

Ion chromatography as a part of green analytical chemistry

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Keywords: environment, water, ion chromatography, green chemistry, reference methods.

Abstract: Due to the increased environmental awareness, green chemistry becomes an important element of environmental protection. Unfortunately, it generate specific environmental costs, which are related to the use of toxic chemical reagents and waste generation. The most frequently determined analytes include inorganic and organic anions and cations. The methods used so far for their analysis in water, sewage and various other types of samples are increasingly being replaced by ion chromatography methods. This paper presents the most important advantages and limitations of ion chromatography in the context of “green analytical chemistry.” The progress of ion chromatography in gradient and isocratic elution, capillary and multidimensional ion chromatography, as well as miniaturization and methods of sample preparation for analysis, which allow to classify this technique as green analytical chemistry, are described.

Introduction

Climate change, environmental pollution and related threats to human health constitute problems of our times. At the beginning of 2020, the world was overrun by the coronavirus pandemic. This difficult time makes us realize how little we know about the world around us and how much we can change in it. But within the realm of what we know and can do to save the environment, there are issues related to so-called green analytical chemistry. Green chemistry includes the search for, design and implementation of chemical products and processes to reduce or eliminate the use and production of hazardous waste. It contributes to the introduction of new environmentally friendly technologies, it also influences people's thinking and lifestyle according to the idea of sustainable development. Analytical chemistry is a key element of chemistry as it ensures evolution in other fields of chemical sciences. The term Green Analytical Chemistry (GAC) was first used in 1988 (de la Guardia and Armenta 2011). In 1998, Anastas and Warner developed 12 principles of green chemistry. These were related to the following activities:

1. Wherever possible, direct measurement methods should be used that do not require preparation of samples for analysis.
2. The number and size of samples should be as small as possible.
3. If possible, the measurement should be done in-situ.
4. Individual processes and analytical operations should be integrated.
5. Automatic and miniaturized methods should be used where possible.

6. If possible, derivatization of samples before analysis should be avoided.
7. The number of waste generated should be significantly reduced and its disposal should be in accordance with the applicable regulations.
8. Where possible, multi-parameter methods should be used.
9. Energy consumption should be minimized.
10. The use of reagents from renewable sources should be preferred.
11. Toxic reagents and solvents shall be eliminated or replaced by alternative non-toxic ones.
12. Safety of analyst chemists should be improved.

It is practically impossible to meet all these conditions in the laboratory, but they are guidelines which should be followed when choosing an analytical method for a specific application. On their basis, several recommendations have been proposed in order to facilitate the evaluation of applied analytical procedures in terms of their compliance with the principles of green analytical chemistry (Namieśnik 2001).

Introduction of the idea of green chemistry was related to the spread of sustainable development principles and the tendency to implement these principles in laboratories and chemical plants (de la Guardia and Garrigues 2011). They also aroused great interest among chemists, especially those who understand that laboratory practices should and can be environmentally friendly (Armenta et al. 2008). Analytical laboratories play an important role in environmental protection by monitoring pollution in air, water or soil. The research conducted requires the use of various reagents and solvents, thus generating waste, including toxic waste. All this has made

the concept of green analytical chemistry a very topical issue, not only in the academic environment, but also in industrial, control and measurement laboratories (Płotka-Wasyłka and Namieśnik 2019). Among analyst chemists, there has always been an awareness of the need to develop methodologies to save solvents and reagents, and to replace the most toxic ones with others, harmless or less toxic (Armenta et al. 2015).

The ideal analytical method should allow for obtaining test results without the use of reagents and consumables, and should be performed on-line, without the need for sample preparation.

Every day, millions of analyses of different liquid, solid and gaseous samples are performed in analytical laboratories around the world. The scope of these tests is very wide and includes both organic and inorganic compounds. Chromatographic methods dominate the determination of organic substances and spectroscopic methods for metals and metalloids. The former are used both on a preparation and analytical scale. Gas chromatography (GC) and liquid chromatography (LC) can be used to separate and determine about 20% and 80% of known chemicals respectively (Witkiewicz and Kałużna-Czaplińska 2019). Unfortunately, in most cases it is required to prepare the sample before chromatographic analysis, which is related to the use of organic solvents. Fortunately, unlike HPLC, organic solvents are not commonly used in ion chromatography. They can be added to eluents that improve the shape of peaks and shorten the retention times of large ions. As most chromatographic determinations are carried out routinely, it is extremely important that they are conducted using methodologies with little environmental impact. The most frequently determined analytes not only in water and wastewater are inorganic anions (e.g. F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) and cations (e.g. Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+}). For their determination, classical methods are still used, such as: titration, colorimetric, gravimetric, turbidimetric and electrochemical methods. Apart from their undoubted advantages (availability, costs of analyses), many of them are characterized by significant influence of interfering factors, high detection and determination limits, low selectivity, high time and labor intensity, as well as the use of expensive and toxic chemical reagents, and lack of possibility of their automation. Currently, ion chromatography dominates in this area of research.

