

Environmental Applications of Ion Chromatography in Eastern and Central Europe

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Abstract

Environmental analytics is one of the most important applications of ion chromatography. It includes determination of ions in water and wastewater as well as in gaseous and solid ones. Nowadays, ion chromatography has almost completely displaced the classical methods of ion determination in these areas. In spite of the fact that the ion chromatography has been officially present in the scientific world for 36 years, its role and popularity is highly diversified in various countries and regions of the world. In highly industrialized countries, it has been a reference method of water and wastewater analysis for years. In other parts of the world, it is not used and appreciated sufficiently despite its undeniable advantages. The following paper is a short overview of the most highly cited scientific and research institutions that conduct research in terms of environmental applications of ion chromatography in Eastern and Central Europe. Furthermore, the paper presents a list of a number of scientific papers referring to the discussed area, published in the years 1996–2009 in some of the most highly cited international scientific journals, and concerning publications of scientists from Eastern and Central Europe seen against the background of Europe and the world.

Introduction

Chromatography as a method of separation was discovered in 1903 when a Russian botanist Mikhail Semyonovich Tsvet, who worked at the University of Warsaw, separated vegetable dyes by using the phenomenon of adsorption in a chromatography column filled with different substances including calcium carbonate (1).

In order to describe this method with Greek words meaning “color” and “writing”, he coined a new term—“chromatography”. Even though many scientists initially ignored the method discovered by Tsvet, its tremendous significance is recognized after over 100 years. Possibly, if its author were still alive, he would be awarded the Nobel Prize.

As it has already been mentioned, at the beginning, chromatography did not arouse chemists’ interest. Actually, its rapid

development began several decades after Tsvet’s historic discovery. Gas chromatography and thin-layer chromatography were developed faster than liquid chromatography, as they were more easily handled in technological terms.

It is estimated that using gas chromatography enables separation and determination of approximately 20% of known chemical compounds, whereas in the case of liquid chromatography it is about 80% of compounds. The chromatographic methods are commonly applied in terms of both preparative and analytical scales, and a gas chromatograph is the most common analytical apparatus in the world. Works related to chromatographic methods were frequently awarded the Nobel Prize (2).

In the 1950s, chromatographic methods (gas chromatography, liquid, and thin-layer chromatography) were successfully applied in chemical analytics, but their applications were limited mostly to the determination of the organic compounds.

The classical techniques such as titration, colorimetric, gravimetric, turbidimetric as well as electrochemical methods were successfully used in order to determine inorganic ions. Despite their obvious advantages (such as the availability or low analysis cost), most of them are highly laborious and characterized by significant influence of matrix interferences, high limits of detection and quantification, and low sensitivity and selectivity. In many cases, those methods require the use of expensive and toxic chemical reagents, and they are characterized by the lack of the possibility of their automation.

At first, the research connected with using chromatographic methods for the inorganic substances analysis was not as effective as estimated. The breakthrough was made at the beginning of the 1970s when a few publications referring to the use of ion exchange chromatography for the separation and determination of inorganic cations and anions were published (3). The two milestones in the ion chromatography development were the publishing of Small, Stevens, and Baumann’s work in *Analytical Chemistry* (4) and the presentation of the first commercial ion chromatograph at the annual American Chemical Society meeting in Chicago in September 1975.

It is estimated that the liquid chromatography market (understood as the value of the yearly apparatus and accessories production) amounted to approximately \$3 billion (including approximately \$165 million as the value of ion chromatographs sale) in 2000 (5). By 2002, about 25,000 ion chromatographs had

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been sold around the world, and the number of applications had exceeded 4,000 (6). Currently, those values are certain to be even higher.

The share of the particular world regions in the ion chromatography market is shown in the Figure 1. It is predicted by the market specialists that the demand for the ion chromatography apparatus and accessories will gradually increase, particularly in regions that have not had significant importance so far such as South American, Asia (except for Japan), and Eastern and Central Europe (7,8).

