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Application of Capillary Electrophoresis for the Analysis of Metal ions in Multimin and Mineral max

Aron Hailemichael[1], A. M. Crouch[2], A. Manohar[1]* and Tesfu Haile[1]

[1]Department of Chemistry, College of Science, Eritrea Institute of Technology, Mainefhi, P. O. Box 12676, Eritrea, N. E. Africa
[2]Department of Chemistry, University of Stellenbosch, Private Bag X1, Matieland, 7602, South Africa

Abstract : Capillary electrophoresis (CE) is a method of choice for analysis of cations in different samples using indirect UV detection. The determination of metal ions can be studied by employing several electrolyte systems with indirect detection at various wavelengths. The indirect detection at 214 nm was performed and resulted in good separation of metal ions with glycolic acid-imidazole background electrolyte (BGE). The method was developed for the identification of metal ions in standard samples and then applied for the analysis of metal ions in real samples. Two samples (Multimin and Mineral max) have been collected from various locations, analysed and compared. Four metal ions (Na^+, Mg^{2+}, Mn^{2+} and Cu^{2+}) were identified. These metals are useful for the animal protection.

Keywords : Water analysis; Background electrolyte composition; Complexation; Cations.

Introduction

Livestock farmers often provide the commercially available minerals for their animals to supplement on brightness, clean colour and photo stability [1]. Multimin and mineral max are commercially available mineral supplement containing Zn, Cu, Mn and Se that are used by the farmers for animal protection [2]. Measuring cations such as sodium, magnesium and copper in water and other samples is important for environmental monitoring, product consistence, fermentation monitoring, process control and spoilage detection [3, 4].

Capillary electrophoresis (CE) has developed into one of the powerful separation techniques for the analysis of ions in complex matrices. The several advantages of ion analysis using CE include resolution, speed, and simplicity and reduced sample preparation [5]. Indirect UV detection has been used successfully for the analysis of non UV-absorbing ions [6, 7]. In this case separation is achieved with an electrolyte containing a UV- absorbing ion plus an electrosmotic flow modifier [8].

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Various methods were employed for the analysis of metal ions present in different samples. The method was developed successfully and studied with the synthetic samples. Then the developed method was applied to routine analysis of real samples. Qualitative and quantitative determinations of the metal ions were obtained. In this particular study, the indirect detection at 214 nm was performed and resulted in good separation of metal ions with glycolic acid-imidazole background electrolyte (BGE). This method was applied to the analysis of metals ions in Multimin and Mineral max samples.

Materials and Methods

Instrumentation

The CE analysis was performed on a Prince Technologies (Emmen, Netherlands) capillary electrophoresis system equipped with a power supply (0 - ± 35 kV) and UV detector (PU 4225 UV detector, Philips) with wavelength of 190-820 nm. Fused-silica capillaries (Polymicro Technology, Phoenix, AZ, USA) of 75 µm I.D, (360 µm O.D) and 108.5 cm long (96.5 cm effective length) were used. The applied voltage was +25 kV. Samples were introduced into the capillary by the hydrodynamic mode (50 mbar) for 12-24 s. Data acquisition and analysis (DAx) soft ware from Prince Technologies was used for the control of instrument settings. All experiments were conducted at 25 ^{o}C. The current was monitored for all evaluated back ground electrolytes and was in the range of 8 to 11 µA.

Materials

Manganese, cadmium, zinc, lead (all Spectro sol grades) and glycolic acid (99%) were obtained from Fluka (Buchs, Switzerland). $MgCl_2.6H_2O$, copper (Spectro Sol), nickel (Spectro Sol) were obtained from Merck (Darmstadt, Germany. NaOH (99%) and HCl (99%) were from Riedel-deHaen (France). $CaCl_2.2H_2O$ (97%) and $FeSO_4.7H_2O$ (97%) were from NT laboratory supplies (Johannesburg). NaCl (99%) and KCl (99%) were from PAL Chemicals. Imidazole (99%) was from Sigma (Steinheim, Germany).

Sampling

The Multimin and Mineral max samples were collected in polyethylene containers and acidified and then kept in refrigerator at +4 ^{o}C. For CE measurements all samples were first screened with CE and their concentration were estimated. When the peak resolution was not satisfactory (high ionic strength) or the ion zones were distorted, the samples were diluted with ultra purified water (Milli-Q water, prepared in the purification unit) and filtered through 0.45µm membranes to achieve better separation for quantification. The samples were not manipulated by pH adjustment or complexation, because we wanted to analyse them by simulating the natural water conditions as closely as possible.