Ion chromatography

Unlike organic compounds, the use of chromatographic methods for the determination of inorganic substances did not bring the initially expected results. The breakthrough came in the early 1970s, when several works on the use of ion exchange chromatography for separation and determination of inorganic anions and cations were published (Small and Bowman 1998). The publication of Small, Steven and Baumann (1975) in *Analytical Chemistry* journal and the presentation of the first commercial ion chromatograph in September 1975 in Chicago during the annual convention of the American Chemical Society is considered a “milestone” in the development of ion chromatography.

Ion chromatography is a part of high-performance liquid chromatography used for separation and determination of anions and cations and other substances after conversion into

ionic forms. Depending on the separation mechanisms used there can be distinguished (Paull and Michalski 2019):

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

Its rapid development and popularity in laboratories carrying out routine analyses is due to the following advantages, among others:

1. Possibility of simultaneous analysis of several ions in a short time (about 5–30 minutes)

The methods previously used for inorganic ion analysis often require the use of expensive and toxic reagents, and in many cases are not sufficiently sensitive and reproducible, moreover they are often time-consuming. Nevertheless, many of them are still used in laboratories due to their availability and low cost. The possibility of simultaneous determination of several or more ions in combination with full automation of this process is one of the most important advantages of ion chromatography.

2. Small amount of sample required for analysis

Ion chromatography is primarily used for routine analyses of water and wastewater. However, in some cases it is necessary to perform the analysis in very small volume samples (e.g. mist samples). The volume of dosing loops used in ion chromatography is usually between 10 μ L and 1000 μ L and the minimum volume of sample needed for analysis is about 0.5 mL.

3. Possibility of using different detectors

Specific conductivity measurements are the most commonly used detection method in ion chromatography, because it is sensitive to all dissociated components and in the low concentration range, the conductivity is a linear function of ion concentration. In addition to the standard conductivity detector, the following detectors are used: UV/Vis, amperometric, fluorescent, chemiluminescent or mass spectrometry (MS), inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectrometry (ICP-OES) (Michalski 2016).

4. Preparation of samples for analysis

If samples with an unloaded matrices are tested, it is sufficient to pre-filter them through a 0.45 μ m pore diameter filter before entering the chromatographic column. For the analysis of samples with loaded matrices (e.g. sewage, emulsions) and solid and gaseous samples other methods of sample preparation are necessary.

5. Possibility of simultaneous analysis of cations and anions or organic and inorganic ions

Although the use of ion chromatography for analysis of anions resulted from its numerous advantages compared to the classical methods applied so far, its use for cation analysis was initially limited, mainly due to the colorimetric, potentiometric and spectroscopic methods used for this purpose. However, the advantage of ion chromatography is the possibility of simultaneous determination of ammonium ions and speciation analysis. This allows for obtaining more complete information about the tested sample using only one analytical method and one instrument.

6. Separation selectivity

Due to the volume of stationary phases used in columns, the maximum concentration of individual ions in the sample should

not exceed several hundred mg/L. Currently, ion exchange columns used, inter alia, for the analysis of bromate(V) traces or ammonium ions can also be determined in samples where the ratio of $\text{Cl}^-/\text{BrO}_3^-$ or $\text{Na}^+/\text{NH}_4^+$ ions is up to 10000:1.

7. Possibility of analyzing ions of the same element at different levels of oxidation (speculative analysis)

This advantage of ion chromatography has started to be appreciated especially in recent years with the development of speculative analytics. Depending on the degree of oxidation, different ions of the same element may differ significantly in their toxicological properties (e.g. $\text{Cr(III)}/\text{Cr(VI)}$; $\text{As(III)}/\text{As(V)}$, $\text{Sb(III)}/\text{Sb(V)}$, $\text{Tl(I)}/\text{Tl(III)}$, $\text{Se(IV)}/\text{Se(VI)}$). From the beginning of its existence ion chromatography has been used in speculative analysis, for simultaneous separation and determination of e.g. anions: $\text{NO}_2^-/\text{NO}_3^-$ or $\text{SO}_3^{2-}/\text{SO}_4^{2-}$. Currently it is the most important method for determination of inorganic by-products of water disinfection (BrO_3^- ; $\text{ClO}_2^-/\text{ClO}_3^-/\text{ClO}_4^-$) (Michalski and Łyko 2013) and ionic forms of metals and metalloids (Michalski et al. 2011).

8. Safety and low operation costs

Compared to high-performance liquid chromatography, in which expensive and toxic organic solvents are used as mobile phases, in ion chromatography, eluants are usually strongly diluted aqueous solutions of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ and NaOH/KOH (for separation of anions) or diluted acids (for separation of cations). Their advantages are low price, availability and safety both in use and disposal ("green chemistry").

