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Full Paper

Simultaneous Determination of Anions in Water, Plant and Soil Samples by Conductometric-Potentiometric Hybrid Detector System

Elif Apaydin,[1,*] and Murat Yolcu[2]

[1]*Giresun University, Center Research Laboratory Application and Research Center, Giresun, Türkiye*
[2]*Giresun University, Faculty of Science and Art, Chemistry Department, Giresun, Türkiye*

*Corresponding Author, Tel.: +90-5435873941
E-Mail: elif.apaydin@giresun.edu.tr

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Abstract- A composite pH sensor based on graphite/quinhydrone by potentiometric flow cells was used for a hybrid detection system that designed conductivity detectors as well as simultaneous detectors in the ion chromatography system. 1.0 mM sodium carbonate solution at 1.0 mL/min flow was used as the eluent in the anion separation system. A simultaneous conductometric-potentiometric hybrid analysis method has been developed for anions (fluoride, bromate, chloride, nitrite, bromide, nitrate, phosphate, sulfate, oxalate, and fumarate). The standard calibration curves for anions were linear with great correlation coefficients. The correlation coefficients (R^2) obtained from the calibration curves were 0.9904–0.9984 for potentiometric detector results. Sample analyses have been successfully performed by this method on some water, plant, and soil samples. It is worthy of note that the quantity of oxalate detected in plants is comparable to that of phosphate and sulfate in both detector systems. The paired t-tests were performed for the statistical analysis of the obtained data.

Keywords- Ion chromatography; Potentiometry; Conductometry; pH sensor; Hybrid system

1. INTRODUCTION

Ion chromatography (IC) has been placed increasingly in scientific studies as an analytical method that enables simple, selective, and rapid determination of various inorganic and organic anions and cations [1-4]. Unexpected properties such as high-temperature coefficient and limited detection capacity of conductivity detection methods, have led to the need the search for alternative detection methods with direct or indirect spectrophotometric and electrochemical detection capabilities [5-10]. In recent years, potentiometric ion-selective electrodes (ISE) have been widely used as detectors for the determination of ionic species in aqueous solutions [11-21]. According to a study data concluded that the detection limits achievable by potentiometric detection for the determination of bromide and ammonium ions are better than those possible with any other ion chromatographic detection method [22-25].

The detectability of inorganic ions especially anions has become routine analysis by IC. The levels of some anion groups in food and drinks are important for all organisms [26]. The presence and type of mineral elements have an important role in the regulation of cellular metabolism such as in creating an acid-base balance in the body, as maintaining optimal osmotic pressure, and as participating in building enzymes and hormones that regulate human activity [27].

Not all fluoride ingested by digestion or inhalation can be absorbed. Some of what is absorbed is excreted in sweat, faeces, and saliva, half of which is excreted in the urine. By protecting the teeth from the effect of acid, it prevents deterioration and decay of teeth. It also prevents calcium loss by retaining calcium in the bones [28]. Chloride is produced when a molecule dissolves in water or other polar solvents, such as hydrogen chloride, or when the element chlorine (a halogen) obtains an electron. In blood, one of the most crucial electrolytes is chloride. Following sodium, chloride is the most prevalent electrolyte in serum, playing a vital role in maintaining electrolyte balance, preserving electrical neutrality, regulating bodily fluids, determining acid-base status, and assisting in the diagnosis of several clinical conditions [29]. Nitrite and nitrate contamination in foods also show their toxic effects through nitrosamines formed by combining with secondary amines in animal products. It has been reported by many researchers that nitrosamines are carcinogenic in both humans and animals [30].

Bromate anion was specially added to the standard purity anion mixture because of its toxic effect and it was aimed to determine. As to new studies have led the International Agency for Research on Cancer (IARC) to classify bromate as a group 2B carcinogen to humans with renal tumour risks at concentrations > 0.05 µg/L. While the World Health Organization (WHO) accepts a limit of 25 µg/L for bromate in drinking water, the US Environmental Protection Agency (EPA) recommends a concentration limit of 10 µg/L at the moment and the Commission of European Union proposes a concentration limit of 10 µg L [31].

