Environmental monitoring of wastewater using capillary ion electrophoresis

Stuart A. Oehrle[*,a], Roger D. Blanchard[b], Chris L. Stumpf[b], Debra L. Wulfeck[b]

[a]Waters Industrial Division of Millipore, 34 Maple Street, Milford, MA 01757, USA
[b]Northern Kentucky University, Department of Chemistry, Highland Heights, KY 41099, USA

Abstract

Capillary ion electrophoresis (CIE) is a capillary electrophoretic technique which has been developed for the rapid analysis of low-molecular-mass inorganic and organic ions. Anion and cation analysis of wastewater samples from a meat processing plant will be discussed. The wastewater samples were collected above, at point of discharge, and at various points downstream from the plant. The purpose of the analysis was to investigate dilution effects of the wastewater as it mixes with the stream water. CIE allows for rapid analysis times (typically less than 5 min) with little sample preparation required.

1. Introduction

Anion analysis using a chromate, high mobility, electrolyte with an osmotic flow modifier (OFM) has been previously shown to be a very sensitive technique for the analysis of anions in several different matrices including environmental wastewater [1–5]. OFM is added to the electrolyte as an additive that reverses the normally cathodic direction of the electroosmotic flow (EOF) that is found in fused-silica capillaries. This creates a co-electroosmotic condition that augments the mobility of the analytes. Cation analysis using a UV Cat-2 and tropolone electrolyte has been shown as well to be a sensitive technique for cation analysis [6,7]. No OFM is required for cation analysis since the natural EOF is in the same direction as the

cation migration and thus augments the separation.

The purpose of this paper is to demonstrate the use of CIE in the analysis of wastewater from an industrial meat processing plant. Wastewater from the plant is discharged from a pipe into a creek which flows into the Licking River in northern Kentucky. The Licking River eventually feeds into the Ohio River. There are no other industrial sites which discharge into the creek. Approximately 200–300 yards (ca. 183–273 m) below the discharge site, water from a lake drains into the creek via a spillway. Sampling of the water at different points along the creek was done during summer, fall, and winter to investigate seasonal concentration loading and dilution rates. Samples of water were taken above (before) the discharge tube, directly from the tube, and at various points downstream. Samples of lake water and from where the lake water and creek water mix were collected as well. No

---

* Corresponding author.

sampling of the mix was done when sampled in the summer because the lake was low and no water was flowing over the spillway.

2. Experimental

2.1. Instrumentation

The capillary electrophoresis (CE) system employed was the Quanta™ 4000E CIA (Waters Chromatography Division of Millipore, Milford, MA, USA). An Hg lamp was used for indirect UV detection at 254 nm for anion analysis and 185 nm for cation analysis. AccuSep™ polyimide fused-silica capillaries of dimension 60 cm × 75 μm I.D. were used throughout. Data acquisition was carried out with a Waters Millennium™ 2010 Chromatography Manager with a SAT/IN module connecting the CE to the data station with the signal polarity inverted from the CE.

2.2. Preparation of electrolytes

High purity water (Milli-Q™) was used to prepare all solutions (Millipore, Bedford, MA, USA). The chromate electrolyte was prepared from a concentrate containing 100 mM sodium chromate tetrahydrate (Fisher Scientific, Pittsburgh, PA, USA) and 0.0056 mM sulfuric acid (J.T. Baker, Phillipsburg, NJ, USA; Ultrex Grade). Osmotic flow modifier (OFM) for reversal of the direction of the electroosmotic flow (EOF), for anion analysis, was a 20 mM concentrate (CIA-Pak OFM anion BT) obtained from Waters. The working electrolyte for anion analysis consisted of 4.5 mM Chromate–0.5 mM OFM-BT, pH 8.1. The working electrolyte for cation analysis was a solution of 1.2 mM UV Cat-2 (Waters) and 3.0 mM tropolone (Aldrich, Milwaukee, WI, USA). All working electrolytes were prepared fresh daily and degassed prior to use.

2.3. Chemicals

All standard solutions were prepared by diluting concentrated stock solutions containing the individual anions or cations. All standard solutions were prepared from their salts and were of ACS grade or better.