Popularity of ion chromatography results from many reasons. For the determination of anions, colorimetric and potentiometric methods commonly known and available are used for the simultaneous determination of just one or several ions. Similar limitations apply to the flow methods (omitting multichannel systems) which are used in standard methods for the analysis of ions such as NO_2^- , NO_3^- and PO_4^{3-} . The situation was slightly different for cation analysis. Colorimetric and electrochemical methods, as well as spectroscopic methods such as Atomic Absorption Spectrometry (AAS), were and still are successfully used for their determination. Ion chromatography is characterized by good cation detection, comparable to spectroscopic methods, and for low concentrations it is even more accurate (Michalski 2009). It is often necessary to determine both anions and cations in a sample and then ion chromatography allowing to obtain more information with one instrument is more useful. Ammonium ions that are not detected by spectroscopic methods should also be considered. These advantages contributed to the fact that soon after ion chromatography was developed, a number of standardized methodologies were developed, which use it as a reference method for the analysis of anions and cations in different types of samples (Michalski 2006).

Progress in ion chromatography and its relevance to green analytical chemistry

Ion chromatography, like other analytical methods, develops rapidly. New more efficient and selective stationary phases, detection methods, sample preparation for analysis or methodological solutions to improve its efficiency are being introduced. In the following section the aspects of ion chromatography are described where the greatest progress is

being made in order to include it among the methods of green analytical and environmental chemistry. These are mainly: methods of sample preparation, types of elution (isocratic or gradient) and the introduction of an automatic eluent generator, capillary and multidimensional ion chromatography, and instrument miniaturization.

Samples preparation for ion chromatography

Sample preparation is usually the most labor-intensive part of the analysis and is the most important source of mistakes. In modern analytical chemistry, especially in trace analysis, sample preparation is often more difficult than the determination (Namieśnik et al. 2000). Sample analysis should be understood as a process consisting of many stages, including: sampling, fixation, transport, storage, preparation, determination and interpretation of obtained results. Determination – often mistakenly identified with analysis – ends the procedure in which one of the most important stages is sample preparation. The proper way of sampling, storing and preparing the sample for analysis is an important part of the final success, which is a reliable result of analysis (Frenzel and Michalski 2016). Due to the state of sample aggregation, sample preparation in ion chromatography can be divided into methods dedicated for:

1. Liquid samples (filtration, dilution, pH change, addition of standard, derivatization, liquid-liquid extraction, solid phase extraction, distillation, microdiffusion, membrane techniques).
2. Gas samples (absorption in solutions, absorption on solid media, sampling by membranes).
3. Solid samples (drying, homogenization, dissolution, extraction/leaching, digestion, combustion).

Most of the samples analyzed by ion chromatography are water and wastewater, which can be filtered through a 0.45 μm filter to remove the solids. In the case of solid samples, they shall be incinerated in oxygen or air and, after absorbing the gaseous products in suitable absorbent solutions, analyzed directly by ion chromatography. This solution is called Combustion Ion Chromatography (CIC). Whereas the analysis of substances in the gaseous phase is usually carried out by absorption in absorbent solutions, on solid sorbents or impregnated filters. Diffusion and permeation denuders can be an effective solution, especially due to the possibility of automated analysis (Slingsby and Kiser 2001).

Isocratic and gradient elution and automatic eluent generators

Until the late eighties of the 20th century, the gradient elution techniques were used only in ion chromatography with conductivity detection. It resulted from the fact that the most important inorganic anions and cations can be separated and determined under simple isocratic conditions. This has changed along with the need to determine other ions, especially in samples with complex matrices (e.g. food, medical and industrial samples). Two gradient elution options can be used in ion chromatography. The first is the so-called concentration gradient, during which the concentration of

eluent changes during the analysis, and the second option is the so-called component gradient, in which the composition of eluent changes by changing a weak eluent to a stronger one. In addition, the use of gradient techniques in ion chromatography was impeded by CO₂ absorption in hydroxide-based eluents, which interferes with the analysis due to unstable baseline and changing retention times of analytes.

