PART 2

DETERMINATION OF CATIONS IN FERTILIZERS BY CAPILLARY ELECTROPHORESIS

CHAPTER 5

INTRODUCTION

5.1 Importance of cations in fertilizer

Determination of inorganic cations such as ammonium, alkali, alkaline earth, and transition metal ions is of great importance in soil, medicine, drinking water, food and fertilizer. In fertilizer industry, these cations were related macronutrients (NH_4^+ and K^+), micronutrients (Ca^{2+} and Mg^{2+}) and trace nutrients (Fe^{2+}, Zn^{2+}, Mn^{2+} and Cu^{2+}). Fertilizers are used to increase productivity of plants, as they provide different essential nutrients to promote plant growth (Table B in Appendix B). Some fertilizers only supply one nutrient. Many supply N, P and K only. A few fertilizers include all of the macronutrients and micronutrients. Due to having different formula, therefore fertilizer is suitable for a variety of plants. The raising demand of chemical fertilizers each year increases its price. This causes fake fertilizers to be spread extensively in fertilizer markets. Fake fertilizers contain fewer nutrients than labeled, and highly impact a farmer's finances. To control quality of fertilizers, a simple, low cost, friendly to the environment and fast analytical method is required for the simultaneous determination of cationic nutrients in fertilizers. Table 5.1 show measuring method and deviation of nutrients in chemical fertilizer under the Ministry of Agriculture and Cooperatives (Thailand) law (Wongsamut, e-mail, March 15, 2009).

Table 5.1

Measuring method and deviation of nutrients in chemical fertilizer

Nutrient	Measuring method	% Nutrient (by wt.)	% Deviation (by wt.)
Total-N	Kjeldahl	> 8.0	± 0.4
		8.0 – 16.0	± 0.6
		16.1 – 24.0	± 0.8
		< 24.0	± 1.0
NH_4^+	-	-	-
K	FAAS or ICP	> 8.0	± 0.4
		8.0 – 16.0	± 0.6
		16.1 – 24.0	± 0.8
		< 24.0	± 1.0
Ca	FAAS or ICP	-	-
Mg	FAAS or ICP	-	-
Mn	FAAS or ICP	-	-

FAAS = Flame Atomic Absorption Spectrophotometry

ICP = Inductively Coupled Plasma

5.2 Current analytical techniques of cations measurement

The determination of alkali and alkaline earth cations such as K^+, Ca^{2+} and Mg^{2+} has long been dominated by atomic absorption spectrometry (AAS) (S. R. Oliveira, Gomes Neto, J. A., Nóbrega, J. A., & Jones, B. T 2010 ; S. R. Oliveira, Raposo, J. L., & Gomes Neto, J. A, 2009). The popularity of inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) (Gorecka, 2006) and ion chromatography (IC) (Bolanc, 2006; Bruzzoniti, 2008) for elemental analysis can be attributed to the ability to analyze numerous elements simultaneous. However, ICP and IC method were high operating costs and consumptions of chemical reagents. In recent year, the use of capillary zone electrophoresis (CZE) for the analysis of cations has grown

significantly. Because of its higher resolution, shorter analysis time and lower consumption of reagents compared to ICP and IC. The CZE has received a great deal of attention for the determination of cations. Numerous applications of CZE have been reported for the determination of ammonium, alkali and alkaline earth metals in various aqueous samples.

5.3 Separation of cations by indirect UV detection

Indirect UV detection is generally used for CZE determination of ions that have no UV absorbance such as alkali and alkaline earth cations including ammonium. Therefore, highly absorbing reagents such as imidazole, methylbenzylamine, etc., have been added to background electrolyte (BGE) and referred as a probe. The electrophoretic mobility of probe should closely to ions of interest in order to obtain symmetrical peak. Ions that migrate faster than the probe will exhibit fronting and ions that migrate slower exhibit tailing. The probe ion provides a constant absorbance at the detection wavelength. When an analyte ion migrates through the BGE, the probe ion is displaced by analyte ions, leading to decreasing of absorbance. The detection signal is usually monitored at a wavelength at which the probe has maximum absorptivity.