2.4. Sampling

Plastic 200-ml bottles (Nalge, Rochester, NY, USA) were used for sampling. The bottles were initially soaked in Milli-Q water overnight and then rinsed several times with Milli-Q water and air dried. Disposable, non-talc, gloves were worn while sampling. Standard sampling techniques were followed at the sampling site [8]. The sample bottles were rinsed several times with the sample water prior to sample collection. The bottles were filled completely to the top with as little air space as possible. Samples were then transported back to the lab and refrigerated until analyzed.

2.5. Calibration

Three standards of different concentrations were prepared for each anion and cation analyte. Triplicate injections were made and the peak areas averaged for each standard concentration. A linear calibration curve was obtained for each standard with the curve forced through zero. Typical correlation constants (r^2) were $0.99X$ or better, with the X being a value of 7 or greater. A new set of standards were prepared from a concentrate for each analysis. Samples were injected in triplicate as well.

3. Results and discussion

Fig. 1 is an example electropherogram of an anion standard. Figs. 2, 3, and 4 are water samples above discharge, at point of discharge, and 200 feet (ca. 61 m) below discharge respectfully. Fig. 5 is an example electropherogram of a cation standard. Figs. 6, 7, and 8 are cation analyses of the same samples as in Figs. 2, 3, and 4. Overall results of the analyses are shown in Tables 1, 2, 3 along with relative standard deviation (R.S.D.) data for triplicate injections of the water samples. CIE enabled fast analysis
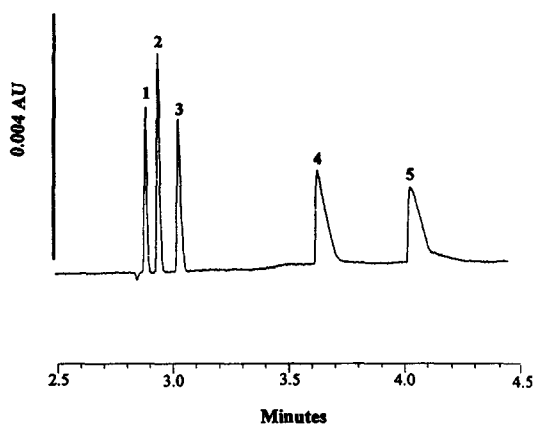
Fig. 1. Electropherogram of anion standard. CIE conditions: fused-silica 60 cm × 75 μm I.D. capillary; voltage: 18 kV (negative); electrolyte: 4.5 mM chromate–0.5 mM OFM; indirect UV detection at 254 nm; hydrostatic injecton (10 cm for 30 s). Solutes: 1 = chloride (2.0 mg/l); 2 = sulfate (6.0 mg/l); 3 = nitrate (4.0 mg/l); 4 = hydrogen phosphate (4.0 mg/l); 5 = carbonate (8 mg/l).

times (less than 5 min) and fairly low R.S.D. values for triplicate injections. As can be seen anion and cation levels increase dramatically (most notably Na^+ and Cl^-) at the point of discharge as compared to the background (before discharge tube) sample. The only real exceptions are magnesium and calcium which remain fairly constant. This is expected due to leaching of these cations from exposed limestone rock in the area along the creek. The main ions

Fig. 3. Electropherogram of water sample at the discharge tube. Diluted 1:100. Conditions as stated in Fig. 1. Solutes: 1 = chloride (1111.7 mg/l); 2 = sulfate (87.6 mg/l); 3 = nitrate (11.7 mg/l); 4 = hydrogenphosphate (20.3 mg/l); 5 = carbonate (not quantitated).