The content of the elements/mineral elements varies in different plants and regions, due to some environmental factors such as atmosphere, environmental contamination, sampling season, plant age, soil condition, and climate effects [32]. Therefore, searching for the mineral compositions of plants is important for people's health. The aim of the present work was to develop an alternative hybrid method for flow-potentiometry based on a graphite/quinhydrone composite pH sensor [33], by designing the detector cell and integrating it with conductivity detectors simultaneously in the IC system. By performing both conductometric and potentiometric anion detections with a single injection, some advantages were provided in parameters such as chemical, solvent, column life, labor, and analysis time, and an accurate, fast, reliable, and reproducible analysis method was developed for anion determination.

2. EXPERIMENTAL SECTION

2.1. Chemical

Quinhydrone, polymethylmethacrylate, and graphite were obtained from Merck. Orthocryl CE was obtained from Dentaurum. Methane sulfonic acid, sodium carbonate, the anion standards were obtained from Dionex-Thermo Scientific.

2.2. Equipment and Method Optimization

For potentiometric measurements; a multi-channel potentiometer device which supported by a computer program designed in our laboratory was used. Ag/AgCl electrode (Basi-MF-2079-RE-5B) was used as the reference electrode. Thermo-Dionex Dual Ion Chromatography (Model: ICS-5000) System was used for IC analysis. The anion (fluoride, bromate, chloride, nitrite, bromide, nitrate, phosphate, sulfate, oxalate, fumarate) separations were performed on Dionex Ion Pac AS 9 HC (4×250 mm with guard column) analytical column with 10 mM sodium carbonate as mobile phase (flow rate: 1 mL/min). Dionex AERS 500 (4 mm, 65 mA) anion suppressor column was used for suppression. The samples were injected into the column (20 µL of volume) by the autosampler of IC system. Thermo conductivity detector (P/N 061830 Model) which supported by Chromeleon® software system was used for anion detections.

Different mobile phase concentrations were tested and 10 mM was selected as optimum. Different flow rates were experimented and 1 mL was selected as the optimum.

2.3. pH Detector Cell Design and Integration in IC System

A pH-sensitive layer prepared with the polymethylmethacrylate-quinhydrone-graphite mixture [30] was attached between two polymethylmethacrylate plates and clamped with a vice for 48 hours, and the cell was left to dry completely for 7 days. Then, the cylindrical holes were drilled with a 0.2 mm driller through the pH-sensitive layer and tubings were connected with the holes in both flow directions. Another cylindrical hole was drilled on the polymethylmethacrylate plate through the flow line as close as possible to the pH-sensitive layer for the reference electrode. The conductivity detector output tubing of the ion chromatographic system was connected to the pH sensitive detector cell. Then potentiometric detection unit was integrated side by side with the conductometric detection unit in the IC system. After system optimization, the sample analyzes were successfully performed by simultaneous potentiometric-conductometric detection method.

2.4. Sample pre-treatment

Tap water, drinking water, waste water and river water were filtred and storaged at +4°C until analyzes. *Smilax excelca leaves* (it is an endemic plant and known as "merevcen" in Giresun), hazelnut sprout, *Ornithogalum Umbellatum L.* (it is an endemic plant and known as "sakarca" in Giresun) and Urtica dioica L. (stinging nettle) which preferred endemic plant species belonged to Giresun region were collected and kept in an oven at 100°C for 5 hours and the samples were shaked for 24 hours in 100 mL deionized water, filtered and storage -8°C until analyzes. Composted and noncomposted soil were kept in an oven at 100°C for 5 hours and the samples were taken into flasks and kept in 200 mL deionized water for 24 hours in a shaker and filtered and storaged at -8°C until analyzes. All samples were used after making the necessary dilutions and filtering through an injector filter with a pore size of 0.22 µm.

3. RESULTS AND DISCUSSION

3.1. Calibration

The conductometric and potentiometric ion chromatograms obtained for standard anion mixtures and their calibration graphs are presented in Figure 1 to 4, respectively. The calibration graphs were constructed by plotting peak area for conductometric and peak height for potentiometric chromatograms against concentration of the anions under the optimum conditions. Retention times (t_R), linear coefficients of determination (R^2) and detection limits (LODs) are given in Table 1.

