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Simultaneous Analysis of Monovalent Anions and Cations with a Sub-Microliter Dead-Volume Flow-Through Potentiometric Detector for Ion Chromatography

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Abstract

A microliter dead-volume flow-through cell as a potentiometric detector is described in this article for sensitive, selective and simultaneous detection of common monovalent anions and cations in single column ion chromatography for the first time. The detection cell consisted of less selective anion- and cation-selective composite membrane electrodes together with a solid-state composite matrix reference electrode. The simultaneous separation and sensitive detection of sodium (Na^+), potassium (K^+), ammonium (NH_4^+), chloride (Cl^-) and nitrate (NO_3^-) in a single run was achieved by using 98% 1.5 mM $MgSO_4$ and 2% acetonitrile eluent with a mixed-bed ion-exchange separation column without suppressor column system. The separation and simultaneous detection of the anions and cations were completed in 6 min at the eluent flow-rate of 0.8 mL/min. Detection limits, at S/N = 3, were ranged from 0.2 to 1.0 μM for the anions and 0.3 to 3.0 μM for the cations, respectively. The developed method was successfully applied to the simultaneous determination of monovalent anions and cations in several environmental and biological samples.

Introduction

Ion chromatography (IC) has become a fundamental analytical method since its introduction by Small *et al.* (1) owing to its wide applicability in determining of ionic species in various water samples (2). IC system based on conductivity detection is one of the most widely used methods (2–13). However, the limitations of the suppressor columns for IC have brought about interest in other means of detection types. IC with potentiometric detection using ion-selective electrodes (ISEs) enables the selective determination of analytes even in complex matrices. A limited number of articles have focused on this subject. Isildak and Asan (14) used poly(vinylchloride) (PVC) membrane electrodes for simultaneous determination of anions and cations in water samples. Lee *et al.* looked for such aforementioned possibilities, discussing various aspects of solid-state electrode (SSE)-array type IC detector systems fabricated with a liquid junction-free reference electrode based on a polyurethane membrane, and they also used IC for determination of some cations (15). Poels *et al.* used an ion-selective field effect transistor (ISFET)-based anion sensor with a PVC matrix membrane for the potentiometric detection of organic acids in liquid chromatography (16). Zielinska *et al.* employed PVC-based liquid membrane coated-wire electrodes, incorporating lipophilic macrocyclic hexaamines to detect carboxylic acids with ion-suppression liquid chromatography (17). Sahin *et al.* used polypyrrole and overoxidized polypyrrole electrodes as a potentiometric detector in IC, in order to

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determine some anions and cations in water samples (18). Akieh *et al.* suggested a mechanism for simultaneous monitoring of the transport of anions and cations across polypyrrole-based composite membranes (19). Isildak developed a simple method using suppressed IC with a pH detection unit to determine inorganic anions in mushrooms (20). Nuñez *et al.* developed an electronic tongue analysis system composed of an array of 15 potentiometric PVC membrane sensors sensitive to cations and anions plus an artificial neural network (ANN) response model for the monitoring of nitrogen stable species in water (21).

On the other side, there was a recognition that the routine separation and detection of common anions and cations at low levels in a simultaneous system is a useful goal for maximizing the overall efficiency of ion chromatographic procedures. Therefore, another area of IC that holds a particular promise for further improvements in ion determination is the achievement of simultaneous analysis of common anions and cations. The main drawback to simultaneous detection of a large variety of anions and cations is nonspecificity of most detection methods used in simultaneous determination. However, simultaneous determination of anions and cations using IC in a single column might not be achieved with suppressed conductivity detection (22, 23). In suppressed conductivity detection, the detector response usually depends on eluent's background conductivity. Anions are normally detected directly as positive peaks in the case of acidic eluents studied, while cations produce negatives peaks by displacement of highly conductive hydronium cations from the eluent, which are detected indirectly (24). Therefore, several other approaches have been envisaged for simultaneous determination of anions and cations. Tandem chromatography is one choice but that doubles the output of high-performance liquid chromatography (HPLC) equipment by simultaneously carrying out two different analyses on the same sample. The sample was split into two at the injection port, and each sample was eluted on a different column, and simultaneous analysis of anions and cations was achieved in tandem mode (25). Potentially, the most straightforward approach is a single channel system in which an anion- and a cation-exchange columns connected in series or a mixed-bed column, which can be used with an eluent that is compatible with the columns (26–28). An outstanding method developed by the present author, in which the simultaneous determination of 14 inorganic and organic anions and cations at sub-ppb levels was demonstrated by using anion- and cation-exchange columns in series (29) or, mixed-bed columns (14), with two all solid-state contact tubular liquid membrane electrodes as detectors in IC.

