Bulgarian Chemical Communications, Volume 49 Special Issue C (pp. 211 – 217) 2017

Application of electrochemical methods in the physicochemical characterization of atmospheric precipitation

P. Orlović-Leko[1]*, D. Omanović[2], I. Ciglenečki[2], K.Vidović[3], T. Brenko[1]

[1]*University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, Zagreb, Croatia,*
[2]*Division for Marine and Environmental Research, RuđerBošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia,*
[3]*National Institute of Chemistry, Hajdrihova 19, p.p. 660, 1001 Ljubljana, Slovenia*

Received November 16, 2016 Revised January 18, 2017

Electrochemical methods play an important role in the environmental analysis. This study demonstrates that electrochemical (voltammetric) methods are a valuable tool with good selectivity and sensitivity for physicochemical analysis of atmospheric precipitation. Studies have been done with daily bulk samples collected in the city of Zagreb (Croatia) in the period of 2009/2010. Heavy metal (HM) content and reduced sulfur species (RSS) were investigated in the precipitation samples by using cathodic striping voltammetry (CSV) and differential pulse striping voltammetry in anodic, DPASV (Zn, Cd, Pb and Cu) and adsorptive cathodic modes, DPAdCSV (Ni), respectively, at the hanging mercury drop electrode. In average, the highest concentrations were found for Zn and the lowest for Cd (Cd < Ni < Pb < Cu < Zn).

Although generally, low correlation between concentrations of these metals was found (statistical significance only between Zn and Cu), the same pattern of concentration changes relative to precipitation events was observed for Zn, Cd, Pb, Cu and dissolved organic carbon (DOC), whereas an opposite pattern was noticed for Ni and pH. Analyses of bulk samples by CSV technique revealed an existence of different sulfur species, providing an excellent tool for study of organic and inorganic RSS in the atmospheric precipitation at nano-levels.

Key words: voltammetric techniques, atmospheric precipitation, heavy metals, reduced sulfur species.

INTRODUCTION

Atmospheric concentrations of many trace metals have been significantly affected by anthropogenic activities, which have changed the biogeochemical cycles and balance of some metals. In an urban environment, metals can be emitted from numerous anthropogenic sources which include traffic-related activities (fossil fuel combustion, wear production from tires, brake lining, leakage of metal-containing motor oils and corrosion in general of vehicle components), industry activities, the disposal of municipal waste, and the corrosion of building materials [1]. In recent study, Gunarwardena et al. [2] found that concentration of Zn is correlated with traffic volume, whereas Pb, Cd, Ni and Cu are correlated with traffic congestion. Metals are removed from the atmosphere by both, dry and wet deposition processes. Quantifying the total trace metal concentrations in atmospheric deposition is important for understanding their geochemical cycling and their impact on ecosystems, especially on the water ecosystem. This is due to the possible post-solubilisation in the water body, having different organic ligands and different pH value [3]. Environmental science is benefiting more and more from the development of sensitive, selective and innovative techniques for the determination of metals in environmental matrices, as well as for the identification and quantification of various elemental forms under which an element may occur [4]. Concentration of heavy metals (HM) in atmospheric aerosols is at the trace level [5] and thus sensitive and selective analytical techniques should be used for their analysis.

Electrochemical techniques, particularly anodic (ASV) and adsorptive cathodic (AdCSV) voltammetry feature both characteristics, while in addition they have a potential to provide speciation information. Detection limits for HM by using stripping voltammetry are in the range down to 10^{-12} M [6]. Metals that could be determined by ASV are those that are soluble in liquid Hg (forming amalgams). In contrast, AdCSV does not require the metal solubility in Hg, so it could be used for the analysis of numerous trace metals [7]. Metal-organic complexation is significant in the atmospheric precipitates.