Conditioning of the capillary

New capillaries were conditioned by purging with 1 M NaOH solution (30 min), Milli-Q water-ultra pure water (30 min) and running electrolyte (30 min) and the sample was injected with the appropriate method. Capillaries were washed after every change of electrolyte with a 5 min rinse of 1 M NaOH solution and then with water and the appropriate electrolyte.

Standard mixtures

Metal ions standard solutions were obtained by dilution in Milli-Q water from 1000 mg/L stock solutions. The mixtures for capillary electrophoretic studies were prepared from the stock solutions to the concentrations needed. All mixtures were ultrasonicated daily before use. The stock solutions were kept in a refrigerator, at 4 ^{o}C.

Calibration solutions

A calibration curve was prepared with 5 mg/L, 25 mg/L, 50 mg/L, 100 mg/L and 200 mg/L measuring 25 µL, 125 µL, 250 µL, 500 µL and 1000 µL respectively of each cation in 5 mL volumetric flasks. The calibration curves were measured only at the ranges suitable for real samples. The linear ranges of each ion were measured at specified injection time.

Results and discussion

Separation of metal ions

The separation of metal ions was carried out using glycolic acid as the complexing agent and imidazole as background electrolyte. This method was developed and applied for the analysis of metal ions in synthetic samples. A mixture of nine metal ions could be separated using imidazole as UV-absorbing species (Figure 1a). All peaks were completely resolved. Detection of Pb^{2+} in this system was problematic because of its small peak height and due to low absorbance of the Pb-glycolic acid complex. The migration time, peak area and corrected peak area of the metal ions are shown in Table 1.

Table 1. The migration time, peak area and corrected peak area of metal ions at a concentration of 10 ppm (n = 6).

Metal ion	Migration time, min (RSD)	Peak area, (RSD)	Corrected peak area, (RSD)
K^+	8.75 (± 1.39%)	3.85E-05(± 10.17%)	4.39E-06(± 9.36%)
Na^+	11.78(± 1.63%)	9.30E-05(± 6.84%)	7.89E-06(± 5.75%)
Ca^{2+}	11.94(± 1.67%)	5.41E-05(± 4.13%)	4.53E-06(± 5.19%)
Mg^{2+}	12.46(± 1.71%)	5.30E-05(± 6.27%)	4.25E-06(± 5.83%)
Mn^{2+}	12.86 (± 1.70%)	2.13E-04(± 3.83%)	1.66E-05(± 2.97%)
Fe^{2+}	13.63 (± 1.72%)	4.08E-05(± 13.16%)	2.99E-06(± 12.13%)
Cd^{2+}	13.89 (± 1.72%)	1.11E-04(± 14.05%)	7.99E-06(± 13.44%)
Ni^{2+}	15.614(± 1.83%)	2.25E-04(± 6.74%)	1.44E-05(± 6.39%)
Zn^{2+}	16.31(± 1.83%)	2.20E-04(± 4.98%)	1.35E-05(± 5.12%)

The electropherograms obtained using glycolic acid and imidazole as complexing agent and as UV-absorbing species respectively for mixtures of nine metal ions are given below. The reproducibility of the method for three runs (red, black and blue) is shown in Figure 1b. Peaks 8 and 9 are distorted due to the strong complexes formed between Ni^{2+} and glycolic acid and Zn^{2+} and glycolic acid.

