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Green Aspects of Ion Chromatography versus Other Methods in the Analysis of Common Inorganic Ions

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Abstract: Due to the increasing environmental awareness of the public, green chemistry has become an important element of environmental protection. In laboratories around the world, millions of analyses of inorganic and organic anions and cations in water and wastewater samples, and solid and gaseous samples are performed daily. Unfortunately, these activities still generate large costs, including environmental costs, which are related to the scale of the studies, the use of toxic chemical reagents, the waste generated, and the energy consumed. The methods used so far for inorganic ion analysis, including classical methods, are increasingly being replaced by instrumental methods, primarily based on ion chromatography. This paper presents the most important advantages and limitations of ion chromatography, and compares them with the costs of classical analyses for the analytes and sample types. Both the financial and environmental costs associated with the determination of common inorganic ions, such as Cl^-, NO_2^-, NO_3^-, and NH_4^+, in 1000 environmental samples, were compared using selected reference wet classical methods and ion chromatography. The advantages and limitations of ion chromatography that allow this separation technique to be classified as a green analytical chemistry method have been described herein.

Keywords: ion chromatography; green chemistry; environment; water; wet classical methods; ions

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1. Introduction

Green chemistry is defined as the search, design, and implementation of chemical products and processes that enable the reduction or elimination of the use and generation of hazardous waste [1,2]. It contributes to the introduction of new environmentally friendly technologies in line with the idea of sustainable development. Analytical chemistry, on the other hand, is a key element of chemistry, as it ensures evolution in other chemical sciences [3]. The term "green analytical chemistry" (GAC) was first used in 1981 by Anastas and Warner [4]. They developed principles that address the activities that analytical laboratories should consider within their work. The following are the criteria and general recommendations:

1. Direct measurement methods that do not require sample preparation for analysis should be used whenever possible;
2. The number and size of samples should be as small as possible;
3. If possible, the measurement should be performed in situ;
4. Individual analytical processes and operations should be integrated;
5. If possible, automated and miniaturized methods should be used;
6. Derivatization of samples prior to analysis should be avoided whenever possible;
7. The amount of waste generated should be drastically reduced and its management should be in accordance with applicable regulations;
8. Multi-parameter methods should be used wherever possible;
9. Energy consumption should be minimized;
10. Preference should be given to the use of reagents from renewable sources;

11. Toxic reagents and solvents should be eliminated or replaced with non-toxic alternatives;
12. Occupational safety of analytical chemists should be improved.

It is not possible to meet all of the above objectives simultaneously in laboratory realities, but they provide guidelines that should be followed when selecting a particular analytical method for a given application [5,6]. A vast majority of organic and inorganic compound determinations are performed using separation techniques, such as gas or liquid chromatography. Thus, it is very important that these common applications have a negligible environmental impact. Among analytical chemists, there has always been an awareness of the need to develop methodologies that allow for solvent and reagent savings, as well as the replacement of the most toxic chemicals with others that are harmless or less toxic. While complete elimination of sample preparation would be an ideal approach, it is not always practical [7]. This is especially true in regard to methods of sample preparation for analysis, including extraction methods [8].

A significant range of routinely carried out analyses concern the determination of various types of inorganic anions (including F^-, Cl^-, NO_2^-, NO_3^-, and SO_4^{2-}) and cations (including Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}) in water and wastewater [9]. This also applies to other important ions, such as inorganic by-products of water disinfection [10,11]. Classical wet methods, such as titration, colorimetric, gravimetric, turbidimetric, as well as electrochemical methods, are still used for the determination of inorganic anions and cations. However, in addition to the advantages of availability and low cost, many of these methods are time consuming and labor intensive. In addition, their frequent disadvantages are the use of expensive and toxic chemical reagents, and the lack of possibility of automation. Currently, ion chromatography (IC) dominates this analytical field [12].

