

UNIVERSITY OF ZAGREB
FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

11th International School of Ion Chromatography



BOOK OF ABSTRACTS

8th– 9th July, 2010
ZAGREB, CROATIA

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EDUCATION PROSPECTS

The program of the two days long education will include invited lectures provided by the leading experts in ion chromatography as well as the lectures and posters presented by the selected participants. The 11 years long tradition of organizing the computer supported workshop and proficiency testing will continue in this particular school.

International School of Ion Chromatography has accomplished a valuable recognition for its quality so performed proficiency test is accepted in accreditation of laboratories.

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Š. Ukić, T. Bolanča

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FINAL PROGRAM

Thursday, July 8th, 2010

Opening of the 11th International School of Ion Chromatography, FCET, Marulićev trg 20

09.00-09.15 S. Kurajica, Dean of FCET, CRO, Š. Cerjan Stefanović (CRO),
T. Bolanča (CRO): Opening remark

Preface to 11th International School of Ion Chromatography, FCET, Marulićev trg 20

09.15-09.45 Š. Cerjan Stefanović (CRO): HISTORY OF INTERNATIONAL SCHOOL
OF ION CHROMATOGRAPHY

Session 1: New achievements in ion chromatography, FCET, Marulićev trg 20

09.45-10.15 N. Avdalovic (USA), Y. Liu (USA), C. Pohl (USA):
CAPILLARY ION CHROMATOGRAPHY – THE FUTURE OF ION
CHROMATOGRAPHY?

10.15-10.45 J. Weiss (Dionex, GER):
STRATEGIES FOR INCREASING SAMPLE THROUGHPUT IN ION
CHROMATOGRAPHY

10.45-11.00 **Coffee break, FCET, Marulićev trg 20, Academic Club**

Session 1: New achievements in ion chromatography, FCET, Marulićev trg 20

11.00-11.30 S. Hoffmann (SUI), T. Hartmann (SUI), S. Czyborra (SUI):
AUTOMATED ION CHROMATOGRAPHIC DETERMINATIONS OVER
SIX ORDERS OF MAGNITUDES

11.30-12.00 Š. Ukić (CRO), Š. Cerjan Stefanović (CRO), T. Bolanča (CRO),
M. Rogošić (CRO):
MATHEMATICAL MODEL FOR SIMULATION OF IC ANALYSIS
RESPONSE

12.00-12.30 M. Ujević Bošnjak (CRO), C. Casiot (FR), Ž. Dadić (CRO),
L. Sipos (CRO):
ARSENIC SPECIATION BY ANION-EXCHANGE
CHROMATOGRAPHY

12.30-13.00 **Poster presentation session; FCET, Marulićev trg 20**

13.00-14.00 **Lunch break (organized by participants them self)**

Session 2: *Computer supported workshop, FCET, Savska cesta 16, Computer Classroom*

14.00-16.00 T. Bolanča (CRO), Š. Ukić (CRO):
OVERVIEW OF VALIDATION PRINCIPLES I:
LINEARITY, WORKING RANGE, SENSITIVITY AND ACCURACY

16.00-16.30 **Coffee break, FCET, Savska 16, Terrace**

16.30-18.30 T. Bolanča (CRO), Š. Ukić (CRO):
OVERVIEW OF VALIDATION PRINCIPLES II:
PRECISION, LOD, LOQ AND ANALYTICAL RESULT

Friday, July 9th, 2010

Session 3: *Applications, FCET, Marulićev trg 20*

09.00-09.30 J. Weiss (GER):
APPLICATIONS OF CAPILLARY ION CHROMATOGRAPHY
SYSTEMS FOR TRACE ANALYSIS

09.30-10.00 D. Kralj (SLO):
ANION DETERMINATION IN THE SECONDARY WATER
AT NUCLEAR POWER PLANT KRŠKO USING ICS 3000

10.00-10.30 T. Tomić (CRO), N. Uzorinac Nasipak (CRO):
ION CHROMATOGRAPHY IN OIL INDUSTRY
Application and experiences

10.30-11.00 **Coffee break, FCET, Marulićev trg 20, Academic Club**

Session 3: *Applications, FCET, Marulićev trg 20*

11.00-11.30 K. Vinković (CRO), C. Crey-Desbiolles (SUI), D. Jensen (SUI):
NITRITE AND NITRATE IN TOBACCO – A CASE STUDY IN
IC METHOD DEVELOPMENT

11.30-12.00 V. Marinović (CRO), G. Mršić (CRO), V. Zechner-Krpan (CRO),
V. Petravić-Tominac (CRO):
ANALYSIS OF METAL IONS IN CROATIAN WINES
USING ION CHROMATOGRAPHY AS FORENSIC METHOD

12.00-12.30 V. Stankov (SRB):
DETERMINATION OF NITRATES/NITRITES IN FRUITS,
VEGETABLES AND THEIR COMMODITIES
BY ION CHROMATOGRAPHY WITH UV DETECTOR

12.30-13.00 **Commercial presentations, FCET, Marulićev trg 20**

13.00-14.00 **Lunch break (organized by participants them self)**

Session 4: *Quality Assessment, FCET, Marulićev trg 20*

14.00-14.30 Š. Ukić (CRO), T. Bolanča (CRO), Š. Cerjan Stefanović (CRO),
K. Margeta (CRO):
9TH PROFICIENCY TEST: CRITICAL REVIEW

14.30-15.30 **Open discussion session - Poster discussion.**

Moderators: N. Avdalović (USA), Š. Cerjan Stefanović (CRO),
T. Bolanča (CRO), Š. Ukić (CRO)

15.30-16.00 **Coffee break, FCET, Marulićev trg 20, Academic Club**

16.00-16.30 **Sample delivery for 10th proficiencie test**

16.30-17.00 **Award of the certificates**

17.00 Š. Cerjan Stefanović (CRO), N. Avdalović (USA), T. Bolanča (CRO):
Closing of 11th International School of Ion Chromatography

PREFACE

Welcome to 11th ISIC 2010

Much of the practice of ion chromatography (IC) today is well established science transformed into easily practiced technology. The number of articles on IC in Analytical Chemistry apparently reached a peak in the mid-'80s. However, the application of IC in a wide number of areas, as judged by the number of articles summarized in Chemical Abstracts, continues to grow at a healthy rate. International School of Ion Chromatography (ISIC) has been providing an ideal forum in the last ten years for ion chromatographers from different regions of Balkan peninsula and neighboring countries. The reliability of IC is taken for granted today. It has become a routine tool for process analysis and control, most notably for trace analysis in the nuclear power and semiconductor industries. The practice is sufficiently widespread such that discussions on diversity of applications, qualitative and quantitative data as well as quality assurance data acquisition become extremely important that they are considered worthy of inclusion in peer reviewed literature. We find above arguments compelling enough to organize ISIC once again.

Furthermore, it is well known that education plays one of the most important roles in the prosperity of particular expert, business economy of the particular company as well as for the global society. Therefore, it is essential to organize education course available to large number of participants. Organizing committee of 11th ISIC recognizes this needs and making IC School totally free of charge we are hoping that our small contribution might make the difference.



President of the organization committee

Ph.D. Tomislav Bolanča, assoc. prof.

We would like to thank sincerely all the lecturers and sponsors for their contributions at 11th ISIC.

***INVITED
LECTURES***

HISTORY OF INTERNATIONAL SCHOOL OF ION CHROMATOGRAPHY

Š. Cerjan Stefanović

*Laboratory of Analytical Chemistry, Faculty of Chemical Engineering and Technology,
Marulićev trg 20, 10000 Zagreb, Croatia
tel. +385 1 4597 205, fax. +385 1 4597 250, e-mail: scerjan@fkit.hr*

The south east European Universities has education about ion chromatography incorporated in graduate program as a part of the course called Chromatography. The ion chromatography course is a part of the Chemical Engineering post graduate study.

However, the incorporation of ion chromatography in Croatian national standards, as a method for water analysis (drinking waters and wastewaters), causes the additional need for education in both theoretical and experimental issues.

International School of Ion Chromatography (ISIC) was organized to become an educational platform using which the knowledge related to fast growing developments in Ion Chromatography could be delivered to people that use it daily as a research tool or in routine analysis. The school is planned to provide the basic knowledge to the newcomers and to deliver up-to-date knowledge to those who are already well familiar with modern Ion Chromatography systems and complex applications.

Program In the program of the school, we endeavoured to include topics, which would prove interesting for daily ion chromatography users. The presentations will focus on the theory of ion chromatography and some of the current instrumentation available, along with method development and column flexibility to solve application requirements, as well as with chance to view a running automated ion chromatography system and witness the maintenance required for its upkeep during the practical workshops.

English is the official language of the school, as it is anticipate for participants from various European countries.

The participants are from Croatia, Slovenia, Serbia, Slovakia, Austria, Hungary, Bulgaria, Macedonia, Romania, Albania and Bosnia and Herzegovina, from different institutions, faculties and industries. This is a very compact group, with good workers which are all very interested in IC. Methodology of ion chromatography is accepted and it is obligated for anion and cation analysis of drinking water samples. Never the less, additional possibilities of ion chromatography applications such as in environmental, pharmaceutical, and food technology chemistry are not forgotten.

Foundation of ISIC Ion chromatography is incorporated in graduate program as a part of the course called Chromatography. The incorporation of ion chromatography in Croatian national standards, as method for water analysis (drinking waters and wastewaters), causes the additional need for education in both theoretical and experimental issues.

For that purpose, since 1997, "International School of Ion Chromatography" has being organized by University of Zagreb, Faculty of Chemical Engineering and Technology, Croatia (prof. Š. Cerjan – Stefanović) and National Institute for Chemistry, Slovenia (Ph.D. Milko Novič) as a part of long life education program.

Ten education schools have been organized so far in Croatia and Slovenia with approximately 40 participants form south eastern part of Europe per seminar.

The history of ISIC

- 1st International School of Ion Chromatography,
27.05.1999., Zagreb – CRO
- 2nd International School of Ion Chromatography,
17. - 18.11.1999., Jezersko – SLO
- 3rd International School of Ion Chromatography,
7.06.2000., Zagreb – CRO
- 4th International School of Ion Chromatography,
24. - 25.05.2001., Bovec, SLO
- 5th International School of Ion Chromatography,
25. - 27.04.2002., Trakošćan, CRO
- 6th International School of Ion Chromatography,
19 - 21.05.2003., Sežana, SLO
- 7th International School of Ion Chromatography,
29.09. - 2.10.2004., Motovun, CRO
- 8th International School of Ion Chromatography
08. - 11.06. 2005., Rogla, SLO
- 9th International School of Ion Chromatography
04. - 07.10.2006., Primošten, CRO
- 10th International School of Ion Chromatography
03. - 06.06.2008., Brijuni, CRO

Program of ICIS includes: Presentations of eminent scientist, Inter-laboratory tests, Computer supported Workshops and Poster sessions.

