

Original Article

## Ion Chromatography - an Advantageous Technique in Soil Analysis

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### Abstract

The content of organic and inorganic substances in soils plays a very important role in their quality and use. The importance of inorganic and organic anions and cations in soil quality is huge, thus we need a suitable analytical methods for their determination in such complex matrices. In this range ion chromatography is an advantageous instrumental analytical technique. It has been used in most areas of analytical chemistry and has become a versatile and powerful technique for the analysis of a vast number of ions present in the environment, food and many other matrices, including soils. The key to valuable data when carrying out ions analyses in soils is the use of correct and reproducible sample preparation methods. The paper reviews the principles of ion chromatography and its application in soil research. Ion chromatography is used to provide information on the fate of nutrient anions resulting from agricultural practices and to determine soil nutrient retention and leaching rates. It is widely accepted as the standard reference methodology for many analytes in different samples matrices including soil analysis.

**Keywords:** *soil analysis, ion chromatography, anions, cations, sample preparation.*

### 1. Introduction

In soils there are organic and inorganic substances in ionic forms. Soil nutrients exist as anions and cations when dissolved. The nutrients which exist as cations are mostly  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . Some of the nutrients which exist as anions are:  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{BO}_3^-$ , and  $\text{MoO}_4^-$ .

Ion exchange capacity is the soil's ability to hold anions and cations.

When soil particles are negatively charged they attract and hold on to cations stopping them from being leached down the soil profile, while negatively charged soil particles repel anions. The implication of this is that negatively charged nutrients such as nitrates, sulfates and chlorides are vulnerable to leaching down the soil profile.

Chromatographic methods are used widely in soil analysis. They help to separate and determine polar and non-polar components; acidic, neutral and alkaline compounds, as well as organic and inorganic substances. It is necessary to use an appropriate chromatography type, which depends on the physicochemical properties of the examined sample and its components. Gas chromatography (GC) and liquid chromatography (LC) can be used to separate

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and determine about 20% and 80% of the known compounds, respectively. Ion chromatography (IC) is a part of high-performance liquid chromatography used to separate and determine anions and cations, and also other substances after converting them into the ionic forms.

Ion chromatography is very useful method used for the determination of common inorganic anions and cations, as well as ionic forms of some metals/metalloids and organic substances [1]. Since its introduction in 1975 [2] ion chromatography has been used as a versatile and powerful technique for the analysis of a vast number of inorganic and organic ions present in samples with different matrices [3].

## 2. The principles of ion chromatography

There are two main types of ion chromatography: suppressed ion chromatography and non-suppressed ion chromatography. In ion chromatography with suppressed conductivity detection an eluent containing a suitable electrolyte is passed through a specialty high performance ion-exchange resin to a suppressor and then to a conductivity detector. Analyte ions are separated on the ion-exchange column and the separated sample ions (together with the eluent) move to the suppressor. In the suppressor, the conductance of the eluent is lowered and the conductance of the eluted analytes is increased, leading to a large increase in the signal to noise ratio of the detection signal. In non-suppressed ion chromatography separation column is connected directly to the conductivity detector.

The background signal is reduced to a manageable level by using an ion-exchange separation column of low exchange capacity that lowers the eluent concentration needed for separation. Both suppressed and non-suppressed modes have been applied to the analysis of various sample matrices. However, suppressed ion chromatography application to anions analysis is much more popular. Ion exchange remains the primary separation mode used in ion chromatography today, although the apparatus used for the separation of the ionic species includes moreover ion-exclusion [4], ion-pairing chromatography [5] and reversed phase liquid chromatography [6].