2. Ion Chromatography

The HPLC (high-performance liquid chromatography) instrument should not be used as an ion chromatograph because of the strongly acidic and basic eluents used in IC, the conductivity detector, and the range of applications. In general, HPLC is mainly used for the analysis of organic compounds (e.g., hydrocarbons, alcohols, sugars), and IC is used for inorganic compounds (and carboxylic acids or amines). Overall, the purchase and daily operation costs of the HPLC apparatus are more expensive than an ion chromatograph. IC is a part of HPLC, used for the separation and determination of anions and cations, as well as other substances when they are converted to ionic forms [13]. Depending on the separation mechanisms used, the following can be distinguished:

- Ion chromatography, with or without conductivity suppression;
- Ion-exclusion chromatography (IEC);
- Ion-pair chromatography (IPC).

Its rapid development and popularity in routine laboratories is primarily due to the following advantages: the possibility of simultaneous analysis of several ions in a short timeframe (about 5–30 min); the small amount of sample needed for analysis (<0.5 mL); the possibility of using different detectors (e.g., conductivity, UV/Vis, amperometric, mass spectrometry); the simple methods of sample preparation for water sample analysis (filtration); the possibility of simultaneous analysis of cations and anions, or organic and inorganic ions; the high selectivity of separations; the possibility of ion analysis of the same element at different oxidation levels (speciation analysis) [14,15]; as well as the safety and cost of daily operation. Compared to HPLC, which uses expensive and toxic organic solvents as mobile phases, in IC, highly dilute aqueous solutions of Na_2CO_3/$NaHCO_3$ and NaOH/KOH (for anion separation), or dilute acids (for cation separation), are usually used as eluents. IC and related techniques are able to detect cations well, comparably to spectroscopic methods, and they are even more accurate for low concentrations [16]. Ammonium ions, which are not conventionally detected by spectroscopic methods, should also be kept in mind. It is often necessary to determine both anions and cations in a sample, and then IC, allowing for more information to be obtained with a single instrument, which is a more useful method. These advantages contributed to the fact that soon after the appearance of IC, a number of standardized methodologies were developed, in which it was used as a reference method for the analysis of anions and cations in various types of sample matrices [17].

2.1. Ion Chromatography Advances for Green Analytical Chemistry

Recently, IC has achieved a very high technological level. An overview of the technological advances in IC was recently presented by Wouters et al. [18]. These advances are mainly related to the introduction of more selective stationary phases, suppressor technologies, detection methods, and capillary [19] and multidimensional IC [20].

In 1983, Rokushika et al. described the theoretical basis of capillary IC, which has been commercially available since 2010 [21,22]. Great credit for the development and popularization of capillary IC belongs to the Japanese scientist Takeuchi, who, with his team, in the late 1980s, began his research related to this subject, which concerned both new stationary phases, detection methods, including a non-contact conductometric detector, and applications [23]. The implementation of capillary IC into laboratory practice has brought many benefits. These include the following: higher laboratory productivity (faster achievement of system stability); possible isocratic and gradient elution; higher determination sensitivity with smaller sample volume; 100-fold increase in absolute sensitivity compared to traditional columns (4 mm); particularly important in the context of green analytical chemistry, lower eluent consumption and minimization of waste generation. A comparison of selected parameters of conventional and capillary IC is given in Table 1.

Table 1. Comparison of selected parameters of conventional and capillary IC [24].

Parameter	Conventional IC	Capillary IC
Column diameter [mm]	4	0.4
Eluent flow rate [mL/min]	1.0	10
Typical injection volume [µL]	25	0.4 (0.1)
Average eluent consumption [L/month]	432	0.432
Limit of quantification [ng]	700	7