ISICs are organized as gathering of eminent scientist from the field of IC, IC every day users and chemicals, and standards production companies.

1. Presentations The presentations will focus on the theory of ion chromatography and some of the current instrumentation available, along with method development and column flexibility to solve application requirements, as well as with chance to view a running automated ion chromatography system and witness the maintenance required for its upkeep during the practical workshops. In school program we endeavoured to include topics which would prove interesting for daily ion chromatography users.

2. Inter-laboratory tests Samples: water, waste water, sea water, different matrices and different concentrations of analytes.

Inter-laboratory tests insure quality control of the ion chromatographic analysis.

3. Computer assisted workshops Incorporated computer assisted workshops provide basic and advanced knowledge of statistics, validation and optimization strategies.

It is imperative to perform practical PC-related work in order to ensure that all participants will fully understand the presented information.

Topics of Computer supported workshops: statistical methods, validation, validation parameters (selectivity, linearity, accuracy, detection limits, quantity limits, working range and robustness).

4. Poster presentations Topics of poster presentations: Applicability and limitations of IC

Conclusion

It is shown that mentioned activities result with significant increase in quality of ion chromatographic analysis and the reputation of ISIC.

References

1. M. Novič, Š. Cerjan-Stefanović, M. Prošek, J. Turšić, T. Bolanča, Međulaboratorijski kružni testovi za analize aniona ionskom kromatografijom, Hrvatska vodoprivreda, **102**, 2001, 49-53.
2. Š. Cerjan-Stefanović, T. Bolanča, M. Novič, J. Turšić, M. Regelja, Kružni testovi u analizi kationa i aniona ionskom kromatografijom, Hrvatske vode, **49** 12 2004, 313-319.



CAPILLARY ION CHROMATOGRAPHY – THE FUTURE OF ION CHROMATOGRAPHY?

N. Avdalovic, Y. Liu, C. Pohl

Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

Ion chromatography (IC) is a widely used analytical technique for the determination of anionic and cationic analytes in various sample matrices. Conventional IC systems typically use separation columns with internal diameters of 2 or 4 mm and perform separations at 0.25 to 2 mL/min. There have been increasing interests in performing ion chromatographic separations using capillary columns. The practice of IC in the capillary format (i.e., using small bore columns with internal diameters of about 1 mm or smaller) has a number of potential advantages. Capillary IC systems typically operate at 1 to 20 $\mu\text{L}/\text{min}$ and thus the amount of eluent consumed is very small. Capillary IC systems offer improved capability for continuous operation with minimal intervention and thus minimize problems associated with system start-up and shutdown. Separation processes in the capillary format require much smaller amount of sample and thus capillary IC systems offer improved compatibility with applications where amount of sample is limited. The operation of capillary IC at low flow rates improves the system compatibility with mass spectrometer. The use of capillary separation columns can improve the separation efficiency and/or speed. In addition, the practice of IC in the capillary format opens the door for the possibilities of offering new selectivity for difficult applications using new columns packed with more exotic and difficult-to-make stationary phases.

In this presentation, we will provide a historical overview of developments of capillary ion chromatography. We will focus the discussion on our own efforts in the development of reagent-free capillary IC systems in recent years. We will discuss the preparation of capillary ion exchange columns, and the design and optimization of capillary-scale electrolytic eluent generators and suppressors. We will demonstrate the advantages of using capillary IC systems in the determination of target inorganic and organic analytes. We will share our view on the future of capillary ion chromatography.



STRATEGIES FOR INCREASING SAMPLE THROUGHPUT IN ION CHROMATOGRAPHY

J. Weiss

*Dionex Corporation, International Operations, Idstein, Germany
joachim.weiss@dionex.com*

One of the most topical subjects in conventional HPLC is the increase of sample throughput without sacrificing resolution by utilizing UHPLC techniques. This is typically achieved by packing separator columns of shorter length and smaller internal diameter with separation materials of smaller particle sizes. However, even at optimal flow rates the resulting backpressure often exceeds the pressure tolerance of traditional HPLC hardware. Therefore, we currently witness the development of HPLC instruments with significantly improved backpressure tolerance well above 80 MPa. Although the stress on wear parts is very high at these high pressures, this development is facilitated with working materials in pumps and valves based on stainless steel.

Since ion chromatography is part of liquid chromatography, it is not surprising that more and more users of ion chromatography would like to have a similar solution for increasing sample throughput in IC as well. The fundamental difference in instrument design, however, is the fact that the fluidic pathways in ion chromatography instruments are made of metal-free components with a significantly lower pressure tolerance which excludes the use of particle sizes of around 2 μm (or smaller) typically employed in UHPLC separations. While particle sizes of common ion-exchange materials used in analytical IC are typically around 8.5 μm , so-called fast ion-exchange columns do exist, featuring 5- μm particle size in a smaller column format (150 mm x 3 mm ID). Thus, the analysis times for anion and cation profiles could be decreased by 50% as compared to conventional ion exchangers. But even under these conditions, typical anion or cation profiles are characterized by a run time of around eight minutes.

One possibility for further decreasing analysis times in IC is a flow rate increase beyond the van Deemter optimum, which goes along with a loss of resolution due to the relatively large particle size of the ion-exchange material. Thus, this approach is only feasible for samples with a simple analyte composition and little or no matrix contamination. Doubling the linear velocity of the mobile phase through the separator column cuts the analysis time in half, while keeping the backpressure of the separator column well below the maximum pressure tolerance of the system, which is currently on the order of 5000 psi (35 MPa). We recently introduced a carbonate-selective, hyperbranched anion exchanger in the 150 x 4 mm ID format, which separates standard anions in less than five minutes utilizing an increased flow rate of 2 mL/min. In comparison to the almost legendary IonPac AS4A more than 20 years ago, which separated standard anions in about eight minutes, the new IonPac AS22-Fast offers significantly higher ion-exchange capacity and resolution.

A more promising approach for increasing sample throughput in IC is the general trend in separation science towards polymeric monoliths, well known today for separating bio-relevant macromolecules such as proteins, peptides, and oligonucleotides. Using ProSwift™, PepSwift™, or DNASwift™ monolith columns, the separation of bio-molecules can be achieved at elevated linear velocities with little or no loss of resolution. In this paper I will discuss a new monolithic platform for separating low-molecular weight ions by ion chromatography and a new generation of ion-exchange columns produced based on this platform.



There are a number of challenges to be resolved in order to design monolith columns specifically for ion chromatography. For example, one of the challenges is a selection of a suitable column wall material with broad range pH stability and pressure robustness. However, the most critical challenge is an elimination of void space between the monolith and the column wall. Traditionally, capillary scale monoliths are prepared with covalent attachment to the wall to avoid formation of an annular void at the capillary wall. In the case of fused silica capillaries, attachment to the wall is usually accomplished via a silyl methacrylate. However, this is not a practical solution for ion chromatography applications due to the susceptibility of the silane to hydrolysis under normal operating conditions. The way out of this dilemma is a covalent attachment of monolithic structures to a PEEK capillary, providing the necessary pH stability for the new family of IonSwift™ columns.

In addition, I will show the comparison of chromatographic performance for monolithic columns with different inner diameters. Especially the development of 1-mm and 250- μm columns will benefit users interested in fast, high-resolution separations performed on conventional and capillary IC systems.



AUTOMATED ION CHROMATOGRAPHIC DETERMINATIONS OVER SIX ORDERS OF MAGNITUDES

S. Hoffmann, T. Hartmann, S. Czyborra

*Metrohm International Headquarters, Oberdorfstrasse 68, Herisau 9101, Switzerland,
sho@metrohm.com (Presenting), ht@metrohm.com, sc@metrohm.com*

Trace-analysis methods require contamination-free sample handling and accurate calibration graphs. In particular, the method calibration in the low-ppb and ppt range is critical, as standard solutions in this range can hardly be handled without introducing errors. Moreover, if the sample concentration is outside the calibration range, laborious and error-prone dilution or preconcentration is required.

These drawbacks are overcome by inline coupling of the patented 800 Dosino and intelligent ion chromatography systems. The Dosino enables high-precision dosing of variable solution volumes into the sample loop or preconcentration column of the ion chromatograph. The Dosino can exactly dose and transfer down to 0.2 μL liquid. Without compromising the accuracy of the results, a whole range of new possibilities opens up for determinations over wide concentration ranges. By using only one analytical setup and without additional rinsing, samples containing both ultratraces and high concentrations can be analyzed.

Furthermore, the Metrohm intelligent Pick-up Technique (MiPuT) and the Metrohm intelligent Preconcentration Technique with Matrix Elimination (MiPCT-ME) enable the user to work with low sample volumes and to remove interfering sample matrices. Combined with automated multipoint calibration, these techniques cover a measuring range of six orders of magnitude.

The combination of intelligent software and hardware allows the system to compare results, take logical decisions and carry them out: if, for example, the concentration of the analyte in the sample exceeds that of the calibration range, the system, after the first injection, compares peak areas, calculates the appropriate injection volume and automatically reinjects the sample. The presented inline techniques reduce the workload, extend the measuring range to six orders of magnitude, are free of carryover effects and significantly improve results accuracy and reproducibility. Applications from different fields will be presented and discussed with regard to flexibility, recovery and accuracy.



MATHEMATICAL MODEL FOR SIMULATION OF IC ANALYSIS RESPONSE

Š. Ukić, Š. Cerjan Stefanović, T. Bolanča, M. Rogošić

*University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19,
10000 Zagreb, Croatia, e-mail: sukic@fkit.hr*

In accordance to common principles of economy, searching for financially more acceptable analytical methods becomes the important part of development policy of modern analytical laboratories; ion chromatographic methods are not an exception.

Although the best peak resolution can be obtained by using isocratic elution mode, the gradient elution mode may provide significant benefits. Due to its capability of reducing the analysis time significantly, gradient elution became inevitable chromatographic technique, despite of inherently more complex method development procedures. In development of new gradient eluted ion chromatographic methods, mathematical models commonly replace the traditional “trial and error” procedures, sometimes with remarkable success. By predicting the chromatographic system response, these models are able to provide an approximation for optimal separation conditions as well.

The aim of this presentation is development of a gradient elution retention model based on isocratic experimental data (IG model). For the purpose of gradient modeling, the quadratic polynomial isocratic elution retention model was set up and tested. The entire experimental part was done on Dionex DX-600 ion chromatographic system. The behavior of a model solution, that contained fluoride (3 ppm), chlorite (10 ppm), chloride (6 ppm), chlorate (25 ppm), nitrate (25 ppm) and sulphate (25 ppm) ions, was tested by separating these anion constituents on AS19 ion chromatographic column. Three different chromatographic properties were predicted: retention time, resolution, and peak asymmetry, in relation to variable eluent ion concentration.

The performed experiments proved that retention times under gradient elution mode could be satisfactorily predicted if quadratic polynomial retention model is used for isocratic prediction. The retention times were predicted directly, using experimental data. However, the properties of resolution and peak asymmetry were obtained indirectly, by calculations using predicted retention times of three characteristic points on the chromatographic peak (50% peak high at fronting side, peak maximum and 50% peak high at tailing side).