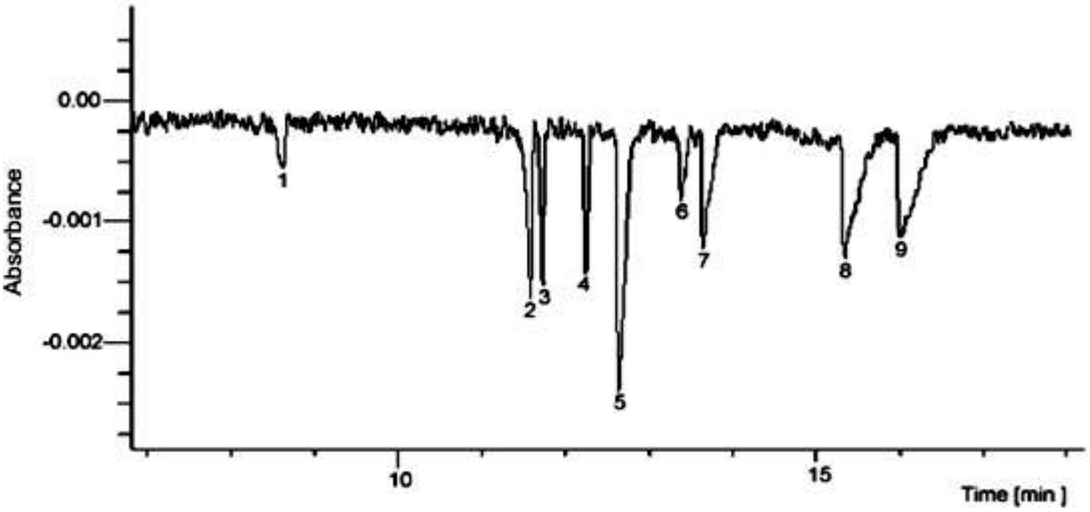

Figure 1a. Electrophoretic separation of nine metal ions. Carrier electrolyte, 12 mM imidazole – 15 mM glycolic acid (pH 4.29); hydrodynamic injection 24 s: voltage, 25 kV, wavelength, 214 nm. Peaks according to sequence: 1= K^+, 2 = Na^+, 3 = Ca^{2+}, 4 = Mg^{2+}, 5 = Mn^{2+}, 6 = Fe^{2+}, 7 = Cd^{2+}, 8 = Ni^{2+}, 9 = Zn^{2+}.

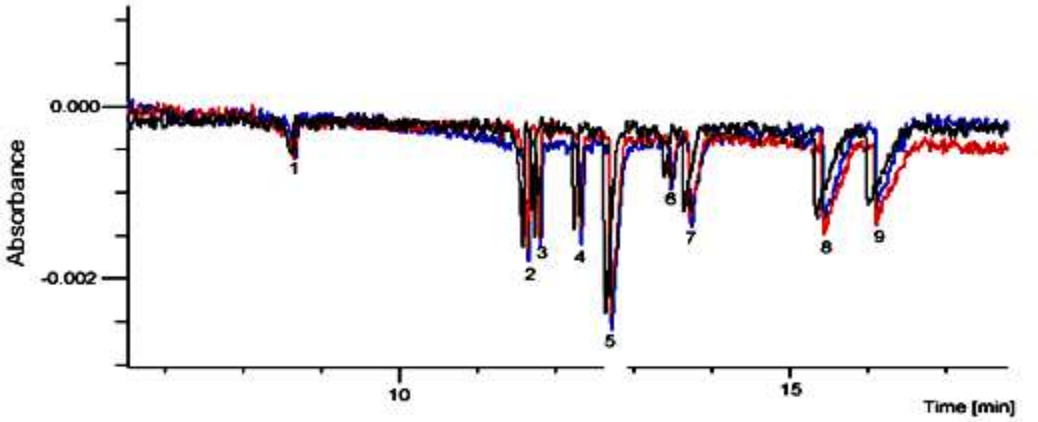

Figure 1b.The reproducibility of metal ions over three runs (within runs). Peaks according to sequence: 1 = K^+, 2 = Na^+, 3 = Ca^{2+}, 4 = Mg^{2+}, 5 = Mn^{2+}, 6 = Fe^{2+}, 7 = Cd^{2+}, 8 = Ni^{2+}, 9 = Zn^{2+}.

Analysis of real samples

Samples from various locations were collected and identification of metal ions in those sample matrices has been performed using some of the developed methods. Identification of peaks was carried by the standard addition method, that is, the addition of single metal species to a metal mixture and identification of the peak with increased height [9, 10].

The two samples (Multimin and Mineral max) that contain metals like sodium, magnesium, copper and zinc either in salt or chelated form and are useful for animal protection have been analysed and compared. CE was performed and a similar electropherograms (Figures 2 and 3) of the two samples have been obtained by decomplexing the chelated sample at lowest pH (≈1.0).

Multimin analysis

The sample was analyzed with glycolic acid-imidazole buffer solution and the electropherogram containing 4 metal ions was obtained. The migration time, peak area, corrected peak area are given in Table 2 and electropherogram of metal ions is given in Figure 2.