Miniaturization is also important when the sample volume is insufficient. Microliter dead-volume flow-through cells are necessary for low detection limits. These have particularly attractive advantages in scenarios involving a very small sample volume for detection, such as in open-tubular micro capillary liquid chromatography (30, 31). One of the advantages of using ISEs as detectors in IC could be the flexibility and permeability in the use of different solutions as eluents for isocratic separations. This is important as most of the desired separations and detections could be achieved with the correct combination of eluent, stationary phase and detection cell. On the other hand, the use of potentiometric detection system could enable elimination of the suppressor system that is mainly required in the mode of conductometric detection of IC. However, in this study, a microliter dead-volume flow-through cell as a potentiometric detector was described for sensitive, selective and simultaneous detection of common monovalent anions and cations in single column IC for the first time. The detection cell was consisted of micro-sized monovalent anion- and cation-selective membrane electrodes and a solid-state composite matrix Ag/AgCl reference electrode. The simultaneous separation and sensitive detection of sodium (Na^+), potassium (K^+), ammonium (NH_4^+), chloride (Cl^-) and nitrate (NO_3^-) in a single run was achieved by using 98% 1.5 mM $MgSO_4$ and 2% acetonitrile eluent with Dionex Ion Pac-CS5 analytical and -CG5 guard mixed-bed columns without suppressor column system. The method developed was successfully applied to sweat, salivary, river, pond, tap and highland water samples.

Experimental

Reagents and solutions

Tetrahydrofuran (THF), high molecular weight PVC, *o*-nitrophenyl octyl ether (NPOE), potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB), tetradodecyl ammonium chloride (TDDA-Cl), dibenzo18-crown-6 (DB18-C6), other chemicals used for preparation of sensing membrane and graphite were obtained from Fluka (Bucks, Switzerland), and dibutylphthalate (DBP) was obtained from Aldrich. The polycarbonate block was obtained from Bayer AG (Darmstadt, Germany). All standard solutions of anions, cations and eluents were prepared from their analytical reagent grade chemicals in deionized and distilled water, and then diluted to the desired concentrations. Samples of river, sea and drinking water taken from local areas in Samsun, Turkey, and were diluted with deionized water if necessary before use.

Construction of a microliter dead-volume flow-through cell and electrodes

An almost 2-µl dead-volume flow-through cell was constructed by the placement of composite membrane electrodes in a polycarbonate detection cell fabricated in the lab. The PVC membrane composition for anion-sensitive electrode consisting of 31% PVC, 4% TDDA-Cl and 65% DBP was prepared in ~3 mL THF. Then, 40% of this membrane cocktail and 60% of graphite as harmonic proportions were mixed to get the composite membrane mixture. The sandpapered tip of the copper wire was dipped into this mixture two to three times. The cation-sensitive electrode membrane was prepared in the similar manner to the anion-sensitive electrode. The PVC membrane composition of the cation-sensitive electrode was 30% PVC, 4% DB18-C6 and 65% NPOE, and 1% KTpClPB. KTpClPB was added as the reducer of the membrane resistivity. The coated electrode surfaces were left to be dried in dark overnight. Finally, the dried micro-sized electrodes were conditioned in 10^{-1} mol L^{-1} NaCl solution for at least 12 h before use. The electrodes prepared were placed into the holes of a 2 × 2.5 × 1-cm sized polycarbonate block. The holes were drilled with a brace in an appropriate size for the electrodes. The tubular detection cell having a flow-line of almost 3 µL dead-volume and ~0.4 mm in diameter and 2.5 cm in length (see Fig. 1). The microliter dead-volume flow-through cell also contained a micro-sized silver/silver chloride reference electrode.