To whom all correspondence should be sent:
E-mail: palma.orlovic-leko@oblak.rgn.hr

Complexation enhances the solubility of metals in aerosols and atmospheric water [8-10]. Beside organic ligands, sulfur species could play important role in speciation of heavy metals. The major reduced sulfur species (RSS) usually found in the atmosphere are carbon disulfide (CS_2), dimethyl sulfide (CH_3SCH_3, DMS), hydrogen sulfide (H_2S), carbonyl sulfide (COS) and ethyl mercaptan (CH_3SH) [11-14]. Some of these compounds have already been electrochemically investigated [15]. Dimethyl sulfide is the dominant biogenic sulfur gas emitted to the atmosphere from the seawater [16]. In the atmospheric aerosols, all these compounds are normally present at very low concentration levels (below ppb levels) [17]. The chemistry of RSS in the atmosphere has significant implications for global climate change, ozone layer depletion and the acidity of precipitation [18 and references therein].

It has already been shown that voltammetry has great potential for detection and characterization of dissolved and particulate sulphur species in water samples without pretreatment [19-22]. For this reason and following our work on model and natural sea- and fresh-water systems [15,23,24], here we have applied for the first time the cyclic voltammetry on mercury electrode in order to study the reduced sulfur species (RSS) in the precipitation samples. The method is based on measurements of inorganic and organic RSS that deposit HgS layer during an accumulation step at the deposition potential, followed by scanning potentials from positive to more negative values at the hanging mercury drop electrode (HMDE). In solutions containing sulfide anions, insoluble HgS layer at the Hg electrode surface can be formed by the reversible process of two-electron-transfer oxidation of Hg at potentials more positive than -0.5 V vs. Ag|AgCl. Organic sulfur compounds are also found to deposit HgS layer by anodic oxidation of Hg at sufficiently positive potentials, around 0 V [20].

In this work, we report results of measurements of the total HM (Cu, Pb, Zn, Cd and Ni), pH, dissolved organic carbon (DOC) and RSS in the atmospheric precipitation. The goal of this study was to demonstrate that electrochemical methods are selective, sensitive and essential for fast and direct qualitative and quantitative characterization of atmospheric deposition. The study has been done with bulk samples collected in the city center of Zagreb (Croatia) in the period of 2009/2010.

EXPERIMENTAL

Samples collection

Samples were collected in the city center (Zagreb, Croatia) near a cross-road characterized by heavy traffic. Sampling was carried out manually on the roof of Faculty building (20 m above ground level) in the period from January 2009 until May 2010. A simple bulk sampler consisting of opaque bottle and a glass funnel were used to collect daily precipitation samples.

Analysis of heavy metals

Concentrations of heavy metals were measured in unfiltered samples by differential pulse ASV, DPASV (Zn, Cd, Pb and Cu) and differential pulse AdCSV, DPAdCSV (Ni). An AUTOLAB potentiostat PGSTAT128N (Eco Chemie, Utrecht, The Netherlands), coupled with a hanging mercury drop working electrode (VA Stand 663, Metrohm, Herissau, Suisse) and CAVRO burette system XL-3000 (Tecan, Männedorf, Suisse) were used for automatic determination of, Cd, Pb, Cu and Zn by the standard addition method. A platinum wire was used as a counter electrode and Ag|AgCl with saturated NaCl as a reference electrode. Prior to the measurements, samples were digested by acidification (pH < 2) with suprapur, Merck, Darmstadt, Germany) and irradiated by UV-light with a mercury lamp 150 W (Hanau, Germany) for at least 24 h. Prepared acidified samples were analyzed without further modifications, except for Zn, for which sodium acetate buffer was added in order to adjust pH to 4. Concentrations of metals in unfiltered samples are referred as total metal concentrations in this study.

The following experimental conditions were applied: equilibration time 10 s; modulation time 0.04 s; interval time 0.1 s; modulation amplitude 20 mV and step potential 2 mV. Specific parameters for DPASV and DPAdCSV technique are presented in Table 1.

Table 1. Specific parameters used for the determination of heavy metals in precipitation samples by DPASV and DPAdCSV.

