>-1</sup> was analyzed. The electropherogram obtained was compared with that obtained only complexing the metal mixture with phenanthroline in the presence of hydroxylamine hydrochloride without using through the process of extraction and preconcentration with magnetic nanoparticles. These results are shown in Fig. 4. In the metal mixture analyzed without preconcentration, the metals cannot identify analyte with any certainty. After performing the preconcentration process, there is a large increase in signal intensity and metals can be easily identified. It is also observed that the complete separation of Mg ion peak with that to the excess 1,10-phenanthroline was not



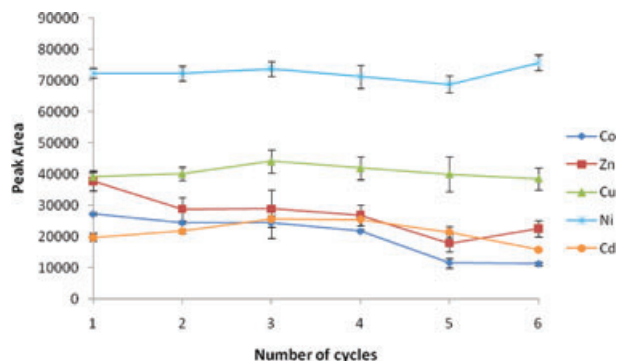
**Figure 4.** Electropherogram of a standard metal mixture at 0.1 mg L<sup>-1</sup> preconcentrated with magnetic nanoparticles (a), and without preconcentration (b). Others conditions are same as in Fig. 2.

obtained, for this reason, we decided to eliminate the Mg from the group of metals to be determined with this methodology.

### 3.2 Reusability

In order to investigate the recycling of magnetic nanoparticles, several extraction and preconcentration cycles with a metal mixture at 0.1 mg L<sup>-1</sup> were carried out. After each cycle, the nanoparticles were washed according to the method described before.

An amount of 2 mg of nanoparticles was stable for at least four cycles, because there was no obvious decrease or increase for the peak area of the analytes. These results are shown in the Fig. 5. Taking into account the amount of nanoparticles used and the price of the product (e.g. a commercial solution of 40 mg cost approximately €75; and using portions of 2 mg, 80 analyses can be performed with this amount of nanoparticles), it can be confirmed that this material is very adequate according to the market prices of this magnetic nanoparticles.



**Figure 5.** Number of cycles of use of 2 mg of carboxylic group functionalized magnetic nanoparticles to extract and preconcentrate metals. Others conditions are same as in Fig. 2.

**Table 1.** Calibration curves and statistical figures of merit for the determination of a metal mixture using carboxylic group functionalized magnetic nanoparticles before CE analysis

Metal	Calibration curve ( $y = mx + b$ )		S <sub>y/x</sub>	R	LOD (mg L <sup>-1</sup> )	LOQ (mg L <sup>-1</sup> )
	m	b				
Co	479 414.8 ± 10 903.9	-480.41 ± 627.75	1955.6	0.9939	0.004	0.013
Zn	475 460.9 ± 11 604.7	-243.69 ± 561.68	1709.7	0.9956	0.003	0.012
Cu	724 854.8 ± 16 115.3	4856.93 ± 890.78	2277.5	0.9971	0.004	0.012
Ni	19 396 660 ± 133 231.4	969.61 ± 5402.77	5891.7	0.9839	0.008	0.028
Cd	468 257.3 ± 21 976.6	-3880.75 ± 1424.24	2394.0	0.9892	0.009	0.030

### 3.3 Validation

Under the optimal experimental conditions, the calibration curves for each metal were established in the range of 0.005–0.12 mg L<sup>-1</sup> by plotting the peak area versus concentration and three repetitions at each concentration were performed. This range was chosen because at higher concentrations it is possible to determine the metals by CE, and complexes with 1,10-phenanthroline can be formed without the need to use a preconcentration method. LOD of each metal determination was calculated for three times the standard deviation of the intercept of the plot divided by its slope, and LOQ at ten times the standard deviation of the intercept of the plot divided by its slope. The figures of merit are shown in Table 1. The proposed method is highly effective to determine Co, Zn, and Cu at low levels.

The LODs achieved by using magnetic nanoparticles before UV-CE has been compared with the experimental LOD (0.3 mg L<sup>-1</sup>) obtained without any preconcentration step before UV-CE analysis, and it can be confirmed that with this new methodology it is possible to reduce the LODs by two orders of magnitude.

The proposed method to extract and preconcentrate metals has been compared with other methodologies used to preconcentrate and determine metals by CE. In the bibliography, we have provided different sorbent types such as chelex-100 [24] or silica gel [25] to carry out a solid-phase extraction to preconcentrate heavy metals before CE analysis. Other alternatives to preconcentrate metals have been reported, for example, the use of electromembranes and electrochemical preconcentration with CE-C<sup>4</sup>D [26, 27] or the online combination of transient isotachopheresis and CE-UV [28]. In all cases, the proposed new simple and cheap methodology is able to reach similar or lower LODs. Taking into account the advantages of the use of magnetic nanoparticles, the proposed methodology in this work is an interesting alternative to improve the sensitivity of UV-CE technique.