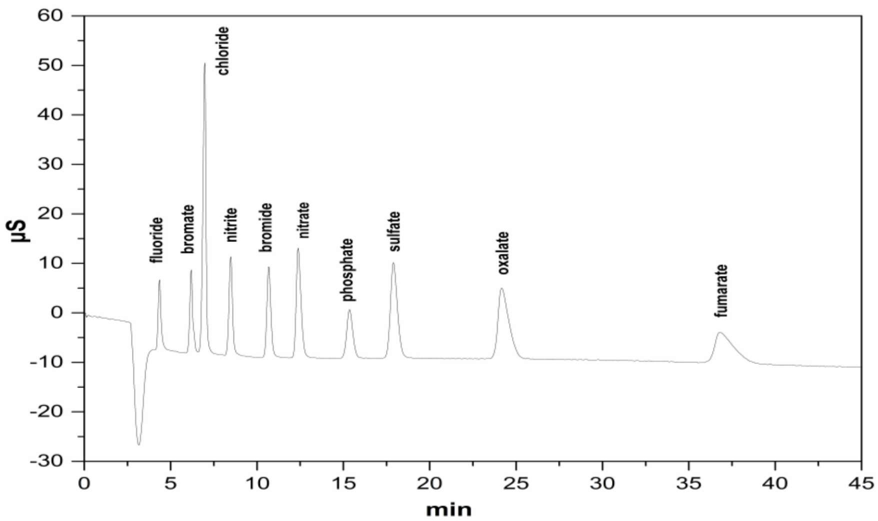


Figure 1. Conductometric ion chromatogram for the standard anion mixture (fluoride, bromate, chloride, nitrite, bromide, nitrate, phosphate, sulfate, oxalate, fumarate)

The formula 3σb/m criteria were used to calculate the detection limit, where σb represents the blank signal's standard deviation and m is the calibration graph's slope [34]. The lowest detection limit observed was 0,18 ppm for Cl^- anion with potantiometric detector. The conductometric and potentiometric results were calculated for the anion contents of the samples (Table 2 and 3 and Figure 5).

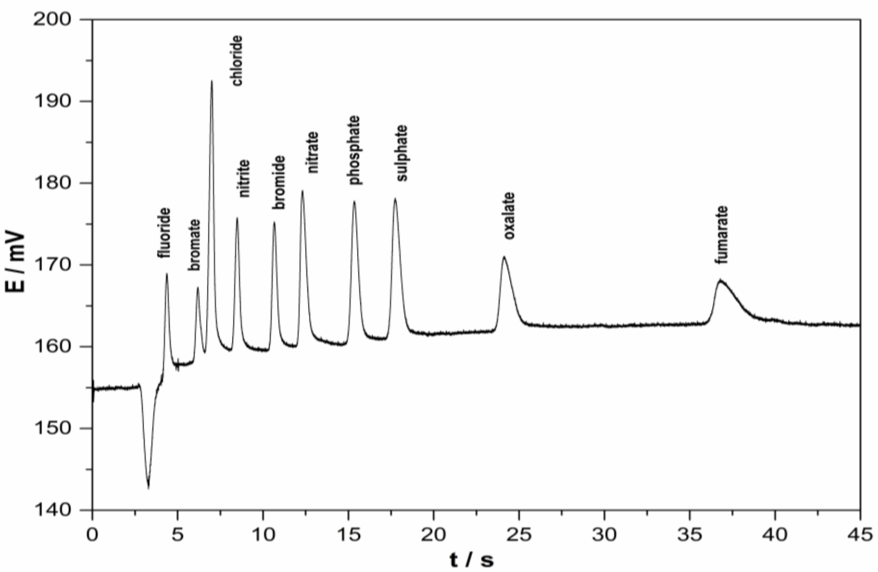


Figure 2. Potentiometric ion chromatogram for the standard anion mixture (fluoride, bromate, chloride, nitrite, bromide, nitrate, phosphate, sulfate, oxalate, fumarate)

Table 1. Retention times (t_R), determination constants (R^2) and detection limits (LOD)