Because of many economical and political reasons at the end of the 20th century, Central and Eastern Europe was out of the main trend of world science. It was often attributed to technological underdevelopment and constant lack of financial provision for the science division in these countries. The situation is under constant improvement, and recently this region is a very attractive place for research. Considering the human potential, Eastern and Central European create an attractive market for companies specializing in ion chromatography and capillary electrophoresis.

Recently developed methods tend to reflect general advances in the field of ion chromatography, such as use of higher capacity columns, larger loop injections, and more complex sample preparation and detection schemes. This, in turn, allows the simultaneous determination of inorganic cations at lower detection limits and expands the range of analytes, which can be measured in different matrix samples such as environmental samples.

The most important advantages of ion chromatography are the possibility of simultaneous determination of several ions, short time of analysis, low limits of detection, a small amount of sample needed for analysis, the possibility of using various detectors (conductivity detectors, UV-Vis, amperometric and potentiometric detectors, ICP-MS, MS, chemoluminescence detectors). Ion chromatography is also a simple method of samples preparation (in the case of waters it is usually sufficient to filter water through a filter with pore diameter of 0.45 μm) and makes possible the simultaneous determination of cations and anions or organic and inorganic ions. Its high selectivity in relation to determined substances in samples with complex matrix and use of inexpensive and safe eluents (these are usually water solutions of sodium carbonate/bicarbonate or highly dilute inorganic acids/bases) also make it a favorable method. Finally, it can determine ions of the same element with different oxidation states [speciation analytics, e.g., $\text{Cl}^-/\text{ClO}_2^-/\text{ClO}_3^-/\text{ClO}_4^-$, $\text{Br}^-/\text{BrO}_3^-$, $\text{NO}_2^-/\text{NO}_3^-/\text{NH}_4^+$, $\text{Cr(III)}/\text{Cr(VI)}$, $\text{Fe(II)}/\text{Fe(III)}$].

The previously mentioned ion chromatography advantages as well as the possibility of full automation of analyses contributed to the fact that a number of normalized methods in which ion chromatography determination of anions and cations was used were elaborated as soon as the 1980s (9,10).

The laboratories usually carry out chromatographic analyses based on research apparatus producers' methodologies, their own methodologies, or the international methods, such as those of the U.S. Environmental Protection Agency (U.S. EPA) or International Organization for Standardization (ISO).

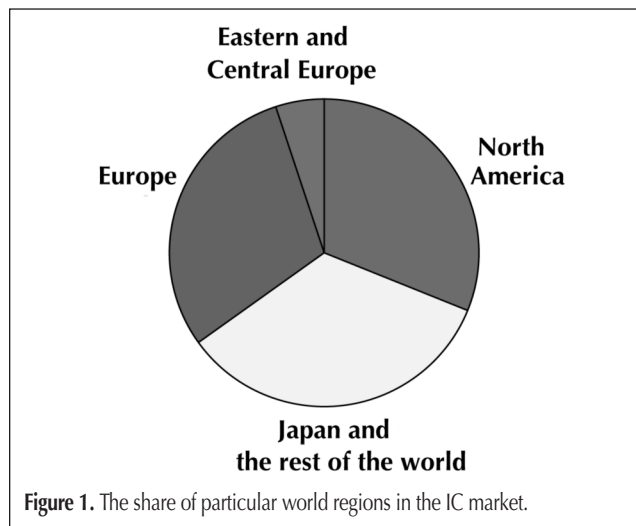
Whereas in the highly industrialized countries the U.S. EPA and ISO standards were used as early as in the 1980s and 1990s,