Ion chromatography system

Chromatography was performed using a quadripartite channel pump and injection valve with a 10 µL sample loop of a spectra series P100 high-performance liquid chromatograph (HPLC). Separations were performed using magnesium sulfate as eluent on Dionex Ion Pac-CS5 analytical and -CG5 guard mixed-bed columns. The flow-through detection cell including the anion- and cation-sensitive electrodes and the micro-sized silver/silver chloride reference electrode were placed immediately after the end of the analytical separation column for the simultaneous detection of anions and cations. Measurements were recorded using a laboratory-made computer-controlled high-input impedance multi-channel potentiometric measurement system. The experimental

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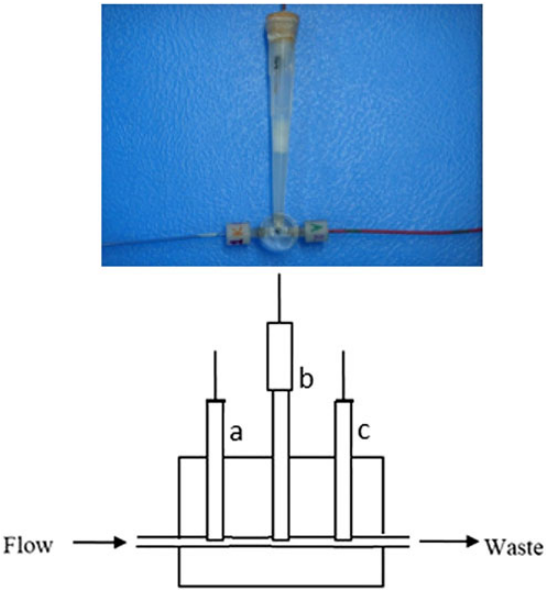


Figure 1. Schematic representation of microliter dead volume flow-through cell (a) composite membrane cation-sensitive electrode, (b) composite membrane anion-sensitive electrode and (c) micro-sized composite Ag/AgCl reference electrode. This figure is available in black and white in print and in color at *JCS* online.

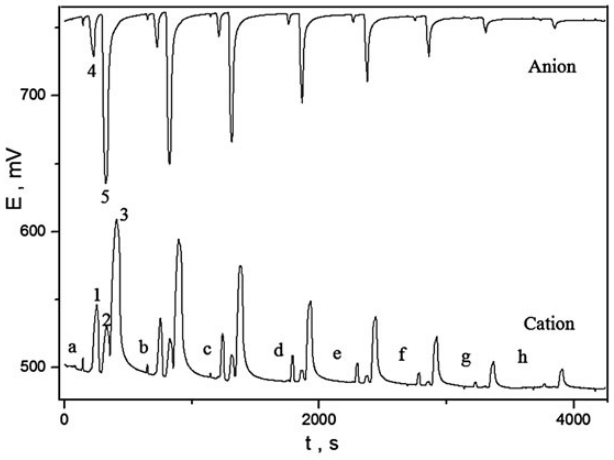


Figure 2. Examples of successive separation and simultaneous detection of anions and cations at different concentrations of standard ion solutions. Column; Dionex Ion Pac-CS5, eluent; 98% 1.5 mM $MgSO_4$ and 2% acetonitrile, flow rate; 0.8 mL/min, injection volume; 10 µL, ions; 1: Na^+, 2: NH_4^+, 3: K^+, 4: Cl^-, 5: NO_3^-. Ion concentrations; a: 1×10^{-2} M, b: 6×10^{-3} M, c: 3×10^{-3} M, d: 1×10^{-3} M, e: 6×10^{-4} M, f: 3×10^{-4} M, g: 1×10^{-4} M, h: 6×10^{-5} M. These concentrations (a–h) were injected consecutively for each anion and cation (1–5) in the chromatograms.