The precision of the proposed method was also assessed in terms of reproducibility and repeatability expressed as RSD%. The values are shown in Table 2. Repeatability of injection was studied over a solution of metals at 0.1 mg L<sup>-1</sup> that was previously extracted and preconcentrated by using 2 mg of magnetic nanoparticles. The re-extracted solution was injected nine times in the CE system. Reproducibility was

**Table 2.** Repeatability and reproducibility of the metal mixture at 0.1 mg L<sup>-1</sup> ( $n = 9$ ) by using the optimized methodology

Metal	Injection repeatability RSD%		Reproducibility RSD%	
	Peak area	Migration time	Peak area	Migration time
Co	9.35	1.99	12.91	2.51
Zn	9.76	3.22	11.86	2.81
Cu	7.06	1.03	6.86	1.27
Ni	14.65	3.10	16.63	1.66
Cd	5.99	1.71	8.58	1.69

calculated by applying the extraction and re-extraction process to three independent aliquots of the metal mixture at 0.1 mg L<sup>-1</sup> using three different portions of 2 mg of magnetic nanoparticles for three consecutive days. Every extract was injected three times in the CE system. The lack of repeatability and reproducibility for some analytes could be attributed to the small volume solution (200 µL) used to extract the metals from the magnetic nanoparticles. Values less than 8% were obtained for Cu and Cd demonstrating the potential of this methodology for the determination of these metals.

Finally, a recovery study was carried out; a pineapple juice sample was spiked with 0.07 mg L<sup>-1</sup> of a metal mixture and all the experimental steps described above were followed before the analysis. The recoveries obtained were 89.8, 87.8, 88.1, 83.1, and 95.9% for Co, Zn, Cu, Ni, and Cd, respectively.

### 3.4 Analysis of juice samples

The developed method was applied to quantify the concentration of metals in four commercial juices (two of pineapple juice and two of peach juice). The results are shown in Table 3. The concentrations of metals have been determined taking into account the calibration curves and the preconcentration factor of the volume in the mineralization of the sample. Any matrix effect was observed since juice samples were effectively mineralized, and the final extract was an aqueous medium.

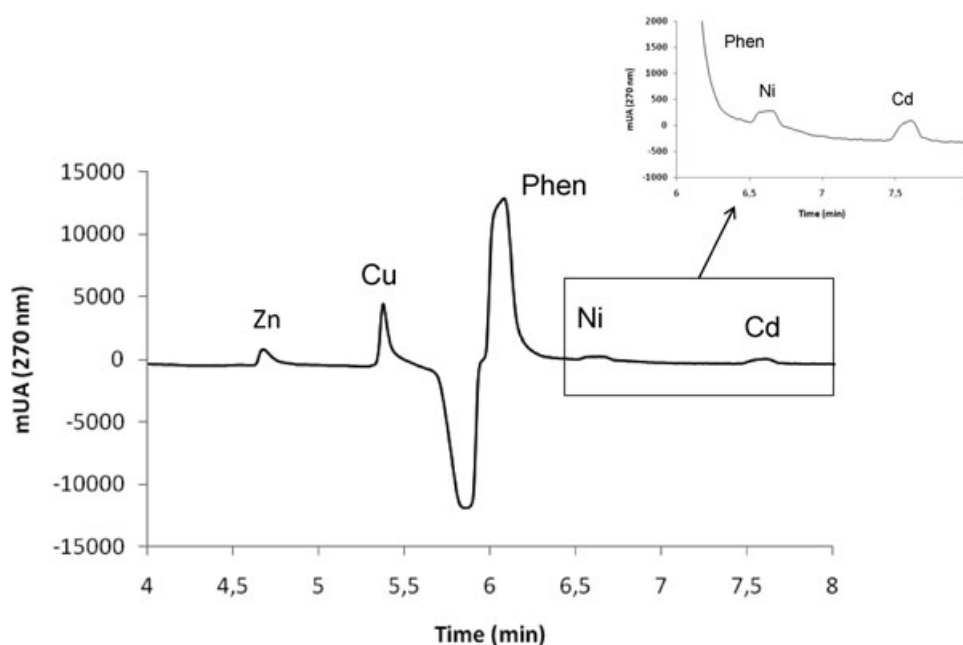
The corresponding electropherogram of a juice sample (sample 1) is shown in Fig. 6. Trace amounts of Zn and

**Table 3.** Determination of metals in juice samples

Number of sample	Type of juice	Analyte (mg L <sup>-1</sup> )				
		Co	Zn	Cu	Ni	Cd
1	Pineapple	–	0.015 ± 0.003	0.0209 ± 0.0008	a)	a)
2	Pineapple	–	0.012 ± 0.001	0.0098 ± 0.0006	–	–
3	Peach	–	0.0169 ± 0.0004	0.030 ± 0.001	a)	–
4	Peach	–	0.041 ± 0.002	–	–	a)

The values shown in this Table take into account that 15 mL of juice samples were used to mineralize the sample and the final residue was dissolved in 10 mL of water.

a) Concentration found below LOQ.



**Figure 6.** Electropherogram of pineapple juice sample applying the extraction and preconcentration steps using carboxylic group functionalized magnetic nanoparticles. Others conditions are same as in Fig. 2.

Cu were found in the pineapple juice. Ni and Cd were also detected, but not quantified.

These results have shown the potential of this carboxylic group functionalized magnetic nanoparticles to be used as preconcentrator of a group of metals before CE analysis. Further studies could be carried out with other food matrices by using the same optimized methodology.

#### 4 Concluding remarks

The potential of the combination of carboxylic groups functionalized magnetic nanoparticles with the chelating reagent 1,10-phenanthroline to extract and preconcentrate metals (Cd, Co, Cu, Ni, and Zn) has been demonstrated. The sensibility improvement of the CE with UV detection was demonstrated in addition to other capabilities such as being an easy and quick technique to separate and deter-

minate metals in juice samples as an example of food matrices.

The main advantages of using carboxylic group magnetic nanoparticles as a sorbent to preconcentrate metals were (i) the low time consumption due to magnetically assisted separation and (ii) their high surface areas; therefore, satisfactory results can be achieved by using less amounts of the sorbents. Consequently, if the sensitivity needs to be enhanced to determine a metal in a food sample by CE, the use of carboxylic group functionalized magnetic nanoparticles represents a very interesting alternative.

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