These features make miniaturized systems inherently "green" [25,26]. Multi-dimensional separations, in which the output of one chromatographic separation is interfaced to a second chromatographic separation, have increased the separation power of analytes in complex sample matrices. In the case of IC, there is significant potential to implement this approach by coupling different ion-exchange separations together, or even by combining ion exchange with some related IC methods (e.g., ion-exclusion chromatography). This approach has led to profound improvements in the ability of IC to handle very complex samples, especially those containing mixtures of inorganic and organic ions. Again, further developments in this area can be anticipated. There is a growing number of applications on multidimensional IC × IC techniques that use columns with significantly different selectivity. The first step involves the initial separation of analytes (or groups of analytes), followed by further, more selective, separation of the individual fractions. Although this procedure is complex and expensive, it provides very good results, especially for samples with complex matrices. As with other analytical methods and techniques, the most important problem is still the sample preparation for analysis, especially for those samples with complex matrices. Sample preparation for analysis by IC requires different steps, and their proper selection is determined by the physical sample state, its composition, and the availability of suitable apparatus. The correct ways of collecting, storing, and preparing the sample for analysis are key elements that affect the reliability of the analyses and the validity of inclusion of the sample in the green analytical chemistry method [27].

The main trends of green analytical chemistry focus on the effective reduction/elimination of organic solvents and other toxic reagents used, as well as the miniaturization and automation of applied methods. Moreover, the minimization of energy consumption, reduction in waste, and reuse of solvents and materials are very important. Compared to the status quo in the 1990s [28], current sample preparation methods tend to be faster, more efficient, more user and environmentally friendly, and easier to automate and miniaturize [29].

Let us assume that we are dealing with a routine analytical laboratory performing analyses of water and wastewater. It has unlimited access to a variety of methods and techniques, both manual and instrumental, with no economical limits. Its only criteria are the use of standardized methodologies and the demonstration of green aspects of applied methods. The comparison of both the financial and environmental costs of determining the same substances using different analytical methods is difficult, and is subject to considerable risks and errors. In order to assess the "environmental friendliness" of a given method more fully, it would be necessary to take into account the costs of energy, labor, analysis time, and the possibility of disposing the waste. In order to prove the thesis that IC has aspects of green analytical chemistry, an attempt has been made below to make such an estimation related to the determination of selected inorganic anions using the IC method. The total costs of single analyses of 1000 samples for the content of major inorganic anions (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) and cations (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}), taking into account the prices in Poland at the end of 2021, are summarized in Table 2. These vary depending on the type of sample matrix (clean water and wastewater), and represent approximate costs that may vary depending on the ion chromatograph manufacturer and the consumables and reagents used.

Table 2. Estimated averaged costs (euro) for determination of common inorganic anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and cations (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) in 1000 water and wastewater samples by isocratic IC.

Costs	**Water**		**Wastewater**	
Type of analysis	Anions	Cations	Anions	Cations
Eluent	2	5	2	5
Suppressor operating	10	-	10	-
Analytical column	2000	2000	2000	2000
Filtration	7	7	20	20
Total costs	2019	2012	2032	2025

2.2. Comparison of Ecological Aspects of Ion Chromatography and Other Standard Methods Case Study

Among the many factors affecting the assessment of applied methods as environmentally friendly, the type and amount of reagents used, their toxicity, and the amount and type of waste generated are very important. The choice of compared methods was based on their common use in laboratories accredited for routine water and wastewater analyses. The amount of reagents needed was calculated per 1000 water samples. The summaries for Cl^-, NO_2^-, NO_3^-, and NH_4^+ are given in Tables 3–6. When using the IC method (according to the ISO 10304-1 standard) for Cl^- determination, the only reagents needed are sodium carbonate and sodium bicarbonate, which are safe and used for eluent preparations. In turn, the determination of Cl^- in 1000 water samples by the Mohr method, according to the ISO 9297 standard, requires the consumption of 100 g of K_2CrO_4 and up to 193 g of $AgNO_3$. This undoubtedly puts this method at a disadvantage compared to IC. It is even worse when the flow methods FIA (flow injection analysis) or CFA (continuous flow analysis) (according to the ISO 15682 standard) are used for the same purpose. In this case, it may be necessary (depending on the variant adopted) to use the highly toxic $Hg(SCN)_2$. Moreover, the ISO 10304-1 standard allows simultaneous determination of not only Cl^-, but also NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} anions. In the case of NO_2^-, NO_3^- determination by using the FIA method (ISO 13395), depending on the option (FIA or CFA), it is necessary to use small, but toxic, amounts of organic compounds (e.g., 4-aminobenzenesulfonamide and *N*-(1-Naphthyl) ethylenediamine dihydrochloride).