In the analysis of multicomponent mixtures, it is extremely important to select the composition of eluent in order to obtain the appropriate separation. Furthermore, the eluent components must not react with each other or with parts of the chromatograph with which they are in direct contact. The eluent can be pressed by a pump through the column in isocratic or gradient mode. During isocratic elution, the composition of mobile phase is constant throughout the chromatographic process, and in gradient elution, during the separation, its concentration changes and the eluting strength of mobile phase increases. The most commonly used anion separation agents using ion chromatography with conductivity suppression in an isocratic system are aqueous solutions of sodium carbonate, sodium bicarbonate or their mixtures. Aqueous solutions of sodium or potassium hydroxide are used in the gradient system. Accurate, reproducible preparation of the eluent and its stability as well as its purity are crucial in ion chromatography. Incorrectly prepared eluent results in unique analysis conditions and measurement errors, which forces their repetition and generates additional financial and environmental costs. Therefore, a very important step in the evolution of ion chromatography has been the development and introduction of automatic eluent generators (Strong et al. 1991). The advantage of the resulting eluent is lack of gaseous pollutants such as CO₂, and the stability and repeatability of eluent composition (Yang et al. 2009). The advantage of this solution is also the fact that only ultra-pure water is used and KOH produced is completely free of CO₂ pollution because it is generated in a closed system. The maximum concentration of KOH produced in such devices is about 1000 mM at a flow rate of 1 mL/min, or 200 mM for capillary systems at 1 µL/min. The lifetime of such a filling depends on many parameters, including programmed KOH concentration, flow rate and operating time. For a KOH concentration of 50 mM/L and a flow rate of 1 mL/min, this means about 100 hours of continuous operation and up to 1.5 years for capillary systems. Moreover, the baseline noise from such an automatic eluent generator does not exceed several dozen nS/cm. The development of automatic eluent generators was initiated by Chen et al. (2012, 2012).

Miniaturization in ion chromatography

Traditional stationary IC systems, due to their size and weight, require large amounts of eluents and relatively large amounts of energy. As a result, it is neither practical nor cost-effective to attempt to use stationary on-situ sample monitoring systems. Environmental aspects such as the separation rate and sensitivity of ion determination can be improved by means of instrument miniaturization. This has many advantages of which space saving is probably the least important. Miniaturized chromatographic systems require less consumables, produce less waste and energy consumption is much lower compared

to full-scale laboratory systems. They can often be moved to a sampling point for on-sit or on-line analysis. This significantly reduces analysis costs and provides faster results. These features make miniaturized systems inherently “green”. Over the past years, several attempts have been made to produce portable IC systems, mainly aimed at monitoring inorganic and organic ions in natural waters. For example, in the 1990s Baram (1996) developed a portable ion chromatograph weighing about 15 kg, for use in a mobile laboratory. Boring et al. (1998) described a portable ion chromatograph weighing only 10 kg, using capillary columns and conductivity detection. Shortly afterwards, Tanaka et al. (1999) used a commercial ion chromatograph powered by a car battery, which weighed 15 kg. At the beginning of the 21st century Kalyakina and Dolgonosov (2003) produced a portable ion chromatograph with a 10 kg conductivity detector. In turn, Kiplagat et al. (2010) developed a lightweight, as weighing < 2.5 kg, ion chromatograph dedicated to cation analysis, while Elkin (2014) developed an autonomous on-situ ion chromatography device. The latter system used standard components and weighed 13 kg without batteries and solar cells.

Another example is the ion chromatograph described by Murray et al. (2018) with a modular design, which allowed for easy modification. It weighed only 0.6 kg and had dimensions of 25 × 25 cm. Isocratic separation of the main anions (F⁻, Cl⁻, NO₂⁻, Br⁻ and NO₃⁻) could be achieved in less than 15 minutes using sodium benzoate eluate at a flow rate of 3 µL/min. The Waters IC-Pak 10 µm capillary column had dimensions (0.150 × 150 mm) and the detector was a UV/Vis detector. There are few publications on the applications of ion chromatography in integrated circuits, mainly due to technical difficulties such as: nano flow control and poor resolution at typical stationary phases and the resulting pressure. This makes ion chromatography in the microchip version more sophisticated technologies than e.g. capillary electrophoresis or capillary electrochromatography in the chip version. The first paper on this issue was published by Murrhiy et al. in 2001.

Capillary and multidimensional ion chromatography

In 1983 Rokushika et al. described the theoretical basis of capillary ion chromatography. Unfortunately, due to the lack of appropriate technology in those years it was not commercialized. It is only thanks to solutions developed by Dionex that capillary ion chromatography has been commercially available since 2010. Technical details and applications of this technique were described by Kuban and Dasgupta (2004) and later by Yang et al. (2012). Unfortunately, due to the cost of applied technologies, the use of capillary ion chromatography in laboratories is not common.

The particle diameters of stationary phase columns used for ion chromatography are usually between 3 µm and 50 µm. The analytical columns are 2 mm to 5 mm in diameter and 25 mm to 250 mm in length. The capillary columns are 10 times smaller in diameter than traditional columns. Although stationary phases used in them are the same, the reduction of column diameter alone forces lower eluent flow rates of about 10 µL/min and a dosed sample volume of about

0.4 μL . The introduction of capillary ion chromatography into laboratory practice has brought many benefits. The most important are higher laboratory performance (faster system stability), lower calibration requirements, possible isocratic and gradient elution, higher sensitivity of determination with a smaller sample volume, 100-fold increase in absolute sensitivity compared to 4 mm systems, multidimensional IC \times IC (2D IC) – detection limits in the ng/L range of only 1 mL of sample, lower cost of use and, what is particularly important in the context of green analytical chemistry, lower consumption of eluent, and less waste. The comparison of selected analytical and capillary IC parameters has been presented in Table 1.

