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Review

Applications of column liquid chromatography to inorganic analysis in agricultural research

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Abstract

Plants absorb their nutrients from soil as inorganic species. Therefore, inorganic assay is of utmost importance in agricultural research. Liquid column chromatography has developed into a powerful analytical tool for inorganic assay during the last two decades. Speed of analysis, simultaneous analysis of several species, low detection limits, high precision, small sample requirements, high reliability, versatility, automation and reasonable cost are some of the reasons for its popularity. New developments in column chemistries and engineering and more sophisticated hardware has been continually expanding its scope. This paper describes the applications of this technology in agricultural research. © 1997 Elsevier Science B.V.

Keywords: Reviews; Inorganic anions; Inorganic cations; Heavy metals

Contents

1. Introduction

Many inorganic species serve as the ‘‘raw materials’’ for agriculture. For example, the three elements required by plants in large quantities, nitrogen, phosphorus and potassium, are absorbed from soils as inorganic ions and are applied by farmers as fertilizers. Clearly, inorganic assay technology is of great importance to agriculture.

The use of column liquid chromatography (CLC) in agriculture, especially for inorganic assay, did not start until the late 1970s. The advent of high-performance liquid chromatography (HPLC) in the mid-1970s coupled with the novel ion-exchange chroma-

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tography method of Small et al. [1], revolutionized the role of CLC in inorganic analysis. The advances made in the microprocessor technology during the 1980s added a new dimension and provided another major boost to the technique via a more reliable and sensitive instrument design. Consequently, many tedious, cumbersome and labor-intensive wet-chemistry techniques have now been replaced by CLC. Versatility, simultaneous multi-component analysis, high precision and speed of analysis, automation, several modes of detection, small sample size requirement and reasonable cost are some of the factors that have contributed to the popularity of the CLC. Bulk of the CLC in use today is primarily practiced as HPLC and has now been utilized by agricultural scientists for the assay of many inorganic solutes in a variety of matrices, materials, and situations, including but not limited to, soil and soil amendments, irrigation, run-off, and rain waters, plants, food and feed items and fertilizers. Continued innovations and developments in column engineering and instrumentation design have continually enlarged the HPLC scope and hence its popularity. The objective of this paper is to describe some of the HPLC applications (including ion chromatography) that have been used in agricultural research.

2. General methodology

Most, if not all, inorganic species important in agriculture may exist as ions. Since many inorganic ions lack suitable chromophores, electrical conductivity (EC) has been used as the main mode of detection although UV absorbance has also been used in some applications. Hence, the inorganic ions have largely been assayed either by the suppressed ion chromatography (SIC) where the analytical column is followed by a second column used for suppressing the background EC of the eluent [1] or by the single-column ion chromatography (SCIC) where eluents of low EC are used [2–6]. Due to suppression of the background EC of affluents, the detection in SIC occurs at a lower background EC which results in a greater sensitivity of analysis. However, the EC suppression column represents added cost and may also cause additional band-broadening and hence, lower the column efficiency [7]. When the analyte detection is done using modes other than conductivity (e.g., UV absorbance), the background EC of the eluent is generally not a consideration.

3. Assay of inorganic anions

The practical development and usage of inorganic anion analysis using CLC seems to have far preceded and exceeded that of inorganic cations, even though the novel ion chromatography technique reported by Small et al. [1] was equally applicable to both. The assay of common inorganic anions, such as, chloride, fluoride, nitrite, nitrate, phosphate and sulfate represents the single biggest application of CLC in agricultural research. Currently, the method is considered a routine and the SIC has been approved for use by many different agencies, including the US Environmental Protection Agency (US EPA method 300.0).

Nitrogen is perhaps the single most important factor that determines crop yields in modern agriculture. The bulk of nitrogen taken up by plants is in the form of nitrate ions. Being a highly water soluble anion, nitrate may also readily leach into the ground water which has caused widespread concern of the potential pollution. Obviously, the assay of nitrate ion is of paramount importance in agriculture. Dick and Tabatabai [8] reported that SIC was highly suitable for the assay of nitrate and sulfate in soil extracts; a number of advantages over wet-chemistry methods were cited. However, sample matrix seemed to have a major effect: calcium acetate as extractant resulted in the best separation relative to calcium phosphate or calcium chloride. The method was shown to be linear up to 5 mg/l of nitrate-N or sulfate-S.

