SIMPLE AND FAST METHOD FOR DETERMINATION OF TRACE CADMIUM IONS IN ENVIRONMENTAL WATER SAMPLES CONTAINING HUMIC SUBSTANCES

M. Grabarczyk

Department of Analytical Chemistry and Instrumental Analysis, Faculty of Chemistry, Maria Curie-Sklodowska University M.C. Sklodowska sq. 3, 20-031 Lublin (Poland)

Abstract

A simple and fast anodic stripping voltammetric procedure for trace determination of cadmium in environmental water samples is described. The interferences caused by humic substances were removed by mixing an analysed sample with resin in a voltammetric cell. The following optimum conditions were found: supporting electrolyte 0.1 mol L^{-1} HCl, the 10 mL of sample was mixing with 0.5 g of resin for 5 min. The proposed procedure was successfully applied for the detection of cadmium in environmental water samples.

Key words: cadmium, environmental waters, humic substances, voltammetric determination

Introduction

The increasing concentration of heavy metals in natural waters is one of the most important elements of environmental contamination and, if they are present in concentrations above norm, may have a negative effect on living organisms and plants. One such metal is cadmium, which as a result of human activity has become one of the main chemical pollutants of the environment.

Cadmium is relatively poorly distributed in the Earth's crust; the average content is about 0.00004% and is present in air, water, soil, and plant and animal tissues. In nature, the metal is not present in a free state, but is present mainly in sulphide ores of zinc, copper, or lead. Rich in cadmium in particular are zinc ores (3%). Their mining and processing releases significant quantities into the atmosphere, hydrosphere, and soil, which contributes to the contamination of the human environment. Cadmium is also present in fossil fuels, for example coal. The share of the combustion process of carbons in cadmium pollution in urban areas is almost 10% [1-3]. Cadmium is also used in many technological processes in various branches of industry and agriculture. In the industry, cadmium is used for the production of dyes and stabilizers for plastics, galvanic protective coatings, solder and alloys, cadmium rods. It is also used for the production

of alkaline nickel-cadmium batteries, fireworks, fluorescent inks. A significant source of cadmium in the environment are fertilizers, which are contaminated with this metal in an amount of 10 to 100 mg/kg. Their long-term and widespread use leads to contamination of the soil with cadmium. Cadmium, once introduced into the environment, is not subject to degradation and remains in continuous circulation. Environmental exposure can lead to the absorption of large amounts of cadmium and the toxic effect of this element on the body [4-7].

Cadmium is an extremely harmful element for living organisms. The greatest damage is caused in organs where it is easily accumulated, i.e. liver, kidneys, bones, testes. Acute poisoning caused by a single high dose of metal in humans is rare. The poisoning caused by the long-term effect of cadmium on the body is much more common. In humans, long-term exposure of the organism to cadmium and the absorption of small amounts of this metal leads to chronic poisoning, which very often for a long time (about a year) may be asymptomatic [4,8-10].

Because, as mentioned above, long-term exposure is very harmful to humans, even at very low concentrations of cadmium, there is a constant need for simple, cheap and fast methods to determine even the lowest concentrations of cadmium in environmental waters. One of the techniques that meets all these requirements is stripping voltammetry. Stripping voltammetry is an electrochemical technique that measures the intensity of a current flowing through an electrode as a function of the potential applied to it after the earlier accumulation of the determined element on this electrode. This method has many advantages, such as fast measurement, cheap equipment, and low detection limits. However, this method has a disadvantage related to interference caused by the presence of humic substances in environmental samples [11-13].

Humic substances (HS) are commonly occurring matrix components in environmental samples. Among humic substances we can distinguish fulvic acids (FA) which are water soluble under all pH, humic acids (HA) which are soluble in water at higher pH, and humins which are water insoluble [14]. Humic substances are a heterogeneous mixture of natural organic substances that are widely distributed in soil, sediments, and different environmental waters, such as river water or lake water. These substances are formed by humification, i.e. the microbiological decomposition of plant and animal residues. The structure of humic substances is complex and diverse and depends on the conditions in which the humification occurred. Humic substances found in environmental water in normal concentrations are not harmful to human and animal health but even their small concentrations, as repeatedly proven in literature, can cause interference in voltammetric measurement [15].