conditions for IC were as follows; eluent flow-rate was 0.8 mL/min and eluent composition was 98% 1.5 mM $MgSO_4$ and 2% acetonitrile. The separation and detection efficiency with synthetic samples was tested for 30 times, and the results were obtained at 95% confidence intervals.

Results

Simultaneous separation and determination of anions and cations

The use of flow injection analysis (FIA) enables the automation of certain ISE methods of analysis, although still only for one analyte at a time. Furthermore, many of these methods suffer from interferences and limited sensitivity, and they can be labor intensive and are often difficult to automate (32). Multiple analytes can be determined by adding additional channels to an FIA system; however, this adds complexity and cost to the instrumentation. Highly selective solvent polymeric ISEs are now routinely used as flow-through detectors for accurate and rapid determination of various ionic species in IC (33, 34). However, direct application of such ISEs to IC systems could not allow the detection of different ions with comparable detectabilities. To balance the detectability of different ions, several different cation ionophores such as valinomycin, nonactin and tetranactin (33) or the use of a less selective ionophore in conjunction with selection of an appropriate plasticizer (34) were examined. It is well known that IC with potentiometric detection combines the advantages of the sensitivity of flow injection analysis with the selectivity freedom from interferences of chromatography. In principle, the routine separation and detection of common monovalent anions and cations at low levels in a simultaneous system is a useful goal for maximizing the overall efficiency of ion chromatographic procedures. However, the present ion chromatography method developed here consisted of micro-sized composite membrane anion- and cation-sensitive electrodes together with a solid-state composite matrix reference electrode for simultaneous detection of common monovalent anions and cations.

The selection of an eluent is important to the success of simultaneous determination of anions and cations using a mixed-bed column and potentiometric detection in IC. In IC employing a potentiometric detector, strength of detector response is based upon the selectivity of the electrode membrane between the eluent ion and the analyte ion. The strength of detector response toward an analyte ion will be much higher if the electrode membrane selective to an analyte ion than that of an eluent ion. If the vice versa is true, there will be no detector response for the analyte ion. As the electrodes prepared here were highly selective to monovalent anions and cations, several polyvalent anions and cations as eluent components were tried. After many trials, $MgSO_4$ were selected as the proper component of the eluent. However during the study, 98% 1.5 mM $MgSO_4$ and 2% acetonitrile mixture as the eluent composition were maintained for the successive elution and sensitive detection of monovalent anions and cations studied. With this eluent, the ions were independently separated and detected using the monovalent anion- and cation-selective composite membrane electrodes at the end of the mixed-bed separation column. The time required for the complete separation of anions and cations was about 6 min with the eluent at the flow-rate of 0.8 mL min^{-1}. Standard solutions of sodium (Na^+), potassium (K^+), ammonium (NH_4^+), chloride (Cl^-) and nitrate (NO_3^-) prepared in the concentration range from 1×10^{-2} to 6×10^{-6} mol L^{-1} were injected into the simultaneous analysis system. Chromatograms obtained from the concessive injections of standard solutions are given in Figure 2. Calibration graphs were constructed by plotting peak height against concentration of the anions and cations under the optimum conditions (Supplementary Figure S1). The repeatability of the separation was moderately good, i.e., relative standard deviations for the retention times of ions varied from 0.3 to 1.6% for n: 8 at 95% confidence. When the concentrations of the ions were low, the standard deviations were small. In the ion chromatographic system, the retention times for each of the anions and cations was calculated using chromatograms produced as a result of 10 µL sample injection. The