Fortunately, nitrate and nitrite ions possess chromophores that absorb UV radiation in the 210 nm region which makes it suitable for detection by a spectrophotometric detector. Thayer and Huffaker [9] reported a method of separating both nitrate and nitrite by using a silica-based anion-exchange column followed by its detection with UV absorbance at 210 nm. The UV detection permitted the use of a stronger eluent with higher EC (e.g., 40 m*M* K-PO_4) and of a column that was relatively a stronger anion exchanger. Naturally, the system would be much less

prone to sample matrix problems as compared to ion chromatography systems (both SIC or SCIC). In this author's opinion, the UV method of Thayer and Huffaker [9] has proved to be superior for nitrite and nitrate assay in water samples and soil and plant extracts over SIC or SCIC; a 100×4.6 mm column is generally sufficient for baseline separation of nitrate from a variety of matrices. It must, however, be emphasized that SIC or SCIC have the added advantage of simultaneous analysis of several other anions which the UV method does not.

Tabatabai and Dick [10] reported a close agreement between SIC and the wet-chemistry methods for measuring nitrate, chloride, sulfate and phosphate in soil extracts and waters. Another study [7] evaluated the potential of SCIC for assaying chloride, nitrite, bromide, nitrate, iodide, chlorate, sulfate and sulfite in soil extracts. The results obtained with SCIC were also in close agreement with those obtained with other methods. The SCIC method was shown to be highly reproducible and sensitive with detection limits of 0.025 mg/l for chloride, bromide, nitrate-N and sulfate-S and of 1.0 mg/l for nitrite-N and sulfite-S. The CLC techniques offered the added advantage of simultaneous multi-ion analysis, speed, sensitivity and small sample size requirement. The use of a octadecyl reversed-phase column with aqueous phosphoric acid–dihydrogenphosphate eluent was proposed by Schroeder [11]. Nitrate was also separated with mobile phase ion chromatography using 2 m*M* tetrabutylammonium hydroxide in 0.05 m*M* sodium carbonate+10% acetonitrile as the mobile phase and detected with a conductivity detector [12]. However, the latter two techniques seem to have found little application in agricultural research.

Many metalloids, especially selenium and arsenic and their derivatives can widely spread throughout the environment due to various processes including the agricultural and natural processes [13]. Both selenium and arsenic are found in soils of many regions and are available for plant uptake and therefore can spread through the food-chain. Although selenium is considered an essential element for many animal species, the difference between essential and toxic levels is rather narrow [14]. Commonly, these ions have been assayed by using: (1) atomic absorption spectroscopy (AAS) with hydride generation [15–17], (2) fluorescence spectrophotometry [18,19], (3) inductively coupled plasma atomic emission spectrometry (ICP-AES) [20–22], (4) neutron activation analysis [23,24], (5) electrothermal graphite furnace [25] and spectrophotometry [26–28]. The inorganic form of both of these elements can exist in two oxidation states, i.e., Se(IV), Se(VI), As(III) and As(V). Since the chemical properties and the ecological fate is determined by the oxidation state, the speciation becomes important. Most of these methods have serious shortcomings. For example, because of their specificity for selenate, acid reduction is required by most methods and after quantifying total selenium by prereduction, selenate is actually estimated by difference [29]. In the hydride generation methods, the oxidative treatment with potassium permanganate destroys the natural distribution of selenium species [30]. The hydride generation technique is also subject to interferences from other elements such as iron and copper [31]. Both SIC [17,32] and SCIC [29,33,34] have been used for the analysis of selenate and selenite. However, sample matrix interference by chloride and sulfate ions has been a serious problem in selenite and selenate analysis by the CLC methods. For example, with SIC, 50 mg/l background sulfate resulted in very poor resolution of selenate [32]. In SCIC, 80 mg/l sulfate background reduced the recovery of selenate to only 58% [29] and chloride above 10 mg/l masked the selenite peak [33]. The US EPA reported [32] that in order to lower the sulfate interference in selenate analysis with chromatography techniques, the samples must be pretreated with barium hydroxide. Chloride ions interfering with selenite analysis in SCIC had to be removed by treating the samples with silver-saturated cation-exchange resin [33]. Matrix problems in soil extracts were avoided by derivatizing selenite with 2,3-diaminonaphthalene (DAN) and its subsequent extraction in cyclohexane. The resulting selenite derivative was separated on a silica gel column and detected fluorometrically [35]. Selenate could be measured after its reduction to selenite after an acid treatment.