Recently, a few voltammetric procedures have been reported for the determination of cadmium in different samples. However, in these procedures it is necessary to remove or destroy the organic matter present in the environmental samples. This is usually accomplished using ultraviolet irradiation, which takes a long time [16-18]. Therefore, the aim of this work will be to present a fast and simple method for determining the trace of cadmium ions in waters containing HS. In order to reduce the interference associated with the presence of HS, it

was proposed to introduce Amberlite XAD-7 resin into the measuring cell. In this case, HS present in the analysed sample do not block the working electrode on which cadmium determination takes place because they are adsorbing on the resin. Optimization of the proposed procedure was aimed at choosing a number of parameters for obtaining the most efficient removal of HS by means of a resin and at the same time quantitatively leaving cadmium ions in solution. The following parameters were selected: supporting electrolyte composition, the ratio of the resin mass to the volume of the sample, the time of mixing the resin with the sample.

Materials and methods

Apparatus

All voltammetric measurements were carried out with an Autolab PGSTAT 10 analyzer (Utrecht, Netherlands) and a hanging mercury drop electrode (HMDE) (MTM Cracow, Poland). A three-electrode cell, volume 10 mL, consisting of HMDE as a working electrode, a Pt as auxiliary electrode and an Ag/AgCl as reference electrode was used.

Reagents

All chemicals used were of analytical reagent grade or Suprapur. A working standard solution of 1×10^{-4} mol L^{-1} Cd(II) was prepared from a dilution of 1 g L^{-1} Cd(II) standard solution (Merck, Darmstadt, Germany). Humic acid sodium salt (HA) was obtained from Aldrich. The fulvic acid (FA) and natural organic matter (NOM) were obtained from the Suwannee River and purchased from the International Humic Substances Society. The Amberlite XAD-7 resin was obtained from Sigma (St. Louis, MO, USA), and the resin was washed four times with triply distilled water and dried at the temperature 50 °C. All solutions were prepared using triply distilled water.

Measurement procedure

The following components were introduced into the volumetric cell:

- analyzed sample or synthetic sample containing Cd(II) and various amounts of humic substances
- 1 mL of 1 mol L^{-1} HCl
- an appropriate amount of H_2O to make up to 10 mL volume
- 0.5 g resin.

The solution prepared in this way was mixed using a magnetic stirrer for 5 min. with simultaneous deoxidization using nitrogen gas. At that time, humic

substances adsorbed onto the resin while Cd(II) ions remained in solution. After this time, a voltamperometric measurement was carried out in two steps:

- accumulation, performed using a potential of -0.9 V for 30 s with stirring; during this time Cd(II) was reduced and deposited as metallic cadmium on the mercury electrode
- after 5 s equilibration time, the differential pulse voltammogram was recorded changing potential towards positive values from -0.9 V to -0.4 V; during this time accumulated cadmium was oxidized with the intensity of the obtained peak on the voltammogram directly proportional to the concentration of Cd(II) in the solution. The peak of cadmium appeared at ~ -0.62 V.

Results

The following parameters were examined in the selection of the most ideal conditions of the proposed procedure: supporting electrolyte composition, the ratio of the resin mass to the volume of the sample, the time of mixing the resin with the sample.

Supporting electrolyte composition

Literature data show that the best effect in the removal of humic substances by Amberlite XAD-7 resin is obtained in an acidic environment [19-21]. Therefore, several acids have been selected for initial testing, such as CH_3COOH, HCl, HNO_3, H_3PO_4. The conducted research was aimed at investigating in the presence of which acid humic substances are most effectively removed from the analyzed sample. This was assessed by carrying out a series of measurements in which the cadmium signal was tested for each acid in the presence of increasing HA concentrations. It was found that the highest cadmium signal in the presence of increasing concentrations of HA was obtained in the presence of HCl. It can be deduced from this that in such a case the humic substances are removed to the greatest extent, thanks to which the cadmium signal is disturbed to the least degree.

The ratio of the resin mass to the volume of the sample

At first, for research aimed at selection, the ratio of the resin mass to the volume of the sample humic acids as the interferent was chosen. The measurements were performed for 10 mL of solution and different mass of resin: 0.2 g, 0.3 g, 0.4 g, 0.5 g and 0.6 g. The time of mixing the resin with the sample was 5 min. The solutions contain a fixed concentration of Cd(II) 5×10^{-7} mol L^{-1}, 0.1 mol L^{-1} HCl and an increasing concentration of HA in the range from 0.25 mg L^{-1} to 4 mg L^{-1}. The obtained results are presented in Fig. 1. As can be seen, as the

resin mass increases, the cadmium signal is less diminished with the increasing concentration of HA. Since the differences in the obtained cadmium signals for 0.5 g and 0.6 g of resin are small at the most optimal conditions, it was proposed to add 0.5 g of resin to 10 mL of the solution.

