



Received: 27 November 2017
Accepted: 23 January 2018
Available online: 15 March 2018

SIMULTANEOUS DETERMINATION OF CHROMATE AND COMMON INORGANIC ANIONS USING SUPPRESSED ION CHROMATOGRAPHY

Joanna Kończyk^{1*}, Edward Muntean², Rajmund Michalski¹

¹ Faculty of Mathematics and Natural Sciences, Jan Długosz University in Częstochowa, 42-200 Częstochowa, 13/15 Armii Krajowej Av., Poland,

² University of Agricultural Sciences and Veterinary Medicine, Faculty of Food Science and Technology, Department of Food Sciences, 3-5 Calea Manastur Str., 400383 Cluj Napoca, Romania

Abstract: Water and waste water analysis is an important area in analytical and environmental chemistry, development of new methods and improvement of existing ones being permanent challenges for researchers. This paper reports the use of isocratic ion chromatography with suppressed conductivity detection for the simultaneous determination of F^- , Cl^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and CrO_4^{2-} , the developed method was applied to analyse surface waters and industrial waste waters from Częstochowa area (Poland).

Keywords: chromate, inorganic anions, ion chromatography, waste water

1. Introduction

Nowadays there is a need for strict control and monitoring of many substances from water and waste water in order to prevent contamination and to protect the environment. The presence in excess levels of the potentially toxic elements such as chromium could have an impact on the environment and our health [1]. Chromium and its compounds are used in many industrial activities such as tanning, plating and stainless steel welding [2]. The different toxicity and bioavailability of Cr(III) and Cr(VI) are a public health concern and therefore require a rigorous control. Trivalent chromium is essential for humans, since it is involved in glucose, lipid and protein metabolism, whereas the deleterious effects on living organism of Cr(VI) are well documented [3]. The hexavalent species exists primarily as chromate CrO_4^{2-} or dichromate $Cr_2O_7^{2-}$ ions, depending upon the pH of the solution. In either state, Cr(VI) is a strong oxidizer and a detrimental contaminant in environmental and biological systems [4].

Many methods for chromium determination have been applied including flame atomic absorption spectrometry [5], electrothermal atomic absorption spectrometry [6], inductively coupled plasma atomic emission spectrometry [7], liquid chromatography with chemiluminescence detection [8], capillary electrophoresis with inductively coupled plasma mass spectrometry and capillary electrophoresis with chemiluminescence detection [9, 10]; all these methods are very useful and can be used for the determination of the total chromium content but not for chromium species.

The results of toxicological tests show that in many cases concentration of different element species, rather than the element total content, influence living organisms. For this reason, understanding the occurrence of various forms of

an element is more important than the knowledge about its total content. Lowering analyte detection limits to extremely low concentration levels results in the fact that some of the applied analytical methods did not meet the necessary requirements so far. Consequently, various separation techniques and detection methods are combined in hyphenated techniques; these techniques are more advantageous due to their extremely low detection and quantification limits, insignificant interference influence as well as high precision and repeatability of the determinations [11]. Nevertheless, hyphenated techniques require expensive instrumentation and are not available in routine laboratories.

Water and waste samples can be analyzed by classical wet chemistry methods, as well as with instrumental ones. Most laboratories use ion chromatography with conductivity detector systems for anion and cation analysis [12], and atomic absorption spectrometry for element determinations [13]. In the range of ions determination, ion chromatography plays a major role, since it offers several advantages over conventional methods such as: short analysis time, sensitivity on the $\mu g/L$ level, high selectivity for analytes in samples with complex matrices, usually a simple sample pretreatment, simultaneous determination of anions and cations, species analysis (e.g., $NO_2^-/NO_3^-/NH_4^+$; Cr(III)/Cr(VI), As(III)/As(V)), as well as use of cheap, safe, and environment friendly chemicals. Moreover, ion chromatography provides a direct method for the simultaneous determination of alkali and alkaline earth cations and ammonia, what is not possible by using spectroscopic methods [14].

Routine laboratories using ion chromatography for water and waste water analysis usually apply only one column and have no capacity and time to conduct research and optimize new methods. They use standardized methods for the determination of common anions (F^- , Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) and cations (Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+}) and usually are not interested to enlarge the range of analytes beyond the official requirements.

* Corresponding author.
E-mail address: j.konczyk@ajd.czest.pl

Therefore the purpose of this research was to investigate whether other non-typical but important ions like chromate, can be determined in standard conditions. The work is focused on the application of isocratic ion chromatography with carbonate/bicarbonate eluents and suppressed conductivity detection for the simultaneous determination of chromate besides common inorganic anions in water and waste water samples.