Compared to conventional columns with a diameter of e.g. 4 mm, reducing the size of column also requires matching other chromatograph elements. This is not a simple transfer of a conventional IC to a miniaturized form (Ng et al. 2011).

Further miniaturization of the chromatographic columns has a “green” nature only when micro and nano-liter pumps are used. Ion chromatography uses single piston pumps, parallel double piston pumps and serial double piston pumps. They can be divided into isocratic or gradient pumps, with gradients on the low or high pressure side. In capillary ion chromatography it is possible to use three types of high capacity micro-pumps such as syringe, electro-osmotic or thermal expansion pumps. Unfortunately they are expensive and with many limitations.

The maximum pressure in commercially available ion chromatography instruments is currently limited to 345 bar. This is not much in contrast to HPLC, and especially to UHPLC, where it can be significantly above 1000 bar (Wouters et al. 2017). This pressure limitation is mainly due to the use of eluants with a wide pH range and also to the diameter of stationary phase particles in the analysis column (De Vos et al. 2015). Among the key elements of capillary ion chromatography system, a detector, especially a conductivity detector, is the easiest to miniaturize. This technology was first developed for capillary electrophoresis and then adopted in capillary ion chromatography. The non-contact C4D conductivity detector introduced in 1998 can be used both in capillary electrophoresis and ion chromatography, mainly due to its robustness, minimum maintenance requirements and low cost (Zemann et al. 1998). The Japanese scientist Takeuchi, who started research on this subject with his team as early as the end of the 1980s, has a great merit in developing and popularizing capillary ion chromatography. They concerned both new stationary phases (Sedyohutomo et al. 2012, Takeuchi et al. 2009, Lim et al. 2014, Rahayu et al. 2015), detection methods, including non-contact conductivity detector (Rong et al. 2012), and their applications (Sedyohutomo et al. 2008).

Multidimensional IC

Taking into account the problems of selectivity of analytic separation, especially in samples with complex matrices, two- or multidimensional ion chromatography may be an effective solution. The possibility to combine analytical columns with different selectivity as well as different separation mechanisms creates unique possibilities to improve separation and simultaneously determine more analytes than is possible in one-dimensional chromatography (Johns et al. 2009, Shellie et al. 2008). An increasing number of published papers concern two-dimensional IC \times IC techniques using columns with significantly different selectivity. The first stage consists in the initial separation of analytes (or groups of analytes) and the next in the further more selective separation of individual fractions. Although such a procedure is more complex and expensive, it provides very good results especially for samples with complex matrices. Improved separation is achieved by both isocratic and gradient multidimensional separation (also with mobile phase flow gradient or pH) (Jandera 2012). Examples include the determination of anions and cations in mineral waters (Fa et al. 2018) or halogenacetic acids in drinking water (Verrey et al. 2013).

Conclusions

Taking into account the above mentioned advantages, can ion chromatography be classified as a method of green analytical chemistry? What criteria should guide such an assessment? Taking into account its efficiency, it is necessary to take into account, among others, the time needed to perform the analysis, labor intensity and types of methods to prepare samples for analysis, amount and type of reagents used and waste generated, as well as energy costs. All this should be compared with analogous parameters for other alternative but often used methods in laboratories. It will not provide a complete image as it is not possible to determine all the factors, nevertheless important information on the ecological aspects of the method will be obtained.

Ion chromatography has been commercially available since 1975. It has evolved from a simple method of separating main inorganic anions and cations in water to an advanced separation method which, combined with modern detection methods, allows for the determination of ionic substances in samples that are not only liquid but also gaseous and solid. The cost of an ion chromatograph is comparable to that of other equipment of a similar class (gas and liquid chromatographs, instruments for atomic absorption spectrometry), which are increasingly becoming standard equipment in laboratories. An

Table 1. Comparison of selected parameters for analytical and capillary ion chromatography

Parameter	Conventional IC	Capillary IC
Column diameters	4 mm	0.4 mm
Eluent flow rate	1.0 mL/min	0.01 ml/min
Typical injection volume	25 μL	0.4 μL
Eluent consumption	432 L/month	0.432 L/month
Limits of quantification	700 ng	7 ng

ion chromatograph used correctly by an experienced analyst who is aware of its advantages and limitations, should be a very important and efficient element of the analytical system in control and measurement laboratories as well as in research and development laboratories. Its availability and universality of use, especially in laboratories performing routine analyses (including environmental) undoubtedly contributes to the protection of both users and the environment.

The progress in development of ion chromatography described in this paper proves that it can be classified as a green analytical chemistry method. Hopefully, it will soon completely replace some of the ion determination methods used so far, especially in waters and wastewaters, which are not only laborious and time-consuming but also sometimes harmful to the environment.