Parameter	DPASV Pb, Cd, Cu	Zn	DPAdCSV Ni
Accumulation potential (V)	-0.8	-1.3	-0.7
Accumulation time (s)	600	60	180
Initial potential (V)	-0.75	-1.15	-0.7
Final potential (V)	0.24	-0.75	-1.2

Analysis of reduced sulfur species (RSS)

Electrochemical measurements of reduced sulfur species (RSS) were performed with µ-Autolab voltammeter controlled by GPES (General Purpose Electrochemical System) 4.6 software (Eco Chemie

B.V., The Netherlands) in a three-electrode cell (663 VA Stand, Metrohm). The RSS were investigated by using cyclic and/or linear sweep voltammetry (CV/LSV) on the HMDE in fresh nonfiltered samples upon addition of NaCl (final concentration 0.55 M) as a supporting electrolyte. In CV and LSV, the accumulation (t_a= 0 – 120 s) of RSS on the Hg electrode surface with stirring was performed at the deposition potential of E = -0.20 and -0.10 V (vs. Ag|AgCl). After accumulation, the potential was shifted in the negative direction (down to E = -1.5 V vs. Ag|AgCl) with a scan rate of 100 mV/s and HgS reduction peak at around -0.6 V, characteristic of many RSS, was recorded [19-22]. Next, the solution was acidified with 30 μL of concentrated HCl (Kemika, Croatia) to pH ~ 2 and purged for 3 min. After restoring the original pH with NaOH (Kemika, Croatia) the accumulation and scan steps were repeated. The result of the first measurement prior to acidification is assigned as total reduced sulfur species, $RSS_T = H_2S/HS^- + S^0$, while the result of the second measurement is assigned to elemental sulfur, S^0, as the model representative for non-volatile reduced sulfur species, RSS_{NV} [19,23].

Other parameters

The pH values of the samples were measured using a digital pH meter, Model Metrohm 691. Calibration was always carried out before measurement using standard buffer solutions of pH 4.00 and 7.00.

Dissolved organic carbon (DOC) was determined in the filtered samples (Whatman GF/F filters, pore size 0.7 μm) using a sensitive, high temperature catalytic oxidation (HTCO) technique. A Model TOC-5000 System (Shimadzu) with high sensitive Pt catalyst and non-dispersive infrared (NDIR) detector for CO_2 measurement was used.

RESULTS AND DISCUSSION

Results of determination of HM and RSS in bulk precipitation samples using electrochemical methods are presented in Table 2, together with pH and DOC values. DOC was selected as the characteristic parameter due to likely association of metals with organic carbon.

Metals in the bulk depositions are derived from both, wet and dry components and therefore the total concentration in the bulk precipitation is controlled by their relative amounts and concentrations. Mean concentrations of heavy metals determined by electrochemical methods are comparable to those measured by HR ICPMS (Table 2).

In the current study, the most abundant HM was Zn, followed by Cu, Pb, Ni and Cd. Similar trend has also been found for atmospheric bulk deposition of metals in other studies, where the highest concentration of Zn in rainwater was mostly observed, while Cd concentration was generally reported as the lowest one [25-28]. This order follows also a common pattern of heavy metals concentrations in natural waters [29,30]. Relationships between elements often provide information about the sources of the particles [31]. On the other hand, according to Kaya and Tuncel [32], these correlations are influenced by physical properties of particles that carry elements. Gunawardena et al. [2] have found that wet deposition mostly contributes by heavy metals associated with fine particles (< 10 μm) such as Pb, Cd, Ni and Cu. In contrast, Zn is mostly associated with relatively large particles (> 10 μm) and dry deposition appears to be the main source of this element. Furthermore, it is important to note that trace elements may be transported over long distances by very small particles and be deposited far from emission sources [33]. According to Azimi et al. [34], HM source investigation appears to be more difficult than that of organics, because for inorganic elements, specific ratios are less developed. As some heavy metals (Cd and Cu) did not pass normality test, the Spearmank rank correlation analysis is applied. Statistically significant correlation factors ($r = 0.87$; $p < 0.05$) were found only between Zn and Cu. The absence of more correlations among metals is most probably due to the specificity of the sampling location, insufficient number of samples and differences in metal concentrations in different samples. However, despite the absence of statistical correlation which would reflect not only the observed trends, but consider also absolute concentrations of each metal, there are obvious common patterns for heavy metal concentrations in here analyzed precipitation (rain) events. This is clearly visible in Fig. 1, where normalized “trends” of metal concentrations, pH and DOC are plotted. Normalization was performed using the last sampling date as the reference point (symbols denote normalized values for each sample). Note that the x-axis technically corresponds to date/time, but dates are not equally distributed (this is why the numbers (dates) are omitted in order to avoid confusion). The concentrations of most of the metals showed two or more maxima, but the relative increase was not the same for each metal and the maxima were not occurring at the same day(s) (Table 2).