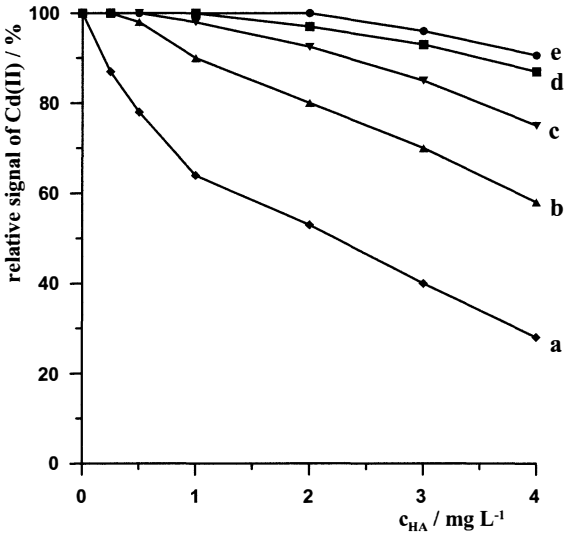

Figure 1. The influence of concentration of humic acid (HA) on Cd(II) relative signal for mixing sample with different masses of resin: 0.2 g (a); 0.3 g (b); 0.4 g (c); 0.5 g (d); 0.6 g (e). The time of mixing the resin with the sample was 5 min. Concentration of Cd(II) 5×10^{-7} mol L^{-1}, accumulation potential and time -0.9 V and 30 s, respectively.

For comparison, identical measurements for selecting the ratio of the resin mass to the volume of the sample using fulvic acids (FA) and natural organic matter (NOM) as interferents were performed. The experiments were carried out using different masses of resin: 0.2 g, 0.3 g, 0.4 g, 0.5 g, 0.6 g and different concentrations of FA or NOM in the range from 0.25 mg L^{-1} to 4 mg L^{-1}. The results obtained were similar to those for HA. So with the increase in resin mass, the voltammetric cadmium signal corresponding to its content in the solution is less suppressed by FA or NOM. Because also in this case the results obtained for 0.5 g and 0.6 g of resin were very similar, it was found that the most optimal resin and resin introduced into 10 mL of the solution is 0.5 g of resin.

The time of mixing the resin with the sample

At first in order to choose the optimal time of mixing resin with the sample, humic acid as an interferent was selected. The measurements were performed for 10 mL of solution and 0.5 g of resin while the time of mixing the resin with the sample was changed from 3 min. to 7 min. The solutions contain a fixed

concentration of Cd(II) 5×10^{-7} mol L^{-1}, 0.1 mol L^{-1} HCl and increasing concentrations of HA in the range from 0.25 mg L^{-1} to 4 mg L^{-1}. The obtained results are presented in Fig. 2. As can be seen, as the mixing time increases from 3 to 5 min. the signal of cadmium increases too; for a mixing time longer than 5 min. the cadmium signal did not change. That is why 5 min. was chosen for further research as the time for mixing the solution with the resin, because further prolonging the mixing time did not increase efficiency in the removal of humic substances.

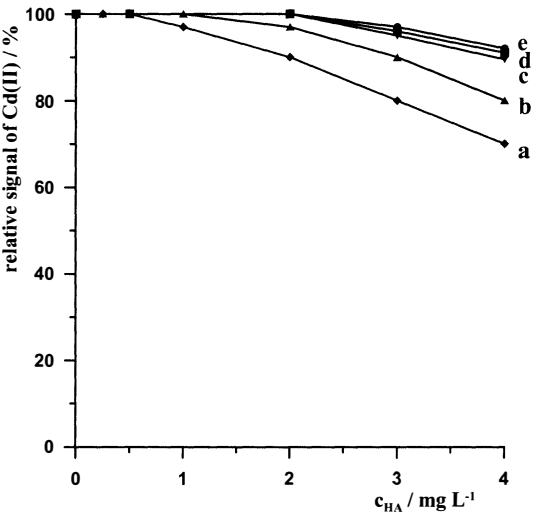

Figure 2. The influence of concentration of humic acid (HA) on Cd(II) relative signal for different times of mixing the resin with the sample: 3 min. (a); 4 min. (b); 5 min. (c); 6 min. (d); 7 min. (e). The mass of resin was 0.5 g. Concentration of Cd(II) 5×10^{-7} mol L^{-1}, accumulation potential and time -0.9 V and 30 s, respectively.

