

ION CHROMATOGRAPHIC TECHNIQUES FOR DETECTION OF INORGANIC ANALYTES IN BIOLOGICAL, ENVIRONMENTAL AND INDUSTRIAL SAMPLES – A REVIEW

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ABSTRACT

Ion chromatography provides a means for separation of polar molecular and ionic species based on their interaction with the ion exchanger. Hence, ion chromatography has been used for the determination of trace inorganic analytes in a variety of biological and environmental samples. Singular ion chromatography has been frequently hyphenated with other detection techniques for enhancing the sensitivity of the ion chromatographic system and to shorten the time of analysis. This review takes into account the recent research work reported on the determination of inorganic analytes in biological, environmental and industrial samples using singular and hyphenated ion chromatographic techniques.

Keywords: *Ion Chromatography, Hyphenated Technique, Singular Technique*

I. INTRODUCTION

Chromatography is a separation technique for resolution of different components of a mixture. The IUPAC defines chromatography as “separation of sample components after their distribution between two phases” [1]. The components present in a mobile phase (liquid or gas) are separated from each other based on their differential interactions with a stationary phase. Components which interact least with the stationary phase are collected faster than those which interact more. The components and the stationary phase may interact with each other in either ionic or non-ionic nature. Ion chromatography (IC) is a separation technique where the interactions between the two phases are ionic. Ions and polar molecules in a mixture are separated on the basis of their charge [2].

The basic components of an IC instrument consist of a liquid mobile phase, an analytical separation column and a detector to determine the species eluted from the column. The eluent is pumped first through the system before sample introduction. The sample then flows through the guard column to the analytical ion-exchange column, where the ion-exchange process occurs. After this separation, a suppressor is used which reduces the conductivity of the eluent and increases the conductivity of the analyte so that it is detected by the detector. A computer system with appropriate software for data handling and processing is used for results processing. Fig. 1 shows the schematic representation of a typical IC system [3].

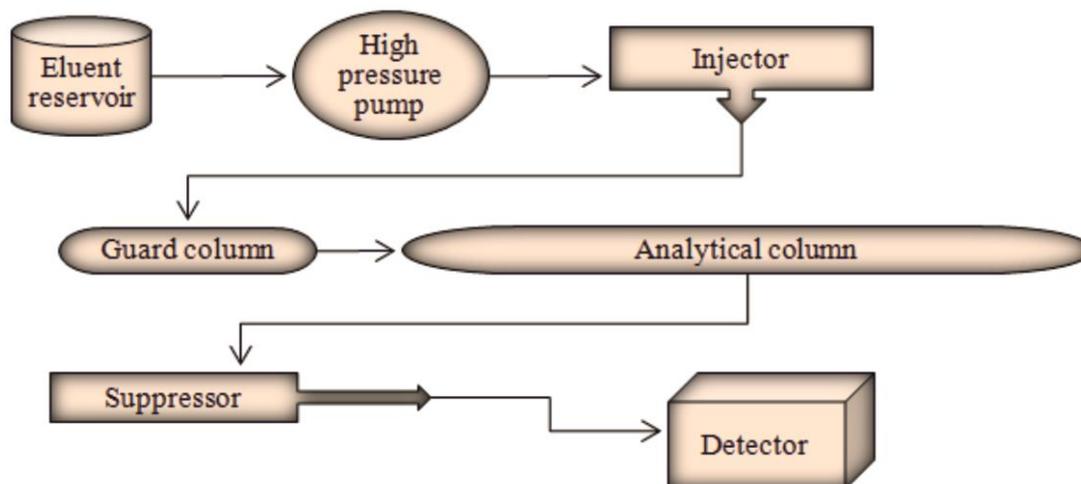


Fig. 1 Schematic Representation of an Ion Chromatographic System

The analytical column consists of an ion exchanger which separates ionic molecules according to charge density, charge distribution, and the size of the molecule. An ion exchanger is a three-dimensional matrix with covalently linked charged groups. If a group is negatively charged, it will exchange positive ions and is a cation exchanger, and vice versa [4]. The use of a guard column prevents clogging of the analytical column with particles or ions which may decrease resolution and sensitivity or create erroneous peaks. Suppressors used in IC are membrane-based devices which convert the ionic eluent to water so that the sensitivity of the detector towards the analyte increases.