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Table I. Calibration Response Equations, Detection Limits and Retention Times of Monovalent Anions and Cations Studied in the Simultaneous Analysis System

Ions	Sodium (Na^+)	Potassium (K^+)	Ammonium (NH_4^+)	Chloride (Cl^-)	Nitrate (NO_3^-)
Detection limit (mol L^{-1})[a]	3×10^{-6}	1×10^{-6}	3×10^{-5}	2×10^{-5}	1×10^{-6}
Retention times (min)[b]	3.0 ± 0.1	5.3 ± 0.3	4.2 ± 0.2	2.4 ± 0.1	4.2 ± 0.2
Calibration response equations and the correlation coefficients	$y = 12.438x + 54.254$ $r = 0.9727$	$y = 36.944x + 168.07$ $r = 0.9904$	$y = 20.175x + 71.064$ $r = 0.974$	$y = 18.952x + 59.284$ $r = 0.991$	$y = 58.614x + 240.39$ $r = 0.9921$

[a]Calculated at S/N = 3.
[b](n: 8 at 95% confidence).

values were given as means ± SD, and the means are produced from three replicates. The retention time and peak height precisions (expressed as % RSD) were determined from three replicate injections of standard samples of mixed ions. Under the optimum ion chromatographic conditions, a linear response was obtained in the concentration range of 1×10^{-2} and 5×10^{-5} mol L^{-1} for each ion, respectively. The limits of detections (LODs) were calculated from the solution concentrations at a signal-to-noise (S/N) ratio of three standard solutions. The detection limit essentially depends on the ability to prepare low level standard samples and handle samples without contamination. The sensitivity of most constructed detectors remained almost constant for at least 2 months. The repeatability of peak heights for repeated injections of all anions and cations was generally better than 2% of the coefficient of variation. Under optimized conditions, the detection limits for all the ions, defined as the amount for a S/N ratio of 3, were of order of few ppm for an injected volume of 10 µL. The reproducibility of peak heights for repeated injections of all anions at all concentrations was generally better than 2%. Some of the reasons for good reproducibility of potential response might be the continuous washing of membrane surface of the electrode with fresh eluent solution, the nature of the eluent and membrane, lack of sample contamination and the design of the detector cell. The selectivity of the all solid-state contact PVC-matrix membrane electrode toward monovalent ions resulted in polyvalent ions being undetected. This can be called monovalent ion-selective detection. The monovalent ion selectivity of the electrode detector can be explained by the ion-exchange process taking place between the free ions in the eluent and the ions bound to the organic site groups in the membranes. When the selectivity is too high toward an ion, the organic ion-exchanger forms a more stable complex with the particular ion in the eluent than with any other ion. Since the ionophores used in the membranes function as a dissociated ion-exchanger for monovalent ions, equilibrium of ion extraction into the membrane is based solely on the difference between the free energy of solvation of the ions in the eluent and in the organic membrane phases. Calibration response equations, detection limits and retention times are summarized in Table I.

It is interesting that the method requires separations of anions and cations independently as there is no interference in the detection for anions from cations or for cations from anions in the ranges studied, and is unlike to most of other simultaneous determination methods in which anions and cations must be separated from each other during the run makes separation difficult and time consuming (22, 23). In the determination, no overlap problem arises when the retention time of a cation is equal to that of anion, i.e., no need to provide better resolution between the cations and anions makes separation easy and less time consuming.

The analysis of salivary, sweat and water samples

The potential application of the developed method was shown for the analysis of sodium (Na^+), potassium (K^+), ammonium (NH_4^+), chloride (Cl^-) and nitrate (NO_3^-) species which are usually found in saliva, sweat and environmental water samples. Assessment of the reproducibility parameters based on the samples was conducted producing % RSD values below 2% for retention time and up to 5% for peak heights measured. Chromatograms obtained from the real sample applications are represented in Figure 3. For each ion, calibration curves were obtained from the peak heights of the chromatogram obtained, and from these curves, the contents of each ion in the analyzed sample were determined. The analytical results for the samples are listed in Table II. The data in Table II compared with the data in similar literature were found reasonable (35–39).