For comparison, identical measurements for selecting the time of mixing the resin with the sample using fulvic acids (FA) and natural organic matter (NOM) as interferents were performed. The experiments were carried out using different mixing times: 3 min., 4 min., 5 min., 6 min. and 7 min. and different concentrations of FA or NOM in the range from 0.25 mg L^{-1} to 4 mg L^{-1}. The results obtained were similar to those for HA. So with the increase of mixing time, the voltammetric cadmium signal corresponding to its content in the solution is less suppressed by FA or NOM. Since, as in the case of HA, differences in the cadmium signal in the presence of both FA and NOM for mixing times of 5 min. 6 min. and 7 min. are insignificant, 5 min. was chosen as the most optimal mixing time. In this case, an important rule was that the total time of the measurement procedure was as short as possible.

Validation

As is known, the best way to validate a procedure is to analyze a certified reference material. It is best that the matrix of such material corresponds to the matrix of samples for analysis, which a given procedure is dedicated to. Therefore, choosing SPS-WW1 Waste Water as a certified reference material seems to be a good choice to validate the proposed procedure. In addition to the organic matrix characteristic for waste water, this material contains, besides cadmium, twelve other elements with concentrations traceable to ultra pure metals or stechiomerically well-defined substances. Concentrations of all elements were as follows: 2000 ± 10 ng/mL Al, 100.0 ± 0.5 ng/mL As, 20.0 ± 0.1 ng/mL Cd, 60.0 ± 0.3 ng/mL Co, 200 ± 1 ng/mL Cr, 400 ± 2 ng/mL Cu, 1000 ± 5 ng/mL Fe, 400 ± 2 ng/mL Mn, 1000 ± 5 ng/mL Ni, 1000 ± 5 ng/mL P, 100.0 ± 0.5 ng/mL Pb, 100.0 ± 0.5 ng/mL V and 600 ± 6 ng/mL Zn. Results of cadmium determination in certified reference material SPS-WW1 Waste Water are presented in Table 1. In order to test the possibility of using the proposed method in samples with more complicated matrices, the SPS-WW1 Waste Water was additionally spiked with different concentrations of humic acid, fulvic acid, and natural organic matter. As can be seen both for the certified reference material and the material enriched in various concentrations of humic substances and natural organic matter, satisfactory results were obtained and the concentrations of determined cadmium ranged from 18.8 ± 0.7 to 20.5 ± 0.4 ng/mL.

Table 1. Results of Cd(II) determination in certified reference material SPS-WW1 Waste Water with certified value of Cd(II) 20.0 ± 0.1 ng/mL. Experiments were performed at the recommended conditions.

Sample	Concentration of added substance [mg L^{-1}]			Cd(II) determined [ng/mL]
	HA	FA	NOM	
SPS-WW1 Waste Water	-	-	-	19.6 ± 0.5
	1	-	-	19.2 ± 0.6
	-	1	-	20.5 ± 0.4
	-	-	1	19.4 ± 0.5
	0.5	0.5	0.5	18.8 ± 0.7

Analytical application

In order to examine the performance of the proposed procedure, it was applied to the determination of trace amounts of cadmium in Bystrzyca river water samples (collected from eastern areas of Poland). To prove that the proposed method of humic substances removal by means of Amberlite XAD-7 resin was proper, the samples of Bystrzyca river water were spiked with 5×10^{-7} mol L^{-1}

Cd(II) and different amounts 1 or 2 mg L^{-1} of HA, FA or NOM. The samples were analysed using the standard addition method. The obtained recoveries of cadmium were in the range from 94.3 to 97.3% with relative standard deviation between 5.2 and 6.4%, confirming that the proposed procedure is a suitable tool for analysis of environmental water samples for cadmium monitoring.

Conclusions

Combination of the anodic voltammetric method for determining trace amounts of cadmium with the simultaneous introduction of resin into the voltammetric cell to the analyzed solution made it possible to elaborate a simple and fast procedure in which interference from humic substances was minimalized. Its main advantage is the possibility of low-cost direct determination of Cd(II) in environmental water samples containing humic substances without the necessity of preliminary UV-irradiation of the samples. This drastically reduces analysis time. The proposed procedure looks promising and can be recommended for monitoring the environment.