An ideal detector in an IC instrument has high signal-to-noise ratio, fast response, wide linear dynamic range, minimal peak broadening, tolerates different types of solvents and can vary flow rate and temperature. In addition, it should not be operationally complex [5]. Thus, depending on the type of detectors, IC techniques can be singular or hyphenated, as shown in Fig. 2. When the detector is in-built into the IC system, the technique is *singular*. However, when an external detector such as standalone detection techniques, for example AAS, ICP (MS/OES), etc. is coupled to IC, then it is said to be *hyphenated*. The term “hyphenation” refers to the coupling of a separation method and a spectroscopic detection technique. These techniques which combine them to utilize the advantages of both are known as hyphenated techniques. Chromatography produces pure or nearly pure fractions of chemical components in a mixture. Spectroscopy provides information for identification of analytes using standards or library spectra [6].

In the past, singular IC has been well exploited for the detection of inorganics in various matrices [7]. However, in the last five years, there has been a momentous shift towards hyphenated IC techniques for trace inorganic determination [8]. The aim of hyphenation of IC is to improve the sensitivity and precision of detection of trace to ultra-trace amounts of the analyte(s) of interest. Also, hyphenated IC techniques are time saving, as the instrumentation combines the features of two techniques and thus, sample preparation time is reduced. IC techniques are today frequently used for the determination of ionic compounds in petrochemicals, foods and beverages, pharmaceuticals, mining and metallurgy [9].

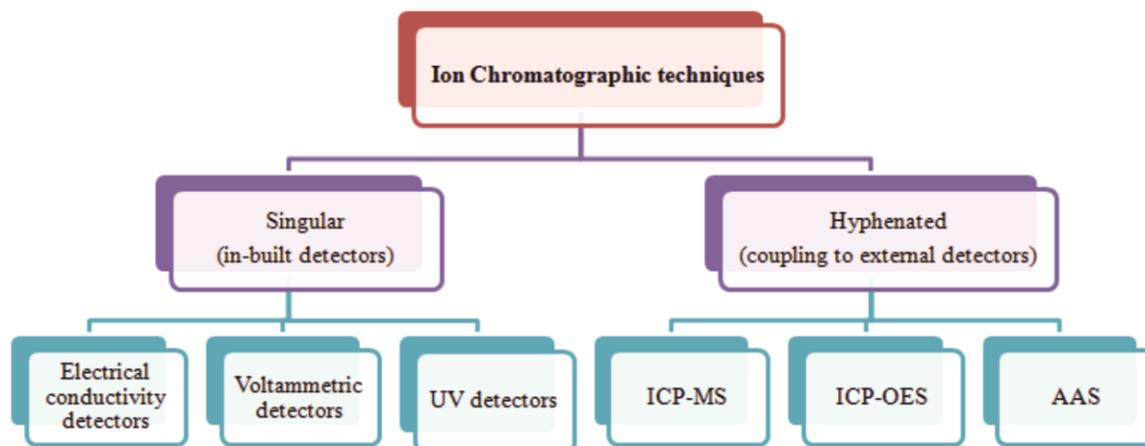


Fig. 2 Singular and Hyphenated Ion Chromatographic Techniques

This review discusses the recent reported work on the use of IC techniques, both singular and hyphenated, for the determination of inorganic analytes in various biological, environmental and industrial samples.

II. SINGULAR IC TECHNIQUES FOR ANALYTE DETERMINATION

Ion chromatography is an excellent analytical technique for the simultaneous determination of anions and cations, and gives good results even for those samples which have a complex matrix [10]. Hence, it has been applied to various matrices in the recent years for the precise detection of inorganic analytes. Some of the recent reported applications of IC to different matrices have been discussed here.