Table 3. Comparison of the amount of reagents needed to determine Cl^- ions in 1000 water samples using different reference methods.

Method Number	Method Name			Reagents	Amount of Reagent per 1000 Samples
ISO 10304-1:2007 [1]	Water quality—determination of dissolved anions by liquid chromatography of ions—part 1: determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate			Na_2CO_3	8.58 g
				$NaHCO_3$	2.12 g
ISO 9297:1989	Water quality—determination of chloride—silver nitrate titration with chromate indicator (Mohr's method)			K_2CrO_4	100 g
				$AgNO_3$	3.08–193 g [2]
				NaCl	0.23 g
ISO 15682:2000	Water quality—determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection	photometric detection [3]	FIA	$Fe(NO_3)_3\ 9H_2O$	22.3–27.9 g
				$Hg(SCN)_2$	0.45–0.56 g
				CH_3OH	108–135 mL
				HNO_3, 65%	2.45–3.06 mL
			CFA	$Fe(NO_3)_3\ 9H_2O$	22.3–26.0 g
				$Hg(SCN)_2$	0.45–0.52 g
				CH_3OH	108–126 mL
				HNO_3, 65%	2.45–9.65 mL
				Detergent (Polyethylene glycol dodecyl ether)	0–1.2 mL
		potentiometric detection	FIA	HNO_3, 65%	0.15 mL
				KNO_3	7.27–36.4 g [4]
			CFA [5]	HNO_3, 65%	0.11–0.19 mL
				KNO_3	27.0–46.1 g
				Detergent (Polyethylene glycol dodecyl ether)	0.53–0.91 mL

[1] Separation conditions: analytical column: Dionex IonPac AS22 (4 × 250 mm); eluent: 4.5 mM Na_2CO_3 + 1.4 mM $NaHCO_3$; eluent flow rate: 1.2 mL/min; detection: suppressed conductivity; injection volume: 25 μL; analytical run time: 15 min. [2] Amount of $AgNO_3$ depends on concentration of chloride in sample (5 mg/L–400 mg/L); without sample dilution. [3] Amount of reagent depends on selected flow diagram, which is involved with concentration range. [4] Amount of KNO_3 depends on concentration range. [5] Amount of reagents depends on selected flow diagram, which is involved with flow rate.

Table 4. Comparison of the amount of reagents needed to determine NO_2^- ions in 1000 water samples by different reference methods.

Method Number	Method Name	Reagents	Amount of Reagent per 1000 Samples
ISO 10304-1:2007 [1]	Water quality—determination of dissolved anions by liquid chromatography of ions—part 1: determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate	Na_2CO_3	8.58 g
		$NaHCO_3$	2.12 g

Table 4. *Cont.*

Method Number	Method Name		Reagents	Amount of Reagent per 1000 Samples
ISO 13395:1996	Water quality—determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection	FIA	H_3PO_4, 85%	36 mL
			4-aminobenzenesulfonamide	3.6 g
			N-(1-Naphthyl) ethylenediamine dihydrochloride	0.36 g
		CFA	H_3PO_4, 85%	13.8 mL
			4-aminobenzenesulfonamide	1.38 g
			N-(1-Naphthyl) ethylenediamine dihydrochloride	0.19 g
			NH_4Cl	19.9 g
			HCl, 37%	1 mL
			Detergent (Polyethylene glycol dodecyl ether)	0.23 mL
			N_2	72 mL
ISO 6777:1984	Water quality—determination of nitrite—molecular absorption spectrometric method		H_3PO_4, 85%	200 mL
			4-aminobenzenesulfonamide	40 g
			N-(1-Naphthyl) ethylenediamine dihydrochloride	2 g

[1] Separation conditions: analytical column: Dionex IonPac AS22 (4 × 250 mm); eluent: 4.5 mM Na_2CO_3 + 1.4 mM $NaHCO_3$; eluent flow rate: 1.2 mL/min; detection: suppressed conductivity; injection volume: 25 µL; analytical run time: 15 min.