of interest are chloride, sodium, potassium, sulfate, hydrogenphosphate and nitrate since they are typically byproducts of meat processing. As can be seen, elevated levels are observed at the point of discharge but the levels eventually reach normal levels just prior to or when mixed with water from the lake runoff. This is especially so in the fall sample, which is summarized in Figs. 9 and 10. These figures consist of bar charts of the ions analyzed at the different sampling
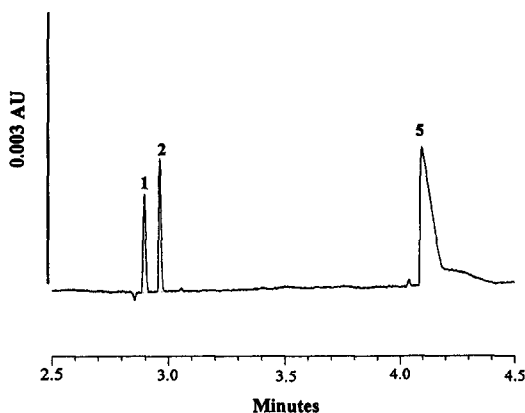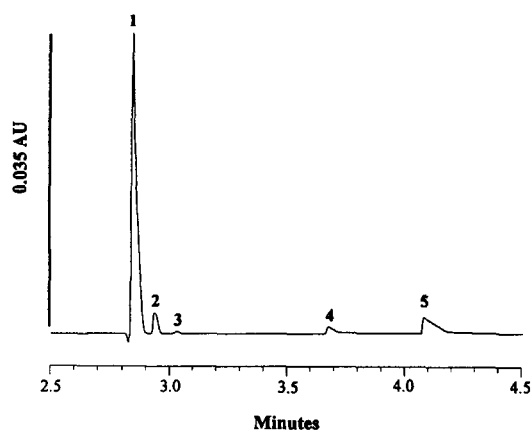

Fig. 2. Electropherogram of water sample before the discharge tube. Diluted 3:100. Conditions as stated in Fig. 1. Solutes: 1 = chloride (17.7 mg/l); 2 = sulfate (25.9 mg/l): 5 = carbonate (not quantitated).
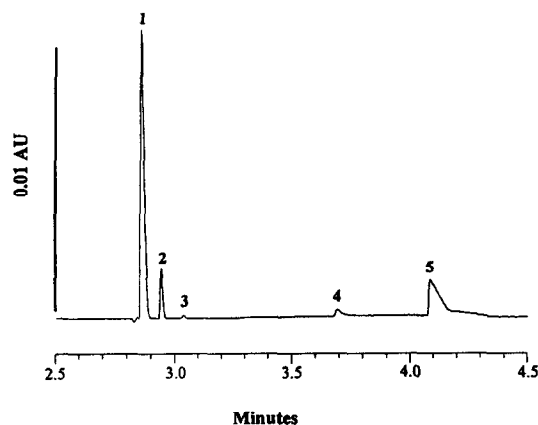

Fig. 4. Electropherogram of water sample 200 feet (ca. 61 m) below discharge. Diluted 3:100. Conditions as stated in Fig. 1. Solutes: 1 = chloride (311.4 mg/l); 2 = sulfate (44.8 mg/l); 3 = nitrate (3.02 mg/l); 4 = hydrogenphosphate (5.38 mg/l); 5 = carbonate (not quantitated).
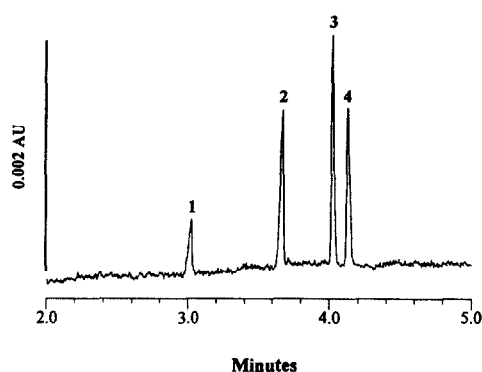
Fig. 5. Electropherogram of cation standard. CIE conditions: fused-silica 60 cm × 75 μm I.D. capillary; voltage: 20 kV (positive); electrolyte: 1.2 mM UV Cat-2-3.0 mM tropolone; indirect UV detection at 185 nm; hydrostatic injecton (10 cm for 30 s). Solutes: 1 = potassium (1.0 mg/l); 2 = calcium (1.0 mg/l); 3 = sodium (1.5 mg/l); 4 = magnesium (0.5 mg/l).

Fig. 6. Electropherogram of water sample before the discharge tube. Diluted 3:100. Conditions as stated in Fig. 5. Solutes: 1 = potassium (5.4 mg/l); 2 = calcium (38.8 mg/l); 3 = sodium (14.3 mg/l); 4 = magnesium (11.1 mg/l).