Arsenate in waters has been assayed using SIC [36]. Mehra and Frankenberger, Jr. [37] reported the use of SCIC coupled with conductivity detection for the assay of arsenate with detection limits of 1430

and 92 mg/l using a sample size of 0.10 and 2.0 ml, respectively.

Electrical conductivity has been the main mode of detection for the inorganic species. However, some species, such as arsenite, can not be detected using conductivity detection. On the other hand, many inorganic species do have suitable chromophores and hence can be detected using UV absorbance detectors [38]. Therefore, the use of UV absorbance detection instead of conductivity detection may provide a useful tool with added selectivity and be able to attenuate, or even eliminate, some interferences caused by sample matrices. Goyal et al. [39] reported a SIC method using UV absorbance detection for the simultaneous assay of arsenite, arsenate, selenate and selenite in waters. Since sulfate does not absorb in the UV region, both selenate and arsenate could be separated and reliably quantified in the presence of very high sulfate concentrations of up to 2000 mg/l. The method was linear over the tested range of 0–5 mg/l with detection limits of 0.1 mg/l for arsenite and selenite and of 0.25 mg/l for arsenate and selenate, using a 0.1 ml sample size. The chloride interference was not tested, however, mainly because the simplicity with which it can be removed from samples by using cation-exchange resin in silver form [33].

Sulfur is not only an essential element for plants but is required in significantly large quantities. Poulson and Borg [40] investigated the possibilities of assaying five sulfur-containing inorganic anions (sulfide, sulfite, sulfate, thiosulfate and thiocyanate) using SCIC. The use of a resin-based anion-exchange column and the gluconate–borate eluent allowed the separation of sulfite and sulfate or thiosulfate and thiocyanate from sulfide. The authors felt that with the use of this eluent and UV absorbance detection of sulfide and electrochemical discrimination of sulfite and sulfate, a single run could be used to differentiate all five anions.

An assay of total content of any element in plant or soil materials generally requires that all organic bonds of the element be destroyed. In some cases (e.g., nitrogen and sulfur), the element must also be converted to a chemical form that can be readily assayed and quantified. For total sulfur analysis, all forms of sulfur in the sample must either be converted to sulfate ions by acid digestion or to sulfide by reduction. None of the procedures would yield a sample suitable for analysis by CLC because of high background ion concentration. To avoid the problem of high sample ion background, some workers resorted to burning the sample in an oxygen atmosphere with no excess ionic material [41,42]. Combustion of samples by using oxygen flask is tedious, time-consuming, difficult to automate and potentially dangerous. Hafez et al. [43] were able to use SIC for the assay of total sulfur as sulfate in plant materials that were digested with concentrated nitric and perchloric acids. In order to eliminate the excessive ionic background, the acid digests were evaporated to dryness. However, it was not possible to eliminate perchlorate ions entirely. While the residual perchlorate ions were not a problem in SIC on a Dionex anion-exchange column (AS4A), the elution of perchlorate peak took in excess of 50 min. Attempts to overlap injections were unsuccessful due to excessive band-width of the perchlorate peak owing to its long retention time. The problem of a long total analysis time (about 60 min) precluded the method from a routine use. In the meantime, Dionex (Sunyvale, CA, USA) introduced a multi-substrate anion-exchange column (Omni Pac-PAX 500) which had a polymeric hydrophobic surface core with an ion-exchange polymeric colloid attached to it. Basically, this column had both anion-exchange and reversed-phase partition activities, concurrently. Since perchloric ions were much less polar than other inorganic anions in the samples, its retention on the column could be easily manipulated by organic solvents, such as acetonitrile. An eluent containing 25 m*M* sodium hydroxide and 45% acetonitrile was able to provide a baseline separation of sulfate and elute the perchlorate peak as well, in 10 min. The method was shown to be highly reproducible and was validated by the analysis of several certified reference materials.

