

Inductively coupled plasma mass spectrometry and its use in assessing water pollution with metals

^{1,2}Alexandra Hoaghia, ¹Oana Cadar, ¹Erika Levei, ¹Cecilia Roman,
¹Claudiu Tănăselia, ²Dumitru Ristoiu

¹ INCDO-INOE 2000, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania; ² Faculty of Environmental Science and Engineering, Babeş-Bolyai University from Cluj Napoca, Cluj-Napoca, Romania. Corresponding author: A. Hoaghia, alexandra.hoaghia@icia.ro

Abstract. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) represents a routine technique used in various fields such as environmental, chemical, forensic, medicine or material sciences. The ICP-MS is suitable for a wide range of concentration levels (from ppt to ppm) and for various types of samples: water, soil, sediments, geological samples or biological fluids and tissues. High sensitivity, accuracy, fast data acquisition and multi-element features makes ICP-MS one of the most used and trusted analytical method. Five well water samples from Copsa Mica area were analysed with respect to metal content (As, Cr, Cu, Fe, Mn, Pb and Zn). Resulting data were used for the calculation of the heavy metal pollution index (HPI) and heavy metal evaluation index (HEI). Results show low metal concentrations and low indices, indicating the good quality of waters in the studied area.

Key Words: inductively coupled plasma mass spectrometry, metal, heavy metal pollution index, heavy metal evaluation index.

Introduction. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is the most versatile analytical technique used for multielement analysis, trace element speciation and isotope ratio measurements (Nelms 2005; Thomas 2013). The first commercial instrument appeared on the market in 1983 and, presently, became one of the fastest trace elemental analysis techniques available for routine laboratory determination (Thomas 2013). Research and applied science, life, environmental and earth science, forensic, geochemistry and industries (chemical, food, nuclear) use ICP-MS technique, because of high speed, high sensibility and quantitation accuracy (Ammann 2007; Schreck et al 2012; Reid et al 2008).

Understanding the water contamination with metals (Cr, Pb, As, Cu, Mn, Zn, Fe) is critical to establish the ecological status of water. The data obtained from the ICP-MS method are the basis for different quality and pollution assessing tools, such as heavy metal pollution index (HPI) and heavy metal evaluation index (HEI). The aim of this study was to present the ICP-MS technique and its importance in providing accurate data regarding the metal content in well water samples used as drinking water sources. Two pollution indices (HPI and HEI) were used in order to assess the metal pollution status of water wells.

Instrument characterization. The inductively coupled argon plasma as ion source for mass spectrometric determinations was used for the first time in 1975 (Gray 1975). In 1978, by coupling the argon ICP with a quadrupole mass spectrometer, the first ICP-MS instrument was developed (Houk et al 1980). Three years later, the first commercial quadrupole ICP-MS (ELAN 250) instrument was launched into the market (Nelms 2005). The principle of operation for the ICP-MS technique is based on ion separation according to their mass to charge ratio, after atomization and ionization of the sample in the plasma (Thomas 2013). The liquid sample is pumped in the nebulizer using a peristaltic pump, where it is converted into fine mist, aerosol or cloud particles with various dimensions. As reaching the spray chamber, the fine droplets are separated from the larger droplets and are carried by argon gas flux into the plasma torch (Thomas 2013). After the introduction into the inductively coupled plasma torch, the aerosol is atomized and ionized. The ions are introduced and transported from plasma operated at atmospheric pressure (760 Torr) to vacuum (1-2 Torr) through the interface region (a set of nickel or platinum cones) into the mass spectrometer. Interface region ensures that the energy spread of ions which enter in the mass spectrometer is low and they are

focused by a system of ion lenses. The mass separation device allows ions with a specific m/z ratio to reach the detector. By setting radio frequencies and voltages applied to the quadrupole rods, a stability region is created along the quadrupole axis for a specific m/z ratio, thus ensuring that only selected ions sequentially pass through the mass filter. Within the detector, ions are individually counted (pulse mode) or, if concentrations are high enough, a Faraday cup can be used to create a measurable current, proportional with the analyte concentration (Thomas 2013; Dean 2005).