2. Experimental

2.1. Reagents

NaHCO₃ and Na₂CO₃ with analytical purity produced by Fluka (Steinheim, Switzerland) were used to prepare eluent. Solutions produced by Fluka were employed to prepare standard solutions of particular anions (F⁻, Cl⁻, Br⁻, NO₃⁻, PO₄³⁻, SO₄²⁻ and CrO₄²⁻) at the concentration level of 1000 ± 2 mg/L. Deionised water used for the eluent preparation came from Hydrolab HLP5, having the electrical conductivity < 0.07 µS/cm. All solutions were stored in high-density polyethylene vessels at room temperature.

2.2. Sample preparation

Waste water samples originated from industry plants are characterized by high ions and metal content, and low pH values; they were diluted 1:9 with deionized water then filtered by membrane filters (0.45 µm pore diameters) before analysis.

2.3. Instruments

Ion chromatographic separations were performed on a 930 Compact IC Flex Metrohm ion chromatographic system (Herisau Metrohm AG, Switzerland), equipped with a conductivity detector, a MSM-HC A chemical suppressor and a 858 Professional Sample Processor. The eluent composition was 5.0 mM Na₂CO₃ + 1.0 mM NaHCO₃; this was delivered at 1.0 ml/min, while the injection volume was 100 µL.

Four Dionex (Sunnyvale, USA) Ion Pac anion-exchange columns (AS4-SC; AS9-HC; AS14, and AS22) were chosen for research (Table 1); the column selection depended both on the popularity of their application in the laboratories that perform routine water and waste water analyses and on their performances, especially in terms of the exchange capacity. The choice of anion-exchange columns resulted from the necessity of proper resolution between common inorganic anions and chromate (which is a highly polarizable ion), while the total analysis time should not be over reasonable time range.

3. Results and discussion

The selected columns have diverse exchange capacity, in a wide range: IonPac AS4-SC is characterized by the lowest capacity (30 µM Cl⁻) whereas IonPac AS22 column have exchange capacities of 310 µM Cl⁻. Since the analytical columns have some optimal chromatographic conditions, recommended by manufacturers, we carried out tests using these ones, recording the behavior of each one during separations. The column exhibiting the best selectivity

Table 1. Characteristics of the used ion-exchange columns [15].

Column	IonPac AS4-SC	IonPac AS9-HC	IonPac AS14	IonPac AS22
Column dimensions [mm]	250 x 4	250 x 4	250 x 4	250 x 4
Material	Polystyrene/Divinylbenzene with latex agglomerated anion exchange (PS/DVB)		Ethylendivinylbenzene/Divinylbenzene (EVB/DVB)	
Particle diameter [µm]	13	9	13	7.5
Cross-linking [%]	2	55	55	-
Organic solvents compatibility [%]	0	100	100	100
Capacity [µeq/column]	30	65	35	310
pH range	0-14	2-11	2-11	0-14

towards the considered analytes and the shortest separation time was Dionex IonPac AS14 column; the chromatogram of anions' standard mixture for this column is presented in Figure 1.

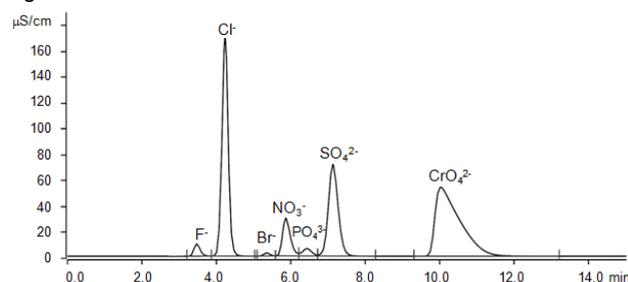


Figure 1. Chromatogram of anions for Dionex IonPac AS14 column.

The Dionex IonPac AS14 was thus selected for anions separation in real samples, such as those of surface and industrial waste water (Figures 2 and 3).

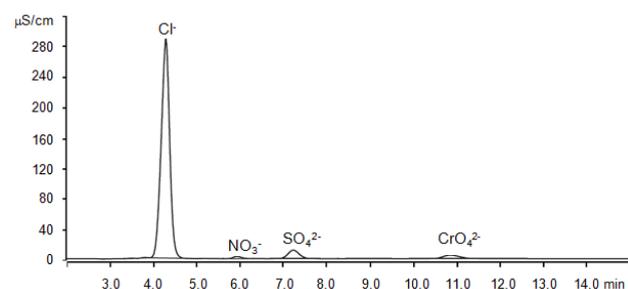


Figure 2. Chromatogram of anions in a selected waste water sample from electroplating company (sample was diluted 1:9 because of the high chloride concentration) - column - Dionex IonPac AS14.