the standards translations appeared in the countries of Eastern and Central Europe a few years later. In terms of water and wastewater analysis, the following ISO standards are available nowadays (the year in brackets is the year when the standard was published in most of Eastern and Central Europe countries): ISO 10304-1:1992 (1998) *Water Quality—Determination of Dissolved Fluoride, Chloride, Nitrite, Orthophosphate, Bromide, Nitrate and Sulphate Ions Using Liquid Chromatography of Ions. Part 1: Method for Water with Low Contamination*; ISO 10304-2:1997 (2000) *Water Quality—Determination of Dissolved Anions by Liquid Chromatography of Ions. Part 2: Determination of Bromide, Chloride, Nitrate, Nitrite, Orthophosphate and Sulphate in Waste Waters*; ISO 10304-3:1997 (2000) *Water Quality—Determination of Dissolved Anions by Liquid Chromatography of Ions. Part 3: Determination of Chromate, Iodide, Sulphite, Thiocyanate and Thiosulfate*; ISO 10304-4:1998 (2001) *Water Quality—Determination of Dissolved Anions by Liquid Chromatography of Ions. Part 4: Determination of Chlorate, Chloride and Chlorite in Water with Low Contamination*; ISO 14911:1998 (2001) *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*; ISO 15061:2001 (2004) *Water Quality—Determination of Dissolved Bromate. Method by Liquid Chromatography of Ions*.

When it comes to the solid samples, there is only one ISO standard (15192) referring to the determination of Cr(VI) ions, and it is entitled *Characterisation of waste and soil—Determination of hexavalent chromium in solid material by alkaline digestion and ion chromatography with spectrophotometric detection*.

For the time being, it has not been translated into Polish and introduced into the standards catalogue of the Polish Committee for Standardization (PCS) yet, nor has it been translated and introduced in other countries of Eastern and Central Europe.

The ISO standards encompassing gaseous pollutants determination include the determination of hydrogen chloride and sulphur dioxide. These are *ISO 1911-1 Air quality—Stationary source emission—Manual method of determination of HCl Part 1: sampling and pretreatment of gaseous (1995)*, *Part 2: Gaseous compounds absorption*, *Part 3: Absorption solutions analysis and calculation* and *ISO 11632: 1998 Stationary source*



emissions—Determination of mass concentration of sulphur dioxide—Ion chromatography method.

Since its beginning, the ion chromatography has had an important place in the chemical analytics of highly industrialized countries, including environmental research. Unfortunately, the method is still seldomly used in the countries of Eastern and Central Europe, and it has not received the place it deserves yet.

This is caused both by a kind of technological backwardness (many laboratories still use manual methods for the routine water and wastewater analyses) and by low popularity of the discussed method in those countries.

The following paper counts Estonia, Lithuania, Latvia, Russia, Ukraine, Belarus, Poland, Slovakia, the Czech Republic, Hungary, Romania, Slovenia, and Croatia as the countries of Eastern and Central Europe.

Eastern and Central Europe Institutions that Work on the Ion Chromatography Applications in Environmental Research

In those countries, the following applications of ion chromatography in environmental analytics might be counted as the most highly cited ones. It is anions and cations determination in various types of water (drinking water, surface and ground water, precipitation) and wastewater (industrial and municipal). Ion chromatography is also used in the air quality and solid samples analysis.

The purpose of this paper is to determine the most important scientific institutions from Eastern and Central Europe that work on the environmental applications of ion chromatography and/or capillary electrophoresis. The presentation does not refer to the use of those methods for routine analyses that are con-

Table IA. Scientific Institutions from Eastern and Central Europe Countries that Carry Out Ion Chromatography and/or Capillary Electrophoresis Applications Research