References

- Anastas, P.T. & Warner, J.C. (1998). *Green Chemistry: Theory and Practice*, Oxford University Press Inc, New York 1998.
- Armenta, S., Garrigues, S. & de la Guardia, M. (2008). Green analytical chemistry, *TrAC Trends in Analytical Chemistry*, 27, 6, pp. 497–511, DOI: 10.1016/j.trac.2008.05.003.
- Armenta, S., Garrigues, S. & de la Guardia, M. (2015). The role of green extraction techniques in Green Analytical Chemistry, *TrAC Trends in Analytical Chemistry*, 71, pp. 2–8, DOI: 10.1016/j.trac.2014.12.011.
- Baram, G.I. (1996). Portable liquid chromatograph for mobile laboratories I. Aims, *Journal of Chromatography A*, 728, 1–2, pp. 387–399, DOI: 10.1016/0021-9673(95)01271-0.
- Boring, C.B., Dasgupta, P.K. & Sjögren, A. (1998). Compact, field-portable capillary ion chromatograph, *Journal of Chromatography A*, 804, 1–2, pp. 45–54, DOI: 10.1016/S0021-9673(98)00139-3.
- Chen, Y., Edwards, B.L., Dasgupta, P.K. & Srinivasan, K. (2012). pH-and concentration-programmable electro-dialytic buffer generator, *Analytical chemistry*, 84, 1, 59–66, DOI: 10.1021/ac2023734.
- Chen, Y., Srinivasan, K. & Dasgupta, P.K. (2012). Electro-dialytic membrane suppressors for ion chromatography make programmable buffer generators, *Analytical chemistry*, 84, 1, pp. 67–75, DOI: 10.1021/ac2023712.
- de la Guardia, M. & Armenta, S. (2011). Origins of green analytical chemistry. In: de la Guardia, M. & Armenta, S. (Eds), *Comprehensive Analytical Chemistry (vol. 57)*, Elsevier Science & Technology, Oxford, pp. 1–23.
- de la Guardia, M. & Garrigues, S. (2011). An ethical commitment and an economic opportunity. In: de la Guardia, M. & Garrigues, S. (Eds), *Challenges in Green Analytical Chemistry*, Royal Society of Chemistry, Cambridge, pp. 1–12.
- De Vos, J., De Pra, M., Desmet, G., Swart, R., Edge, T., Steiner, F. & Eeltink, S. (2015). High-speed isocratic and gradient liquid-chromatography separations at 1500 bar, *Journal of Chromatography A*, 1409, pp. 138–145, DOI: 10.1016/j.chroma.2015.07.043.
- Elkin, K.R. (2014). Portable, fully autonomous, ion chromatography system for on-site analyses, *Journal of Chromatography A*, 1352, pp. 38–45, DOI: 10.1016/j.chroma.2014.05.046.
- Fa, Y., Yu, Y., Li, F., Du, F., Liang, X. & Liu, H. (2018). Simultaneous detection of anions and cations in mineral water by two dimensional ion chromatography, *Journal of Chromatography A*, 1554, pp. 123–127, DOI: 10.1016/j.chroma.2018.04.017.
- Frenzel, W. & Michalski, R. (2016). Sample preparation techniques for ion chromatography, In: Michalski, R. (Ed.), *Application of IC-MS and IC-ICP-MS in Environmental Research*, John Wiley & Sons Inc, New York, pp. 210–266.
- Jandera, P. (2012). Programmed elution in comprehensive two-dimensional liquid chromatography, *Journal of Chromatography A*, 1255, pp. 112–129, DOI: 10.1016/j.chroma.2012.02.071.
- Johns, C., Shellie, R.A., Pohl, C.A. & Haddad, P.R. (2009). Two-dimensional ion chromatography using tandem ion-exchange columns with gradient-pulse column switching, *Journal of Chromatography A*, 1216, 41, pp. 6931–6937, DOI: 10.1016/j.chroma.2009.08.018.