Strengths and limitations. The main advantages of ICP-MS are the low detection capabilities, multi-element capabilities, wide analytical range, high sensitivity accuracy and precision, good sample throughput and isotopic analysis capabilities (Beauchemin 2010; Potter 2008). Among the ICP-MS limitations are polyatomic, isobaric and matrix-induced interferences, relative high price tag and maintenance (costs) and instability caused by samples with high levels of dissolved solids (L'Vov 1997; Todol et al 2002; Boss & Fredeen 2004; Moldovan et al 2004; Dean 2005; Wang & Kalinitchenko 2005; Cordos et al 2007; Mermet 2008; Potter 2008; Vale et al 2008; Burguera & Burguera 2009; Thomas 2013).

Quantification of hazardous substances represents an important part of environmental assessment. Classical environmental applications of ICP-MS are trace element measurements in water samples as the method can detect and measure almost the entire periodic table of elements (Profrock & Prange 2012). Released high quantities of toxic metals have adverse effects on the environment, so that metal analyses have significant aim in environmental monitoring (Amaral et al 2014; Markiewicz et al 2015).

Case study. Copsa Mica was a significant industrial point and a pollution hotspot recognized in Europe, due to the metal (Cd, Pb, Sn, Zn) and carbon black pollution (Curseu et al 2006; Paulette et al 2015). Copsa Mica is located towards north western part of Sibiu County, in the central west part of Tarnavelor Plateau (fragmented and very long narrow ridges dominant east-west direction plateau, formed on Myocene - Pliocene sediments) at the confluence of Tarnava Mare and Visa rivers. The climate is transition temperate continental with oceanic influences, average temperatures of 6-8°C and average rainfall of 700-1000 mm/year (Horhoi 2001; Reti & Rosian 2007).

Material and Method. Five water samples (S1-S5) were collected from private water wells Copsa Mica, Tarnava and Medias. Samples were collected in polyethylene 500 mL bottles and were stored at 4°C until the chemical analysis. On site, samples were filtered with 0.45 µm cellulose acetate filters and acidified at pH < 2 with 63% HNO₃. The metal content (As, Cr, Cu, Fe, Mn, Pb, Zn) was measured using a ELAN DRC II Perkin-Elmer ICP-MS. The metal concentrations were used for the calculation of HPI and HEI, according to the following equations (Mohan et al 1996; Edet & Offiong 2002):

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad (I)$$

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \times 100 \quad (II)$$

Where:

W_i – represents the unit weightage of i^{th} parameter; n is the total number of the considered parameters;

Q_i – represents the sub-index of the i^{th} parameter

M_i – represents the monitored value of metal of i^{th} parameter

S_i – as the standard value of the i^{th} parameter, taken according to drinking water standards of U.S. EPA (2006) and WHO (2011);

I_i – as the desirable value of the i^{th} parameter, taken according the drinking water standards of U.S. EPA and WHO;

(-) – indicates the numerical difference of the two values, ignoring the algebraic sign.

Mohan et al (1996) establish a critical value for the *HPI* of 100. Water samples with a higher score as 100 are considered polluted factors.

$$HEI = \sum_{i=1}^n \frac{H_c}{H_{mac}} \quad (III)$$

Where:

H_c – represents the determined value of the i^{th} parameter

H_{mac} – the maximum admissible concentration (MAC) of the i^{th} parameter, according to U.S. EPA (2006) and WHO (2011) drinking water guidelines.

Results and Discussion. The metal (As, Cr, Cu, Fe, Mn, Pb and Zn) concentrations in the studied well waters are below the corresponding MAC (U.S. EPA 2006; WHO 2011) and are comparable in all samples. Sample S1 presents the highest concentrations of As ($1.0 \mu\text{g L}^{-1}$), Cr ($5.0 \mu\text{g L}^{-1}$), Fe ($150 \mu\text{g L}^{-1}$) and Pb ($4.0 \mu\text{g L}^{-1}$), while S2 presents highest of Cu ($7.0 \mu\text{g L}^{-1}$), S3 the highest Mn ($8.0 \mu\text{g L}^{-1}$) and S5 the highest Zn ($180 \mu\text{g L}^{-1}$) concentration (Figure 1).