Anion	**t_R(min)**	**R^2 (conductometric)**	**R^2 (potentiometric)**	**LOD* (conductometric)**	**LOD* (potentiometric)**
Fluoride	4.35	0.9991	0.9984	0.05	0.30
Bromate	6.15	0.9994	0.9904	0.24	4.94
Chloride	6.98	0.9993	0.9943	0.03	0.18
Nitrite	8.45	0.9973	0.9979	0.08	1.54
Bromide	10.62	0.9999	0.9926	0.08	1.50
Nitrate	12.25	0.9997	0.9915	0.08	1.25
Phosphate	15.32	0.9982	0.9901	0.13	2.21
Sulphate	17.69	0.9918	0.9913	0.08	2.06
Oxalate	24.06	0.9975	0.9921	0.40	9.52
Fumarate	36.75	0.9949	0.9918	0.52	12.23

*Results given S/N=3 as ppm

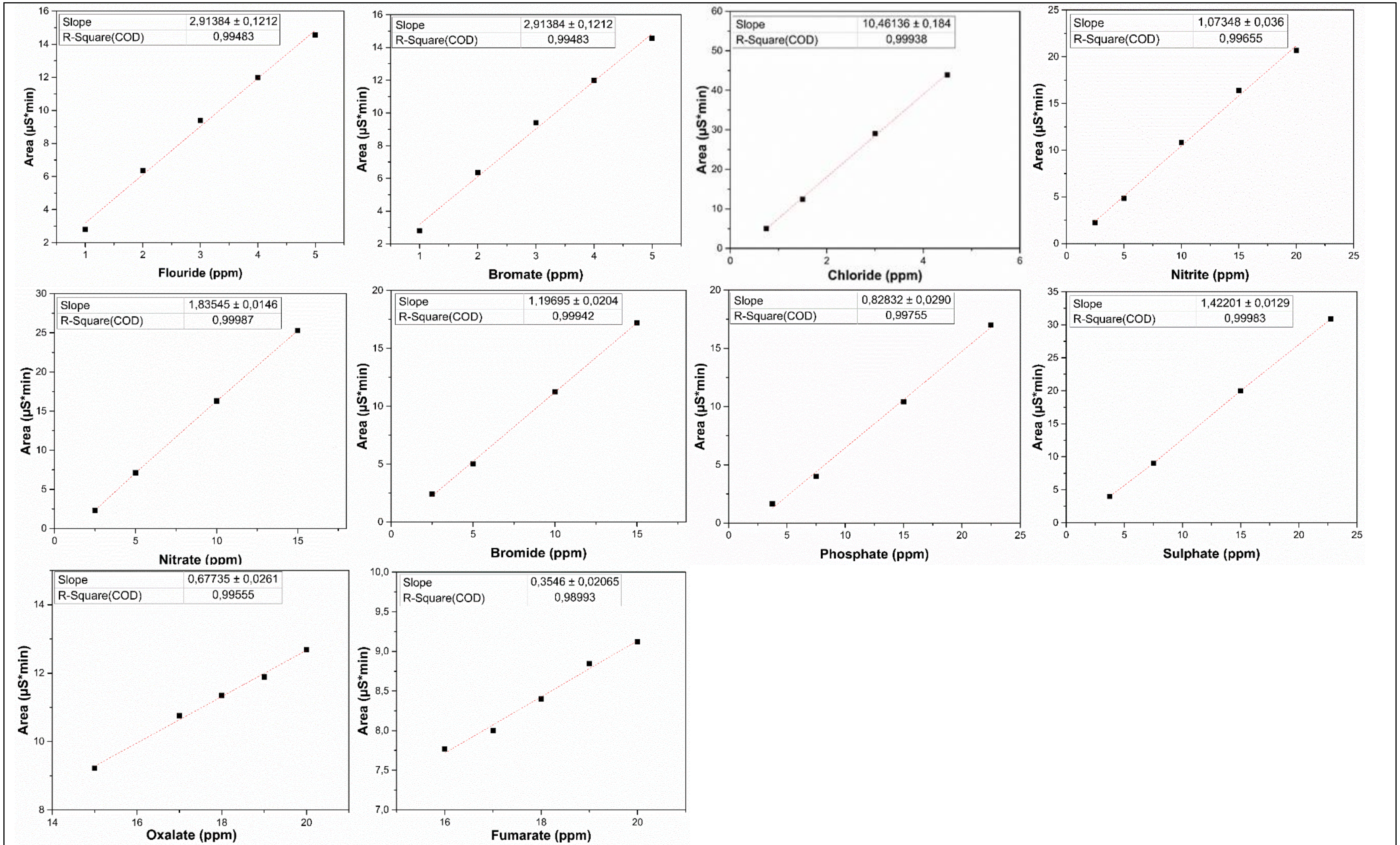