The generalized logistic function was chosen for the peak shape prediction. This three-parameter distribution function was able to model all test chromatograms satisfactorily. By combining gradient elution model with the selected peak shape function, a number of real elution simulations was performed. The simulations were compared with experimental gradient chromatograms, and in most cases good fit was obtained.

This approach offers, to every day chromatography users, a possibility for significant reducing of experimental efforts in optimization of ion chromatographic methods. In combination with one or more optimization criteria, the approach offers possibility to become an excellent basis for new ion chromatographic optimization software. This conjunction is already applied in optimization software OptIC, what is the distinct topic at one of 11th ISIC's poster presentations.



ARSENIC SPECIATION BY ANION-EXCHANGE CHROMATOGRAPHY

M. Ujević Bošnjak¹, C. Casiot², Ž. Dadić¹, L. Sipos³

¹Croatian National Institute of Public Health, Rockefellerova 7, Zagreb, Croatia
magdalena.ujevic@hzjz.hr, zeljko.dadic@hzjz.hr

²HydroSciences Montpellier, UMR 5569, Université Montpellier 2, CC MSE, Pl. E. Bataillon,
34095 Montpellier cedex 05, France, casiot@msem.univ-montp2.fr

³University of Zagreb, Faculty of Chemical Engineering and Technology
Marulićev trg 19, Zagreb, Croatia, laszlo.sipos@zg.t-com.hr

The presence of arsenic in the groundwater of Eastern Croatia was found more than twenty years ago. Moreover, during the last decade, drinking water contamination by arsenic has been considered a global problem. Arsenic toxicity depends on its chemical form, thus the knowledge of arsenic species distribution in aqueous systems is required in order to determine the relative hazards to consumers. Various analytical techniques have been used to determine arsenic species in environmental samples. The most commonly used speciation techniques often involve a combination of chromatographic separation with spectrometric detection. For the purposes of this paper, arsenic species in groundwater samples from Eastern Croatia were separated by anion-exchange chromatography (AEC) and detected by inductively coupled plasma-mass spectrometry (ICP-MS). Two ways of sample preservation were tested: preservation by Ethylenediaminetetraacetic acid (EDTA) and by mixture of EDTA, and acetic acid.

Key words: arsenic, speciation, groundwater, anion-exchange chromatography (AES), ICP-MS, Eastern Croatia

Introduction

Arsenic exists under different chemical species in groundwater; inorganic: arsenite As(+3) and arsenate As(+5) are predominant and more toxic than organic species (monomethyl- and dimethylarsenic).¹ Furthermore, the efficiency of arsenic removal from drinking water depends on its speciation, As(+5) being more easily removed than As(+3).² Thus, the knowledge of arsenic speciation is necessary for risk assessment as well as for appropriate choice of arsenic removal technology. Arsenic species are very unstable in natural waters; their distribution depends on the redox conditions, pH, and the presence of precipitating metals such as iron, organic matter, as well as on microbial activity.³ Thus, the preservation of arsenic species before laboratory analyses is very important, and different preservation techniques have been used.⁴⁻⁷ Sample preservation with EDTA is preferred for determination of As(+3), As(+5), Monomethylarsonic acid MMA(V) and Dimethylarsinic acid DMA(V) by HPLC-ICP-MS.⁸⁻¹⁰ However, some authors showed that EDTA was ineffective in preservation of the inorganic As species in groundwater^{5,7}, and Samanta and Clifford³ used a mixture of EDTA and acetic acid. The interconversion of As(+3) and As(+5) is matrix dependent and any investigation of arsenic species in water would require first the establishment of the optimal storage conditions.¹¹

The objective of the present study is to compare two ways of groundwater arsenic species preservation (with EDTA and mixture of EDTA and acetic acid) prior to separation by anion-exchange chromatography (AEC) and detection by ICP-MS.

Materials and Methods

Groundwater samples were collected in December 2008 from six wells used for water supply in Eastern Croatia. Samples were split immediately into one subsample for total As determination, preserved with 1% HNO₃, and two subsamples for As speciation analysis were preserved: (i) a volume of 500 µL of 0,25 M EDTA were added to 10 mL of the sample previously filtered through 0.2-µm pore size filters; (ii) 5 mL of 8,7 M acetic acid (HAc) and 5 mL of 50000 µg·g⁻¹ EDTA were added to 500 mL sample previously filtered through 0.2-µm pore size filters. All samples were stored at 4 °C until further analyses. The analyses were performed in the Laboratory of Hydrosociences, Montpellier, France and analyzed within a week after collection.

Arsenic species were separated by anion-exchange chromatography (AEC) using a polymeric anion-exchange column, PRP-X100 Hamilton, Reno, NV (25 cm × 4.1 mm i.d.) and detected online by ICP-MS (Thermo X7 Series). VARIAN ProStar HPLC was used for solvent delivery. Eluent suppression was not used prior to ICP-MS detection, because DMA(V) is lost during the suppression step.¹²

Separation of As(+3) and As(+5) was achieved in ten minutes using a 30-mM ammonium phosphate buffer at pH 8.0. A gradient program was used for simultaneous determination of As(+3), As(+5), MMA and DMA using two ammonium phosphate buffers: (i) Sol A, 5 mM and pH 4.7, and (ii) Sol B, 30 mM and pH 8.0. From 0 to 4.1 min, Sol A was pumped then Sol B from 4.1 to 10.1 min. Sol A was pumped again from 10.1 to 20.0 min in order to equilibrate the column before further analysis. The flow rate through the column was maintained at 1 ml·min⁻¹.

Total As concentration was independently determined in a parallel HNO₃-preserved sample by ICP-MS.

All reagents were of analytical reagent grade. Deionised Milli-Q water was used to prepare all solutions. Calibration was performed with mixed standard solutions. Primary standards of 1000 mg·L⁻¹ of each species were prepared from: sodium arsenite (Rectapur, Prolabo, France) for As(+3); sodium arsenate (Sigma, St. Louis, MO) for As(+5); sodium dimethylarsinic (Merck, Germany) for DMA(+5) and di-sodium monomethylarsonate (Carlo Erba, Italy) for MMA(+5).

Results and Discussion

In studied groundwater samples MMA(+5) and DMA(+5) were not detected. As(+3) was the predominant component of the inorganic As in groundwater samples since As(+3) was > 85% and > 90% of the total arsenic, in EDTA and EDTA+HAc preserved samples respectively. Although the concentrations of As(+3) found in the samples preserved with EDTA were very similar to that found in the samples preserved with EDTA+HAc (Figure 1), in three samples (D23, D24 and S8) higher As(+5) concentrations were found in the samples preserved with EDTA. As(+3) is readily oxidized to As(+5) upon storage as well as adsorbed on particulate matter. Thus, preservation by EDTA+HAc could be more effective. However, more samples, as well as comparison with the field separation results, are necessary to provide better understanding of sample preservation for arsenic speciation in the studied groundwater.

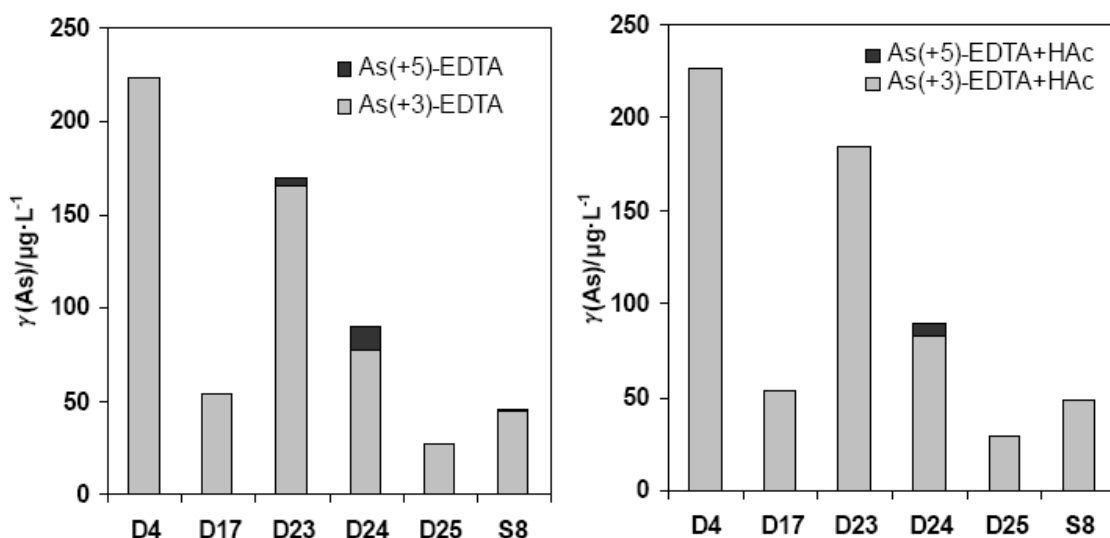


Figure 1. Arsenic species determined by AEC-ICP-MS in Eastern Croatian groundwater samples preserved in EDTA and EDTA+HAc.

Total arsenic concentrations determined by ICP-MS were between 32 and 214 $\mu\text{g}\cdot\text{L}^{-1}$. The Croatian drinking water limit ($50 \mu\text{g}\cdot\text{L}^{-1}$) was exceeded in four groundwater samples while the WHO-recommended threshold ($10 \mu\text{g}\cdot\text{L}^{-1}$) was exceeded in all six samples. The total arsenic concentrations obtained from the sum of As(+3) and As(+5) determined by AEC-ICP-MS were in very good agreement with the total arsenic concentrations determined by ICP-MS (Figure 2). The lower results obtained from preserved samples imply arsenic retention on colloidal or particulate matter.

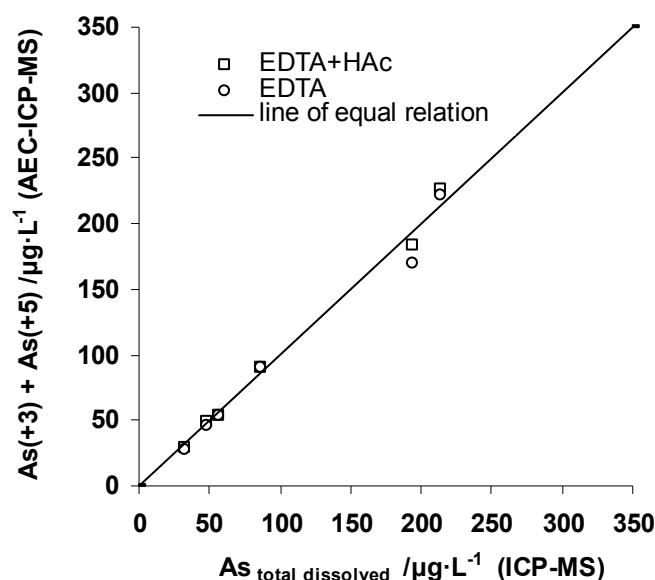


Figure 2. Comparison of the total arsenic concentrations determined in HNO_3 -preserved sample by ICP-MS and total arsenic concentrations obtained from sum of As(+3) and As(+5) concentrations obtained by AEC-ICP-MS in EDTA (open circles) and EDTA+HAc (open squares) preserved groundwater samples from Eastern Croatia.