Table 2. Concentrations of HM, RSS, pH and DOC in bulk precipitation samples.

		DPASV				DPAdCSV		DOC	RSS
No	Date	Zn (µg/L)	Cd (µg/L)	Pb (µg/L)	Cu (µg/L)	Ni (µg/L)	pH	(mg/L)	nM
1	22/01/2009	3.75±0.23	0.060±0.002	1.96±0.08	1.65±0.04		5.28	1.44	
2	28/01/2009	7.72±0.42	0.092±0.005	1.43±0.08	1.71±0.05		5.28	1.18	
3	02/02/2009	18.74±0.87	0.077±0.004	3.45±0.18	9.04±0.28	1.16±0.08	5.28	2.71	
4	10/02/2009	9.75±0.45	0.046±0.002	1.42±0.05	5.52±0.20	2.19±0.15	6.21	1.08	5.0
5	03/03/2009	12.85±0.82	0.102±0.006	5.98±0.13	9.20±0.36	0.72±0.05	4.38	3.64	
6	05/03/2009	9.89±0.61	0.055±0.003	1.39±0.05	1.81±0.06	0.73±0.11	6.30	1.26	
7	20/04/2009	5.97±0.42	0.030±0.003	1.47±0.07	1.75±0.03	0.32±0.09	5.91	2.17	7.0
8	21/04/2009	11.88±0.99	0.467±0.023	2.44±0.14	2.08±0.04	0.57±0.07	5.40	1.72	4.0
9	24/04/2009	25.22±1.87	0.415±0.008	6.65±0.13	7.56±0.19	1.28±0.08	6.76	4.86	
	Mean	11.75	0.149	2.91	4.48	0.99	5.64	2.23	
	STD	6.64	0.167	2.05	3.35	0.62	0.72	1.29	
	Min.	3.75	0.030	1.39	1.65	0.32	4.38	1.08	
	Max.	25.22	0.467	6.65	9.20	2.19	6.76	4.86	
	Median	9.89	0.077	1.96	2.08	0.73	5.40	1.72	
	HRICPMS*	7.56	0.060	1.17	3.37	0.63	5.46	1.59	

Among studied metals, Zn, Cd, Pb and Cu followed the same trend, which is also consistent with the trend of DOC, while Ni and pH showed the opposite trends. Similar patterns without statistical correlation point on general common physicochemical processes related to pre-rainy and rainy periods. It is obvious that there are differences between the amounts of metals deposited and "washed-out" during separate precipitation events, but in general this process is similarly reflected in the "drift" of heavy metal levels (increase/decrease) in water samples collected among different events. The pH values are one of the most important factors controlling the dissolution of trace metals in deposition samples [35, 36]. In the current study, pH values were in the range between 4.38 and 6.76. Generally, metals are more soluble at low pH conditions. However, in our case, no correlation between pH and HM concentration was observed for each compound. Similar result has been obtained in another bulk deposition study [37].

In the bulk deposition, DOC concentrations were strongly correlated only with Pb (Spearman's correlation coefficient r = 0.90). This suggests that the sources of organic ligands and HM in the samples could be multiple. Copper did not correlate with DOC (r = 0.58), but it is known that Cu forms very stable organic complexes.

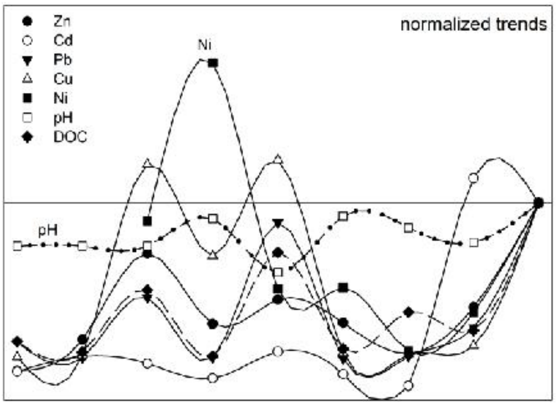

Fig. 1. Normalized values of heavy metal concentrations, pH and DOC concentrations. Symbols represent normalized values for each sampling event, while lines are plotted in order to highlight the observed common patterns.