Country and Scientific Institution	The most highly cited published works
Lithuania Vilnius State University, Department of Analytical and Environmental Chemistry, Vilnius Lithuanian University of Agriculture, Forest Monitoring Laboratory, Vilnius	– Application of capillary electrophoresis for research into inorganic ions in water (11) – Changes of the precipitation chemical composition in Lithuania in the years 1981–2004 (12) – Applications of ion chromatography for research into the environmental condition of forests (13)
Latvia University of Latvia, Department of Analytical Chemistry, Riga	– New ion-exchange materials research
Estonia Tallinn Technical University, Institute of Chemistry, Tallinn Tartu State University, Institute of Environmental Physics, Tartu	– Application of ion chromatography in monitoring research (14) – Polar research (15) – Air quality research (16)
Russia Lomonosov State University, Division of Analytical Chemistry, Moscow Russian Academy of Sciences, Moscow Vernadskii Institute of Geochemistry and Analytical Chemistry, Moscow	– Research on hydrazine and the products of its decomposition in soil samples (17) – Simultaneous determination of trace anion contents in water (18) – River water quality research (19)
Ukraine National Academy of Sciences, Institute of Geology and Geochemistry, Lvov	– Determination of inorganic ions in sea water (20) – Research on the Chernobyl disaster effects (21)
Belarus Belarus Academy of Sciences, Institute of Physical Organic Chemistry, Minsk	– Research on the new ion-exchange materials used for environmental samples analysis (22)
Slovakia Comenius University, Faculty of Natural Sciences, Department of Nuclear Chemistry, Bratislava Slovak Technical University, Institute of Analytical Chemistry, Bratislava	– Determination of selected inorganic ions in water (23)
The Czech Republic Charles University, Department of Analytical Chemistry, Prague Academy of Sciences of the Czech Republic, Institute of Analytical Chemistry, Brno Masaryk University, Department of Analytical Chemistry, Brno Mendel University of Agriculture and Forestry, Brno	– Determination of alkali metals and alkali earth metals in water (24) – Research on the polluting of watercourses with nitrate (V) and sulphate (VI) (25) – Determination of anions in uranium ores (26) – Research on precipitation (27) and air (28) quality

ducted by relevant national environmental monitoring units.

This part of the paper was developed on the basis of the on-line information available in the global databases that cover, among other things, publications in acknowledged international scientific journals, with the following criteria: the significant use of ion chromatography methods and/or capillary electrophoresis in the scientific research carried out in the given institution, the subject of the works referring to environmental analysis, and the authors' affiliation.

An important fact ought to be emphasised at this point. Many outstanding scientists from Eastern and Central Europe countries work and live abroad, conducting their research in places such as the U.S., Canada, Japan, Australia, or the countries of Western Europe. In such a case, the authors' affiliation and the place of work were assumed as a criterion not their nationality.

The most important institutions from particular Eastern and Central Europe countries that carry out environmental research using ion chromatography techniques and/or capillary elec-

trophoresis are given in Table I. In addition, chosen publications of authors from the discussed countries that include the issues related to the use of ion chromatography/capillary electrophoresis in the environmental research are presented.

Due to the fact that it was difficult to access some data in particular countries, such as the information about grants realization, what is taken into consideration are above all the publications in the acknowledged international journals that were prepared by scientists from Eastern and Central Europe or with their participation.

This criterion seems to be extremely important and reliable when assessing particular institutions, and their achievements as the requirements that have to be met by authors published in the most prestigious international periodicals are high. The chosen research grants realized by the Polish scientific institutions in the years 1995–2009 and relating to the uses of ion chromatography/capillary electrophoresis in the environmental analytics are shown in the Table II.

Table IB. Scientific Institutions from Eastern and Central Europe Countries that Carry Out Ion Chromatography and/or Capillary Electrophoresis Applications Research