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OVERVIEW OF VALIDATION PRINCIPLES I: LINEARITY, WORKING RANGE, SENSITIVITY AND ACCURACY

T. Bolanča, Š. Ukić

*University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19,
10000 Zagreb, Croatia, e-mail: Tomislav.Bolanca@fkit.hr*

Most measurement techniques make use of a calibration graph to estimate the analyte concentration in unknown samples. This implies that a decision concerning the nature of the relationship between the concentration and the response has to be taken. Very often a simple straight line relationship is preferred and many measurement techniques are designed to achieve proportionality between response and concentration. In practice, however, deviations from linearity are frequently observed. Therefore, it is essential for a method validation program to include a linearity test. Such tests and closely related parameters (working range and sensitivity) are discussed in this session.

Accuracy and bias are of course in close relation with linearity estimation. Systematic errors are characterized by terms such as trueness and bias related to term accuracy. Systematic errors may be constant (absolute) or proportional (relative). A constant error refers to a systematic error independent of the true concentration of the analyte and should be expressed in concentration units. A proportional error depends on the concentration of the analyte and should be expressed in relative units, such as percentage. The main sources of constant error are insufficient selectivity, which is caused by another component that also yields a response, and inadequate blank corrections. Proportional errors are caused by errors in the calibration, for instance by different slopes of the calibration lines of the standards and in the sample (matrix interference). The incorrect assumption of linearity over the range of analysis will also cause errors related to the concentration to be determined.

The experimental design and statistical background necessary for estimation of linearity working range, sensitivity and accuracy will be discussed and presented. Moreover, practical examples will be calculated on sight using MS Excel offering easy transfer and implementation of presented know-how in participants own laboratory.



OVERVIEW OF VALIDATION PRINCIPLES II: PRECISION, LOD, LOQ AND ANALYTICAL RESULT

T. Bolanča, Š. Ukić

University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19,
10000 Zagreb, Croatia, e-mail: Tomislav.Bolanca@fkit.hr

The precision is a measure for the size of the random errors. From a statistical point of view, precision measures the dispersion of the results around the mean, irrespective of whether that mean is a correct representation of the true value. Therefore, it requires the measurement of the standard deviation. How this is done depends on the context. Two extreme types of precision are usually distinguished, namely the repeatability and the reproducibility. In short, repeatability is the precision obtained in the best possible circumstances (same analyst, within one day when possible) and reproducibility in the most adverse possible circumstances (different laboratories, etc.). Intermediate situations may and do occur (intermediate precision). Fourth term used in the context of precision is robustness or ruggedness. Small departures from defined details of analytical procedure often occur when one carries out the in practice. Controlling such parameters may lead to better reproducibility or to avoid sources of laboratory bias.

An important characteristic of an analytical method is the smallest concentration of the analyte that can be detected with a specified degree of certainty. The fact that both blank and sample measurements are subject to error requires the problem of chemical detection to be treated in a statistical way. This implies that detection decisions are prone to the two kinds of errors associated with any statistical testing: false positive decisions (type I or α -error) and false negative decisions (type II or β -error). Therefore, three limiting levels are required to completely describe the detection capabilities of an analytical method:

- the decision limit at which one may decide *a posteriori* whether or not the result of an analysis indicates detection,
- the detection limit at which a given analytical procedure may be relied upon to lead *a priori* to detection and
- the determination limit (or quantification limit) at which a given procedure will be sufficiently precise to yield a satisfactory quantitative estimate.

The experimental design and statistical background needed for estimation of precision, LOD, LOQ and analytical result presentation will be discussed. Furthermore, practical examples will be calculated on sight using MS Excel offering easy transfer and implementation of presented know-how in participants own laboratory.

APPLICATIONS OF CAPILLARY ION CHROMATOGRAPHY SYSTEMS FOR TRACE ANALYSIS

J. Weiss

Dionex Corporation, International Operations, Idstein, Germany
joachim.weiss@dionex.com

There has been significant growth in the applications of HPLC using capillary columns. As an analytical tool, capillary HPLC offers several important advantages:

- It facilitates the direct interface to mass spectrometry
- It significantly reduces solvent consumption and associated waste disposal
- It provides higher mass sensitivity than conventional HPLC
- It is ideal for applications where sample volumes are limited

The recently introduced first capillary ion chromatography system offers similar benefits, although the above-mentioned benefits differ in their significance for typical ion chromatography applications. The biggest advantage of IC in the capillary format is the drastically reduced eluent consumption, which allows the continuous operation of the system over a long period of time, creating as little as 5 L of waste in an entire year. In conventional water analysis, sample volume is usually not an issue, but customers studying corrosion, working in atmospheric chemistry, or investigating metabolomic pathways will definitely benefit from the much smaller injection volumes ($\ll 1 \mu\text{L}$) required for Capillary IC. The higher mass sensitivity of Capillary IC as compared to conventional IC has a huge impact on the applicability of IC for trace analysis.

Ion chromatography is the preferred analytical technique for the determination of standard anions and cations at trace levels in a variety of sample matrices. To achieve the required sensitivity in trace analysis, established IC methods utilize either direct injection of a large sample volume ($\geq 1000 \mu\text{L}$) or a concentrator column to pre-concentrate analytes of interest from a large volume of sample (10 mL or more). In a conventional IC system with 4-mm ID separator columns operating at a flow rate of 1 mL/min, sample volumes can vary from 0.5 mL to 50 mL. Capillary IC systems typically use 0.4-mm ID capillary separator columns operating at a flow rate of 10 $\mu\text{L}/\text{min}$. To achieve the same concentration sensitivity, the sample volume can be reduced by a factor of 100 in capillary IC systems. For example, a 10- μL injection in a capillary IC system is equivalent to a 1000- μL injection in a conventional IC system. Instead of loading 50 mL of sample onto a concentrator column with a loading pump in a conventional IC system, a 500- μL sample volume can be injected onto a capillary concentrator column much more easily and conveniently. Capillary IC systems offer significant benefits for trace analysis, especially in applications where sample volumes are limited.

In this presentation, I will discuss the performance of capillary IC systems with on-line electrolytic eluent generation and suppressed conductivity detection and will demonstrate the advantages of capillary IC systems in determining anionic and cationic analytes at parts-per-trillion levels in different sample matrices.

ANION DETERMINATION IN THE SECONDARY WATER AT NUCLEAR POWER PLANT KRŠKO USING ICS 3000

D. Kralj

*Nuklearna elektrarna Krško, Vrbina 12, 8270 Krško
e-mail: Dejan.Kralj@nek.si*

The main goal of chemistry program in NPP Krško is to identify all important chemistry parameters which are directly related to Plant performance parameters (Chemistry performance indicator), considering quality assurance and quality control criteria. In corrosion monitoring process dissolved anion concentrations originated from hard acids (Cl^- , SO_4^{2-}), moderately hard acids (CH_3COO^- , HCOO^-) and from acids added as corrosion inhibitors (NO_2^- , NO_3^-) are most important indicator parameters.

Compounds present in demineralized water media of secondary side that can be characterized as impurities, could be divided in two groups in most general way: non-volatile and moderately volatile organic compounds, and CO_2 . The dissolved non-volatile impurities in the secondary side are affecting mainly the SG corrosion performance, when they concentrate beneath the deposits or in the flow restricted heat transfer crevices. Corrosion damages by non-volatile impurities are experienced seldom in other parts of the secondary side, due to absence of concentration mechanism in the other components and pipe work. The volatile impurities can harm the turbine corrosion performance, if they concentrate for example in the turbine blade key ways.

For dissolved anion concentration determination until 2008 Dionex DX-500 ion chromatograph was employed and it was replaced by the Dionex ICS 3000. Main parts of Dionex ICS 3000 instrument, as was recommended by Kemolab d.o.o. and Dionex Germany, are:

- Analytical column AS18, 4x250 mm
- Guard column AG18, 4x50 mm
- Ultra trace concentrator ATAC-LP1, 4x35 mm
- KOH eluent generator cartridge
- Self-Regenerating Suppressor ASRS 300, 4 mm
- Autoprep Large Volume Loop

For anion separation process analytical column AS18 is employed coupled with concentrator column. A larger sample volume may be injected into the concentrator column (up to 20 ml) which reduces the limits of anion determination (below 0.1 $\mu\text{g/l}$ for most anions – Table 1). Anion concentrations in secondary process water are very low and approach very closely to the LOQ determination limit for anions or even fall below it. Repeatability and reproducibility are very good (Figure 1).

The analytical method was evaluated with statistical parameters and the LOD limit of detection and the LOQ limit of quantification were determined for each individual anion. In addition to the calibration lines it is also determined the limit of a linear area and thus defined accurately the determination area for individual anions.

LOQ in NPP Krško is determined according to American standard INPO 88-021 [1]:

$$\text{LOQ} = 10 \times S_R$$

S_R – Standard deviation of 10 replicates of the blank

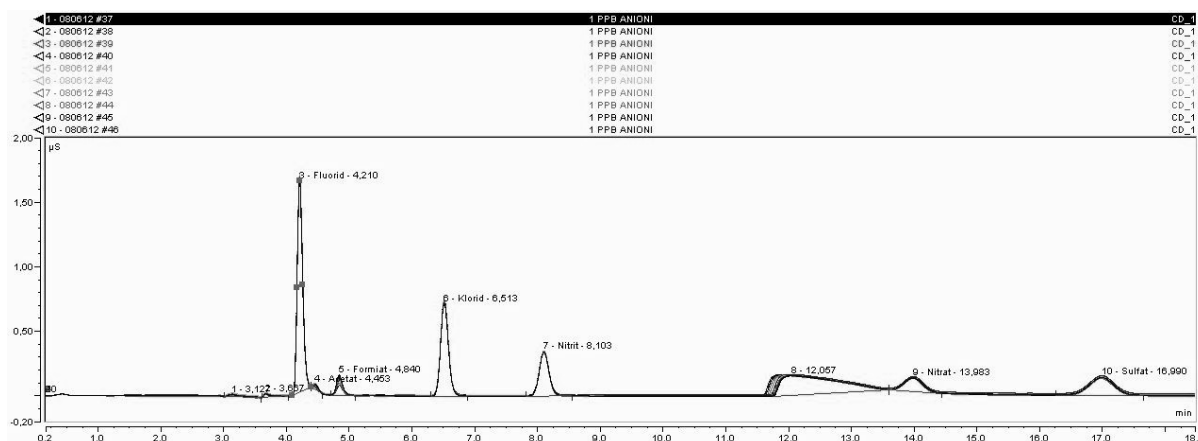


Figure 1. 1 ppb F⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻ - Repeatability

Method Description:

- Single Analysis Time: 42 min
- EGC/KOH Concentration: 16 mM
- Isocratic Pump
- T_{Col} = 30°C
- Sample Volume = 10 ml
- Flow rate: 1 ml/min

Calibration:

Linear calibration is used for all anions (Table 2). Correlation Coefficient is higher than 0.999 for all anions (Figure 2).