Table 5. Comparison of the amount of reagents needed to determine NO_3^- ions in 1000 water samples by different reference methods.

Method Number	Method Name		Reagents	Amount of Reagent per 1000 Samples
ISO 10304-1:2007 [1]	Water quality—determination of dissolved anions by liquid chromatography of ions—part 1: determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate		Na_2CO_3	8.58 g
			$NaHCO_3$	2.12 g
ISO 13395:1996	Water quality—determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection	FIA	H_3PO_4, 85%	72 mL
			4-aminobenzenesulfonamide	7.2 g
			N-(1-Naphthyl) ethylenediamine dihydrochloride	0.72 g
			NH_4Cl	40.8–102 g [2]
			HCl, 37%	1 mL
			Cadmium granulate	5.43 g

Table 5. *Cont.*

Method Number	Method Name	Reagents	Amount of Reagent per 1000 Samples
	CFA	H_3PO_4, 85%	22.8 mL
		4-aminobenzenesulfonamide	2.28 g
		N-(1-Naphthyl) ethylenediamine dihydrochloride	0.29 g
		HCl, 37%	1 mL
		NH_4Cl	39.3 g
		Detergent (Polyethylene glycol dodecyl ether)	0.70 mL
		Cadmium granules	5.43 g
		N_2	276 mL
ISO 7890-1:1986	Water quality—determination of nitrate—part 1: 2,6-Dimethylphenol spectrometric method	CH_3COOH	5 L
		2,6-dimethylophenol	6 g
		H_2SO_4, 98%	17.5 L
		H_3PO_4, 85%	17.5 L
		Amidosulfonic acid	1.4 g

[1] Separation conditions: analytical column: Dionex IonPac AS22 (4 × 250 mm); eluent: 4.5 mM Na_2CO_3 + 1.4 mM $NaHCO_3$; eluent flow rate: 1.2 mL/min; detection: suppressed conductivity; injection volume: 25 µL; analytical run time: 15 min. [2] Amount of reagent depends on selected flow diagram, which is involved with concentration range.

Table 6. Comparison of the amount of reagents needed to determine NH_4^+ ions in 1000 water samples using different reference methods.

Method Number	Method Name	Reagents	Amount of Reagent per 1000 Samples
ISO 14911:1998 [1]	Water quality—determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography—method for water and waste water	Methanesulfonic acid (MSA), 99%	52 mL
ISO 7150-1:1984 [2]	Water quality—determination of ammonium—part 1: manual spectrometric method	Strong cation exchange resin in hydrogen form	80 g
		H_2SO_4, 98%	0.8 mL
		Sodium salicylate	520 g
		Trisodium citrate dihydrate	520 g
		Sodium pentacyanonitrosylferrate dihydrate	3.88 g
		NaOH	128 g
		Sodium dichloroisocyanurate dehydrate	8 g

Table 6. *Cont.*

Method Number	Method Name	Reagents	Amount of Reagent per 1000 Samples
ISO 5664:1984	Water quality—determination of ammonium—distillation and titration method	H_3BO_3	1000 g
		Methyl red	0.25 g
		Methylene blue	0.15 g
		Bromothymol blue	0.5 g
		H_2SO_4, 98%	10–34 mL [3]
		Strong cation exchange resin in hydrogen form	1000–3400 g [3]
		MgO	250 g
		HCl, 0.02N	0.18–35.7 L [4]

[1] Separation conditions: analytical column: Dionex IonPac CS16 (5 × 250 mm); eluent: 30 mM MSA; eluent flow rate: 1.0 mL/min; detection: suppressed conductivity; injection volume: 25 µL; analytical run time: 26 min. [2] Without interferences. [3] Amount of reagents depends on analytical sample volume. [4] Amount of HCl (0.02N) depends on concentration of ammonium in sample.