Country and Scientific Institution	The most highly cited published works
Hungary <i>University of Pannonia,</i> Department of Analytical Chemistry, Veszprém <i>Eötvös Loránd University,</i> Institute of Chemistry, Budapest <i>Debrecen Agriculture University,</i> Debrecen	– Characteristics of ion exchangers used in analytical columns (29) – Water-monitoring research (30) – Chromium speciation analysis (31) – Determination of carboxylic acids in environmental samples (32)
Romania <i>Technical University,</i> Bucharest <i>Research Institute for Analytical Instrumentation,</i> Cluj-Napoca <i>University of Agriculture Sciences</i> <i>and Veterinary Medicine,</i> Timisoara	– Determination of inorganic cations in mineral waters (33)
Bulgaria <i>Bulgarian Academy of Sciences,</i> Institute of Organic Chemistry, Sofia	– Research on the influence of the environmental conditions on the quality of olives (34)
Slovenia <i>National Institute of Chemistry,</i> Ljubljana <i>University of Ljubljana,</i> Faculty of Chemistry and Chemical Technology <i>University of Maribor,</i> Faculty of Chemistry and Chemical Engineering, Maribor <i>Laboratory for Environmental Research,</i> Nova Gorica Polytechnic	– Determination of inorganic anions and cations in various types of water (35) – Research on the chemical composition of sea water (36) – Determination of chlorine, bromine, and iodine ions (37) – Simultaneous determination of Cr(III)/Cr(VI) ions (38)
Croatia <i>University of Zagreb,</i> Faculty of Chemical Engineering and Technology, Zagreb	– Application of ion chromatography in the analysis of PM ₁₀ dust samples (39) – Metal monitoring in the national parks (40) – Industrial sewage analysis (41) – Determination of inorganic cations in sea water (42)
Poland <i>Gdansk Technical University,</i> Faculty of Chemistry, Gdansk <i>Nicolaus Copernicus University,</i> Faculty of Chemistry, Torun <i>Warsaw University,</i> Faculty of Chemistry <i>Adam Mickiewicz University,</i> Faculty of Chemistry, Poznan <i>Polish Academy of Sciences</i> Institute of Environmental Engineering, Zabrze	– Research on runoff water quality (43) – Application of isotachopheresis for water quality research (44) – Applications of IC for the determination of nitrogen ions in environmental samples (45) – Selenium speciation analysis (46) – Application of passive methods for the determination of nitrogen and sulphur oxides in atmospheric air (47) – Chromium speciation analysis (48) – Determination of inorganic by-products of water disinfection (49,50)

Publications of the Scientists from Eastern and Central Europe Against the Background of Europe and the World

The publication of scientific articles, especially in the most influential international journals, is one of the markers of importance of the given analytic technique and particular research subject significance.

The key words “ion chromatography” as well as the authors’ affiliation and place of work were a decisive criterion for the lists presented in this part of the paper. It is important as many acknowledged scientists from Eastern and Central Europe work abroad.

Table III. The Percentage Rate of Articles Concerning the Theoretical Background and Applications of IC in the Listed International Scientific Journals

Journal	Total number of articles in years 1996–2009	(%)
<i>Journal of Chromatography A</i>	17548	4.63
<i>Talanta</i>	6703	2.21
<i>Journal of Separation Science</i>	2632	2.14
<i>Journal of Chromatographic Science</i>	1472	2.11
<i>Analytica Chimica Acta</i>	11362	1.91
<i>Chromatographia</i>	3955	1.71
<i>Analytical and Bioanalytical Chemistry</i>	4948	1.53
<i>Analytical Chemistry</i>	14572	0.81
<i>Electrophoresis</i>	6702	0.55
<i>Journal of Chromatography B</i>	2538	0.51
<i>Water Research</i>	6730	0.38
<i>Chemosphere</i>	9284	0.29

The presented statistical data covers the information dating from the year 1996 until August 2009. The journals that were taken into consideration are the international scientific journals that publish articles on chromatography and related methods, such as *Journal of Chromatography A*, *Journal of Chromatography B*, *Journal of Chromatographic Science*, *Chromatographia*, *Talanta*, *Analytical Chimica Acta*, *Analytical Chemistry*, *Water Research*, *Chemosphere*, *Analytical and Bioanalytical Chemistry*, *Journal of Separation Science*, and *Electrophoresis*.

The choice of the journals was influenced by their prestige and importance, which are expressed by the value of the “impact factor” (IF), and the number of published articles concerning the theory and practice of ion chromatography. The percentage rate of those publications in relation to the total number of articles published in the given journal is stated in Table III. The number of publications with the key words “ion chromatography” published in the discussed journals between the year 1996 and August 2009 is given in Table IV.

Summary and conclusions

The remarkable progress made in terms of the preparation methods of samples for the analysis, new generations of filling materials used in analytical columns, the improvement in the working of suppressors as well as the use of such sophisticated detection methods as ICP–MS or MS (51) have contributed to the ion chromatography expansion into the new areas of applications (52).