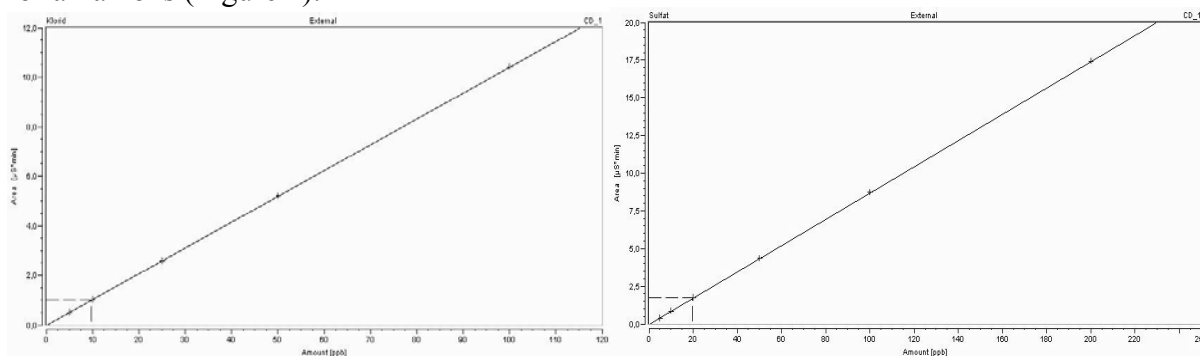


Figure 2. Calibration curves for Cl⁻ and SO₄²⁻; correlation coefficient > 0.999

Table 1. Low level LOQ

	F ⁻ µg/l	Cl ⁻ µg/l	SO ₄ ²⁻ µg/l	NO ₃ ⁻ µg/l	NO ₂ ⁻ µg/l	CH ₃ COO ⁻ µg/l	HCOO ⁻ µg/l
LOQ	0.1	0.1	0.1	0.1	0.1	3.0	3.0

Table 2. Linearity range

	F ⁻ µg/l	Cl ⁻ µg/l	SO ₄ ²⁻ µg/l	NO ₃ ⁻ µg/l	NO ₂ ⁻ µg/l	CH ₃ COO ⁻ µg/l	HCOO ⁻ µg/l
LR	0.1 - 50	0.1 - 100	0.1 - 60	0.1 - 200	0.1 - 100	3 - 200	3 - 200

QC Check and Control Charting:

Check standard is analysed at the beginning of the run, every 10th sample and at the end of the run. Table 3 shows check standard concentration.

Table 3. Check standard concentration

	F ⁻ µg/l	Cl ⁻ µg/l	SO ₄ ²⁻ µg/l	NO ₃ ⁻ µg/l	NO ₂ ⁻ µg/l	CH ₃ COO ⁻ µg/l	HCOO ⁻ µg/l
LOQ	3.5	5.0	5.0	5.0	5.0	5.0	5.0

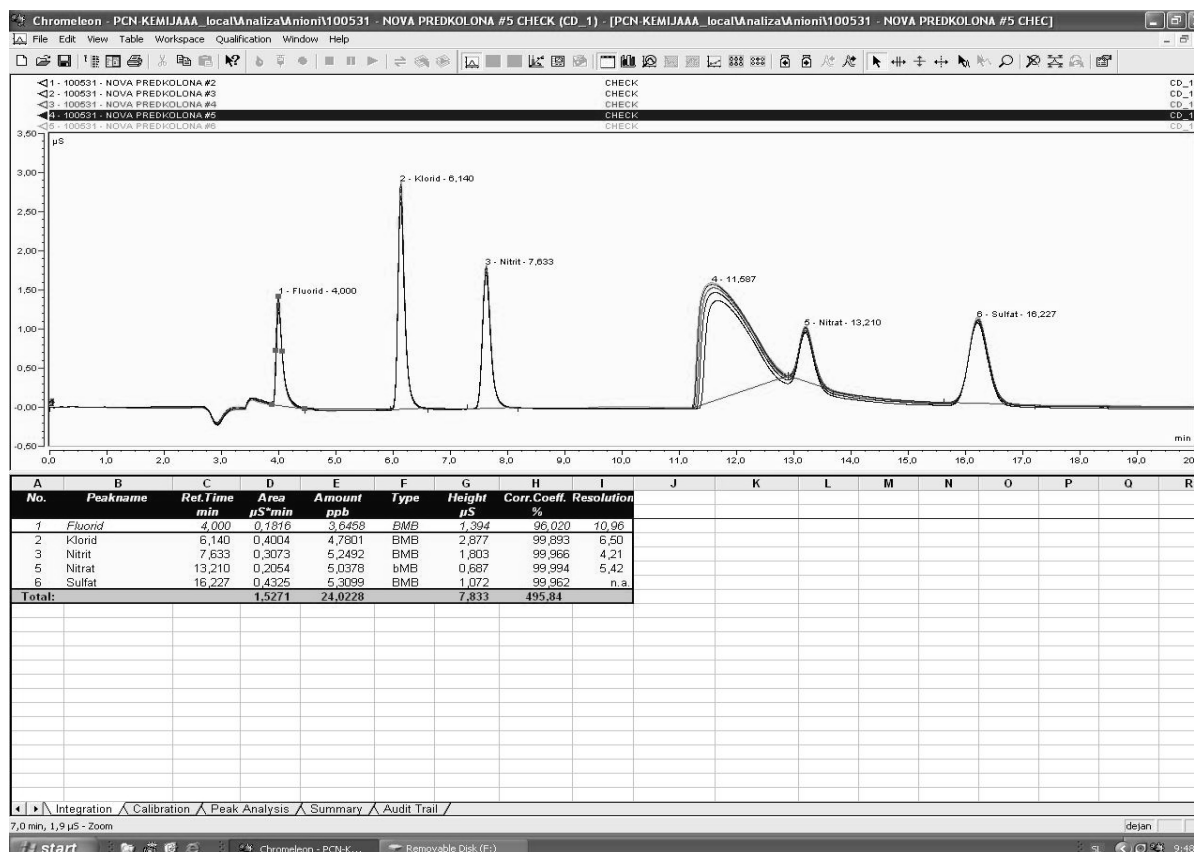


Figure 3. QC check for F⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻ - Repeatability

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ION CHROMATOGRAPHY IN OIL INDUSTRY

Application and experiences

T. Tomić, N. Uzorinac Nasipak

INA - Industrija nafte d.d.

Ion chromatography is a powerful tool for water sample analysis in oil industry. Replacement of the classic analytical method leads to the use of smaller sample content, faster analysis, multiple information in a single analysis. In oil industry we can find numerous ion chromatography uses, of which some are connected to oil investigations and some to ecological demands and control. Different sample matrices can be analyzed. Water is most frequently used as matrix but waste samples, amine solutions and other matrices can be analyzed as well.

Water samples in oil industry are as follows:

a) Oilfield water samples

- formation water – water that occurs naturally within the pores of a rock
- connate water – water trapped in the pores of a rock as it was formed. The chemistry of connate water can change in terms of composition throughout the history of the rock. Connate water can be dense and saline compared with seawater. Formation water in contrast is simply water found in the pore spaces of a rock and might not have been present when the rock was formed. Connate water is also described as fossil water
- sedimentary water – used as injection water in order to increase recovery from an oil bed. Composition is similar to formation water but with oilfield chemicals included
- brine – saline liquid usually used in completion operations and, increasingly, when penetrating a pay zone. Brines are preferred because they have higher densities than fresh water. Classes of brines include chloride brines (calcium and sodium), bromides and formates
- injection water – water injected into a reservoir to pressurize and displace hydrocarbons to producing wells. Injection water is also used in water-storage operations in offshore and remote locations with economic and environmental constraints. Sedimentary water is used usually as injection water in order to increase recovery from an oil bed

Oilfield water investigation has two main reasons:

1. qualitative determination of some or few ions in water, which geologists can use in identifying mineral constitution because oilfield water samples like crude oil are typical for their corresponding geological formation
2. quantitative determination of particular ion concentration aimed at classifying the water sample

b) Other water samples connected with oil industry

- groundwater – water in the subsurface below the water table. Groundwater is held in the pores of rocks and can be connate, from meteoric sources or associated with igneous intrusions
- wellspring water – water samples from wells near oil fields
- surface water – parts of river watercourse
- sea water – near oil refinery
- waste water

Except water as matrix, there are other sample matrices as well:

- amines which are used to remove acid gases (H₂S, CO₂) from natural gas or gasoline
- waste, waste elutes

The significance of oilfield water analyses is the analysis of liquid samples from exploration wells, characterization of water produced together with oil, quality check of injection water, prediction of corrosion rate, prediction of scale formation rate, monitoring of chemicals used for water treatment and analytical backup for projects in oil industry.

Main analytical problems in IC oilfield water analysis are the following: high chloride contents, separation of chloride and nitrate, separation of sodium and ammonium, presence of organics – hydrocarbons, oils and fats and interference of artificial added compounds.

Solutions to these problems are sample filtration to remove insoluble particles (e.g. 0.45 µm cellulose filters), dilution to bring analytes into working range, multiple analysis to cover all important ion determinations, use of OnGuard Ag/H cartridges to easily remove chloride, bromide and iodide from concentrated matrices or OnGuard II P cartridges to remove organic matter.

In this paper we have presented IC anion and cation analysis of different samples under different conditions. Each sample was treated separately under specific working conditions. We have worked with IC chromatographs of two different manufacturers, with different chromatographic columns and with or without suppression. Detection has been performed on conductivity detector on both systems. Every system has its advantages and disadvantages but we have obtained satisfactory results for anion and cation separation and determination on both systems.

NITRITE AND NITRATE IN TOBACCO – A CASE STUDY IN IC METHOD DEVELOPMENT

K. Vinković¹, C. Crey-Desbiolles², D. Jensen²

¹*Kemolab d.o.o., Drinska 27b, 10000 Zagreb, Croatia*

²*Dionex (Europe) Management AG, Soloturnerstrasse 259, 4600 Olten, Switzerland*

Conductivity detection is very often considered as the standard detection technique in ion chromatography (IC). While most of the IC-applications indeed use suppressed conductivity, other detection techniques like UV and amperometry are commonly used as well. In case of demanding sample matrices the combination of both, improved separation and optimized detection conditions can help to solve the analytical task.

The determination of Nitrite and Nitrate in aqueous tobacco extracts was chosen as a real-life example to explore different detection techniques. This matrix and analytes were chosen, as nitrites are precursors in the formation of carcinogenic nitrosamines. Since nitrosamines are found in tobacco smoke, concentration of nitrites should be kept under control.