Tungstate and molybdate in waters have been analyzed by using SIC [44], with a detection limit of 1 μg/l after a 100-fold pre-concentration of the sample. The detector was used at a setting of 10 μS full scale. The modern conductivity detectors are relatively much more stable and sensitive. Hence, a significantly lower detection limit for this assay may easily be expected. Trace amounts of molybdate in soil extracts were determined by using SCIC [45]. A

polymethacrylate gel analytical column with 5 m*M* *p*-hydroxybenzoic acid (pH 8.25) as the eluent was able to separate molybdate ions from other inorganic anions (chloride, nitrate, phosphate and sulfate) encountered in soil extracts. Ammonium oxalate as extractant was able to recover greater quantities of molybdate from soils as compared to hot water. A detection limit of 45 μg molybdate/l with a 2 ml injection was reported without any pre-concentration step. The results agreed closely with those obtained with ICP-optical emission spectrometry (OES). Again, the use of newer conductivity detectors would surely result in lower detection limits for molybdate and additional sensitivity may be achieved by suppressed chromatography.

Orthophosphate in aqueous soil extract was determined by SCIC [46]. The eluent consisted of 1.5 m*M* phthalic acid adjusted to pH 2.7 with formic acid and a Vydac anion-exchange (250×4.6 mm) column was used. The results agreed closely with those obtained with conventional auto-analyzer assay and had a detection limit of as low as 0.8 μg/l phosphate-P using a 0.5 ml sample injection.

Certain metal ions that generally exist as cations, may be analyzed as anions [47]. It is an interesting approach where the metal cations were complexed with ethylenediaminetetraacetic acid (EDTA) prior to injection onto a SIC system. The metal–EDTA complexes of lead, zinc and copper ions were separated as anions along with other inorganic anions, such as, chloride and nitrate. A polystyrene–divinylbenzene column agglomerated with a completely aminated anion-exchange latex (AS9, Dionex) with a sodium carbonate–sodium bicarbonate eluent, was used. The method was shown to be linear for the tested range of up to 15 mg/l with detection limits of 6, 40.5 and 17 ng for Cu–EDTA, Pb–EDTA and Zn–EDTA complexes, respectively. This being a newer approach has not yet been used in agricultural research. However, the technique appears potentially powerful and hence, it is only a matter of time.

4. Assay of inorganic cations

The applications of CLC in agricultural research for inorganic cation assay have been far fewer than those for inorganic anions. The simultaneous assay of mono and divalent inorganic anions has now been available for nearly two decades. Whereas, until recently, two separate analyses (either one column and two different eluents or two columns and two eluents) were generally required for the assay of common monovalent (lithium, cesium, sodium, ammonium and potassium) and divalent (calcium, magnesium, barium and strontium) cations in both SIC and SCIC. The cation SIC had an additional shortcoming; a convenient and practical suppression device was not available in the past. The cation micro-membrane suppressor required tetrabutyl ammonium hydroxide as the regenerant at a concentration of 100 m*M*. This was very expensive to operate. However, a self-regenerating cation suppressor has now become available which is certain to enhance the cation SIC applications. For these reasons, the usefulness of the cation assay in the past using CLC may have been limited. Two good general review articles on cation analysis by ion chromatography have recently been published on (I) stationary phases and separation methods [48] and (II) detection methods by Dugay et al. [49].

The separation of alkali metal cations (lithium, sodium, potassium, rubidium and cesium) and that of magnesium and calcium, in two different runs, using SIC was reported by Small et al. [1]. The simultaneous analysis of inorganic monovalent cations (lithium, sodium, potassium, ammonium, rubidium and cesium) in drinking waters, using SCIC with nitric acid as eluent, was first reported by Fritz et al. [50]. By the use of ethylene diammonium dinitrate as eluent, the divalent inorganic cations (barium, strontium, calcium and magnesium) could also be separated and assayed. One of the first direct applications of CLC for the assay of inorganic cations in agricultural research was reported by Basta and Tabatabai in 1985 [51]. They assayed sodium, potassium, calcium and magnesium in plant materials after dry ashing with subsequent extraction in 5 m*M* HCl. In a separate study, the same authors [52] reported the assay of the same cations in soil extracts. The inorganic cations (exchangable bases) from soils were extracted by 1 *M* ammonium acetate. Due to high ionic concentration, the resulting soil extracts were not suitable for SIC. Hence, the ammonium acetate extracts were evaporated to dryness and the