Discussion

In this study, a microliter dead-volume flow-through cell as a potentiometric detector was described for sensitive, selective and simultaneous detection of common monovalent anions and cations in single column IC. The results obtained from the developed simultaneous detection system exhibited high selectivity and reasonable sensitivity for the ions that are usually present in the environmental and biological samples. The method required no pretreatment step and exhibited high selectivity toward monovalent anions and cations such as Na^+, K^+, NH_4^+, Cl^- and NO_3^- in the presence of many interfering ions. It required a small sample volume of 10 µL or less and was capable of high analytical throughput almost 8 min for per sample. The method exhibited good response stability of almost 4 mV for 10 successive injections, low cost and simple equipment and applicability of wide range of ion concentrations (1×10^{-2}–6×10^{-5}) with detection limits ranged from 0.2 to 1.0 µM for the anions and 0.3 to 3.0 µM for the cations respectively, at S/N = 3. The chromatographic results reveal that the developed method was successively applied to the sensitive, selective and simultaneous determination of sodium (Na^+), potassium (K^+), ammonium (NH_4^+), chloride (Cl^-) and nitrate (NO_3^-) in the environmental and biological samples.

Conclusion

A high speed single column IC-potentiometry system has been developed by bringing the correct combination of an eluent–column–detector trios which is critical for the success of sensitive, selective and simultaneous determination of common anions and cations. The use of the micro-sized composite membrane electrodes within the detection cell made it possible to minimize the potentiometric detector system of IC. The developed system does not require the suppressor column that

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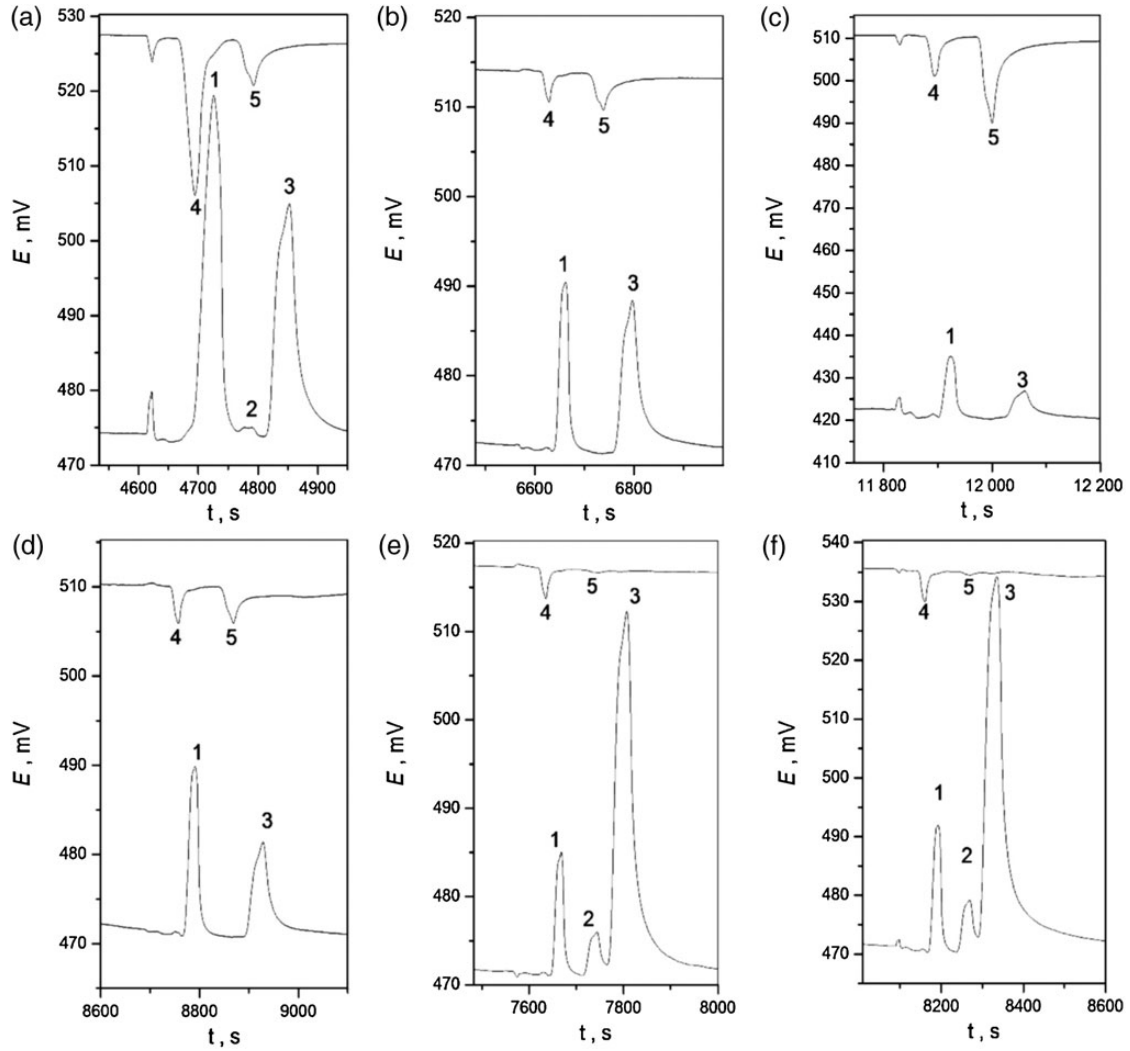