Method development started with nitrite and nitrate separation on IonPac AS19 column with potassium hydroxide eluent and suppressed conductivity detection. As the extracts contained high concentrations of organic acids initially KOH-gradient elution was applied to allow the determination of the target analytes. Since the extracts contained high concentrations of chloride eluting next to nitrite, its trace determination was hampered. The use of parallel UV-detection was considered, but the end user voted for a method allowing the selective determination of nitrite and nitrate in combination with a shorter cycle time of analysis.

In a different approach we tested the separation on AS9-HC column applying UV detection. The eluent chosen was 30 mmol L⁻¹ sodium chloride, eluting all interesting components while being UV-transparent. Good correlation coefficients (> 0.999) were achieved for both, nitrites and nitrates, in the range from 0.01 to 1.00 mg L⁻¹. Signal to noise ratio at 0.01 mg L⁻¹ was 18.1 for nitrite and 31.5 for nitrate for aqueous standard solutions. Unfortunately, in real samples organic interferences prevented identification of nitrite at concentrations lower than 0.2 mg L⁻¹. Several sodium chloride gradients were tested in order to achieve better separation between nitrite and interfering compounds. pH value of the eluent was set to 7.5 trying to transfer most organics to neutral molecules. Unfortunately, neither gradients, buffering of the eluent, wavelength changes on the UV-detector or choosing a column of different selectivity (e.g. CarboPac PA100) did improve the chromatographic resolution of nitrite from matrix components. In addition we tested an SPE sample preparation using OnGuard P and RP cartridges. The total amount of UV-absorbing organics was reduced, though the determination of nitrite was difficult. Hence amperometric detection was chosen to solve the issue.

As working electrode glassy carbon was chosen being superior to other electrode materials in terms of sensitivity. Applying an isocratic elution with 30 mmol L⁻¹ NaCl on an IonPac AS9-HC all ionic components were eluted in 35 min. Due to the high specificity and sensitivity of the amperometric detection it was possible to reliably quantify nitrite in aqueous tobacco-extracts at concentrations down to 0.01 mg L⁻¹ with excellent reproducibility. The approach chosen uses UV-detection in parallel to detect Nitrate selectively, interference-free and with high specificity at concentration levels from 10 to 800 mg L⁻¹.

During method development the chromatographic and the detection conditions, as well as the sample preparation prior to the analytical separation were evaluated to generate a robust and reliable method suited for routine application. Pros and Cons of three detection techniques were examined and evaluated for specific samples. This application might be of interest also for other food samples, if the determination of nitrite is hampered by other matrix components. As limits on the amount of nitrites used in meat products are established in order to decrease cancer risk in the population, the experiments shown could become the basis for wider usage of the same approach or similar methods.

ANALYSIS OF METAL IONS IN CROATIAN WINES USING ION CHROMATOGRAPHY AS FORENSIC METHOD

V. Marinović¹, G. Mršić¹, V. Zechner-Krpan², V. Petravić-Tominac²

¹Forensic Center "Ivan Vučetić", Ilica 335, 10000 Zagreb, Croatia

²Faculty of Food Technology and Biotechnology, Department of Biochemical Engineering, Pierottijeva 6, 10000 Zagreb, Croatia

Ion chromatography (IC) was used to analyze concentrations of four metals (sodium, potassium, magnesium and calcium) in two Croatian wines (sample 1 and sample 2), both produced in 2009. Comparison of the results for two wine samples showed that levels of all four metals differed in tested samples. The highest differences were found for sodium (146.7 %) and the lowest for magnesium (7.5 %).

Conclusion: Therefore, ion chromatography can be regarded as suitable method for differentiation of different wine samples.

Table 1. Results of metal ions analysis of two Croatian wines.

ION CONCENTRATION (mg/L)	SAMPLE 1	SAMPLE 2
Sodium	109.69	270.66
Potassium	1091.11	1541.35
Magnesium	108.99	101.39
Calcium	100.22	112.24

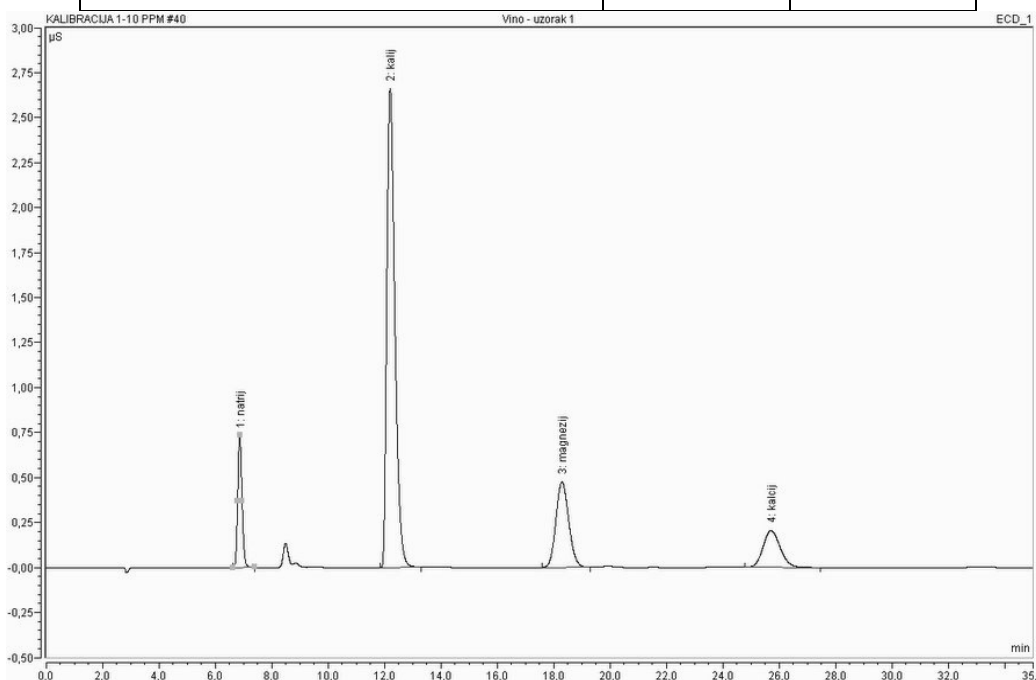


Figure 1. Chromatogram of sample 1.

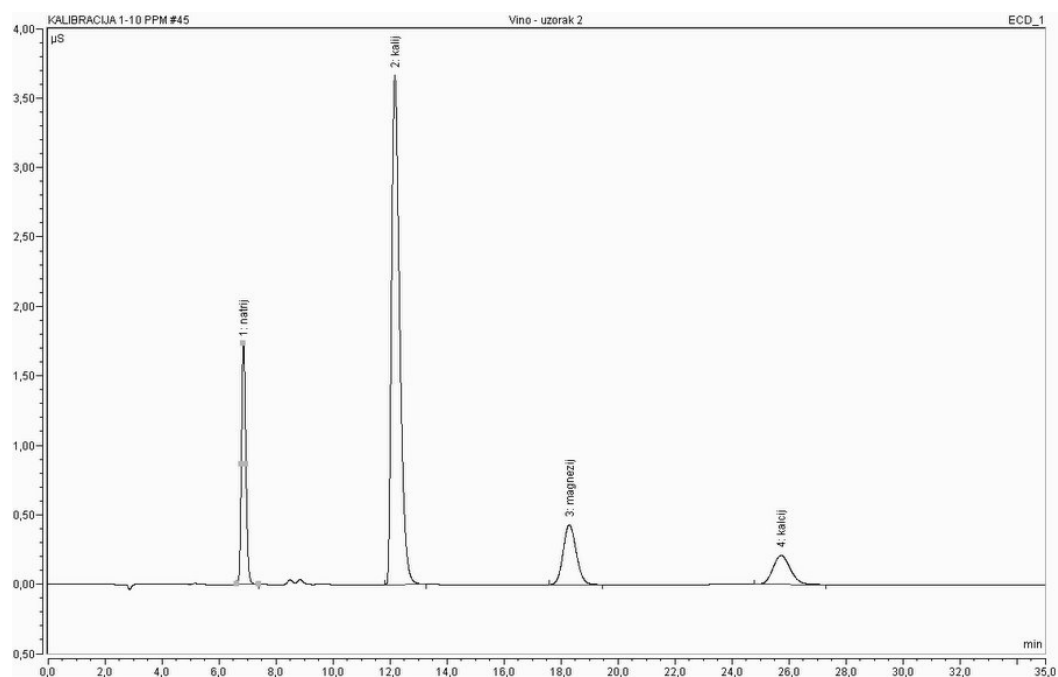


Figure 2. Chromatogram of sample 2.

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**DETERMINATION OF NITRATES/NITRITES IN FRUITS,
VEGETABLES AND THEIR COMMODITIES
BY ION CHROMATOGRAPHY WITH UV DETECTOR**

V. Stankov

*SP Laboratorija, Industrijska zona bb, Bečej,
e-mail:splaboratorija@soyaprotein.com*

Nitrates and nitrites are chemicals that can be found naturally in our environment. They are essential nutrients for plants to grow and its content is an important quality characteristics of fruits and vegetables. Plants naturally release nitrogen when die and decompose. The nitrogen from the rotting plants oxidize (combine with oxygen) to form nitrates or nitrites.

During a rainfall, surface water can move through the soil and carry these nitrates or nitrites down to the underground drinking water (ground water). Other ways that water can be contaminated with nitrates is through the use of products that contain large amounts of ammonia-ion, fertilizer. Ammonia oxidize and form nitrite. Heavy applications of nitrogen fertilizer can cause nitrates to accumulate in vegetables. Farmers tend to apply large amounts of fertilizers, especially nitrogen. This is a reasonable insurance against yield losses from nutrient deficiencies, especially if fertilizers are fairly cheap. However, applying too much nitrogen fertilizer may be bad for human health.

Once taken into the body, nitrates may be converted to the more toxic nitrites. Nitrite and N-nitroso compounds, which form when nitrite binds to other substance before or after ingestion (for example, the amines derived from proteins) can lead to severe pathologies in humans. The best-known effect of nitrite is its ability to react with hemoglobin (oxyHb-Fe²⁺) to form methemoglobin (metHb-Fe³⁺) and nitrate. Because of that, oxygen delivery to tissue is impaired. The condition where the nitrite reacts with the iron and hemoglobin is known as methemoglobinemia (often called "blue baby syndrome").

To protect public health, the European Member States agreed an EC Regulation setting limits for nitrate in lettuce, spinach and processed cereal-based foods and baby foods (Commission Regulation EC No.1881/2006). Serbian legislation defines the concentration of nitrates (max 100mg/kg) and nitrites (0.2mg/kg) in baby food and concentration of nitrates (max 250mg/kg) and nitrites (2mg/kg) in children's food, but for fruits and vegetables we don't have maximum levels.