2.1 Application to Biological Samples

In the past, IC has been used for determination of various ions in matrices such as food products and animal/human tissues and biological fluids. A study done on ovine and goat milk samples from different cattle farms (Calabria, Italy) reports the concentrations of several anions using IC. The in-built detector was a conductivity detector. The results show that phosphates were the most abundant anion ($1409 - 3050 \text{ mg L}^{-1}$) followed by chloride ($679 - 2568 \text{ mg L}^{-1}$) and sulfates ($25 - 341 \text{ mg L}^{-1}$). Nitrates were found to be lower than 146 mg L^{-1} . There was no significant difference found between the goat and ovine milk samples. Nitrite concentrations were below the detection limits and bromide (potential carcinogen) was absent, indicating that there is low risk of contamination of the food chain in that particular region [11]. Table 1 below lists the relative standard deviation (RSD) and detection limits of each of these anions.

Table 1 Figures of merit for anion detection in milk samples using IC

Anion	RSD (%)	Detection limit ($\mu\text{g L}^{-1}$)
Br^-	2.0 – 3.1	21.1
Cl^-	1.9 – 3.3	2.4
NO_2^-	1.2 – 3.7	7.7
NO_3^-	1.6 – 2.5	7.5
PO_4^{3-}	1.3 – 2.0	12.2
SO_4^{2-}	2.2 – 3.6	20.2

In another recent study, the concentration of the carcinogen Cr(VI) in *Colla corii asini*, using IC has been determined. *Colla corii asini* is a type of gelatin made from the skin of *Equus asinus*, and is a popular Chinese medicine. However, in the recent years, use of dichromate-rich leather in the production of *Colla corii asini* has become prevalent, which can be a serious hazard to human health. Thus, Yang et al reported an on-line pre-treatment method for isolation of Cr(VI) from the organic matrix and determination using IC equipped with variable wavelength UV–Vis detector. Cr(VI) detected by the detector at 545 nm by complexing it with 1,5-diphenylcarbazide in the reaction coil before the detector. The detection limit for Cr(VI) was $1.4 \mu\text{g L}^{-1}$ and the RSD for six replicate measurements was 1.5 %. The accuracy of the method was tested by comparing the chromatogram of standard Cr(VI) solution with the suggested method. Spike recovery tests gave recoveries between 93.4 – 102.0 %. Thus, Cr(VI) could be reliably detected using this method in a highly organic sample matrix [12].

In 2013, Linda et al reported a method for detection of common inorganic ions in human saliva using IC equipped with UV-Vis detector. The column used was a modified commercial TSK gel NH2-60 column. To improve the selectivity and affinity of the column material towards the analytes of interest, modification was carried out by reacting TSK gel NH2-60 with tosylated-poly(ethylene oxide). The effect of eluent and retention time was studied. The RSD for the anions studied (iodate, bromate, bromide, nitrate, iodide, and thiocyanate) were between 1.1 – 4.3 % [13].

2.2 Application to Environmental Samples

IC has been extensively applied to environmental matrices, primarily soils and waters. Rong et al reported an IC method for the determination of iodide in seawater samples. The column used was C30 modified with HDMB, and the IC detector was UV detector. The eluent conditions were optimized and the effect of organic substrates on iodide determination was studied. It was found that iodide concentration in seawater samples could be determined without any pre-treatment, and the best eluent was NaCl–acetonitrile. The RSD for 6 replicates of measurement was 2.4 % and detection limit was $6.4 \mu\text{g L}^{-1}$. The modified column material was found to be stable for two months with 6 h daily continuous operation [14].

Another seawater based high performance IC determination of strontium was carried out by Nesterenko et al. Alkaline earth metals in the seawater samples were removed by the use of IDA modified silica columns. *o*-cresolphthalein was used as the reagent for complexation with Sr^{2+} in a post-column reactor and the complex

was detected at 570 nm using UV detector. The variation in the reproducibility of measurements (RSD) was within 1.1 %. Sample volumes as low as 4 μL were used for the analysis. This paper presents the first reported Sr^{2+} determination in seawater samples without any prior treatment or dilution [15]. There is a similar report for iodide determination in seawater samples using IC and making use of chemically modified column material. The stationary phase (silica gel) was modified with vitamin-U. The detection limit was $8.2 \mu\text{g L}^{-1}$ and RSD was $> 2.4 \%$. The modified stationary phase remained stable and gave reproducible results even after 3 months of usage at 6 h per day [16].