Reference:

1. Czeczot, H., Skrzycki, M. (2010) Kadm – pierwiastek całkowicie zbędny dla organizmu. Postępy Higieny i Medycyny Doświadczalnej, 64: 38 – 49.
2. Ostrowska, P. (2008) Kadm, występowanie, źródła zanieczyszczeń i metody recyklingu. Gospodarka Surowcami Mineralnymi, 24: 255 – 260.
3. Thornton, I. (1992) Sources and pathways of cadmium in the environment. International Agency for Research on Cancer Scientific Publications, 118: 149-162.
4. Czeczot, H., Majewska, M. (2010) Kadm – zagrożenie i skutki zdrowotne. Toksykologia, 66: 243-250.
5. Jakubowski, M., Muszer, J., Slota, P. (1995) The risk of exposure on cadmium in chosen the bronches of industry. Medycyna Pracy, 46: 109-122.
6. Satarug, S., Baker, J.R., Urbenjapol, S., Haswell-Elkins, M., Reilly, P.E.B., Williams, D.J., Moore, M.R. (2003) A global perspective on cadmium pollution an toxicity in non-occuptionally exposed population. Toxicology Letters, 137: 65-83.
7. Ostrowska, P. (2008) Kadm, występowanie, źródła zanieczyszczeń i metody recyklingu. Gospodarka Surowcami Mineralnymi, 24: 255-260.
8. Bonda, E., Włostowski, T., Krasowska, A. (2007) Metabolizm i toksyczność kadmu u człowieka i zwierząt. Kosmos Problemy nauk Biologicznych, 57(1–2): 87-97.
9. Floriańczyk, B. (1995) Toksyczne i kancerogenne właściwości kadmu. Nowiny Lekarskie, 6: 737-754.
10. Järup, L., Berglund, M., Elinder, C.G., Nordberg, G.,Vahter, M. (1998) Health effects of cadmium exposure: a review of the literature and risk estimate. Scandinavian Journal of Work, Environment and Health, 24: 1-51.
11. Kipcak, I., Akin, C. (2019) Cadmium removal from aqueous solution by iron oxide coated sepiolite: preparation, characterization and batch adsorption studies. Desalination and Water Treatment, 146: 245-256.

12. Korolczuk, M., Grabarczyk, M. (2002) Determination of Cr(VI) in the presence of Cr(III) and humic acid by cathodic stripping voltammetry. Microchemical Journal, 72: 103-109.
13. Grabarczyk, M., Koper, A. (2011) Direct determination of cadmium traces in natural water by adsorptive stripping voltammetry in the presence of cupferron as a chelating agent. Electroanalysis, 24: 33-36.
14. Nieder, R., Bendi, D.K. Carbon and nitrogen in the terrestrial Environment. Springer, 2008.
15. Kaleta, J., Puszkarewicz, A. (2019) Influence of water hardness on the effectiveness of coagulation of humic compounds. Journal of Ecological Engineering, 20: 126-134.
16. Cao, L., Jia, J., Wang Z. (2008) Sensitive determination of Cd and Pb by differential pulse stripping voltammetry with in situ bismuth-modified zeolite doped carbon paste electrodes. Electrochimica Acta, 53: 2177-2182.
17. Yang, G., Yan, J., Qi, F., Sun, Ch. (2010) High sensitivity and reproducibility of a bismuth/poly(bromocresol purple) film modified glassy carbon electrode for determination of trace amount of cadmium by differential pulse anodic stripping voltammetry. Electroanalysis, 22: 2729-2738.
18. Yi, W.J., Li, Y., Ran, G., Luo, H.Q., Li, N.B. (2012) Determination of cadmium(II) by square wave anodic stripping voltammetry using bismuth–antimony film electrode. Sensors and Actuators B, 166-167: 544-548.
19. Grabarczyk, M., Wardak, C. (2014) A new voltammetric strategy for sensitive and selective determination of gallium using cupferron as a complexing agent. Journal of Environmental Science and Health, Part A, 49: 1142-1148.
20. Grabarczyk, M. (2017) Optimization of adsorptive stripping voltammetry procedure using chloranilic acid as a complexing agent for the determination of ultra-trace germanium in natural water samples. Journal of the Electrochemical Society, 164: H872-H876.
21. Węgiel, K., Grabarczyk, M., Kubiak, W.W., Baś, B. (2017) A reliable and sensitive voltammetric determination of Mo(VI) at the in situ renovated bismuth bulk annular band electrode. Journal of the Electrochemical Society, 164: H352-H357.