Figure 3. Chromatograms of (a) Kurtun river, (b) Pond water, (c) Tap water, (d) Highland water, (e) 1:30 diluted salivary and (f) 1:30 diluted sweat. The other chromatographic conditions were similar as in Figure 2. Peaks of anions and cations: (1) Na^+, (2) NH_4^+, (3) K^+, (4) Cl^- and (5) NO_3^-.

Table II. Concentrations of Monovalent Anions and Cations in Environmental and Biological Samples Obtained With the Ion Chromatography and Potentiometry Hybrid System

Sample	Concentration of cations and anions found in real samples (mg L^{-1})				
	Sodium (Na^+)	Potassium (K^+)	Ammonium (NH_4^+)	Chloride (Cl^-)	Nitrate (NO_3^-)
River water	5,302.186 ± 31.23	7.67 ± 0.25	5.72 ± 0.02	369.26 ± 29.54	6.24 ± 0.10
Pond water	29.79 ± 1.15	3.18 ± 0.05	<LOD	38.74 ± 1.39	5.75 ± 0.12
Tap water	14.66 ± 0.50	1.63 ± 0.07	<LOD	92.98 ± 10.17	8.95 ± 0.27
Highland water	30.07 ± 1.37	2.12 ± 0.31	<LOD	44.75 ± 1.91	5.70 ± 0.07
Sweat	1,517.59 ± 32.14	1,574.29 ± 52.19	443.73 ± 11.34	1,474.01 ± 51.00	150.85 ± 0.28
Saliva	364.82 ± 10.99	429 ± 13.42	283.68 ± 5.02	1,245.20 ± 53.07	149.26 ± 0.17

opens up the use of new type of eluents for more efficient elution of anions and cations in IC. The method required separations of anions and cations independently as there was no interference in the detection for anions from cations or for cations from anions in the ranges studied. The system is simple and cheap, and allows rapid and sensitive determination of common monovalent anions and cations simultaneously for several sample matrices. This fast, sensitive and accurate determination method would further be developed for in-place and in-time analysis of water samples where faster measurement needed.

Supplementary material

Supplementary materials are available at *Journal of Chromatographic Science* (http://chromsci.oxfordjournals.org).

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