Table II. Grants Awarded for Research on IC and/or Capillary Electrophoresis Applications Realized in Polish Scientific Institutions

Years	Project title	Institution
1995–1996	The study on methods development of SO ₂ and NO ₂ determination in air by using IC	<i>Cracow Technical University</i> , Faculty of Engineering and Chemical Technology
1999–2000	The study on AOX determination using IC	<i>Cracow Technical University</i> , Faculty of Engineering and Chemical Technology
1996–1997	Application of flow injection analysis and IC in selenium speciation	<i>Warsaw University</i> , Faculty of Chemistry
2001–2002	Application of IC in air pollution analysis	<i>Wroclaw Technical University</i> , Faculty of Environmental Protection, Wroclaw
2002–2003	Application of hyphenated techniques in speciation of arsenium, antimonium, and selenium—IC method coupled with atomic absorption spectrometry	<i>Adam Mickiewicz University in Poznan</i> , Faculty of Chemistry
2004–2005	New solutions in species analysis of bromide/bromate and Cr(III)/Cr(VI) in environmental samples using ion chromatography method	<i>Institute of Environmental Engineering</i> , Polish Academy of Sciences
2005–2006	Neutron activation analysis and IC as a tool for the determination of lanthanides in environmental samples	<i>Institute of Nuclear Chemistry and Technology</i> , Warsaw
2004–2005	Method optimization of cyanide determination in wastewaters; Comparison of flow injection analysis and IC	<i>Institute of Environmental Engineering</i> , Polish Academy of Sciences
2006–2007	Research on application of IC for anions determination in ionic liquids	<i>Gdansk University</i> , Faculty of Chemistry
2008–2010	The study on simultaneous determination of anions and cations in ionic liquids by using ion chromatography with conductivity detection	<i>Gdansk University</i> , Faculty of Chemistry

Table IV. The Number of Articles with Key Words "Ion Chromatography" Published in the Listed Scientific Journals in the Years 1996–2009

Journal	Total number of articles	Number of articles with key words "ion chromatography"		
		World	Europe	Countries of Eastern and Central Europe
<i>Journal of Chromatography A</i>	17548	768	311	74
<i>Talanta</i>	6703	158	62	14
<i>Journal of Separation Science</i>	2632	61	29	12
<i>Journal of Chromatographic Science</i>	1472	31	6	1
<i>Analytica Chimica Acta</i>	11362	213	99	14
<i>Chromatographia</i>	3955	74	36	12
<i>Analytical and Bioanalytical Chemistry</i>	4948	87	41	8
<i>Analytical Chemistry</i>	14572	116	37	1
<i>Electrophoresis</i>	6702	40	16	9
<i>Journal of Chromatography B</i>	2538	14	3	0
<i>Water Research</i>	6730	27	15	1
<i>Chemosphere</i>	9284	30	14	1

Even though the ion chromatography has been a reference method in water and wastewater analysis for many years, the technique is still being developed. The most important challenges and problems to solve for ion chromatography in the near future relate to new methods of sample preparation, new ion-exchange materials, improvement in the suppressors effectiveness, lowering the limits of detection and limits of quantification of analyte ions, extending the analyses range by including new organic and inorganic substances, development of new reference methods, introducing new detection methods, and the miniaturization of the ion chromatographic systems.

The information presented in this paper allows one to reach several conclusions. The share of scientists from Eastern and Central Europe in the papers published in the international scientific journals and concerning the applications of ion chromatography in the environmental research is not substantial. A similar conclusion can be drawn in relation to the role and significance of ion chromatography in the discussed countries expressed by the number of the carried out research projects and realized grants. Also, a lot of papers concerning the applications of ion chromatography are published in the discussed countries. Nevertheless, these publications are written in the national languages, which hinders the possibility of access to research results. Such a situation is caused, among other things, by poor knowledge of English and high requirements of prestigious international journals that have to be met. Finally, many distinguished scientists born in Eastern and Central Europe live and work abroad. The reason for such a condition is that the financing of science and the accessibility of the latest apparatus and technologies are very limited. Despite the fact that this backwardness is gradually being overcome, it is still estimated to be a matter of not a few but of several decades.

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