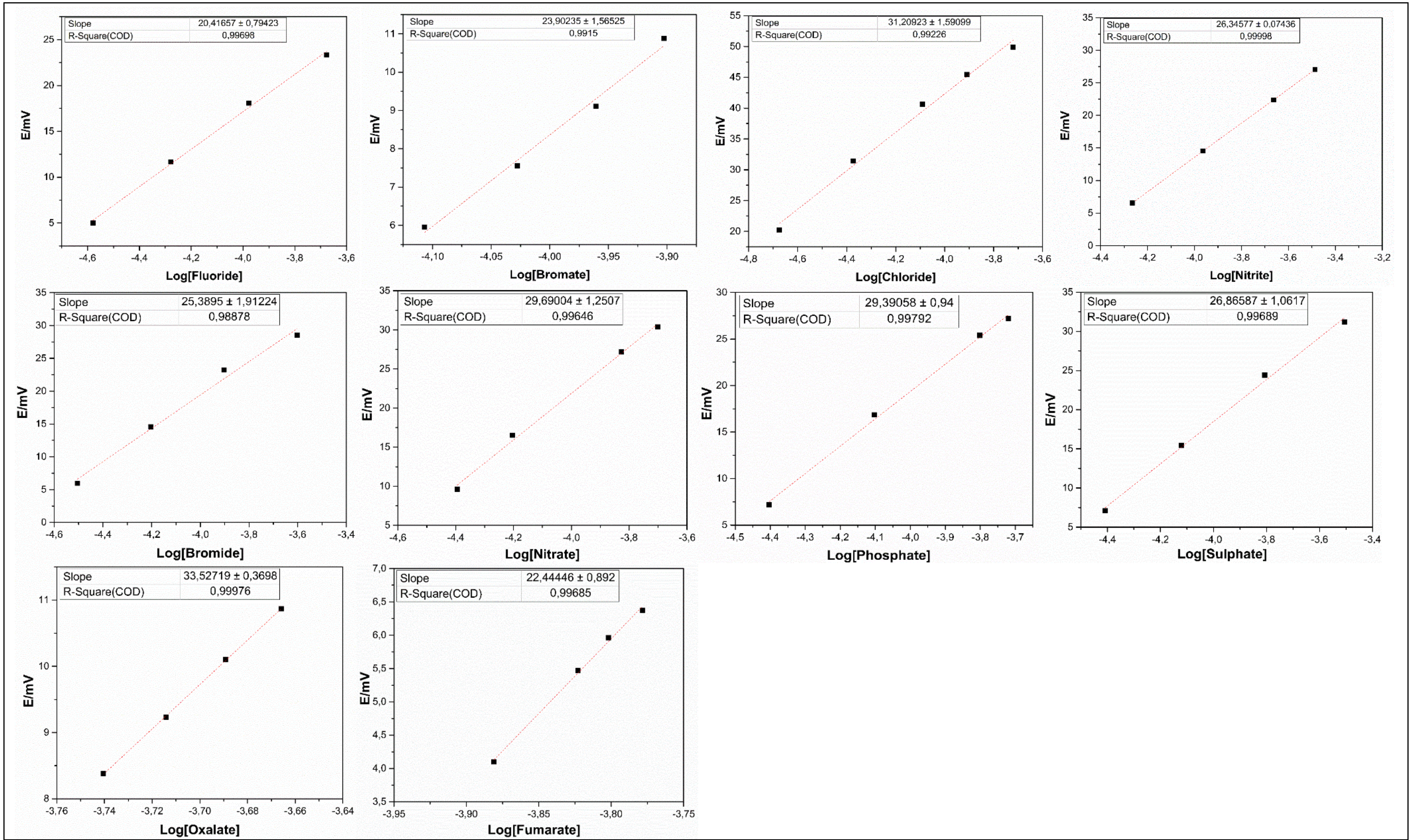


Figure 3. The calibration graphs for the anions by conductometric detection



0 **Figure 4.** The calibration graphs for the anions by potentiometric detection

It is seen that the calibration graphs, which were created using the chromatograms obtained from the consecutive injections of standard anion mixtures at varying concentrations, are highly linear (~R^2 = 0.999) for both conductometric and potentiometric detectors. It was concluded that these results were sufficiently linear for real sample analysis.