In the second set of precipitation samples analyzed by HR ICPMS, investigation of organic matter content was performed by DPASV [38, 39, and unpublished results]. In comparison with the unfiltered sample, the filtered sample of bulk precipitation showed much lower concentration of binding ligands (up to 33%) evaluated by electrochemical measurements of the complexing capacity value for Cu ions. This pointed to the fact that significant part of Cu could be bound to particles and/or ligands present in the particulate organic fraction, POC. In the same samples, the POC values were in the range between 0.042 and 2.522 mg/L, *i.e*. it represents up to 39% of the total content of organic carbon.

Reduced sulfur species

Typical voltammograms of RSS studied in precipitation samples are presented in Fig. 2. From the presented voltammograms, the presence of two peaks is clearly visible at around -0.75 V (Figs. 2A, B) and -0.55 V (Fig. 2B, and as a shoulder in Fig. 2A), indicating two different sulfur species. The more negative peak, usually in our papers designated as C2, represents the well-known dissolution/reduction of HgS layer on the Hg electrode surface [19-23]:

$$HgS + H^+ + 2e^- \rightarrow HS^- + Hg^0 \qquad (1)$$

This peak is usually taken as a measure for “free” and labile sulfur species content ($H_2S/HS^-/S^{2-}$, S^0, S_n, S^{2-}, thiols, labile metal sulfide complexes and nanoparticles). The more positive peak can be ascribed to the presence of different organosulfur species (DMS, 3-mercaptopropionat, thio-compounds) [15, 23]. So far, in oxic seawater, in addition to C2, a peak around -0.5 V (vs. Ag|AgCl) can frequently be revealed. This peak is usually ascribed to organosulfur species (DMS) which at applied experimental conditions oxidize the Hg electrode, but do not deposit HgS layer on its surface [15,40]. Therefore, this peak is revealed more positively than the HgS reduction peak.

In Fig. 3, the voltammetric response obtained in natural anoxic seawater sample, where presence of free sulfide (in concentration of 50 nM) was determined by revealing of HgS reduction peak, is shown together with the responses of the same sample after additions of dissolved elemental sulfur (S^0) and DMS. With addition of DMS, new and more positive peak with respect to HgS reduction peak was revealed, similarly as was obtained in some of the precipitation samples represented here in Fig. 2B. As expected, addition of dissolved S^0 caused an increase of the HgS reduction peak [15, 23].

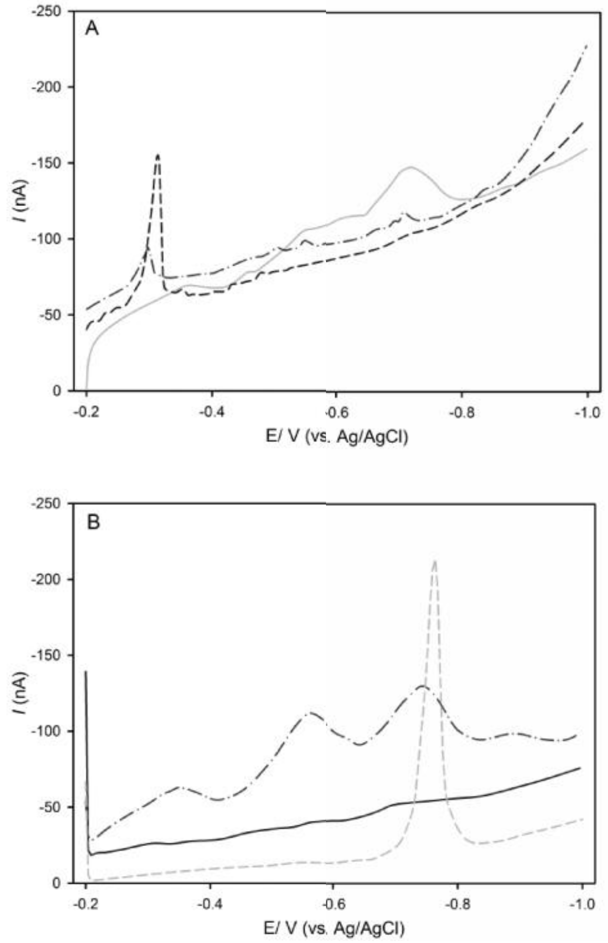

Fig. 2. Voltammetric curves obtained in precipitation samples: A) original sample taken in April 2009 (solid), after addition of HCl (pH ~ 2) (dotted-dash), and after addition of Na_2S (dashed) when increase of the voltammetric peak proving presence of RSS was observed; B) sample taken in February 2009 measured without (solid) and with accumulation step of 120 s with stirring (dotted-dash) at the starting potential E = -0.2 V vs.Ag|AgCl; the same sample after addition of Na_2S (dashed).