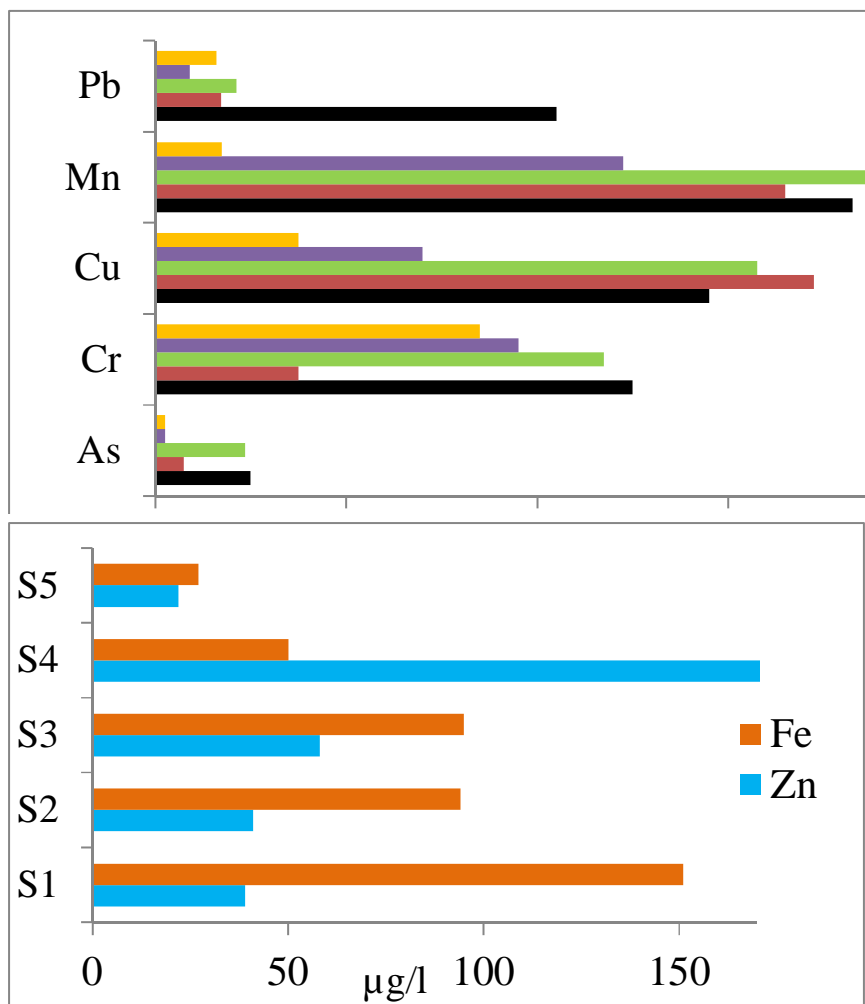


Figure 1. Metal concentrations (As, Cr, Cu, Fe, Mn, Pb, Zn) in well water samples.

The scores for the pollution indices are lower as the critical scores (100), which means no metal pollution for the studied water wells. Sample S1 presents the higher values for HPI and HEI, while S5 shows the lower values (Table 1).

Table 1

Evaluation of metal pollution indices

	S1	S2	S3	S4	S5	SI*	I*	Wi	Q	Wi x Q
As $\mu\text{g L}^{-1}$	1.0	0.30	0.94	<0.1	<0.1	10	0	0.10	4.5	0.45
Cr $\mu\text{g L}^{-1}$	5.0	1.5	4.7	3.8	3.4	50	0	0.02	7.3	0.15
Cu $\mu\text{g L}^{-1}$	5.8	6.9	6.3	2.8	1.5	1300	1300	0.001	0.00	0.00
Fe $\mu\text{g L}^{-1}$	151	94	95	50	27	300	0	0.003	28	0.09
Mn $\mu\text{g L}^{-1}$	7.3	6.6	7.7	4.9	0.7	50	0	0.02	11	0.22
Pb $\mu\text{g L}^{-1}$	4.2	0.69	0.85	0.36	0.64	15	0	0.07	8.9	0.59
Zn $\mu\text{g L}^{-1}$	39	41	58	176	22	5000	0	0.0002	1.3	0.00
HPI	17	4.9	8.9	2.8	2.2					
HEI	1.1	0.56	0.73	0.40	0.22					

*according to the Guidelines for Drinking Water WHO (2011); U.S. EPA (2006).