The key concept in the evolution of ion chromatography was suppressor [7]. In the suppressor, the conductance of the eluent is lowered, or suppressed, and the conductance of the sample ions is increased, leading to a large increase in the signal-to-noise ratio of the detection signal. The stationary phase used in ion chromatography consists of polystyrene (PS), ethylvinylbenzene (EVB), or methacrylate resins copolymerized with divinylbenzene (DVB) and modified with ion-

exchange groups. Furthermore polyvinyl, silica-based and many other materials were used [8]. At the beginning of ion chromatography development stationary phases utilized particles greater than 40  $\mu\text{m}$  and generated only about 120 and 300 theoretical plates efficiency in relation to column dimension. In the first commercial column used for ion chromatography (Dionex AS-1), the particle size was reduced to 25  $\mu\text{m}$  and efficiencies increased to 700 theoretical plates. Modern high-capacity columns have efficiencies over 8000 plates and particle size < 3  $\mu\text{m}$  [9].

Next, the combination of positively and negatively charged sites in a single particle, or within the functional groups of a single molecule attached to the surface of an absorbent, provides unique opportunities to vary the selectivity of separation [10]. Carbonate and bicarbonate eluents have been used as the mainstay of anion-exchange ion chromatography for many years.

However, the ideal eluent is hydroxide since, after suppression, it forms water that has virtually zero conductance and, therefore, provides the perfect conductivity baseline. Unfortunately, hydroxide eluent is difficult to use because it readily absorbs carbon dioxide and forms carbonate. The type of eluent for cation-exchange chromatography depends on the detection method being used. The most popular eluents used in cation analysis are low concentration mineral acids such as HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, sometimes containing organic modifiers (e.g., ethylenediamine, 2,3-diaminopropionic acid), these have significant influence on the retention time and resolution [11]. Although the conductivity detector is still the most popular, other types of detection modes such as amperometric, potentiometric, UV/Vis, chemiluminescence, fluorescence, as well as atomic absorption spectrometry, atomic emission spectrometry, inductively coupled plasma–optical emission spectrometry, inductively coupled plasma–mass spectrometry and mass spectrometry can be applied for different analytes [12].

## 3 Sample preparation method

As in other analytical methods, the key stage of analysis (especially of such complex samples as the soil) is the proper preparation of samples for analysis. The analysis of soils by ion chromatography requires either the transfer of the whole sample, or at least the ions of interest, into an aqueous phase. Sample preparation methods for ion chromatography are very numerous and the apparatus and time required for sample preparation vary considerably [13]. Dissolution of the sample or extraction of the ions to be determined is normally carried out at room

temperature, but can also be accelerated by gentle warming or by heating the solvent up to the boiling point. The choice of extracting solution is dependent on both the soils matrix and upon the nature of the determined ions [14].

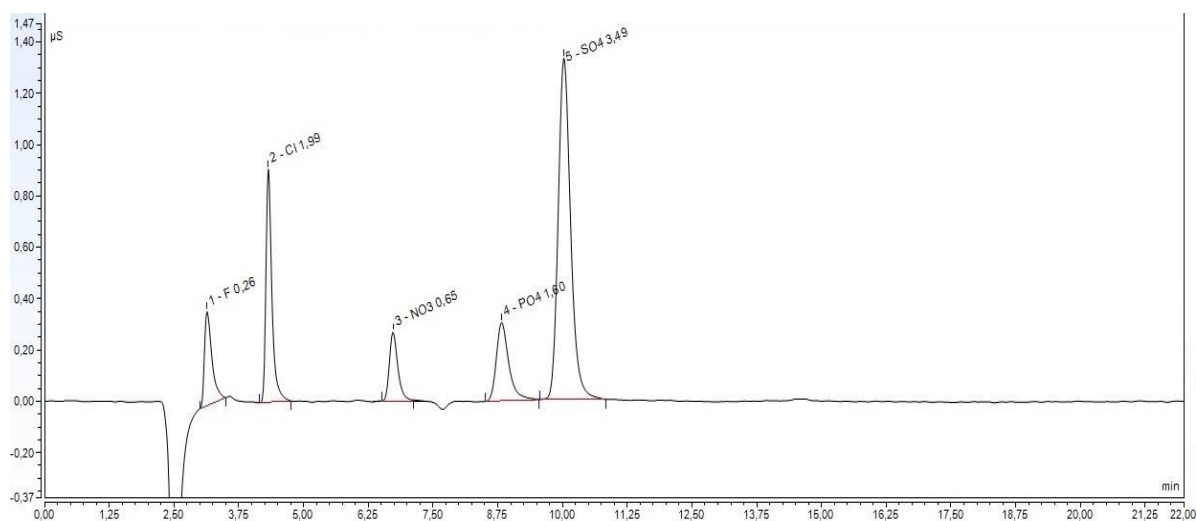
Water is preferred, in order to avoid introducing extraneous peaks into the final chromatogram. Sometimes, water combined with a miscible solvent such as methanol, solutions of dilute acid or base, dilute salt solutions, or even the eluent, can be used [15]. If an aqueous extraction is not sufficient, it may be necessary to consider a wet chemical digestion. Acid digestion with concentrated mineral acids is basically inappropriate for ion chromatography because the excess of the acid co-anion can lead to the appearance of a large interfering peak in the final chromatogram and can also cause column overloading.