residue was ignited at 400°C to volatilize the ammonium acetate. The clean residue was taken up in 5 m*M* HCl. A SIC system with conductivity detection was used for both studies with 5 m*M* HCl and 2.5 m*M* HCl+2.5 m*M* phenylenediamine dihydrochloride as eluents for the separation of mono and divalent cations, respectively. The reported detection limits for sodium, potassium, calcium and magnesium were 0.05, 0.1, 0.1 and 0.03 mg/l, respectively. While monovalent cations were fully separated, a true baseline separation of divalent cations was not shown. A slight sample matrix or column problem could actually deteriorate the separation even further. Nevertheless, the applications represented a major step forward in the application of SIC in agricultural research. Nieto and Frankenberger, Jr. [53] evaluated the suitability of SCIC for the analysis of ammonium, alkali metals and alkaline earth metals in soil extracts. Basically, the SCIC system reported by Fritz et al. [50] was used and two separate injections were made to separate the mono- and divalent cations. Since water was used as the soil extractant, sample matrix problems were not encountered. However, the method only extracted soluble cations and not total or exchangeables. The assay was reported to be highly linear, precise and the results were in agreement with those from AAS. The detection limits using a 0.5 ml sample loop were: 0.05 mg/l for sodium, calcium, magnesium; 0.10 mg/l for lithium and barium; 0.5 mg/l for ammonium and 1.0 mg/l for potassium and strontium.

A method for the simultaneous determination of mono- and divalent cations (sodium, potassium, calcium and magnesium) in plant materials with one injection was reported by Goyal et al. [54], using SCIC and conductivity detection. The cation-exchange column used was IC Pac CM/D (Waters, Milford, MA, USA) with 0.1 m*M* EDTA+3 m*M* nitric acid as eluent. A total analysis time of 16 min for all four cations could be reduced to 12 min by including 10% acetonitrile in the eluent. Acetonitrile accelerated the migration of magnesium and calcium ions but did not affect the retention of sodium or potassium. The authors preferred to use the nitric-perchloric acid digestion for elemental recovery. The excessive ionic background problem as a result of acid digestion was solved by evaporating the acids to dryness and reconstituting the sample in 10 m*M* HCl. The results agreed very closely with certified values. The detection limits for sodium, potassium, magnesium and calcium were 0.05, 0.2, 0.025 and 0.05 mg/l, respectively. A bulk of the cation work in agricultural research involves the assay of these four inorganic cations in soil and plant materials. In the past, these cations have been determined using AAS or ICP. In this author's opinion, the single-injection simultaneous assay method reported by Goyal et al. [54] offers a very useful, practical, and convenient alternative to AAS and ICP. The author's laboratory has rarely used AAS for the assay of these four cations ever since the SCIC method became available about five years ago.

CLC has also been used for the simultaneous determination of urea and ammonium in soil extracts [55]. The workers used a silica-based cation-exchange column which retained ammonium while urea molecules eluted in the void volume. With the use of an in-line solid-phase urease catalytic column, placed after the cation-exchange column, urea was hydrolyzed, on-line, to ammonium. Both urea and ammonium peaks were detected flurometrically as ammonium after a post-column, on-line derivatization with *o*-phthalaldehyde (OPA) and mercaptoethanol [56]. The OPA chemistry reported in this paper was selective to ammonium only.

SIC has also now been used for the single-injection simultaneous assay of nitrogen, potassium, calcium and magnesium in acid digests of plant samples [57]. All nitrogen in the plant material was converted to ammonium during digestion. Sodium, ammonium, potassium, magnesium and calcium were well separated. A cation-exchange column and a cation self-regenerating suppressor (Ionpac CS 12A and CSSR-1, respectively; both Dionex) were used with 12 m*M* sulfuric acid as the eluent. The excessive ionic background problem was solved by diluting the acid digests by 100-fold. The results matched closely with the certified value of different elements assayed. It is, however, not clear as to how the authors were able to obtain full recovery of nitrogen without the use of a catalyst that is generally required for complete Kjeldahl digestion (boiling point of sulfuric acid is 290°C). SCIC was also used for the simultaneous analysis of cationic nutrients (sodium, potassium, magnesium and calcium) in food

stuffs, following microwave acid digestion [58]. The problem of high ionic background due to acid digestion was solved by diluting the samples 10 000-fold.

5. Assay of heavy metal ions

Heavy metals are important from an environmental standpoint. Many soils and waters may contain heavy metals some of which may be highly toxic. Historically, AAS or ICP has been used for the assay of heavy metals. However, neither of these methods can distinguish between various species an element may exist as. CLC can be used to separate species with different oxidation states.