In 2014, Nojavan et al reported a method for determination of inorganic ions in various water samples and water miscible organic solvents using IC equipped with a conductivity detector. Electromembrane extraction (EME) was done for isolation of inorganic analytes from water samples and organic solvents. The advantage of EME is the reduction in the time of extraction to 5 – 20 min. The figures of merit for the EME based IC determination of some anions is given in Table 2. Comparison with other reported IC methods showed that EME – IC method was better in terms of detection limit, lower consumption of sample and decrease in extraction time [17].

Table 2 Figures of merit for anion detection using EME – IC

Anion	RSD (%)	Detection limit ($\mu\text{g L}^{-1}$)
F^-	13.4	0.6
Cl^-	9.5	0.6
NO_3^-	10.7	1.5
NO_2^-	9.9	1.5
Br^-	12.8	3.0
PO_4^{3-}	11.3	7.5
SO_4^{2-}	13.5	4.5

2.3 Application to Industrial Samples

The quality assessment of industrial products and by-products has been an important issue. IC can be applied to various matrices without any necessary pre-treatment. Raw *Jatropha curcas* oil is a potential feedstock for biodiesel as it has high phosphorus content. Thus, Zhang et al reported an IC method for the determination of inorganic phosphate. The oil was extracted and dissolved in acetone and was directly injected into the IC system having conductivity detector. Total phosphorus content (inorganic phosphates and organic phospholipids) was determined by a standard colorimetric procedure. The difference between total phosphorus and inorganic phosphate gave the phospholipid content. The detection limit obtained was 0.1 mg L^{-1} and RSD was between 3 – 11 % [18].

The determination of bromide and iodide in certain pharmaceutical products was carried out using an IC system with incorporated UV detector. Silica modified with polyaniline was studied for its properties and was optimized for the retention of the anions. Detection limit obtained for Br^- and I^- were found to be 0.012 and 0.004 mg L^{-1} . The RSD was below 2.01 % and recoveries of both Br^- and I^- from the pharmaceutical samples were $> 97 \%$ [19].

In 2014, Silveira et al reported a simultaneous IC determination of several anions in biodiesels prepared from soy, canola and sunflower vegetable oils, from crude soy oil, and from bovine fat. The inorganic anions were separated from the matrix by ultrasound-assisted extraction into water, which highlights that this method is green. Acetate, formate, chloride, phosphate and sulfate anions were determined simultaneously without requirement of individual separation. The detection limits were in the range of 0.1 – 1.36 mg L⁻¹ and the RSD were between 1.5 – 12.8 %. The method is free from organic solvents and water was the only solvent used [20].

III. HYPHENATED IC TECHNIQUES FOR ANALYTE DETERMINATION

The hyphenation of IC with other analytical techniques such as atomic spectrometry (Fig. 3) minimizes sample pre-treatment time, thus increasing sampling frequency. In addition, the sensitivity of IC is enhanced significantly, which is reflected in the detection limits obtained. This section discusses the recent papers where IC coupled techniques have been used to determine various analytes from different matrices.