To confirm that the more negative peak in precipitation samples belongs to RSS which deposit HgS at the starting deposition potential, the same sample was measured without and with accumulation step at the starting potential, as well as in acidic conditions and after addition of standard Na_2S. Accumulation step caused increase of both peaks, as well as their movement to more positive potentials in acidic conditions. After addition of Na_2S and/or S^0, increase of more negative peak was recorded. These observations present typical behavior of the RSS at the Hg electrode [15,19 and references therein]. The first RSS peak at -0.55 V was removed by acidification and purging of samples, while the second one, corresponding to nonvolatile RSS, remained [23].

Concentration of volatile and nonvolatile RSS in all studied precipitation samples ranged between 2-5 nM, equivalent to sulfide. Usually the same concentration range of nonvolatile RSS can be found in oxic seawater layers [15, 23 and references therein] and freshwaters [41]. Owing to the relatively small number of samples, it is very difficult to talk about a serious correlation with DOC values measured in the same samples, but it is interesting, however, that the highest RSS were found in the sample with higher DOC concentration. Similar correlation between RSS and DOC in the oxic seawater has already been reported in the literature [23].

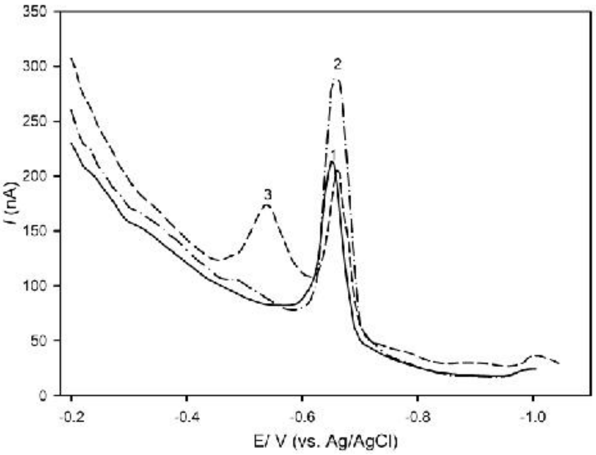

Fig. 3. Natural anoxic water sample with detected free sulfide (curve 1), the same sample after addition of dissolved S^0 (curve 2) and DMS (curve 3).

CONCLUSIONS

Electrochemical techniques, CSV, ASV and AdCSV used in this paper are shown to be important tool for determination of heavy metals and reduced sulfur species content in atmospheric deposition (bulk samples). These methods do not require complex sample pre-treatment and show good selectivity and high sensitivity. The average concentrations of elements followed the order: Cd < Ni < Pb < Cu < Zn. The DOC concentrations were significantly correlated with Pb, while for heavy metals the correlation was found only between Zn and Pb. Despite weak correlations (in general) between metals and the relatively small number of samples (N=9), it was observed that heavy metals (Zn, Cd, Pb and Cu) and DOC followed the same pattern of concentration changes related to precipitation events, while the opposite pattern was found for Ni and pH. Cyclic sweep voltammetry at the HMDE show interesting possibilities for study of nano-levels of organic and inorganic RSS in the atmospheric precipitation.