Fruits, vegetables and their commodities if contain nitrates or nitrites, can be identified by Ion-exchange chromatography. This separation method is based on ion-exchange processes occurring between the mobile phase and ion-exchange groups bonded to the support material. Separation of anions is accomplished with quaternary ammonium groups attached to the polymer of stationary phase.

In SP Laboratory, determination of nitrates and nitrites in vegetables, fruits and their commodities was done by ICS-1000 system with UV Detector by Dionex, USA. Separation and identification of nitrates and nitrites was done with analytical column AS14 and guard column AG14 and with mobile phase 3.5mM Na₂CO₃/1mM NaHCO₃ buffer system. Sample preparation of fruits, vegetables and their commodities is based on sample clarification by Carrez I (K₄[Fe(CN)₆]*3H₂O) and Carrez II (ZnSO₄*7H₂O) reagents.[1]

Nitrates and nitrites are well separated by this method. As far as the detection of ions, we used UV detector because there wasn't interferences with matrix unlike conductometric

detector where was disturbance. The method was validated on green beans, peach, apple, cucumber, apple juice, frozen green beans, peas and frozen peas and baby food with fruits.

Validation parameters of the nitrate ion (NO_3^-): range of calibration curve 2.5-25mg/l, range of method 0.01-250mg/kg, recovery 96.41-104.8%, repeatability 0.004-1.372%, reproduction 0.011-5.35%, precision 0.011-5.410%, uncertainty of measurement 5.32-8.10% and LoQ 0.01mg/kg. Validation parameters of the nitrite ion (NO_2^-): range of calibration curve 0.25-2mg/l, range of method 0.01-10mg/kg, recovery 92.95-101.13%, repeatability 1.190-3.088%, reproduction 6.682-9.854%, precision 7.039-10.327%, uncertainty of measurement 6.36-14.53% and LoQ 0.01mg/kg.

During the last year, most of the commercial samples (about 600 samples), which were analyzed didn't contain nitrate and nitrite, about 85% of samples contained under 10mg/kg nitrates and under 1mg/kg nitrites, whereas a few samples had a higher content of nitrate - spinach (about 3000mg/kg), lettuce (about 1500mg/kg), strawberry (about 300mg/kg) and baby food with vegetables (about 80mg/kg). In SP Laboratory that is the routine technique for nitrate and nitrite determination in fruits, vegetables and their commodities.

Reference:

1. EN 12014-2 Foodstuffs - Determination of nitrate and/or nitrite content - Part 2: HPLC/IC method for the determination of nitrate content of vegetables and vegetable products

9TH PROFICIENCY TEST: CRITICAL REVIEW

Š. Ukić, T. Bolanča, Š. Cerjan Stefanović, K. Margeta

University of Zagreb, Faculty of Chemical Engineering and Technology, Laboratory for Analytical Chemistry, Marulićev trg 20, 10 000 Zageb, Croatia,
e-mail: Tomislav.Bolanca@fkit.hr

In an inter-laboratory experiment, different laboratories determine some characteristic, e.g. the concentration of an analyte in one or various homogeneous samples under documented conditions. Several subtypes of inter-laboratory studies can be distinguished. *Collaborative trials or method performance studies* are used to test the performance (generally the precision) of a single analytical method. A standard method, which is routinely used in several laboratories, can also be examined collaboratively to test for a possible bias of either the method (method bias) or the laboratories (laboratory bias) that routinely use it. The comparison of different laboratories that perform comparable analyses with their own individual method is often called *proficiency testing or laboratory performance studies*; sometimes, the term “round robin study” is used. It is an essential part of the requirements for laboratory accreditation and the participating laboratories have to prove their technical competence regularly. In proficiency testing, the defined test schemes are organized individually for the analysis of a certain analyte (or a group of analytes) in a certain matrix. All proficiency testing schemes are run regularly, but each scheme has its own frequency of test rounds.

The most commonly used evaluation tool in proficiency testing is *z*-score. A *z*-score is the ratio of the bias estimate and the target value for the standard deviation of the results. Several estimators can be used for this target value:

- A fixed arbitrary value, possibly adapted after a certain number of rounds performed if general analytical improvements allow for a better precision.
- A precision estimate required for a specific task of data evaluation.
- The reproducibility standard deviation observed from a collaborative study in method validation.
- The (average) reproducibility standard deviation observed in the previous rounds.
- The expected standard deviation for the concentration range considered according to Horwitz or the slight modification of this method for proficiency tests.
- A robust estimator of spread of the data, e.g. Huber’s *M*-estimator.
- The standard deviation of the results after removal of the outliers.

Based on an adequate estimator for the standard deviation, the absolute values of the *z*-scores, which are standardized, allow a direct estimation of the performance of the laboratory by comparison with the following quality limits:

- $|z| < 2$: the performance of the laboratory is considered satisfactory.
- $2 < |z| < 3$: the performance of the laboratory is considered questionable.
- $|z| > 3$: the performance of the laboratory is considered unsatisfactory.

As an alternative to these symmetric acceptance intervals, asymmetrical acceptance intervals are suggested for trace analysis. Based on the standard deviation of the test itself, this method takes into account that negative lower acceptance limits are not reasonable.

The final report has to be send to the participants. It comprises a description of the preparation of the material and the test for homogeneity, an anonymous (coded) list of all valid data and the statistical results. The *z*-scores have to be tabulated or graphically



expressed. Moreover, abstracts of the methods as well as the remarks of the participants should be added if it is possible.

***POSTER
PRESENTATIONS***

VALIDATION OF METHOD FOR ANIONS DETERMINATION IN DRINKING WATER AND COMPARISON OF DIFFERENT SEPARATION COLUMNS FOR ANIONS ANALYSIS

M. Kopričanec, M. Mihovec-Grdić, R. Čalić

Zagrebački holding d.o.o., Podružnica vodoopskrba i odvodnja, Sektor vodoopskrbe, Služba kontrole kvalitete vode i HSZ, E. Patačić 1b, 10000 Zagreb, martina.kopricanec@vio.hr, mira.mihovec@vio.hr, romana.calic@vio.hr

The analysis of anions (fluorides, chlorides, nitrites, orthophosphates, bromides, nitrates and sulphates) in underground and drinking water of the Zagreb water-supply system is carried out by means of ion chromatography method, HRN EN ISO 10304-1:1998 [1]. Anions are separated on the Dionex AS15 anion separation column, and are then transformed, using suppressor, to related acids determined by the conductivity detector. The anions analysis is carried out on the ICS-3000 instrument (Dionex), with hydroxide eluents.

This study will provide the description of the method validation procedure for the determination of anion concentration in underground and drinking water. The validation procedure includes linearity, repeatability, determination of detection and quantification limits. The results obtained show that the method is precise and accurate for the determination of low and high anion concentrations in underground and drinking water, and that the method meets the requirements of the Ordinance on Sanitary Quality of Drinking Water.^[2]

In addition, the study will also show basic differences in the anion analysis on the following separation columns: AS9-HC (carbonate eluents), AS14 (carbonate eluents), AS23 (carbonate eluents) and AS15 (hydroxide eluents)

1. HRN EN ISO 10304-1:1998, Water quality- Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulphate ions, using liquid chromatography of ions.
2. Ordinance on Sanitary Quality of Drinking Water, (OG 47/08)

QUANTIFICATION OF TOTAL SULPHUR CONTENT IN THE PLANT MATERIAL BY USING A HIGH PERFORMANCE ION CHROMATOGRAPHIC (HPIC) METHOD

M. Pazalja, D. Krešić, A. Šapčanin

*Faculty of Pharmacy, University of Sarajevo, Čekaluša 90,
71000 Sarajevo, Bosnia and Herzegovina,
ida@bih.net.ba*

Objectives Presence of sulphur (S) compounds in the plants like Cauliflower (*Brassica oleracea* var. botrytis), Nasturtium (*Tropaeolum majus*), Garlic (*Allium sativum* L.), Kale (*Brassica oleracea* var. sabauda), Cabbage (*Brassica oleracea* var. capitata L.), Leek (*Allium ampeloprasum* var. porrum L.) and Ramson (*Allium ursinum* L.) has a great gastronomic nutritional and pharmacological importance. This work has been aimed to assess total S content in a different plant material by using a High Performance Ion Chromatographic (HPIC) method. **Materials and Method** Samples from seven different plants (leaves, flowers and roots) were prepared by digestion and oxidation with a mixture of perchloric and nitric acid and addition of small portion of magnesium oxide. HPIC method was performed with a Shimadzu Ion Chromatograph equipped with conductivity detector CDD-10A, pump LC-10AD, auto sampler SIL-10Ai, degasser DGU-14A and oven CTO-10A. Degassed and diluted samples were analyzed on Shodex IC SI-90G strong exchange column, using a mobile phase: carbonate buffer NaHCO_3 (0.0017 M) and Na_2CO_3 (0.0018 M), during the 20 minutes at 40°C and 1.0 mLmin^{-1} flow rate. Magnesium sulphate was used for the preparation of calibration curve. **Results** The total S content in analyzed plants varies from 0.09 mg/g to 1.72 mg/g. **Conclusion** Used HPIC method is simple, sensitive and accurate and can be applied for the determination of total S content in the different plants. Results of this analysis suggest consumption of Ramson as a significant pharmacological source of organo-sulphur compounds and Garlic as a food supplement like an equal prevention from hazard effects of cardiovascular diseases.

UTILIZATION OF HIGH PERFORMANCE ION CHROMATOGRAPHY (HPIC) METHOD FOR THE DETERMINATION OF TOTAL SULFUR CONTENT IN A FARMYARD MANURE

D. Krešić, M. Pazalja, A. Šapčanin

*Faculty of Pharmacy, University of Sarajevo, Čekaluša 90,
71000 Sarajevo, Bosnia and Herzegovina,
ida@bih.net.ba*

Objectives Sulphur (S) is assimilated from the soil as a sulphate ion and further being reduced to the organo-sulphide species. The application of farmyard manure is a core principle in organic farming systems and enables management of soil organic matter. Soil organic matter is crucial to maintain and improve physical, chemical and biological properties of agricultural soils and is essential for the storage of energy and nutrients, as a structural stabilizer and as a chemical buffer for introduced xenobiotics. This work has been aimed to assess total S content in different farmyard manure (cow, chicken, sheep, horse) by using a High Performance Ion Chromatographic (HPIC) method. **Materials and Method** Samples from seven different manure (fresh and commercially available) were prepared by digestion and oxidation with a mixture of perchloric and nitric acid and addition of small portion of magnesium oxide. HPIC method was performed with a Shimadzu Ion Chromatograph equipped with conductivity detector CDD-10A, pump LC-10AD, autosampler SIL-10Ai, degasser DGU-14A, oven CTO-10A. Degassed and diluted samples were analysed on Shodex IC SI-90G strong exchange column, using a mobile phase: carbonate buffer NaHCO_3 (0.0017 M) and Na_2CO_3 (0.0018 M), during the 20 minutes at 40°C and 1.0 mLmin^{-1} flow rate. Magnesium sulphate was used for the preparation of calibration curve. **Results** The total S content in analysed farmyard manure varies from 0.5 mg/g to 5.1 mg/g. **Conclusion** Used HPIC method is simple, sensitive and accurate and can be applied for the determination of total S content in the farmyard manure. This experiment illustrates the utility of HPIC as a reliable analytical tool. Results of this analysis could recommend soil fertilization with chicken manure for the cultivation of the plants with highest S metabolic needs.