If mineral acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, or HNO<sub>3</sub> have to be used, the difference in retention times between the sample anions and the solvent anion should be as large as possible. For acid extraction followed by the determination of the standard anions chromatography with direct conductivity measurement, tartaric acid, perchloric acid and/or formic acid can be used. For chemical suppression ion chromatography, acetic acid, or formic acid can be used for determining common anions. In general, acid digestion is better suited to preparing samples which are to be analyzed for cations (e.g., transition metals and rare earth elements) using ion chromatography with post column reaction detection. An alternative to the acid digestion of solid samples

is fusion under alkaline conditions. The procedure is usually very labor intensive, takes a long time, and involves a high risk of errors from contamination and loss of analyte. This method can be used for the determination of fluoride and chloride in geological materials after fusion with sodium carbonate and subsequent injection into an ion chromatography column [16].

#### 4. Applications of ion chromatography in soil analysis

Ion chromatography offers several advantages over conventional methods for determination of ions: short time of analysis; sensitivity at the µg/L level; high selectivity in samples with complex matrices; small sample volume; possibility to use different detection modes; simultaneous determination of anions and cations, or inorganic and organic ions; species analysis; use of cheap, safe, and environment friendly chemicals [17]. In the range of applications of ion chromatography, inorganic anions are, by far, the most important. The primary reason for this is the lack of alternative methods for anion analysis, which is not the case for cation analysis where many other instrumental techniques are readily available. However, ion chromatography has an advantage over spectroscopic techniques for cation analysis in the area of metal/metalloids ions, and ammonia determination [18]. An example chromatograms of anions and cations in soil are given on Figure 1 and 2, respectively.



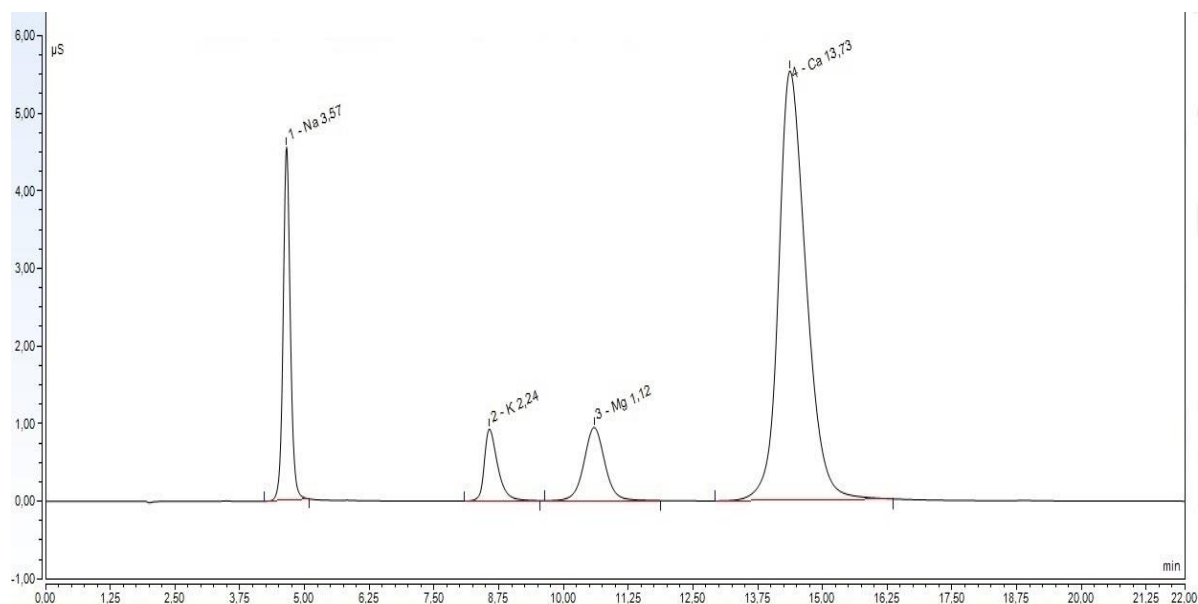
**Figure 1.** Chromatogram of anions in soil from Pyskowice (Poland)