The conductometric and potentiometric results for anion contents of the samples are given in Table 2 and Table 3, respectively. As could be seen from the tables, fumarate was not detected in any sample.

For the water samples, fluoride was detected only in river water. Nitrite, bromide, phosphate and oxalate were not detected in any water sample. Bromate, chloride and nitrate were detected in all water samples. Sulfate was detected in all water samples except wastewater. The lowest and highest levels of anions determined by conductometric and potentiometric detections were in the range of 0.36±0.04-0.35±0.01 mg/L for fluoride in river water, and in the range of 3306.20±0.09-1189.75±2.80 mg/L for nitrate in wastewater, respectively.

For the plant samples, nitrite, bromide and nitrate were not detected in any plant sample. Fluoride and chloride were detected in all plant sample. Bromate was detected only in the stinging nettle sample. Phosphate and sulfate were detected in all plant samples except *Ornithogalum umbellatum L.* sample. Oxalate was detected in the *Smilax excelsa* and hazelnut sprout samples. The lowest levels of anions determined by conductometric and potentiometric detections were in the range of 26.14±0.51 – 8.72±0.09 mg/kg for fluoride in *Smilax Excelca,* respectively. The highest levels of anions determined by conductometric and potentiometric detections were 2345.16±7.02 mg/kg for phosphate in nut sproud and 3847.54±5.17 mg/kg for oxalate in *Smilax Excelca*, respectively.

For the soil samples, the bromide was not detected in the natural soil sample. Other anions were detected in both soil samples. The lowest and highest levels of anions determined by conductometric and potentiometric detections were in the range of 3.14±0.01 mg/kg - 2.45±0.04 mg/kg for fluoride in composed soil, and in the range of 169.61±1.72 mg/kg - 129.55±1.06 mg/kg for sulfate in composed soil, respectively.

There are various parallel studies in the literature. One application for this is in series nonsuppresor ion chromatography systems with flow cells [35]. Another one is a potentiometric and conductometric analysis of anions and cations using polypyrrole and overoxidised polypyrrole electrode [36]. In addition to the use of the electrode used in potentiometric detection and simultaneous detection of integrated ion chromatography, it is important to note that while the standard anion mixture contains 7 anion species, bromate, oxalate and fumarate were added to the mixture and a system was developed that contains 10 anion species and can detect all of them simultaneously, which makes our study special and subjective.

Table 2. The conductometric results for anion contents of the samples

Sample No	Sample Type	Anion Contents (ppm)*								
		F^-	BrO_3^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	$C_2O_4^{2-}$
1	Tap water	<LOD	3.18±0.05	2.92±0.10	-	-	4.84±0.19		66.64±2.38	-
2	Drinking water	-	0.37±0.01	0.42±0.01	-	-	1.55±0.03	-	6.77±0.16	-
3	Waste water	-	203.79±0.03	12.81±0.24	-	-	**3306.20±0.09**	-	-	-
4	River water	0.36±0.04	0.62±0.01	0.87±0.07	-	-	6.44±0.71	-	35.50±5.27	-
5	*Smilax Excelca*	26.14±0.51	-	159.07±0.94	-	-	-	1497.49±9.66	811.06±5.12	863.44±8.81
6	Hazelnut sproud	**770.13±0.94**	-	228.06±1.42	-	-	-	**2345.16±7.02**	**1309.61±6.74**	**1031.21±5.97**
7	*Ornithogalum Umbellatum L*	361.69±1.28	-	**1024.85±10.30**	-	-	-	-	-	-
8	Nettle plant	740.97±14.01	**1349.29±10.32**	356.61±8.01	-	-	-	314.89±7.53	778.11±12.52	-
9	Noncomposed soil	11.81±0.03	21.52±0.02	8.07±0.09	<LOD	-	14.27±0.18	26.0±0.33	169.61±1.72	26.13±0.08
10	Composed soil	3.14±0.01	22.14±0.79	6.60±0.02	3.61±0.03	6.15±0.07	7.82±0.06	19.20±0.07	128.85±0.02	26.92±0.18