Conclusions. The ICP-MS represents an easy, accurate and fast metal determination technique. The metal content can be used in different water quality assessing tools in order to evaluate the quality and contamination status of the waters. The pollution indices (HPI and HEI) show that the studied well water samples are not contaminated with As, Cr, Cu, Fe, Mn, Pb and Zn. Metal concentrations did not exceed the MAC established by drinking water guidelines (U.S. EPA 2006; WHO 2011).

Acknowledgements. This paper is a result of a doctoral research made possible by the financial support of the Sectorial Operational Program for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project POSDRU/159/1.5/S/133391 - "Doctoral and postdoctoral excellence programs for training highly qualified human resources for research in the fields of Life Sciences, Environment and Earth".

References

- Amaral C. D. B., Nobrega J. A., Nogueira A. R. A., 2014 Investigation of arsenic species stability by HPLC-ICP-MN in plants stored under different conditions for 12 months. *Microchemical Journal* 114:122-126.
- Ammann A. A., 2007 Inductively coupled plasma mass spectrometry (ICP-MS): a versatile tool. *Journal of Mass Spectrometry* 42:419-427.
- Beauchemin D., 2010 Inductively coupled plasma mass spectrometry. *Anal Chem* 82:4786-4810.
- Boss C. B., Fredeen K. J., 2004 Concepts, instrumentation and techniques in inductively coupled plasma optical emission spectrometry. Third Edition, Perkin Elmer, U.S.
- Burguera J. L., Burguera M., 2009 Recent on-line processing procedures for biological samples for determination of trace elements by atomic spectrometric methods. *Spectrochimica Acta B* 64:451-458.
- Cordoş E., Frenţiu T., Şenilă M., Ponta M., Tănăselia C., 2007 Analytic atomic spectrometry with plasma sources. Edit. INOE, Bucharest, 236 pp.
- Curseu D., Popa M., Sirbu D., Moldovan Z., 2006 Water pollution in the Copsa Mica region after Romanian revolution. International Conference on Automation, Quality and Testing, Robotics, (AQTR'08), May 22-25, Cluj-Napoca, Romania, IEEE Catalog Number: CFP08AGT-CDR, ISBN: 978--4244-2577-81.
- Dean J. R., 2005 Practical inductively coupled plasma spectroscopy. John Wiley & Sons, Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, 184 pp.
- Edet A. E., Offiong O. E., 2002 Evaluation of water quality pollution indices for heavy metal contamination monitoring. A study case from Akpabuyo-Odukpani area, Lower Cross River Basin (southeastern Nigeria), *GeoJournal* 57:295-304.