An excellent compilation of various CLC methods used for the assay of heavy metal ions is available [59]. The separation of heavy metal ions has been achieved after complexing the metal ions with other ions or compounds. This form of chromatography is usually referred to as ''ion-pair chromatography'' and is a hybrid between ion-exchange and partition chromatography. The pairing ion can be conveniently included in the mobile phase. The sensitivity of heavy metal ions detection with conductivity detectors is usually low. Therefore, various indirect detection methods have been developed. The application of a post-column reactor, using a color-forming and complexing agents that form UV–visible absorbing derivatives, have been useful in a wide variety of applications, including those for mercury, lead, chromium, copper, iron, aluminum and zinc [60]. Post-column reaction with 4-(2-pyridylazo) resorcinol (PAR) has found a useful application for the detection of many heavy metal ions. Some heavy metal ions (e.g., copper, zinc, nickel, cobalt, cadmium) can also be assayed with a coulometric detector [61].

An impressive separation of twelve metal ions [iron (III), copper, lead, zinc, nickel, cobalt, cadmium, iron (II), calcium, manganese and magnesium] was demonstrated on a silica-based ion-exchange resin with 0.16 m*M* tartrate buffer, pH 3.2 [62]. The detection was carried out photometrically at 520 nm after a post-column reaction with PAR–zinc–EDTA reagent [62]. SCIC was found suitable for the separation and determination of chromium(VI) in aqueous soil and sludge extracts [63]. Detection was based on EC and 5 m*M* *p*-hydroxybenzoic acid was used as the eluent. The method had a detection limit of 92 μg/l.

6. Sample matrix problems

While most analytical methods may be affected by sample matrices, the CLC techniques are particularly vulnerable. Hence, sample matrix problems constitute one of the biggest limitation of CLC methods. In CLC, the most commonly encountered sample matrix problems arise when the analyte of interest is present at a relatively much lower concentration than other species chromatographed under the same conditions. For analyte detectability, a certain minimum sample size must be injected. Consequently, the species present at high concentrations overwhelm and saturate the column and disturb its equilibrium. As a result, the peak of interest is either totally masked or distorted (loss of resolution), making quantification difficult and inaccurate. In some cases, sample matrix may also affect the quantitative detection, despite no loss in peak resolution. Therefore, the potential sample matrix affects should be carefully examined before a CLC method is used for analysis. The most commonly applied approach to solving these problems has been the removal of interfering species (or significantly lowering its concentration) via precipitation, evaporation or decomposition by heat. In some instances dilution of sample prior to injection or use of a smaller sample size, may also be helpful. But this approach is limited by the analyte detectability. Use of an alternate mode of detection (e.g., UV absorbance instead of conductivity) may provide additional selectivity and lower the interference. A number of studies reporting specific sample matrix problems and their attempted remedies were cited earlier in this paper [29,32,33,39,43,52,54,57].

7. Future trends and needs

A number of CLC technologies are in various stages of development at this point. The author wishes to point out some needy areas and where

some of these technologies are most likely to find applications in future agriculture research.

A healthy environment is now a concern of most people. Due to their widespread presence (in soils and water) and potential high toxicity, the trace metal analysis has assumed a great importance. While CLC is not yet popular for trace metal analysis in agriculture, the available background information may be helpful to the reader. Timerbaev and Bonn [64] provided an excellent overview for the trace metal analysis using complexation techniques coupled to ion chromatography. Methods for pre-concentration of metal ions prior to assay [65] and on-line pre-concentration of transition metals for ultra-trace metal analysis [66] were recently reported. These represent important and useful approaches as the metal ions usually exist at trace levels.

As mentioned before, sample matrix problems continue to preclude the use of CLC for many applications. A relatively new approach to solving matrix problems is the use of column or eluent stream switching valves. For instance, phosphate could be successfully assayed in the presence of large quantities of sulfate by using a column-switching technique [67]. This approach could possibly be extended to many other applications. Another area which the author strongly feels for is the simultaneous analysis of inorganic anions and cations which is bound to revolutionize the inorganic analysis using CLC. Some preliminary work in this direction using SCIC and column switching devices has been reported [68]. A novel and interesting approach called ''electrostatic ion chromatography'' for inorganic solute assay has recently been introduced by Hu and coworkers [69–71]. This concept offers a new approach for the simultaneous analysis of inorganic anions and cations. However, it remains to be seen if this technique will find applications in agricultural research in light of usual sample matrix problems.

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