*Mean values with standard deviations for N=3 (mg/L for water samples, mg/kg dry matter for plant and soil samples) The bolds have the highest value in the group

Table 3. The potentiometric results for anion contents of the samples

Sample No	Sample Type	Anion Contents (ppm)*								
		F^-	BrO_3^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	$C_2O_4^{2-}$
1	Tap water	<LOD	6.08±0.03	2.75±0.37	-	-	3.43±0.23	-	65.35±0.06	-
2	Drinking water	-	5.52±0.04	0.23±0.01	-	-	1.45±0.02	-	4.36±0.45	-
3	Waste water	-	156.79±1.77	5.97 ±0.10	-	-	**1189.75±2.80**	-	-	-
4	River water	0.35±0.01	5.90±0.02	0.43±0.03	-	-	3.35±0.10	-	21.73±1.62	-
5	*Smilax Excelca*	8.72±0.09	-	86.02±0.49	-	-	-	951.62±5.24	914.74±6.03	**3847.54±5.17**
6	Hazelnut sproud	440.95±3.12	-	119.97±2.84	-	-	-	**1463.37±5.72**	**1120.12±5.04**	3272.89±5.77
7	*Ornithogalum Umbellatum L*	263.09±3.61	-	**178.72±4.72**	-	-	-	-	-	-
8	Nettle plant	**1767.57±9.70**	**1430.41±6.01**	130.89±4.62	-	-	-	599.34±5.24	684.24±4.84	-
9	Noncomposed soil	4.47±0.09	37.19±0.15	4.41±0.07	<LOD	-	11.21±0.40	17.68±0.34	129.55±1.06	70.22±0.95
10	Composed soil	2.45±0.04	38.90±0.79	3.50±0.08	10.71±0.08	<LOD	9.42±0.25	15.63±0.04	81.98±0.66	69.54±0.40

*Mean values with standart deviations for N=3 (mg/L for water samples, mg/kg dry matter for plant and soil samples) The bolds have the highest value in the group

