

New methods for determination of arsenic, bromate, chlorite, and heavy metals in waters



E. Beinrohr¹, A. Manová¹, M. Střelec¹, J. Dzurov²

¹ Department of Analytical Chemistry, Slovak Technical University, Radlinskeho 9, 812 37 Bratislava, e-mail: ernest.beinrohr@stuba.sk

² ISTRAN, Ltd., Radlinskeho 27, 811 07 Bratislava, e-mail: istran@istran.sk



Introduction

Some ground water sources are contaminated with arsenic originating from some minerals. The maximum allowable arsenic level decreased recently to 10 µg/l for drinking waters challenged the analytical chemists to develop more sensitive and generally available methods for arsenic determination. The same is valid for some heavy metals such as nickel, chromium (VI), mercury and cadmium entering the water sources from industrial plants. Novel water disinfection methods such as those with chlorine dioxide and ozone may be sources of dangerous disinfection byproducts such as chlorite and bromate.

Recently, an automatic measuring system similar to potentiometric stripping analysis [1] has been developed for a reliable, simple and fast determination of the above species in water samples. The method is based on flow-through coulometry [2-8] and computer controlled signal processing enabling the measurement of concentrations down to low ppb (µg/l).

EXPERIMENTAL

Instrument:

* Flow-through system EcaFlow[®] model GLP 150, ISTRAN Ltd., Bratislava, Slovakia.

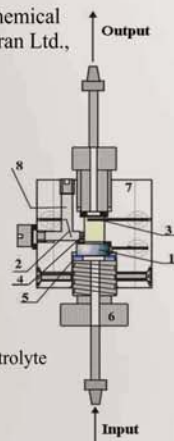


* Portable Coulometric Analyser model PCA, ISTRAN Ltd., Bratislava, Slovakia



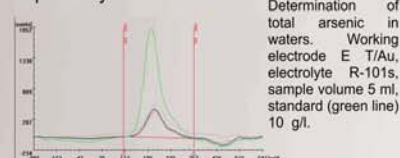
* Flow-through electrochemical cell Eca Cell[®] 353b, Istran Ltd., Bratislava, Slovakia

- 1 - working electrode,
- 2 - reference electrode,
- 3 - auxiliary electrode,
- 4 - membrane,
- 5 - packing,
- 6 - screw,
- 7 - plexiglass body,
- 8 - space for reference electrolyte



RESULTS AND DISCUSSION

Arsenic, cadmium, mercury and nickel are measured by making use of a stripping technique, where the metal traces are collected on a flow-through electrode then are stripped by constant current. The detection limits for As, Cd, Hg, Ni were found to be 0.2 µg/l, 0.2 µg/l, 0.1 µg/l, 0.5 µg/l, respectively.



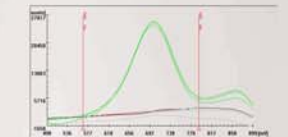
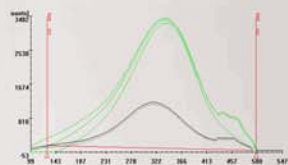
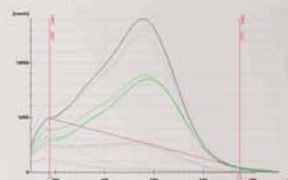
Analysis of ground water samples from an earlier antimony mine.

Sample No.	As(III) µg/l	Total As µg/l
1	< LOD	0.43 ± 0.3
2	< LOD	2.43 ± 0.34
3	< LOD	5 680 ± 240
4	3.89 ± 0.23	14.6 ± 1.2
5	< LOD	6,91 ± 0,79
6	2.40 ± 0.18	4.00 ± 0.11
9	447 ± 32	480 ± 15
11	3 700 ± 300	3 440 ± 75

LOD: detection limit (0.2 µg/l).

Cr(VI), bromate and chlorite are determined by making use of the "In-Electrode Coulometric Titration" method based on the direct electrochemical conversion of the analyte species in a porous or thin-layer electrode. Chromium (VI) can be measured down to 2 µg/l, the detection limit for chlorites is about 5 µg/l.

The determination of bromates was tested in various tap and bottled water samples. The procedure is simple and straightforward: The stabilised water sample is boiled short and on cooling down the reagent solutions are added. The sample is then aspirated by the analyser and analysed automatically. The method enables the measurement of 0.5 to 50 µg/l bromates with a detection limit of 0.15 µg/l. The method for bromate determination has been adopted to commercially available systems enabling the measurement by means of a portable analyser, as well as with laboratory and process analysers. Regarding metrological parameters, the developed method can compete the ion chromatographic method but is significantly cheaper and faster.



SUMMARY

Species	Detection limit µg/l	Linear range µg/l
As	0.2	0.5 - 200
Cd	0.2	0.5 - 1 000
Hg	0.1	0.2 - 1 000
Ni	1.0	2 - 500
Cr(VI)	2.0	5 - 1 000
ClO ₂	5.0	10 - 5 000
BrO ₂	0.2	0.5 - 50

ACKNOWLEDGEMENT

The study was supported by the VEGA 1/2464/05 project.

REFERENCES

- [1] D. Jagner, A. Granelli: Potentiometric stripping analysis. Anal. Chim. Acta 83, 19-26, (1976).
- [2] E. Beinrohr, M. Németh, P. Tschopel. G. Tolg: Design and characterization of flow-through coulometric cells with porous working electrodes made of crushed vitreous carbon. Fresenius J. Anal. Chem. 343, 566-575, (1992).
- [3] E. Beinrohr, P. Csémi, F. J. Rojas, H. Hofbauerová: Determination of manganese in water samples by galvanostatic stripping chronopotentiometry in a flow-through cell. Analyst 119, 1355-1359, (1994).
- [4] E. Beinrohr, M. Čákr, J. Dzurov, P. Kottáš, E. Kozáková: Calibrationless determination of mercury by flow-through stripping coulometry. Fresenius J. Anal. Chem. 356, 253-258, (1996).
- [5] Beinrohr E., Manová A., Dzurov J., Broekaert J.A.C.: Flow-through Stripping Chronopotentiometry for the Monitoring of Mercury in Waste Waters, Fresenius J. Anal. Chem., 362, 201-204 (1998).
- [6] Jurica L., Manová A., Dzurov J., Beinrohr E., Broekaert J.A.C.: Calibrationless Flow-through Stripping Coulometric Determination of Arsenic(III) and Total Arsenic in Contaminated Water Samples after Microwave Assisted Reduction of Arsenic(V), Fresenius J. Anal. Chem., 366, 260-266 (2000).
- [7] Kozáková E., Bodor R., Jursa J., Beinrohr E. Flow-through coulometric determination of mercury in soils and soil extracts Chem. Papers 54, 144-147 (2000).
- [8] Beinrohr E., Flow-through coulometry as a calibrationless method in inorganic trace analysis. Accred. Qual. Assur., 6, 321-324 (2001).