Analytical column:	Dionex IonPac 22 4 x 250 mm	Eluent flow rate:	1,2 mL/min
Eluent:	4.5 mM Na <sub>2</sub> CO <sub>3</sub> + 1,4 mM NaHCO <sub>3</sub>	Detection:	Suppressed conductivity
		Injection volume:	25 µL

Sample preparation: Air dried soil samples were ground and sieved.

To prepare a water extract 10g of soil were

flooded 100ml of deionized water and shaken for 24 hours. Obtained extract were filtered by syringe filters (PES 0.22 $\mu$ m).



**Figure 2.** Chromatogram of cations in soil from Pyskowice (Poland)

Analytical column: Dionex IonPac CS16 5 x 250 mm  
 Eluent: 30mM Methanesulfonic acid (MSA)  
 Eluent flow rate: 1,5mL/min  
 Detection: Suppressed conductivity  
 Injection volume: 25  $\mu$ L

Sample preparation: Air dried soil samples were ground and sieved. To prepare a water extract 10 g of soil were flooded 100 mL of deionized water and shaken for 24 hours. Obtained extract were filtered by syringe filters (PES 0.22 $\mu$ m).

Both ion chromatography and ion exclusion chromatography have been used extensively for the determination of low-molecular-weight organic acids in soil extracts [19]. To separate complex mixtures (e.g. inorganic and organic acids) two-dimensional chromatographic techniques can be used. The organic acids are separated in the first dimension, whereas the fraction of the nearly unresolved, highly dissociated inorganic acids were passed to an anion concentrator column by means of a column switching valve. These techniques require the compatibility of the eluent with both columns.

Recently, ion chromatography has also found increased application in the field of species analysis. Toxicological test results show that in many cases specific forms of a given element, rather than its total content, have a decisive impact on living organisms. For that reason, the information on the total element content in a given sample is less important than understanding the occurrence of various element

forms. One of the most popular examples of species analysis is simultaneous separation and determination of nitrogen ions ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) [20]. Studying low analyte concentrations, particularly in complex matrix samples, requires meticulous and sophisticated analytical techniques. The latest trends embrace the so-called hyphenated methods, which combine different separation and detection methods [21]. Hyphenated methods (e.g. IC-MS and IC-ICP-MS) has incredibly developed over the last years, it is still a relatively new field of the analytical chemistry [22]. Its further development depends on many factors, such as developing new methods of separation, detection and sample preparation as well as the availability of new certified reference materials. Hyphenated methods offer great possibilities and their main advantages include: extremely low limits of detection and quantification, and very good precision and repeatability of determinations [23]. On the other hand, they have

their specific limitations, such as high price and complexity of the apparatus. The application of hyphenated methods requires perfect understanding of analytical methodologies and apparatus. Those systems are expensive and used in scientific research, rather than for routine analyses.