- Kalyakina, O.P. & Dolgonosov, A.M. (2003). Ion-chromatographic determination of fluoride ions in atmospheric precipitates and natural waters, *Journal of Analytical Chemistry*, 58, 10, pp. 951–953.
- Kiplagat, I.K., Kubáň, P., Pelcová, P. & Kubáň, V. (2010). Portable, lightweight, low power, ion chromatographic system with open tubular capillary columns, *Journal of Chromatography A*, 1217, 31, pp. 5116–5123, DOI: 10.1016/j.chroma.2010.06.017.
- Kuban, P. & Dasgupta, P. K. (2004). Capillary ion chromatography, *Journal of separation science*, 27, 17–18, pp. 1441–1457, DOI: 10.1002/jssc.200401824.
- Lim, L.W., Tokunaga, K. & Takeuchi, T. (2014). Development of chemically bonded crown ether stationary phases in capillary ion chromatography, *Chromatography*, 35, 2, pp. 95–101, DOI: 10.15583/jpchrom.2014.012.
- Michalski, R. (2006). Ion chromatography as a reference method for determination of inorganic ions in water and wastewater, *Critical Reviews in Analytical Chemistry*, 36, 2, 107–127, DOI: 10.1080/10408340600713678.
- Michalski, R. (2009). Applications of ion chromatography for the determination of inorganic cations, *Critical Reviews in Analytical Chemistry*, 39, 4, pp. 230–250, DOI: 10.1080/10408340903032453.
- Michalski, R. (2012). Hyphenated methods for speciation analysis, In: Meyers, R.A. (Ed.), *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*, John Wiley & Sons Inc., New York, pp. 1–20.
- Michalski, R. (Ed.). (2016). *Application of IC-MS and IC-ICP-MS in environmental research*, John Wiley & Sons Inc., New York 2016.
- Michalski, R. & Łyko, A. (2013). Bromate determination: state of the art, *Critical Reviews in Analytical Chemistry*, 43, 2, pp. 100–122, DOI: 10.1080/10408347.2012.747792.
- Michalski, R., Jabłonska, M., Szopa, S. & Łyko, A. (2011). Application of ion chromatography with ICP-MS or MS detection to the determination of selected halides and metal/metalloids species, *Critical Reviews in Analytical Chemistry*, 41, 2, pp. 133–150, DOI: 10.1080/10408347.2011.559438.
- Murray, E., Li, Y., Currivan, S.A., Moore, B., Morrin, A., Diamond, D., Macka, M. & Paull, B. (2018). Miniaturized capillary ion chromatograph with UV light-emitting diode based indirect absorbance detection for anion analysis in potable and environmental waters, *Journal of separation science*, 41, 16, pp. 3224–3231, DOI: 10.1002/jssc.201800495.
- Murrihy, J.P., Breadmore, M.C., Tan, A., McEnery, M., Alderman, J., O'Mathuna, C., O'Neill, A.P., O'Brien, P., Avdalovic, N., Haddad, P.R. & Glennon, J.D. (2001). Ion chromatography on-chip, *Journal of chromatography A*, 924, 1–2, pp. 233–238, DOI: 10.1016/S0021-9673(01)00855-X.
- Namieśnik, J. (2001). Green analytical chemistry – some remarks, *Journal of separation Science*, 24, 2, pp. 151–153, DOI: 10.1002/1615-9314(20010201)24:2<151::AID-JSSC151>3.0.CO;2-4.
- Namieśnik, J., Łukasik, J. & Jamrógiewicz, Z. (2000). *Przygotowanie próbek środowiskowych do analiz*, WNT, Warszawa 2000. (in Polish)