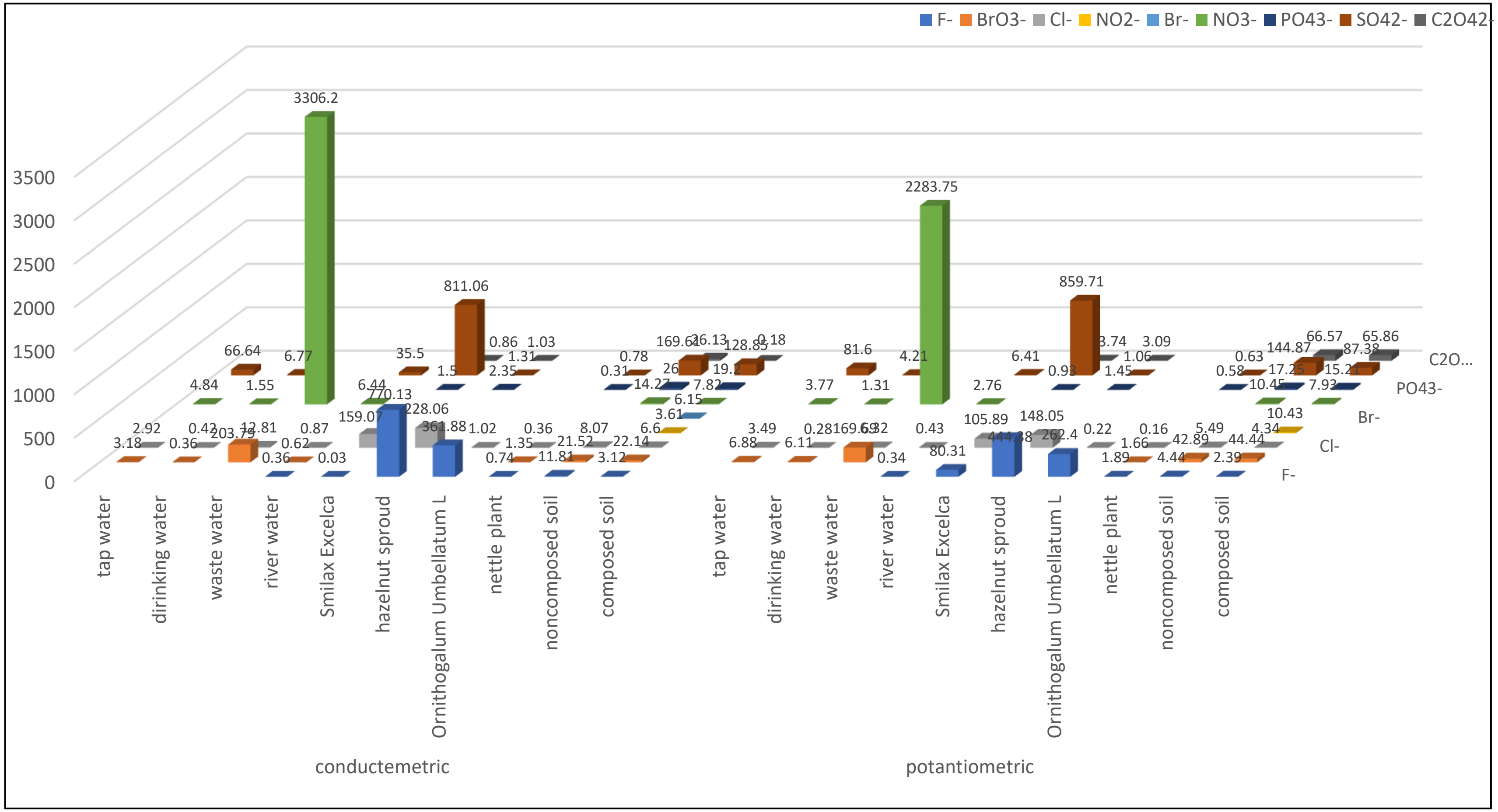


Figure 5. Column graph of anion values detected by conductometric and potentiometric detectors (ppm)

3.3. Statistical Analysis

The paired t-tests were applied to the ion chromatographic results obtained for the anion contents of the samples. For this purpose, the conductometric and potentiometric results were compared separately for each anion and the experimental t-values (Table 4) were calculated according to the equation given below.

$$t_{\text{exp}} = \frac{X_d - \mu}{S_d/\sqrt{N}}$$

Table 4. The paired t-test results for the anion contents of the samples

Anions	***t*-experimental ***	***t*-critical**	**N-1**
Florur	0.500	2.45	6
Bromate	0.804	2.45	6
Chloride	1.523	2.26	9
Nitrate	1.003	2.57	5
Phosphate	1.095	2.78	4
Sulphate	1.196	2.36	7
Oxalate	1.754	3.18	3

*Results are given in comparison with critical values at 95% confidence level (P=0.05) for N-1

As a result of the statistical analyzes (paired t-tests) made for the purpose of comparing the conductometric and potentiometric methods, it has been determined that the experimental t values calculated at the 95% confidence level are smaller than the critical t values. It was concluded that it is not significantly differences between the data obtained by potentiometric detection and the data obtained by conductometric detection, which is accepted as a reference method.

4. CONCLUSION

In this study, the performance of the flow-cell designed as a pH detector was tested in a batch conditions, and then simultaneous tests were carried out as a potentiometric detector in the ion chromatography system alongside the conductometric detector. Optimum operating conditions (eluent composition, flow rate, column, temperature, time, flow cell, etc.) have been studied in detail for this combined hybrid system. pH electrod based on Graphite/quinhydrone can be used for 60 days. As a result of the studies, an accurate, fast, simultaneous and reproducible conductometric-potentiometric hybrid analysis method has been developed for the anions (fluoride, bromate, chloride, nitrite, bromide, nitrate, phosphate, sulfate, oxalate, fumarate) found in the water, soil and plant samples. This method has advantages in terms of important parameters such as chemicals, solvents, column life, workmanship, and time etc.

Declarations of interest

The authors declare no conflict of interest in this reported work. The result in this article was derived from Elif Apaydın's doctoral thesis.

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