3. Conclusions

The concept of green analytical chemistry is a very current topic, not only in theoretical academia discussions, but also in industrial, control and measurement laboratories [30]. In the range of determination of major inorganic ions, IC is currently the dominant method. Its availability and widespread use, especially in laboratories performing routine analyses (including environmental analyses), undoubtedly contributes to environmental protection. Its "green aspects" are mainly the use of low-cost and safe eluents; the speed and reproducibility of analyses; the small amount of sample needed for analysis and the waste generated; the non-use of organic solvents (in the vast majority of applications). Advances that have greatly accelerated the development of IC in recent years include the introduction of gradient elution and high-performance suppressors, more selective and dedicated stationary phases, capillary and multidimensional IC, or the miniaturization of instruments and combined techniques. An undoubtedly "green" aspect of IC is the miniaturized systems that require fewer consumables, generate less waste, and have much lower energy consumption compared to full-scale laboratory systems. They can often be moved to the sampling location, enabling "in situ" or "on-line" analysis. This significantly reduces the cost of performing the analysis and reduces the analysis time. Ion chromatography has large potential to be greener in all steps of the analysis, from sample collection and preparation to separation and final determination.

Similarly to any other analytical method, it also has some limitations [31]. Our needs are moving towards even better repeatability and selectivity, and lower limits of quantification and analysis costs. Other limitations include the time required for sample preparation because high accuracy in dilutions is required, which often requires attention to detail and good laboratory practice. The total analysis time per sample can also be significantly longer compared to manual and fully automated analyzers. The typical run times are approximately 20 min per sample. If the analysis was to be repeated three times for each sample, the total time would be 1 h. The additional limitations of operating costs are associated with consumable parts, which are usually made from plastic, which is harmful to the environment.

Fully automated methods, such as IC, contribute to increased unemployment in laboratories because a given number of analyses can be carried out by a much smaller number of analysts than would be needed to perform the same work using classical wet methods. In terms of routine anion and cation analysis, there are several methods available that are "greener" than IC. These are capillary electrophoresis methods [32], especially on microchips [33] and, above all, miniaturized flow methods [34]. Microfluidic devices offer many functionality advantages, mainly due to their structural and mechanical properties and high efficiency [35].

However, the estimates presented in this paper, and the comparison of IC with other selected classical methods for the determination of major inorganic ions, indicate that some of the advantages of IC provide a basis to include it among the methods of green analytical and environmental chemistry. IC continues to be a highly dynamic technique and shows no signs of stagnation. However, at this stage of IC development, the question of whether it is a green analytical method cannot be answered unequivocally. Here, it is worth quoting the former head of Greenpeace Paul Watson, "It doesn't matter what the truth is, only what people believe.

Table 7 summarizes a comparison of the compliance level to the 12 principles of green chemistry with respect to IC and classical wet methods for the determination of major inorganic anions and cations.

Table 7. Comparison of the degree of fulfillment of the 12 principles of green chemistry with respect to IC and classical methods for the determination of major inorganic anions and cations.

Principles of Green Chemistry	Green IC?	Wet Classical Methods
Wherever possible, direct measurement methods should be used that do not require preparation of samples for analysis	+ + +	+
The number and size of samples should be as small as possible	+ +	+
If possible, the measurement should be performed in situ	+	+ +
Individual processes and analytical operations should be integrated	+ +	+ +
Automatic and miniaturized methods should be used where possible	+ + +	+
If possible, derivatization of samples before analysis should be avoided	+ +	+ +
The amount of waste generated should be significantly reduced and its disposal should be in accordance with the applicable regulations	+ + +	+
Where possible, multi-parameter methods should be used	+ + +	+
Energy consumption should be minimized	+	+
The use of reagents from renewable sources should be preferred	+	+
Toxic reagents and solvents shall be eliminated or replaced by alternative non-toxic	+ + +	+
Safety of analyst chemists should be improved	+ + +	+

Degree of compliance with green analytical chemistry requirements. + + +: significantly, + +: rather yes, +: little or no.

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