- Ng, B.K., Shellie, R.A., Dicoski, G.W., Bloomfield, C., Liu, Y., Pohl, C.A. & Haddad, P.R. (2011). Methodology for porting retention prediction data from old to new columns and from conventional-scale to miniaturised ion chromatography systems, *Journal of Chromatography A*, 1218, 32, pp. 5512–5519, DOI: 10.1016/j.chroma.2011.06.050.
- Paull, B. & Michalski, R. (2019). Ion Chromatography Principles and Applications. In: Worsfold, P., Poole, C., Townshend, A. & Miró, M. (Eds.), *Encyclopedia of Analytical Science*, Elsevier Health Sciences, London, pp. 178–189.
- Płotka-Wasyłka, J. & Namieśnik, J. (Eds.). (2019). *Green Analytical Chemistry: Past, Present and Perspectives*, Springer, Singapore 2019.
- Rahayu, A., Lim, L. W. & Takeuchi, T. (2015). Preparation of a hybrid monolithic stationary phase with allylsulfonate for the rapid and simultaneous separation of cations in capillary ion chromatography, *Journal of separation science*, 38, 7, pp. 1109–1116, DOI: 10.1002/jssc.201401264.
- Rokushika, S., Qiu, Z.Y. & Hatano, H. (1983). Micro column ion chromatography with a hollow fibre suppressor, *Journal of Chromatography A*, 260, pp. 81–87, DOI: 10.1016/0021-9673(83)80009-0.
- Rong, L., Liu, Z., Ma, M., Liu, J., Xu, Z., Lim, L. W. & Takeuchi, T. (2012). Simultaneous Determination of Inorganic Cations by Capillary Ion Chromatography with a Non-suppressed Contactless Conductivity Detector, *Analytical sciences*, 28, 4, pp. 367–367, DOI: 10.2116/analsci.28.367.
- Sedyohutomo, A., Lim, L.W. & Takeuchi, T. (2008). Development of packed-column suppressor system for capillary ion chromatography and its application to environmental waters, *Journal of Chromatography A*, 1203, 2, pp. 239–242, DOI: 10.1016/j.chroma.2008.07.055.
- Sedyohutomo, A., Suzuki, H. & Fujimoto, C. (2012). Determination of inorganic anions by capillary ion-exchange chromatography using polyethylenimine-coated octadecyl-bonded phases, *Analytical Sciences*, 28, 6, pp. 625–629, DOI: 10.2116/analsci.28.625.
- Shellie, R.A., Tyrrell, É., Pohl, C.A. & Haddad, P.R. (2008). Column selection for comprehensive multidimensional ion chromatography, *Journal of separation science*, 31, 19, pp. 3287–3296, DOI: 10.1002/jssc.200800286.
- Slingsby, R. & Kiser, R. (2001). Sample treatment techniques and methodologies for ion chromatography, *TrAC Trends in Analytical Chemistry*, 20, 6–7, pp. 288–295, DOI: 10.1016/S0165-9936(01)00069-3.
- Small, H. & Bowman, B. (1998). Ion chromatography: A historical perspective, *American laboratory (Fairfield)*, 30, 21, pp. 56C–62C.
- Small, H., Stevens, T.S. & Bauman, W.C. (1975). Novel ion exchange chromatographic method using conductometric detection, *Analytical Chemistry*, 47, 11, pp. 1801–1809, DOI: 10.1021/ac60361a017
- Strong, D.L., Dasgupta, P.K., Friedman, K. & Stillian, J.R. (1991). Electrodealytic eluent production and gradient generation in ion chromatography, *Analytical chemistry*, 63, 5, pp. 480–486, DOI: 10.1021/ac00005a019.
- Takeuchi, T., Oktavia, B. & Lim, L.W. (2009). Poly (ethylene oxide)-bonded stationary phase for capillary ion chromatography, *Analytical and bioanalytical chemistry*, 393, 4, pp. 1267–1272, DOI: 10.1007/s00216-008-2533-7.
- Tanaka, K., Ohta, K., Haddad, P.R., Fritz, J.S., Lee, K.P., Hasebe, K., Ieuji, A. & Miyanaga, A. (1999). Acid-rain monitoring in East Asia with a portable-type ion-exclusion-cation-exchange chromatographic analyzer, *Journal of chromatography A*, 850, 1–2, pp. 311–317, DOI: 10.1016/S0021-9673(99)00286-1.
- Verrey, D., Louyer, M.V., Thomas, O. & Baurès, E. (2013). Direct determination of trace-level haloacetic acids in drinking water by two-dimensional ion chromatography with suppressed conductivity, *Microchemical Journal*, 110, pp. 608–613, DOI: 10.1016/j.microc.2013.07.012.
- Witkiewicz, Z. & Kałużna-Czaplińska, J. (2019). *Podstawy chromatografii i technik elektromigracyjnych*, PWN, Warszawa 2019. (in Polish)
- Wouters, S., Bruggink, C., Agroskin, Y., Pohl, C. & Eeltink, S. (2017). Microfluidic membrane suppressor module design and evaluation for capillary ion chromatography, *Journal of Chromatography A*, 1484, pp. 26–33, DOI: 10.1016/j.chroma.2016.12.078.
- Yang, B., Zhang, F. & Liang, X. (2009). A simplified ion exchange bead-based KOH electrodyalytic generator for capillary ion chromatography, *Talanta*, 79, 1, pp. 68–71, DOI: 10.1016/j.talanta.2009.03.004.
- Yang, B., Zhang, F. & Liang, X. (2012). Recent development in capillary ion chromatography technology, *Central European Journal of Chemistry*, 10, 3, pp. 472–479, DOI: 10.2478/s11532-011-0148-x.
- Zemann, A.J., Schnell, E., Volgger, D. & Bonn, G.K. (1998). Contactless conductivity detection for capillary electrophoresis, *Analytical chemistry*, 70, 3, pp. 563–567, DOI: 10.1021/ac9707592.

Chromatografia jonowa jako część zielonej chemii analitycznej

Streszczenie: Ze względu na zwiększoną świadomość ekologiczną, zielona chemia staje się ważnym elementem ochrony środowiska. Laboratoria na całym świecie przeprowadzają miliony analiz różnych substancji. Niestety generują one określone koszty środowiskowe, co związane jest stosowaniem toksycznych odczynników chemicznych i wytwarzaniem odpadów. Do najczęściej oznaczanych analitów należą aniony i kationy. Dotychczas stosowane metody ich analiz są coraz częściej zastępowane metodami chromatografii jonowej. W pracy przedstawiono najważniejsze zalety i ograniczenia chromatografii jonowej w kontekście „zielonej chemii analitycznej”. Opisano postępy w zakresie elucji gradientowej i izokratycznej, kapilarnej i wielowymiarowej IC, miniaturyzacji i metod przygotowania próbek, które pozwalają na jej zaliczenie do metod zielonej chemii analitycznej.