ANALYSIS OF AIRBORNE PARTICULATE MATTER BY PILS-IC

S. Hoffmann¹, P. Jones²

¹*Metrohm International Headquarters, Oberdorfstrasse 68, Herisau 9101, Switzerland,
sho@metrohm.com (Presenting)*

²*Metrohm U.K. Ltd., Metrohm House, Evenwood Close, Daresbury Court, Runcorn WA7 1LZ,
UK, sc@metrohm.com*

Airborne particulate matter at sizes less than 1/20th the width of human hair can cause respiratory aggravation and may be linked to other more serious and chronic conditions. These particles are identified by their largest component sizes (e.g., 2.5 µm or Particulate Matter 2.5 – PM_{2.5}) and can be separated from larger particles by use of a cyclone. The ADI 2018 Particle Into Liquid Sampler (PILS) is a device used to capture the particles in an air flow and dissolve the soluble constituents in a steam jet for analysis (in this case by ion chromatography – IC). The PILS-IC system provides analysis with fast cycle times giving the concentration of water-soluble components of the PM_{2.5} such as nitrate, chloride and sulfate that may adversely impact human health.

In this poster, a comparison between the 30 day results obtained by the PILS-IC system and the results obtained by manual extraction and analysis of air filters will be presented. The PILS-IC system reported results for anions in the fine particles every twenty minutes. During the period of operation the PILS-IC system recorded a significant increase in the levels of the particulates at the monitoring site (over 50 µg·m⁻³ on two separate occasions). Comparable data from the filter systems was not available for several days, but corroborated the high-level events previously reported by the PILS-IC system.

LIQUID HANDLING APPLIED TO AUTOMATED SAMPLE PREPARATION IN LIQUID CHROMATOGRAPHY

S. Hoffmann, S. Czyborra

*Metrohm International Headquarters, Oberdorfstrasse 68, Herisau 9101, Switzerland,
sho@metrohm.com (Presenting), sc@metrohm.com*

Sample preparation plays an important role in all fields of liquid chromatography. While in the past a lot of tedious manual steps were required, nowadays automated sample preparation is gaining importance.

State-of-the-art equipment for automated sample preparation usually allows filtration, solid-phase extraction and dilution. More recently, ultrafiltration, intelligent dilution, combustion and dialysis have been made available as fully automated techniques.

In this presentation, we focus on liquid handling operations used for efficient automated sample preparation.

We discuss a so-called liquid handling module, that is a setup combining a selection manifold with dosing devices, reagent and mixing vessels, peristaltic pump and injection valve. In combination with an ion chromatograph, this system offers almost unlimited flexibility for all kinds of automated liquid handling operations.

Selected key applications involving, for example, chemical reactions of the samples before separation, pH adjustment by addition of acids or bases, dilution and spiking demonstrate the scope of liquid handling as applied to automated sample preparation.

SAMPING AND ANALYSES OF ATMOSPHERIC DEPOSITION IN FOREST ECOSYSTEM OF CROATIA IN FRAMEWORK OF ICP FORESTS

T. Jakovljević¹, A. Marchetto², K. Berković³

¹*Croatian forest reserach institute, Cvjetno naselje 41, 10450 Jastrebarsko,
tamaraj@sumins.hr*

²*Institute of Ecosystem Study, Largo Tonolli 50, 28922 Verbania Pallanza, Italy,
a.marchetto@cnrise.it*

³*University of Zagreb, Faculty of Food Technology and Biotechnology, Pierrotieva 6,
10000 Zagreb, kberkovic@pbf.hr*

The Integrated Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) and EU regulation aim to conduct intensive and continuous monitoring of forest ecosystems in Europe as a mean of evaluating the damage caused by atmospheric pollution and other factors influencing forest condition. They also try to improve the understanding of the casual relationship between changes in forest ecosystems and the factors influencing these changes, with particular focus on the atmospheric deposition (concentrations, amount of deposition, fluxes) and soil loads at the sites, on which intensive monitoring is performed. The chemistry of atmospheric deposition and its transformation in contact with vegetation are of great importance in understanding its effects on forests. Therefore, methods of sampling, sample treatment, chemical analysis, and quality control are harmonised and detailed in ICP Forests manual. The objective of this kind of research in Croatia is to determinate the flux of ions from atmosphere to forest ecosystem on yearly basis, in order to assess the condition of forests of Croatia.

Two type of samples are used. One is the bulk open field sample that represents a flux of dissolved components from the atmosphere in open field with rain, snow, hail. It is sampled with a continuously open plastic funnel and bottle, which also collects parts of particulate and gaseous deposition during dry periods. The other, the throughfall method estimates the deposition to forests and these samples are sampled beneath the forest canopy and containing bulk+leached+dry deposition-absorbed ions. The collectors are placed, with the opening area horizontal at a height of approximately 1 m above the ground level to avoid contamination by soil. Throughfall collectors are distributed evenly over the plot. The precipitation samples were collected biweekly and their volume was measured separately and marked on the mailing form to be sent with the samples to the laboratory.

According to ICP Forests manual analytical methods and parameters to be analysed in the collected samples are divided into mandatory parametars, which are considered necessary to measure on European scale: the amount of precipitation, pH and conductivity at 25°C, ions NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-} using ion chromatography. Validation checks and relationships are performed according to the ICP Forests manual: checks of ion balance, the comparison between measured and calculated conductivity value, the ratio between Na^+ and Cl^- ions and the comparison between conductivity value and the sum of cations/ between conductivity value and the sum of anions.

The results give an opportunity to extend the research on other permanent plots in Croatia. Therefore, it is desirable to improve the coherency and efficiency of the existing monitoring activities and networks, reliability, comparability and accuracy of forest related information at national as well as European level.

DEHALOGENATION OF ORGANIC COMPOUNDS BY REDUCTIVE RADICALS

B. Matasović, M. Bonifačić

*Institut "Ruđer Bošković", Bijenička cesta 54, 10000 Zagreb
bmatasov@irb.hr, bonifacic@irb.hr*

γ -Radiolysis and measurements of halide ions by means of ion chromatography have been employed to investigate reductive dehalogenation of chloro-, bromo-, and iodophenols, halogenated aliphatic compounds and 5-bromouracil by carbon-centred radicals, $\bullet\text{CH}(\text{CH}_3)\text{OH}$, $\bullet\text{CH}_2\text{OH}$, and $\bullet\text{CO}_2^-$, in air-free aqueous solutions in the presence of ethanol, methanol or sodium formate as precursors of reductive organic radicals. The influence of different bases on the reaction efficiency has also been investigated. The presence of sodium hydrogencarbonate and ammonium acetate significantly influences reduction power of carbon-centred radicals (except $\bullet\text{CO}_2^-$), while presence of stronger base, potassium hydrogenphosphate, does not improve reduction power of those radicals which is otherwise insufficient for dehalogenation of brominated and chlorinated compounds. In systems where reduction is operative, dehalogenation has been observed to occur by a chain process. Additionally, complex between base and reductive radical is formed in case of $\bullet\text{CH}(\text{CH}_3)\text{OH}$ and $\bullet\text{CH}_2\text{OH}$. Mechanisms of the abovementioned reduction reactions, simple electron transfer mechanism for $\bullet\text{CO}_2^-$ and proton-coupled electron transfer for $\bullet\text{CH}(\text{CH}_3)\text{OH}$ and $\bullet\text{CH}_2\text{OH}$, have been investigated. System with the concentration of NaHCO_3 of 10 mmol/dm^3 gives the optimal outcome, i.e. the highest yield of halide ions with as low concentration of other components as possible but even better rate constants have been achieved with $\bullet\text{CO}_2^-$ (for one to two orders of magnitude). Equilibrium constants of complexes observed in this work has been estimated to be (almost) the same.

OptIC, NEW SOFTWARE FOR PREDICTION AND OPTIMIZATION IN IC

T. Bolanča, Š. Ukić, M. Rogošić, B. Brigljević, A. Dizdar, P. Žuvela

*University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19,
10000 Zagreb, Croatia, e-mail: sukic@fkit.hr*

The aim of this work is presentation of a new software for prediction and optimization in ion chromatography; OptIC. The predictions are based on empirical mathematical model that calculates retentions (for both: isocratic and gradient mode) by using isocratic experimental data. Retention prediction of different points on chromatographic peak was used for further estimation of other relevant chromatographic values (resolution, peak asymmetry). Moreover, in order to provide IC users a complete schematic view of IC analysis, generalized logistic function was applied for description of component distribution inside chromatographic band. Selection of optimal conditions and faster scanning of gradient domain are based on four in-house developed criteria incorporated in overall algorithm routine. The extensive model testing approved all above mentioned software attributes; the testing results are presented in this work.

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Početak našeg poduzeća seže u 1922. godinu. Od tog razdoblja do danas postali smo jedan od vodećih proizvođača visoko kvalitetnih mjernih instrumenata i analizatora koji svoju primjenu nalaze u industriji ali i znanosti.

Inovativnost zaposlenih i predanost kvaliteti pokretačka su sila našeg rada tijekom svih godina djelovanja. Prepoznavanje i razumijevanje potreba naših korisnika osnova su za ideje novih proizvoda. Razvijen centar za istraživanja te sudjelovanje sa mnogim istraživačkim institutima omogućavaju nam da te ideje sjedinimo u novonastalim instrumentima koristeći sve što tehnologija pruža.

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Stručno znanje i dugogodišnje iskustvo zaposlenih stoji na usluzi savjetom, robom, ljubaznošću, korektnom i brzom uslugom te razumnim cijenama.

Na osnovi dugogodišnjeg iskustva u suradnji s laboratorijima raznih industrija dajemo stručne savjete u

- Odabiru laboratorijskog namještaja
- Opremanju laboratorijskim uređajima i priborom
- Mjerama osiguranja i zaštite osoblja
- Odabiru analitičkih metoda
- Izboru i traženju proizvođača potrebnih roba

Od ožujka 2005 godine potvrdili smo svoju kvalitetu certificirajući se pri RWTÜV Croatia, ovlaštenom predstavništvu njemačke tvrtke RWTÜV Essen.

Ako nas do sada niste upoznali - pokušajte - isplatit će se.



PRODAJNI PROGRAM

LABORATORIJSKE KEMIKALIJE



MIKROBIOLOGIJA

STANDARDNI REFERENTNI MATERIJALI



LABORATORIJSKA OPREMA I PRIBOR