Several previous papers used methylbenzylamine (Fukushi, et al., 2006; Fung & Lau, 2006; Hirogawa, Okamoto, Gosyo, Tsuda, & timerbaev, 2007; Shakulashvili, Faller, & Engelhardt, 2000) or imidazole (Abe, Murayama, Maeda, & Arakawa, 2006; Carducci, Dabas, & Muse, 2000; Gao, et al., 2008; K.G. Hopper, H. Leclair, & B.R. McCord, 2005b; Johns, Yang, Macka, & Haddad, 2004; Piovezan, Costa, Jager, Leal de Oliveira, & Micke, 2010; Sekar & Azhaguvel, 2007; Suarez-Luque, Mato, Huidobro, & SimalLozano, 2006; Sze, Yeung, & Fung, 2007; Warren & Adams, 2004) as absorbing probe in electrolytes for determination of cations by CE, due to both compounds having high molar absorptivity. The applications in different samples including total analysis time and detection limits of NH_4^+, K^+, Ca^{2+} and Mg^{2+} were showed in Table 5.2. From several previous papers, optimized concentration of 18-crown-6 ether was added in background electrolytes to delay the K^+ peak, otherwise superimposed to the NH_4^+ peak.

Table 5.2

Selected examples of inorganic cation separations by capillary electrophoresis

Cations	Samples	Background electrolyte	Detector	Separation time (min)	LOD (S/N=3), mg L^{-1}				Refs.
					NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}	Jelly fish	10 mM N- methyl- benzylamine,0.5 mM citric and 16 mM 18-crown-6 at pH 4.8	214 nm	4.5	0.28	0.30	0.13	0.21	(Fukushi, et al., 2006)
Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+} and Cu^{2+}	Coconut milk and jasmine tea	12 mM imidazole, 1 mM 18-crown-6, 5 mM malic acid and 20% D_2O at pH 4.25	214 nm	9	0.12	0.17	0.24	0.18	(Gao, et al., 2008)
Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+} and Cu^{2+}	Orange juice	10 mM N,N-dimethyl benzylamine, 8 mM lactic acid and 2 mM 18-crown-6	214 nm	6	0.040	0.047	0.013	0.016	(Fung & Lau, 2006)
Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Zn^{2+}, Co^{2+} Fe^{2+}, Cd^{2+}, Li^+, Pb^{2+}, Cr^{3+}, Ni^{2+} and Cu^{2+}	Water	10 mM 4-aminopyridine, 6.5 mM HIBA pH 4.5	214 nm	20	-	0.100	0.105	0.092	(Shakulashvili , et al., 2000)
Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}	Human sweat	10 mM 4- dimethyl- benzylamine, 6.5 mM HIBA and 2 mM 2 mM 18-crown-6 at pH 4.25	214 nm	15	0.025	0.035	0.024	0.060	(Hirogawa, et al., 2007)

Table 5.2 (Continued)

Cations	Samples	Background electrolyte	Detector	Separation time (min)	LOD (S/N=3), mg L^{-1}				Refs.
					NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+}, Li^+ and Cu^{2+}	Pineapple and Grape juice	10 mM imidazole and acetic acid at pH 3.6	185 nm	4	-	0.57	0.06	0.12	(Suarez-Luque, et al., 2006)
Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}	Ethanol fuel	20 mM HIS/lactic acid and 2.5 mM 18-crown-6	CCD	6	0.12	0.18	0.14	0.14	(Munoz, Richter, Jesus, Lago, & Angnes, 2004)
Na^+, NH_4^+, K^+, Mg^{2+}, $Ca^{2+}$and Li^+	-	6 mM imidazole, 12 mM HIBA, 0.1 mM DDAB, 2 mM 18-crown-6 at pH 4.0	210 nm	3.2	0.084	0.117	0.022	0.038	(Johns, et al., 2004)
Na^+, K^+, Mg^{2+}, $Ca^{2+}$and Li^+	Blood serum and urine	6.5 mM maleic acid/7.5 mM L-arginine and 1.5 mM 18-crown-6 at pH 5.5	CCD	4.8	0.006	0.018	0.014	0.012	(Wan, Kubáň, Tanyanyiwa, Rainelli, & Hauser, 2004)
Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}	Leaf extracts	10 mM imidazole and 2 mM 18-crown-6 at pH 4.2	200 nm	5	0.180	0.293	0.007	0.016	(Warren & Adams, 2004)