Manufacturers of IC instrumentation are taking great efforts to offer users a wide range of instrumentation which, with respect to their flexibility, robustness and cost, generally satisfy the considerably different requirements in the various

fields of application, including soil analysis. Real world applications of IC vary greatly but there is virtually no scientific field in which this method cannot be used for the routine determination of ions or for solving special problems.

Besides the methods recommended by ISO, EN and U.S. EPA, there exist many methods developed by manufacturers of chromatography equipment. Examples of IC standards and application notes recommended dedicated to soils analysis are given in Table 1.

Table 1. Examples of ISO, US EPA, Dionex and Metrohm application notes for soil analysis by using IC method

Method number	Method name
<b>ISO/EN</b>	
EN 13368-1: 2001	Fertilizers – Determination of chelating agents In fertilizers by ion chromatography. Part 1: EDTA, HEDTA and DTPA
EN 13368-2: 2001	Fertilizers – Determination of chelating agents In fertilizers by ion chromatography. Part 2: EDDHA and EDDHMA
EN 15192 (2006)	Characterization of waste and soil. Determination of chromium (VI) in solid material by alkaline digestion and ion chromatography with spectrophotometric detection
EN 16318 (2013)	Fertilizers. Determination of trace elements. Determination of chromium(VI) by photometry (method A) and by ion chromatography with spectrophotometric detection (method B)
<b>US EPA</b>	
6860	Perchlorate in water, soils and solid wastes using ion chromatography/electrospray ionization/mass spectrometry (IC/ESI/MS OR IC/ESI/MS/MS)
300.0	Determination of inorganic anions by ion chromatography
9056	Determination of inorganic anions by ion chromatography
9056A	Determination of inorganic anions by ion chromatography
3060A	Alkaline digestion for hexavalent chromium
<b>Dionex (Thermo Scientific)</b>	
AN69	Determination of aluminum in complex matrices using chelation ion chromatography
AN1113	Determination of chloride and sulfate in water and soil
AU165	Separation of Cr(III) and Cr(VI) by ion chromatography
AN1079	Simultaneous determination of trivalent chromium and hexavalent chromium using accelerated solvent extraction and ion chromatography
AN123	Determination of perchlorate levels in food and soil samples using accelerated solvent extraction and ion chromatography
<b>Metrohm</b>	
AN U-77	Chromate in strongly alkaline digestion solution according to EN ISO 15192 (digested soil) and EN 16318 (fertilizer)
AN S-360	Soluble tungsten and molybdenum in soil
AN M-11	Determination of soluble Cr(III) and Cr(VI) in alkaline soil extract applying IC-ICP/MS
AN M-12	Iron speciation analysis in soil using IC-ICP/MS in accordance with EPA SW846 Method 6800
AN S-142	Silicate, sulfate, and phosphate in a clay extract
AN S-58	Iodide in the presence of the standard anions in a leach solution
AN S-9	Six standard anions in soil eluate
AN CIC-12	Halogens and sulfur in clay using Metrohm combustion IC
AN C-99	Lanthanides in a rock sample by ion chromatography using non-suppressed conductivity detection
AN C-40	Calcium and magnesium in rock extracts

## 5. Conclusions

Until 1975, only a small range of analytical parameters could be measured automatically; therefore, it was necessary to develop and validate new methods to extend the scope of such parameters. An alternative that has almost replaced most of the wet chemical methods used in anions and cations analysis is ion chromatography. It is an attractive technique, especially for laboratories that need to determine numerous anions and cations in several thousand samples but do not have the throughput to justify the purchase of large automatic analyzers that are usually based on colorimetric procedures. Ion chromatography eliminates the need to use the hazardous reagents that are often integral to wet chemical methods.

The most important recent challenges related to the development and application of ion chromatography in soils analysis are: new sample preparation methods; improving the speed and selectivity of the separation of analytes; lowering of limits of detection and limits of quantification; development of new standard methods and extending the scope of the analysis for new group of substances.

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