Table 2. The migration time, peak area, corrected peak area metal ions (n = 6).

Metal ion	Migration time, min (RSD)	Peak area, RSD	Corrected area, RSD
Na^+	12.32(± 0.48%)	3.40E-03(± 1.56%)	2.76E-04(± 1.55%)
Mn^{2+}, Zn^{2+}	12.60(± 0.56%)	1.15E-03(± 4.68%)	9.00E-06(± 4.21%)
Cu^{2+}	15.53(± 0.71%)	8.95E-04(± 8.75%)	5.00E-06(± 9.06%)

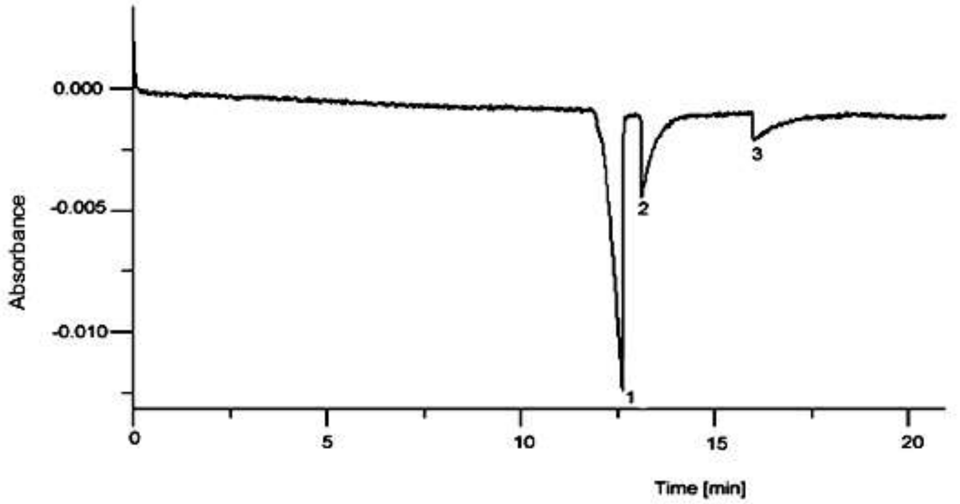

Figure. 2. Electrophoretic separation of metal ions. Carrier electrolyte, 12 mM imidazole – 15 mM glycolic acid (pH 4.29): hydrodynamic injection, 0.6 s: voltage 25 kV. Peaks according to sequence: 1 = Na^+, 2 = Mn^{2+} (Zn^{2+}), 3 = Cu^{2+}.

Synthetic (standard) samples of respective metals have been injected to identify the peaks in the sample. The highest peak for Na^+ was obtained. The tail in the second peak is due to the overlap of Mn^{2+} and Zn^{2+}. Different attempts have been made to resolve the two peaks, that is, by varying the pH of the buffer and concentration of the sample. However, these attempts proved to be inconclusive. Strong peak distortion of Cu^{2+} peaks is caused by the formation of very stable complex with glycolic acid with only small mobility [11].

Mineral max analysis

Table 3 The migration time, peak area, corrected peak area of metal ions (n = 6).

Metal ion	Migration time, min (RSD)	Peak area, RSD	Corrected area, RSD
Na^+	12.33(± 0.48%)	3.40E-03(± 1.56%)	2.76E-04(± 1.55%)
Mn^{2+}, Zn^{2+}	12.79(± 0.57%)	1.08E-03(± 5.16%)	8.40E-05(± 5.47%)
Cu^{2+}	15.53(± 0.71%)	8.94E-04(± 8.72%)	5.00E-06(± 9.10%)