Fig. 7. Electropherogram of water sample at the discharge tube. Diluted 1:100. Conditions as stated in Fig. 5. Solutes: 1 = potassium (44.0 mg/l); 2 = calcium (42.1 mg/l); 3 = sodium (792.8 mg/l); 4 = magnesium (12.6 mg/l).
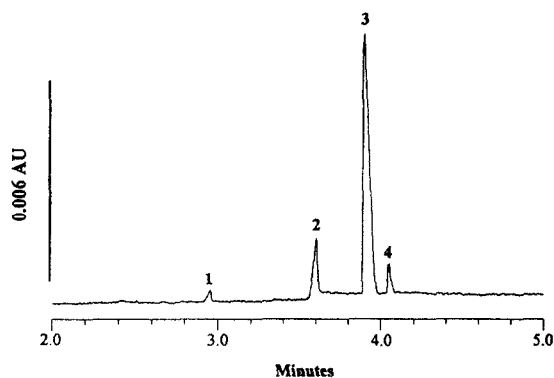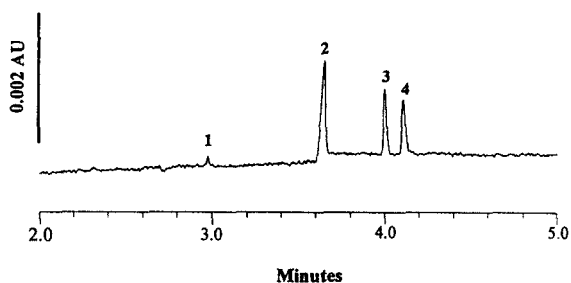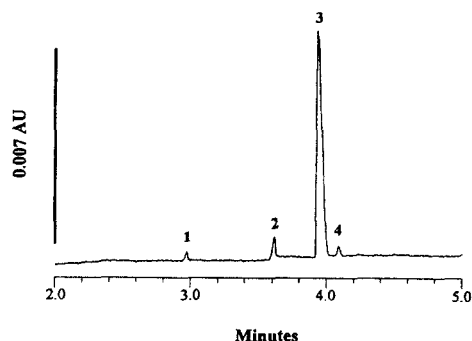
Fig. 8. Electropherogram of water sample 200 feet (ca. 61 m) below discharge. Diluted 3:100. Conditions as stated in Fig. 5. Solutes: 1 = potassium (19.6 mg/l); 2 = calcium (48.1 mg/l); 3 = sodium (247.7 mg/l); 4 = magnesium (11.2 mg/l).

points. The increase in ion concentration above background levels at the discharge tube is dramatically shown. As mentioned above, they decline significantly at sampling points farther downstream from the discharge tube, as dilution takes place. The summer sample remained at high levels of chloride, potassium, sodium, sulfate, and hydrogenphosphate even downstream prior to where lake runoff was. This can be explained by the fact that the creek was dry before the discharge tube and the only flow in the creek was from water that came out of the discharge tube. The water analyzed above the tube was collected from a standing pool of water. There was no summer sampling from the lake runoff since it was at low level and no water was running over the spillway. It is interesting that nitrate was not found in the summer sampling. One possible factor was that the sampling was done on a day of low (ions) discharge.

There was very little water flowing over the spillway for the winter sampling. There was no sampling at the mix point for the winter sampling due to heavy snow and thick ice at the mixing point. The creek was flowing above the discharge tube and lake spillway for the fall sampling. Ion levels dropped off very quickly at the sampling sites after the discharge tube. This is due to dilution with the surrounding water which by the time samples were taken at the lake had diluted the ion levels to very near the original (back-

Table 1
Average amounts found in triplicate injections from the summer sampling

	Above discharge	At discharge	200 ft. below	200 yd. below	Lake
Cl^-	20.0 (0.15)	1150.5 (0.14)	1140.9 (0.67)	77.7 (0.80)	6.9 (1.03)
SO_4^{2-}	12.7 (0.92)	116.7 (0.60)	115.6 (0.88)	48.5 (0.90)	31.6 (0.80)
NO_3^-	ND	ND	ND	ND	ND
HPO_4^{2-}	ND	21.8 (0.73)	23.0 (1.20)	18.5 (1.12)	ND
K^+	16.7 (1.30)	52.3 (0.95)	44.7 (1.35)	40.0 (1.05)	2.9 (1.80)
Ca^+	39.2 (0.85)	39.0 (0.20)	41.5 (1.02)	39.6 (0.93)	28.7 (1.20)
Na^+	14.6 (0.88)	721.7 (0.25)	665.4 (0.23)	600.8 (1.20)	6.8 (1.74)
Mg^+	11.1 (0.98)	13.3 (0.85)	13.7 (0.90)	14.2 (1.39)	6.1 (1.85)

Amounts in mg/l; $n = 3$; R.S.D. in parentheses; ND = none detected.