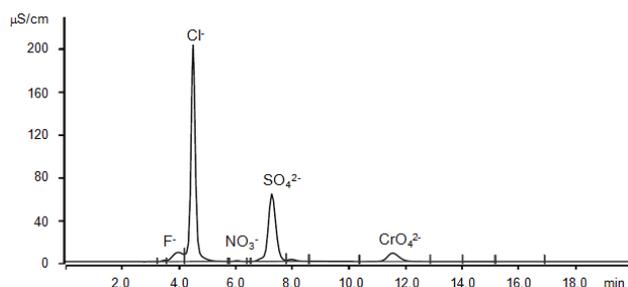


Figure 3. Chromatogram of anions in a selected surface water sample (column - Dionex IonPac AS14).

The quality of ions separation and the obtained results are mostly dependent on issues such as the type of stationary phase (cross-linking, exchange capacity, particles size), as well as the eluent type and its flow rate. As most laboratories conducting routine analyses of ions in water and waste water with ion chromatography frequently have only one specific analytical column, then what might be altered within the optimization process framework are usually the last two parameters, *i.e.* the eluent type and its flow rate. The conducted tests point out the advantages and limitations of all used anion-exchange columns and analytical conditions and indicate the need to adapt the appropriate column to specific determinations.

4. Conclusions

The proposed isocratic ion chromatography method uses an anion-exchange column, carbonate/bicarbonate eluent and suppressed conductivity detection; it can be applied to the determination of F^- , Cl^- , NO_3^- , Br^- , PO_4^{3-} , SO_4^{2-} and CrO_4^{2-} in complex matrix industrial waste water samples, being a simple, robust and low operational costs method comparing to wet methods used for inorganic anions' analysis and hyphenated methods currently used for chromium determination.

Acknowledgements

The authors would like to thank Metrohm Poland and A.G.A. Analytical companies for free of charge lending ion chromatograph and accessories which were used in the present research.

References

- [1] R. J. Vitale, G. Mussoline, K.A. Reinhimer, *Reg. Toxicol. Pharmac.* **1997**, *26*, S80–S85. doi: 10.1006/rtp.1997.1144.
- [2] P.C. Nagajyoti, K.D. Lee, T.V.M. Sreekanth, TVM. *Environ. Chem. Lett.* **2010**, *8*(3),199–216. doi: 10.1007/s10311-010-0297-8.
- [3] Piechova, L. Pavlata, *Veterinari Medicina*, **2007**, *52*(1), 1–18.
- [4] J. Kotas, Z. Stasicka, *Environ. Poll.*, **2000**, *107*, 263–283. doi: 10.1016/S0269-7491(99)00168-2.
- [5] Z. Sun, P. Liang, *Microchim. Acta*, **2008**, *162*, 121–125. doi: 10.1007/s00604-007-0942-0.
- [6] K.L.Mandiwana, N. Panichev, T. Resane, *J. Hazard. Mat.*, **2006**, *136*(2), 379–382. doi: 10.1016/j.jhazmat.2005.12.030.
- [7] T. Sumida, A. Sabarudin, M. Oshima, S. Motomizu, *Anal. Sci.*, **2006**, *22*(1), 161–164.
- [8] Gammelgaard, Y.-P. Liao, O. Jons, *Anal. Chim. Acta*, **1997**, *354*, 107–113.
- [9] N. Kovachev, M.A. Aguirre, M. Hidalgo, K. Simitchiev, V. Stefanova, V. Kmetov, A Canals, **2014**, *117*, 27–33. doi:10.1016/j.microc.2014.06.005.
- [10] W.P.Yang, Z.J. Zhang, W. Deng, *J. Chromatogr. A*, **2003**, *1014*(1-2), 2013–214. doi: 10.1016/S0021-9673(03)00940-3.
- [11] R. Michalski, M. Jablonska, S. Szopa, A. Łyko, *Crit. Rev. Anal. Chem.*, **2011**, *41*, 133–150. doi.org/10.1080/10408347.2011.559438.
- [12] J. Weiss, *Handbook of Ion Chromatography*, Fourth, Completely Revised and Enlarged Edition, vol.1,2,3, Wiley-VCH, Verlag GmbH&Co. KGaA, Weinheim, Germany, **2016**.
- [13] E. Dillon, *Principles and Applications of Atomic Absorption Spectroscopy*, NY Research Press, **2015**.
- [14] R. Michalski, *Crit. Rev. Anal. Chem.* **2006**, *36*, 107–127. doi:10.1080/10408340600713678.
- [15] <https://www.thermofisher.com/us/en/home/industrial/chromatography/dionex.html> [read: 20.11.2017]