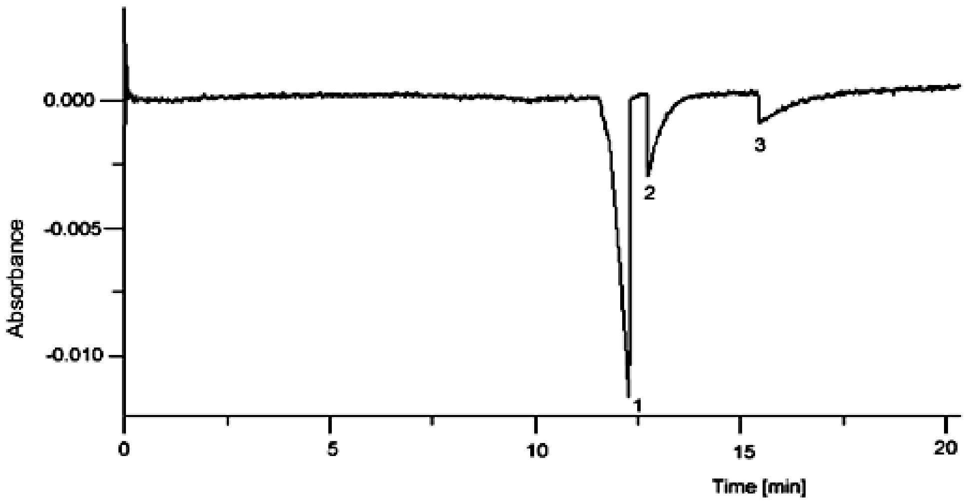

Figure. 3. Electrophoretic separations of metal ions. Carrier electrolyte, 12 mM imidazole-15 mM glycolic acid (pH 4.29): hydrodynamic injection, 0.6 s: voltage 25 kV. Peaks according to sequence: 1 = Na^+, 2 = Mn^{2+} (Zn^{2+}), 3 = Cu^{2+}.

A similar electropherogram of Mineral Max was obtained as it shown in Figure 3. The electrophergrams obtained from Multimin and Mineral max were overlapped to compare the two samples. The degree of overlap was very high as it shown in Figure 4. The migration time and peak area were similar for the two samples (Tables 2 and 3).

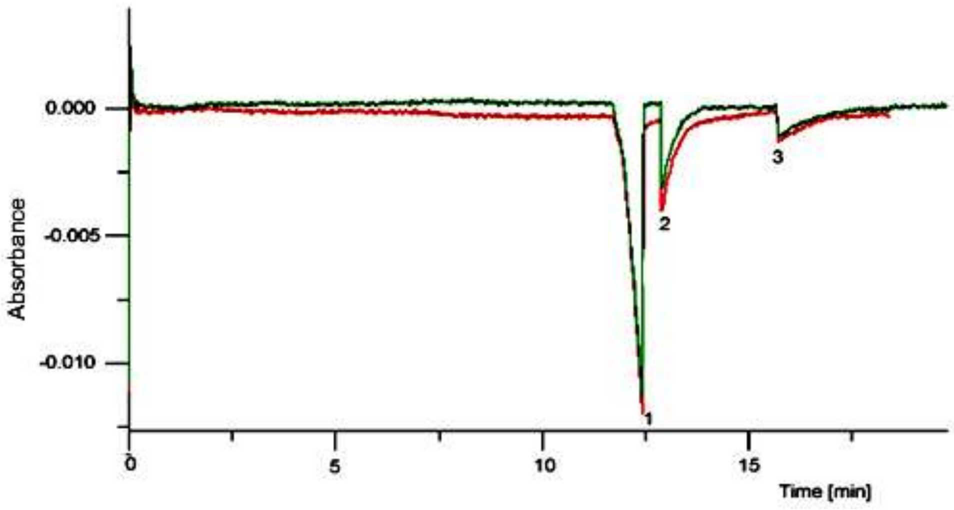

Figure 4. The reproducibility between the two samples: Multimin (red electropherogram) and Mineralmax (green electropherogram). Carrier electrolyte, 12 mM imidazole – 15 mM glycolic acid (pH 4.29): hydrodynamic injection, 0.6 s: voltage 25 kV. Peaks according to sequence: 1 = Na^+, 2 = Mn^{2+} (Zn^{2+}), 3 = Cu^{2+}.

It can be mentioned that the two samples are identical with regard to Na^+ and Cu^{2+}. But it is difficult at this stage to conclude with respect to Mn^{2+} and Zn^{2+} since they show different degree of overlapping. It can be concluded the electropherogram of the samples are similar and very good reproducibility between the two samples has been obtained.

Conclusion

Different methods have been developed for the simultaneous detection of alkali, alkaline earth and transitional metal ions in aqueous samples. A glycolic acid with imidazole method was developed for the detection of metal ions present in mineral wax and multimin samples. The method was able to detect four metal ions (Na^+, Cu^{2+}, Mn^{2+} and Zn^{2+}). This method was found as the most efficient one and it was the potential method for quantitative and qualitative analysis of metal ions in mineral wax and multimin samples.

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