- Gray A. L., 1975 Mass-spectrometric analysis using an atmospheric pressure ion source. *Analyst* 100:289-299.
- Horhoi E. D., 2001 Environment quality of Tarnava Mare corridor: geological study. Edit. Logos 1994, Oradea [in Romanian].
- Houk R. S., Fassel V. A., Flesch G. D., Svec H. J., Gray A. L., Taylor C. E., 1980 Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements. *Analytical Chemistry* 52:2283-2289.
- L'Vov B. V., 1997 Forty years of electrothermal atomic absorption spectrometry. Advances and problems in theory. *Spectrochimica Acta Part B: Atomic Spectroscopy* 52:1239-1245.
- Markiewicz B., Komorowicz I., Sajnog A., Belter M., Baralkiewicz D., 2015 Chromium and its speciation in water samples by HPLC/ICP-MS-technique establishing metrological traceability: a review since 2000. *Talanta* 132:814-828.
- Mermet J. M., 2008 Limit of quantitation in atomic spectrometry: an unambiguous concept? *Spectrochimica Acta Part B* 63:166-182.
- Mohan S. V., Nithila P., Jayarama Reddy S., 1993 Estimation of heavy metals in drinking water and development of heavy metal pollution index. *Journal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology: Toxic/Hazardous Substances and Environmental Engineering* 31(2):283-289.
- Moldovan M., Krupp E. M., Holliday A. E., Donard O. F. X., 2004 High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: a review. *Journal of Analytical Atomic Spectrometry* 19:815-822.
- Nelms S. M., 2005 Inductively coupled plasma mass spectrometry handbook. Blackwell Publishing Ltd.
- Paulette L., Man T., Weindorf D. C., Person T., 2015 Rapid assessment of soil and contaminant variability via portable x-ray fluorescence spectroscopy: Copsa Mica, Romania. *Geoderma* 243-244:130-140.
- Potter D., 2008 A commercial perspective on the growth and development of the quadrupole ICP-MS market. *Journal of Analytical Atomic Spectrometry* 23:690-693.
- Profrock D., Prange A., 2012 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for quantitative analysis in environmental and life sciences: a review of challenges, solutions, and trends. *Applied Spectroscopy* 66(8):843-868.
- Reid H. J., Bashammakh A. A., Goodall P. S., Landon M. R., O'Connor C., Sharp B. L., 2008 Determination of iodine and molybdenum in milk by quadrupole ICP-MS. *Talanta* 75:189-197.
- Reti K. O., Roşian G., 2007 Premises of the location and development of urban structures Basin Târnavelor. *Environment & Progress* 11:412-415.
- Schreck E., Foucault Y., Sarret G., Sobanska S., Cecillon L., Castrec-Rouelle M., Uzu G., Dumat C., 2012 Metal and metalloid foliar uptake by various plant species exposed atmospheric industrial fallout: mechanisms involved for lead. *Science of the Total Environment* 427-428:253-262.
- Thomas R., 2013 Practical guide to ICP-MS: a tutorial for beginners. Third Edition (Practical Spectroscopy), CRC Press, 418 pp.
- Todol J. L., Gras L., Hernandez V., Mora J., 2002 Elemental matrix effects in ICP-AES. *Journal of Analytical Atomic Spectrometry* 17:142-169.
- Vale G., Rial-Otero R., Mota A., Fonseca L., Capeloro J. L., 2008 Ultrasonic-assisted enzymatic digestion (USAED) for total elemental determination and elemental speciation: a tutorial. *Talanta* 75:872-884.
- Wang X. D., Kalinitchenko I., 2005 Principles and performance of the collision reaction interface of the Varian 820-MS, Varian Instruments ICP-MS Advantage Note, 1, October. http://www.varianinc.com/image/vimage/docs/applications/apps/icpms_an1.pdf.
- *** U.S. Environmental Protection Agency (EPA) National Primary and Secondary Drinking Water Regulations (NPDWRs and NSDWRs or secondary standards): Guidance for Nuisance Chemicals, 2006 Online sources: <http://water.epa.gov/drink/contaminants/#List>.
- *** Guidelines for drinking water quality, Fourth edition, World Health Organization, 2011. Online source: http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/.

Received: 23 April 2015. Accepted: 26 May 2015. Published online: 30 June 2015.

Authors:

Alexandra Hoaghia, INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, RO-400293 Cluj-Napoca, Romania, e-mail: alexandra.hoaghia@icia.ro

Oana Cadar, INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, RO-400293 Cluj-Napoca, Romania

Erika Levei, INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, RO-400293 Cluj-Napoca, Romania

Cecilia Roman, INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, RO-400293 Cluj-Napoca, Romania

Claudiu Tănăselia, INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, RO-400293 Cluj-Napoca, Romania

Dumitru Ristoiu, Babeş-Bolyai University, Faculty of Environmental Science and Engineering, 30 Fântânele, RO-400294 Cluj-Napoca, Romania

This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited.

How to cite this article:

Hoaghia A., Cadar O., Levei E., Roman C., Tănăselia C., Ristoiu D., 2015 Inductively coupled plasma mass spectrometry and its use in assessing water pollution with metals. *Ecoterra* 12(2):18-23