Acknowledgements. *This work is supported by the Croatian Science Foundation projects: "The Sulphur and Carbon Dynamics in the Sea and Fresh-Water Environment" (IP-11-2013-1205 SPHERE) and "New methodological approach to biogeochemical studies of trace metal speciation in coastal aquatic ecosystems" (IP–2014–09–7530 MEBTRACE). The authors thank Zdeslav Zovko for the DOC measurements.*

REFERENCES

1. C. Wong, X. LI, I. Thornton, *Environ. Poll.*, **142**, 1 (2006).
2. J. Gunawardena, P. Egodawatta, G.A. Ayoko, A. Goonetilleke, *Atmos. Environ.*, **68**, 235 (2013).
3. A. Baker, P. Croot, *Mar. Chem.*, **120**, 4 (2010).
4. P. Smichowski, D. Gómez, *Comprehensive Anal. Chem.*, **70**, 239 (2015).
5. A. Allen, E Nemitz, J. Shi, R. Harrison, J. Greenwood, *Atmos. Environ.*, **35(27)**, 4581(2001).
6. D. Omanović, C. Garnier, K. Gibbon-Walsh, I. Pižeta, *Electrochem. Commun.*, **61**, 78 (2015).
7. C. van den Berg, *Analyst.*, **114**, 1527 (1989).
8. H. Okochi, P. Brimblecombe, *Sci. World J.*, **2**, 767 (2002).
9. M. Witt, S. A. Skrabal, R. Kieber, J. Willey, *Atmos. Environ.*, **41**, 3619 (2007).
10. M. Plavšić, P. Orlović-Leko, Z. Kozarac, E. Bura-Nakić, S. Strmečki, B. Ćosović, *Atmos Res.*, **87(1)**, 80 (2008).
11. S. Watts, *Atmos. Environ.*, **34**, 761, 2000.
12. L. Nunes, T.M. Tavares, J. Dippel, W. Jaeschke, *J. Atmos. Chem.*, **50**, 79 (2005).
13. Z-H. Shon, K-H. Kim, E.-C. Jeon, M-Y. Kim,Y-K. Kim, S-K. Song, *Atmos. Environ*. **39**, 4803 (2005).
14. Z-H. Shon, K-H. Kim, *Chemosp.*, **63**, 1859 (2006).
15. I. Ciglenečki, B. Ćosović, *Mar.Chem.*, **52**, 87 (1996).
16. K-H. Kima, L. Gangwoong, Y. P. Kim, *Environ. Poll.*, **110**, 147 (2000).
17. S.K. Pandey, K.H. Kim, *Air Environ. Sci. Technol.*, **43**, 3020, (2009).
18. H. Guo, I.J. Simpson, A.J. Ding, T. Wanga, S.M. Saunders, T.J. Wang, H.R. Cheng, B. Barletta, S. Meinardi, D.R. Blake, F.S. Rowland, *Atmos. Environ.*, **44**, 3805 (2010).
19. I. Ciglenečki, B. Ćosović, *Electroanal.*, **9**, 775 (1997).
20. D. Krznarić, I. Ciglenečki, B. Ćosović, *Anal. Chim. Acta*, **431**, 269 (2001).
21. I. Ciglenečki, D. Krznarić, G. R. Helz,. *Environ. Sci. Technol.*, **39**, 7492 (2005).
22. E. Bura-Nakić, D. Krznarić, D. Jurašin, G. Helz, I. Ciglenečki, *Anal. Chim. Acta*, **594**, 44 (2007).
23. E. Bura-Nakić, G. Helz, I. Ciglenečki, B. Ćosović, *Geochim. Cosmochim. Acta*, **73**, 3738 (2009).
24. P. Orlović-Leko, K. Vidović, M. Plavšić, I. Ciglenečki, I. Šimunić, T. Minkina, *J. Solid State Electrochem.*, **20(11),** 3097 (2016).