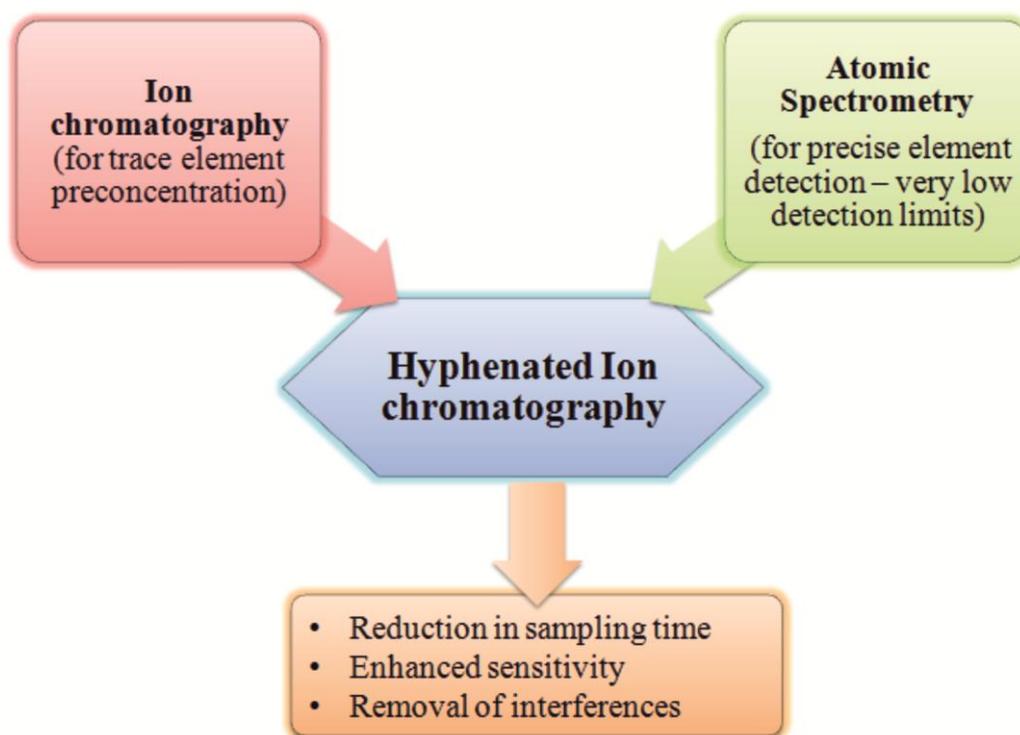


Fig. 3 General Principle of Hyphenated Ion Chromatographic Techniques

3.1 Application to Biological Samples

The speciation and determination of mercury and its compounds in seawater and marine fish was studied using an IC-ICP-MS system. Two strong cation exchange guard columns were connected in series and used together as an analytical column. Parameters such as mobile phase flow rate, pH, retention time and concentration of eluting agent were optimized. Under the optimized conditions, speciation between Hg²⁺ and MeHg⁺, EtHg⁺, PhHg⁺ could be achieved by varying the retention time for each. The detection limits and RSD of the four mercury species are given in Table 3. The proposed method was applied to seawater samples and samples of marine fishes. The validation of method was carried out using certified reference materials (seawater and fish

tissue) supplied by National Standard Material Center (Beijing, China). The recoveries of the analyte obtained from all experiments were with the range of 94–102 % [21].

Table 3 Figures of Merit for Speciation and Determination of Mercury Species

Species	Retention time (s)	RSD (%)	Detection limit ($\mu\text{g L}^{-1}$)
Hg ²⁺	20.3	1.3 – 1.7	0.019
MeHg ⁺	57.7	1.6 – 2.3	0.027
EtHg ⁺	78.1	2.1 – 2.7	0.031
PhHg ⁺	124.0	1.9 – 2.3	0.022

An IC method for the speciation and determination of selenium in human urine was developed by Jäger et al. Nine different selenium species were determined by coupling ICP-MS with different IC systems (ion-pairing, anion-exchange and cation-exchange). The separation of SeSug1 (methyl-2-acetamido-2-deoxy-1-seleno-b-D-galactopyranoside), SeSug3 (methyl-2-amino-2-deoxy-1-seleno-b-D-galactopyranoside), SeMet (selenomethionine), SeEt (selenoethionine) and SeMeG (methylselenogluthathione) was done using ion-pairing chromatography, whereas Se(VI), Se(IV), SeMCys (methylselenocysteine) and TMSe (trimethylselenium ion) were studied using both anion and cation exchange chromatography. Using the three methods of determination, the detection limits for the nine species were in the range of 0.10 – 0.19 $\mu\text{g L}^{-1}$. The precision for six replicates of measurements (RSD) was found to be between 3.0 – 13.5 %. The recoveries of all the selenium species were between 89 – 111 %. The results obtained were found to be in agreement with the standard selenium levels in human urine. The study concluded that more studies needed to be done to properly understand the mechanism of selenium metabolism as it is an essential trace element in humans [22].

Another technique based on IC-ICP-MS was carried out most recently for the bio-monitoring of iodide in human blood serum and urine. In the past, very few studies have reported iodide concentration in blood serum [23]. The method reports high sample throughput and detection limit of iodide in serum and urine were found to be 0.12 and 0.05 $\mu\text{g L}^{-1}$, respectively. The RSD for determination of seven replicates of serum was in the range of 4.86 – 5.30 %. For six replicates of urine, the RSD was found to be between 1.40 – 2.28 %. In both matrices, recovery between 100 – 105 % was obtained. The method accuracy was validated using certified reference material for serum and urine from various agencies. It was concluded that the iodide concentration in urine varies according to the actual iodine uptake by an individual [24].