Table 5.2 (Continued)

Cations	Samples	Background electrolyte	Detector	Separation time (min)	LOD (S/N=3), mg L^{-1}				Refs.
					NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
Sr2+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}	Explosives residue	15 mM HIBA, 6mM imidazole, 4 mM 18-crown-6 and 5% CAN at pH 6.5	215 nm	2	14	11	9.5	15	(K.G. Hopper, H. LeClair, & B. R. McCord, 2005a)
Ethylammonium, Na^+, NH_4^+, K^+, Mg^{2+} Ca^{2+} Sr^{2+}, Mn^{2+}, Zn^{2+} and Pb^{2+}	Postblast residues	10 mM chrysoidine in MeOH and 0.7% glacial acetic acid	LED	9	0.20	0.22	0.13	0.23	(Hutchinson, et al., 2007)
Na^+, NH_4^+, K^+, Mg^{2+} Li^+ and Ca^{2+}	Homeopathic liquid formulation samples	12.5 mM imidazole, 10 mM HIBA and 3 mM 18-crown-6 at pH 3.6	215 nm	4.5	0.6	0.8	0.6	0.6	(Sekar & Azhaguvel, 2007)
Na^+, NH_4^+,Ba^{2+}, Sr^{2+}, K^+, Mg^{2+} Li^+ and Ca^{2+}	Mineral water and tap water	7.5 mM Cu(II) acetate, 15 mM ethylenediamine and 2 mM triethanolamine at pH 8	230 nm	4	0.15	0.45	0.12	0.18	(Padarauskas, Olsauskaite, & Paliulionyte, 1998)
Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}	Natural water	9 mM pyridine-12 mM glycolic acid and 5 mM 18-crown-6 at pH 3.6	254 nm	9	0.06	0.08	0.02	0.03	(Hiissa, Sirén, Kotiaho, M., & Hautojärvi, 1999)

Table 5.2 (Continued)

Cations	Samples	Background electrolyte	Detector	Separation time (min)	LOD (S/N=3), mg L^{-1}				Refs.
					NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
Na^+, NH_4^+, Mn^{2+}, K^+, Mg^{2+} and Ca^{2+}	Drainage water	20 mM MES/HIS, 1.5 mM 18-crown-6 at pH 6	CCD	3.5	10	13	8	15	(Kubán, Karlberg, Kubán, & Kubán, 2002)
Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}	Well water	11 mM HIS, 50 mM acetic, 1.5 mM 18-crown-6 and 0.1 mM citric acid at pH 4.1	CCD	10	0.3	0.2	0.3	0.2	(Kuban, Nguyen, Macka, Haddad, & Hauser, 2007)
Na^+, NH_4^+, K^+, Mg^{2+} Li^+ , $Ca^{2+}$and creatinine	Urine	2 M acetic acid and 2% w/v PEG	CCD	9.5	0.052	0.098	0.019	0.032	(Tůma, Samcová, & Duska, 2008)
Ethylammonium, Na^+, NH_4^+, K^+, Mg^{2+} Ca^{2+} Sr^{2+}, Mn^{2+}, Ba^{2+}, Zn^{2+} and Pb^{2+}	Postblast explosive residue	10 mM HIS, 50 mM acetic, 1 mM HIBA and 0.7 mM 18-crown-6 at pH 4.2	CCD	7	0.031	0.053	0.073	0.048	(Hutchinson, et al., 2008)

In our knowledge, the application of CZE for the determination of NH_4^+, K^+, Ca^{2+} and Mg^{2+} in fertilizers has never been done before. Thus, CZE method was developed for the determination of cationic nutrients in fertilizers sample.

5.4 Aim of this research

The aim of this work was to develop fast and high selectivity CZE method for the simultaneous determination of the cationic nutrient in fertilizers using optimized electrolyte containing imidazole. Optimization conditions of the applied potential and composition in background electrolytes were investigated. The developed CZE method was applied for analysis of cationic nutrients in different formula of solid and fluid fertilizer samples, and the accuracy was confirmed with a flame atomic absorption spectrophotometer.