Table 2
Average amounts found in triplicate injections from the fall sampling

	Above discharge	At discharge	100 ft. below	200 ft. below	Lake	Mix
Cl^-	17.7 (0.63)	1112.5 (0.11)	511.7 (0.17)	311.2 (0.22)	6.8 (1.0)	12.2 (1.1)
SO_4^{2-}	25.9 (0.34)	87.3 (0.64)	74.8 (0.54)	45.2 (0.60)	27.2 (0.56)	27.0 (0.42
NO_3^-	ND	11.7 (1.05)	4.8 (1.21)	3.08 (1.12)	ND	ND
HPO_4^{2-}	ND	20.2 (0.40)	9.6 (1.28)	5.4 (0.92)	ND	ND
K^+	5.5 (1.73)	43.8 (1.22)	22.8 (1.62)	19.4 (2.10)	5.9 (1.89)	6.8 (2.21)
Ca^+	39.2 (0.98)	42.4 (1.52)	53.6 (1.36)	48.5 (1.22)	43.9 (1.18)	40.0 (1.33)
Na^+	14.1 (1.02)	790.3 (0.47)	336.1 (0.82)	246.7 (0.34)	7.1 (1.35)	11.2 (1.20)
Mg^+	11.2 (1.14)	12.8 (1.32)	14.5 (1.62)	11.4 (1.45)	8.6 (1.78)	8.4 (1.56)

Amounts in mg/l; $n = 3$; R.S.D. in parentheses; ND = none detected.

ground) levels. As can be seen from this data the sodium and chloride levels remain about the same at discharge for all the times sampled but the others vary depending on the time of sampling. Also dilution effects from the creek flow plays a very important role in how quickly the

Table 3
Average amounts found in triplicate injections from the winter sampling

	Above discharge	At discharge	100 ft. below	200 ft. below	Lake	Mix[a]
Cl^-	11.7 (0.65)	977.8 (0.20)	734.5 (0.29)	673.6 (0.18)	12.4 (1,15)	
SO_4^{2-}	54.4 (0.60)	49.6 (1.00)	49.2 (1.10)	54.7 (1.09)	93.1 (0.19)	
NO_3^-	ND	33.4 (1.10)	23.8 (0.69)	22.6 (1.00)	ND	
HPO_4^{2-}	ND	18.6 (0.95)	13.1 (1.11)	11.8 (1.18)	ND	
K^+	1.6 (1.52)	46.5 (1.25)	38.3 (1.43)	27.7 (2.21)	1.8 (1.70)	
Ca^+	89.9 (0.29))	33.7 (0.87)	44.4 (2.21)	36.9 (1.73)	33.1 (1.91)	
Na^+	19.7 (0.87)	762.1 (0.35)	613.6 (0.20)	518.5 (0.19)	26.0 (1.84)	
Mg^+	25.9 (0.62)	7.5 (1.95)	11.4 (2.50)	11.4 (1.45)	10.0 (1.35)	

Amounts in mg/l; $n = 3$; R.S.D. in parentheses; ND = none detected.
[a] No sampling of mix was done due to heavy snow and thick ice.

Bar Plot for Cl (Fall)

Bar Plot for SO₄ (Fall)