25. B. Başak, O. Alagha, *Environ. Monit. Assess.*, **67**, 493 (2010).
26. I. Fernández-Olmo, M. Puente, L. Montecalvo, A. Irabien, *Atmos. Res.*, **145-146**, 89 (2014).
27. H. Hou, T. Takamatsu, M.K. Koshikawa, M. Hosomi, *Atmos. Environ.*, **39(20)**, 3583 (2005).
28. A. Lawlor, E. Tipping, *Poll.*, **121**, 153 (2003).
29. J. Gaillardet, J. Viers, B. Dupré, in: Heinrich, D.H., Karl, K.T. (eds.), Treatise on Geochemistry. Pergamon, Oxford, 2003, p. 225.
30. A. Cindrić, C. Garnier, B. Oursel, I. Pižeta, D. Omanović, *Mar. Poll. Bull.*, **94**, 199 (2015).
31. C. Johansson, M. Norman, L. Burman, *Atmos. Environ.*, **43 (31)**, 4681 (2009).
32. G. Kaya, G. Tuncel, *Atmos. Environ.*, **31**, 3985 (1997).
33. C. Meyer, M. Diaz-de-Quijano, F. Monna, M. Franchi, M. Toussaint, D. Gilbert, N. Bernard, *Atmos. Environ.*, **101**, 286 (2015).
34. S. Azimi, V. Rocher, M. Muller, R. Moilleron, D.R. Thevenot, *Sci. of the Total Environ.*, **337**, 223 (2005).
35. P.Tanner, A. Wong, *Water, Air and Soil Poll.*, **122**, 261 (2000).
36. A. Okubo, S. Takeda, H. Obata, *Atmos. Res.*, **129-130**, 20 (2013).
37. A. Motelay-Massei, D. Ollivon, K. Tiphagne, B. Garban, *Water, Air, and Soil Poll.*, **164(1)**, 119 (2005).
38. P. Orlović-Leko, S. Strmečki, J. Dautović, Z. Kozarac, B. Ćosović, M. Plavšić, in: Croatian Waters Facing the Challenge of Climate Changes (Proc. 5th Croatian Water Conference with international participation, Opatija, 2011), D. Biondić, D. Holjević, Lj. Tropan (eds), Croatian Water, Zagreb, 2011, Part 1, p. 169.
39. P. Orlovic-Leko, D. Omanović, M. Plavšić, in: Ecology and biology of the soil (Proc. of the international scientific conference, Rostov-on-Don, 2014), K. Kazeev (ed.), Southern Federal University, Rostov-on-Don 2014, p. 157.
40. I. Ciglenecki, M. Marguš, E. Bura-Nakić, I. Milanović, *J. Electrochem. Sci. Eng.*, **4**, 155 (2014).
41. P. Superville, I. Pižeta, D. Omanović, G Billon, *Talanta*, **112(15)** 55 (2013)

ПРИЛОЖЕНИЕ НА ЕЛЕКТРОХИМИЧНИ МЕТОДИ ЗА ФИЗИКОХИМИЧНО ОХАРАКТЕРИЗИРАНЕ НА АТМОСФЕРНА ВЛАГА

П. Орлович-Леко[1] *, Д. Оманович[2], И. Сигленечки[2], К. Видович[3], Т. Бренко[1]

[1] Загребски университет, Факултет по минно дело, геология и петролно инженерство,
Пиероттижева 6, Загреб, Хърватия
[2]Отдел за изследване на морето и околната среда, Институт Руджер Бошкович, Биеничка 54, 10000
Загреб, Хърватия
[3]Национален институт по химия, Хаджрихова 19, п.п. 660, 1001 Любляна Словения

Постъпила на 16 ноември 2016 г.; коригирана на 18 януари 2017 г.

(Резюме)

Електрохимичните методи играят основна роля при анализ на околната среда. Това изследване показва, че електрохимичните (волтамметрични) методи са ценен инструмент с добра селективност и чувствителност при физико-химичен анализ на атмосферни валежи. Изследванията бяха осъществени при ежедневно вземане на проби в град Загреб (Хърватия) през периода от 2009 до 2010г. Беше изследвано съдържанието на тежки метали (ТМ) и редуцирани серни частици (РСЧ) в проби от дъждовна вода с помощта на катодна стрип волтамметрия (КСВ) и диференциална импулсна стрип волтамметрия: при аноден, DPASV (Zn, Cd, Pb и Cu) и при адсорбционно катоден режим, DPAdCSV (Ni), съответно, на капков живачен електрод. Като цяло най-високи концентрации са открити за Zn и най-ниски на Cd (Cd <Ni <Pb <Cu <Zn). Независимо от установената слаба корелация между металите (статистически значима бе само корелацията между Zn и Cu), същата тенденция на промяна в концентрациите бе наблюдавана за Zn, Cd, Pb, Cu и DOC, докато за Ni и pH беше наблюдавана противоположна тенденция. Анализът на обемни проби по метода CSV установи наличие на различни серни частици, осигурявайки отлични възможности за изучаване на органични и неорганични RSS в атмосферна влага при нано-нива.