3.2 Application to Environmental Samples

Environmental snow and ice samples from Antarctica were collected and perchlorate concentration in these was determined using ion chromatography coupled with tandem mass spectrometry using an automated sample on-line preconcentration method. The on-line preconcentration system consisted of a 6-port injection valve, a separate column and an autosampler, specifically for preconcentration of perchlorate and removal of matrix anions. The preconcentrated perchlorate was then sent to the analytical column of the IC system, and then further to the electrospray ionization – MS (ESI-MS) for detection. The detection limit for perchlorate was found to be 0.2 ng L^{-1} . The RSD for five replicates of samples was obtained between 2.7 – 9.1 %. Antarctic snow and ice samples were found to contain perchlorate in the range of 10 – 340 ng L^{-1} . Spike tests for perchlorate gave recoveries between 93 – 139 % [25].

Table 4 Retention Times for Speciation of Seven Arsenic Species

Species Name	Formula	Retention time (s)
Arsenite	$H_nAs^{III}O_3^{n-3}$	0.00
Thioarsenite	$H_nAs^{III}S_3^{n-3}$	0.61
Arsenate	$H_nAs^VO_4^{n-3}$	9.50
Monothioarsenate	$H_nAs^VSO_3^{n-3}$	10.87
Dithioarsenate	$H_nAs^VS_2O_2^{n-3}$	12.46
Trithioarsenate	$H_nAs^VS_3O^{n-3}$	14.01
Tetrathioarsenate	$H_nAs^VS_4^{n-3}$	15.38

The speciation and determination of seven species of As(III) and As(V) was carried out in natural sulfidic geothermal water samples, using IC coupled with hydride generation-atomic fluorescence spectrometry (IC-HG-AFS). Speciation of all the arsenic species was achieved at different retention times on the IC column (Table 4). The peak identification was based on analysis of standard arsenic compounds using this proposed method. The detection limits for all the species were in the range of 1 – 3 $\mu\text{g L}^{-1}$. The RSD for all determinations was found to be < 5 %. The strength of the proposed method is the instrumental mobility for analysis of natural waters [26].

3.3 Application to Industrial Samples

An IC method coupled to ICP-MS was used for the speciation of inorganic tin, namely the Sn(II) and Sn(IV) species in industrially contaminated water samples. ESI-MS was used as a complementary method to study the formation of Sn(II) and Sn(IV) complexes with diethylene triamine pentaacetic acid (DTPA), which was used as the eluent. The speciation of tin was carried out in water samples and was detected by the IC-ICP-MS system. The detection limits for Sn(II) and Sn(IV) were found to be 0.1 and 0.3 $\mu\text{g L}^{-1}$, respectively. The RSD for five replicates was found to be 2.7 and 2.1 %, respectively. Spike tests in industrial water samples gave recoveries of both tin species in the range of 96.8 – 103.4 % [27].

IV. CONCLUSION

Ion chromatography is one of the most widely used analytical techniques for the determination of inorganic analytes in a variety of samples, as there is little or no requirement of sample pre-treatment. Also, IC shows good sensitivity in terms of detection limit. The removal of interferences from the sample is also relatively simple. However, to reduce the time of analysis and further enhance the detection limit, IC system is often coupled with other analytical detection techniques. In the recent years, this hyphenation has led to increased sample throughput and enhanced detection limits often in the range of ppt (ng L^{-1}). Also, since samples do not usually require pre-treatment steps, hence, hyphenated ion chromatographic techniques have been applied for determination of various trace ions in different complex matrices such as mammalian tissues and fluids, industrially contaminated water samples, different environmental samples, etc. Moreover, the simultaneous

determination of several ions in one analytical run has also been made accurate and precise by the hyphenation of IC. Thus, hyphenated IC techniques can be applied for the routine analysis of various inorganic analytes in samples with complex matrix components.

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