Bar Plot for NO₃ (Fall)
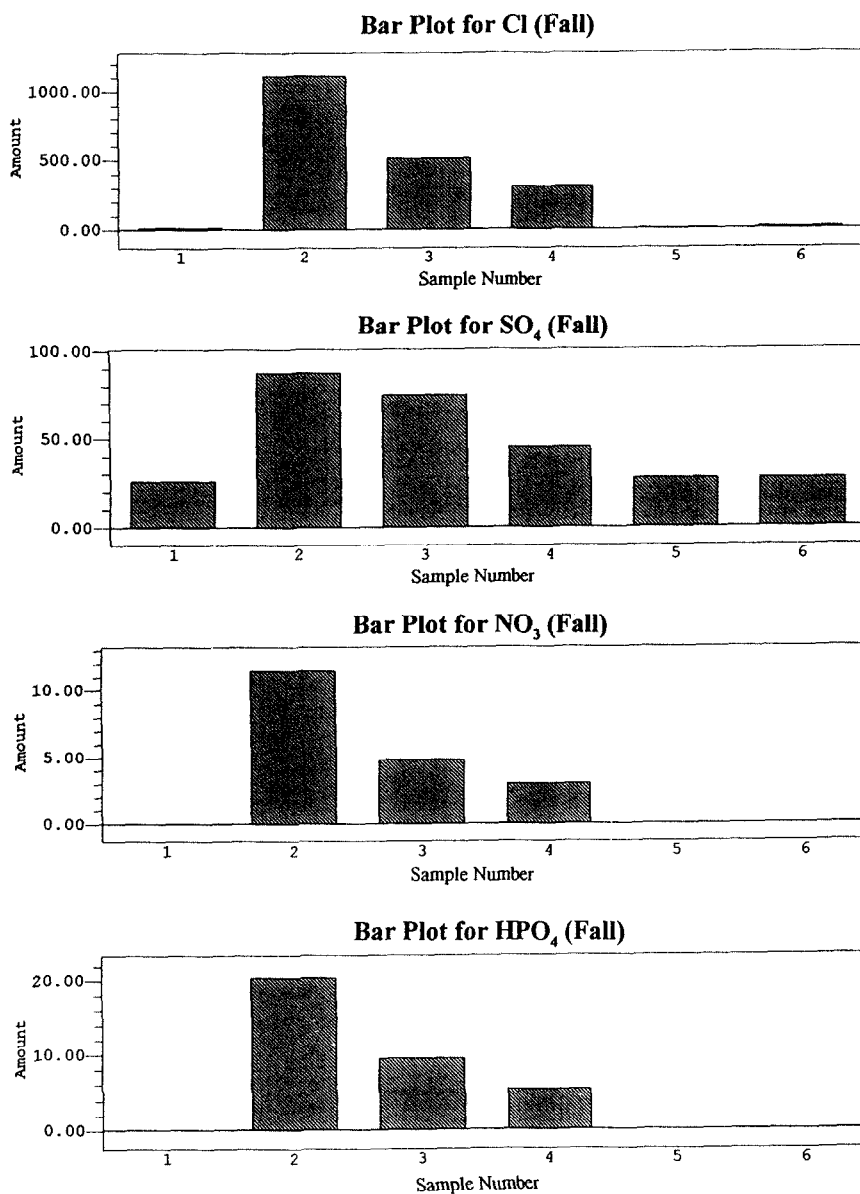
Bar Plot for HPO₄ (Fall)

Fig. 9. Summary bar plot for anion analysis of samples collected in fall. Amounts are in mg/l. Sample number corresponds to sample point: 1 = above discharge tube; 2 = at discharge tube; 3 = 100 feet (*ca.* 30 m) below; 4 = 200 feet (*ca.* 61 m) below; 5 = lake water from spillway; 6 = mix of both.

ion levels in the water return to typical levels. This plays an important role in evaluating the environmental impact of the ion content on aquatic life in the creek. CIE offers a reliable means of monitoring with little sample preparation and fast analysis times.

Bar Plot for K (Fall)

Bar Plot for Ca (Fall)

Bar Plot for Na (Fall)
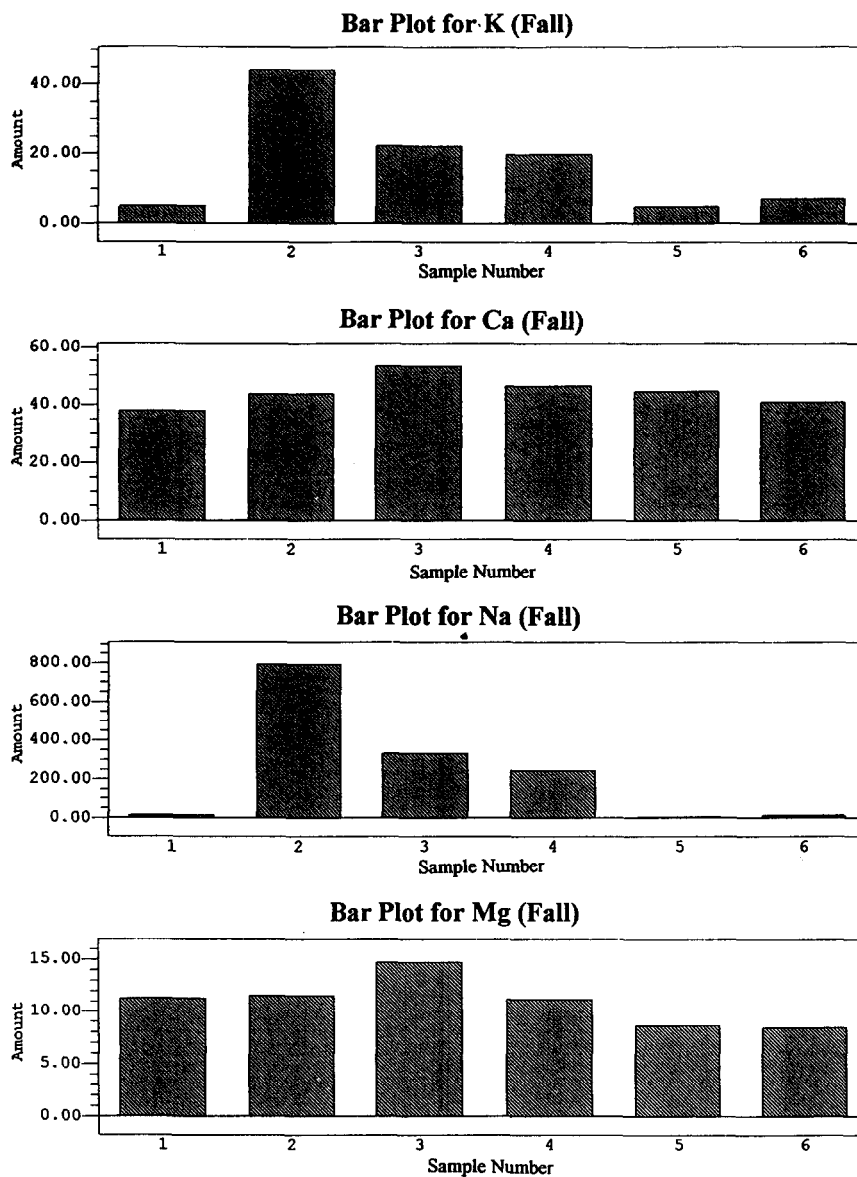

Bar Plot for Mg (Fall)

Fig. 10. Summary bar plot for cation analysis of samples collected in fall. Amounts are in mg/l. Sample number corresponds to sample point: 1 = above discharge tube; 2 = at discharge tube; 3 = 100 feet (*ca.* 30 m) below; 4 = 200 feet (*ca.* 61 m) below; 5 = lake water from spillway; 6 = mix of both.

6. Further work

Further investigations of the wastewater for anions and cations will continue. One other area of possible interest is also in the area of organic acid monitoring of wastewater using CIE. A group from the Biological Sciences Department will also be investigating the effects of these high

levels of ions on the aquatic ecosystem of the creek.

References

[1] P. Jandik and W.R. Jones, *J. Chromatogr.*, 546 (1991) 431.

[2] G. Bondoux, P. Jandik and W.R. Jones, *J. Chromatogr.*, 602 (1992) 79.

[3] W.R. Jones and P. Jandik, *J. Chromatogr.*, 546 (1991) 445.

[4] J.P. Romano and J. Krol, *J. Chromatogr.*, 640 (1993) 403.

[5] P.E. Jackson and P.R. Haddad, *J. Chromatogr.*, 640 (1993) 481.

[6] A. Weston, P.R. Brown, P. Jandik, A.L. Heckenberg and W.R. Jones, *J. Chromatogr.*, 593 (1992) 289.

[7] A. Weston, P.R. Brown, P. Jandik, A.L. Heckenberg and W.R. Jones, *J. Chromatogr.*, 608 (1992) 395.

[8] S.E. Manahan, *Environmental Chemistry*, Lewis, Chelsea, 5th ed., 1991.