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ADSORPTIVE CATHODIC STRIPPING VOLTAMMETRIC DETERMINATION OF SEVERAL HEAVY METALS (Ni , Co, Cu, Pb) IN NATURAL WATERS

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ABSTRACT

Adsorptive cathodic differential pulse stripping voltammetry (AdDPSV) was applied to determination of Ni(II), Co(II), Cu(II) and Pb(ll). For determination Ni(II) and Co(II) the mercury film on the surface rotating disc electrode prepared ex situ was employed as working electrode and dimethylglyoxime was employed as the surface active ligand. For the determination of Cu(ll) and Pb(ll) the hanging mecury drop electrode (HMDE) was employed as working electrode and 8-oxin was employed as the surface lingand. Methods have high detection sentitivity, good accuracy and precision which was applied to determination of Co (II) and Ni(II) in natural waters.

Key word: absorptive, vóltammetric, nickel, cobalt, copper, lead

Introduction

Electrochemical stripping methods have become popular for the determination of traces and ultratraces of heavy metals because these methods have very low limits of detection, high accurace and precision. For the developing countries as Vietnam these methods are very suitable as low cost of apparatus and low cost to client [1-2]. Since last fifteen years a new method of stripping analysis - Adsorptive stripping technique - has been steadily increasing. This technique is based on accumulation of the analyte on the surface of working electrode by using chemical or electrochemical adsorptive effect in the suitable conditions. For the determination of heavy metals the organic reagent was employed as the surface - active ligand for complexation . After adsorptive accumulation at a suitable potential the cathodic or anodic sripping process was carried out [3-5].

In this paper we summarize the main results of the research of our group in the field adsorptive cathodic stripping analysis of Co(II), Ni(II), Cu(II) and Pb(II) in natural waters.

Experimental

Instrumentation and chemicals

The voltammetric and stripping voltammetric measurements were carried out with the polarographic system 693 VA Processor (Metrohm, Switzerland) using the three electrodes system. The worlcing electrode was rotating disc or haing mercury drop (HMDE). The referent electrode was a double-lunction Ag/AgCl (3M KC1, satured AgCl and 3M KC1 in the bridge). For determination of Ni(Il) and Co (II) the mercury film on the surface of a disc electrode prepared ex situ by electrolysis of $5.10^{-3}M$ Hg^{2+} solution at Ee = - 1,0V for 2 min. For the determination of Cu(II) and Pb(II) the HMDE as employed as working electrode.

All chemicals employed were of p.a or special chemical purity. In some cases the suprapure chemicals (MERCK) were applied. All solutions of metal ions and reagents were prepared from double - didtilled water using the quartz apparatus . The blanck experiment had shown that chemicals and studied solutions were not contaminated.

Results and discussion

Determination of Ni(II) and Co(II)

In the basic medium of (NH_4^+ - NH_3) buffer Ni(II) and Co(II) were complex formed with dimethylglyoxime (DMG) and gave differential pulse adsorptive cathodic strpping peaks.

After carried out series of experiments for investigation of effect of many factors on the determination of Co(II) and Ni(II) we have found the optimal and suitable conditions for theire determination (see tab.1).

Tab. 1. Optimal conditions for the determination of Ni(II) and Co(II) by DP-AdCSV

1	Concentration of buffer ($C_{buf.}$)	0.100; (0.500 – 1.00)[a]
2	pH of solution	9.0; (9.5 – 10.0)[a]
3	Concentration of DMG (CDim.)	1.0 mM
4	Removal of dissolved oxygen by	bubbling nitrogen for 10 min or adding Na_2SO_3
5	Potential for adsorptive accumulation	$E_{ads.}$ = -700 mV (- 1000 mV)[b]
6	The time for adsorptive accumulation	$t_{ads.}$ = 20 - 60 s
7	The rest time	t_{rest} = 30 s
8	Velocity of rotating disc electrode	1000 - 1700 rpm
9	Technical parameters:	
	Amplitude	E = 50 mV
	Duration of a pulse	50 ms
	Scan rate	v = 10 mV/s
	Potential range	from - 700 mV to - 1200 mV
10	Volume of solution	V = 10 ml
11	Temperature	t° = 20 - 30 °C

[a] The conditons for determination of Ni(II) in presence of a lager amount of Co
[b] The condition for determination of Co(II) in the presence of a lager amount of Ni

In the optimal conditions given above Ni(II) gave a peak at Ep (Ni) = -1000 mV and Co(II) gave a peak at Ep (Co) = -1100 mV.

In the optimal conditions the mesurements of DP-AdCSV peaks of Ni(II) and Co(II) were received very good reproducibility. With a mercury film prepared ex situ and a analyzed solution the results of mesurement got the related standard deviation (RSD) 5% when 10 times of mesurement were repeated.

The limit of detection of Ni(II) by this method is 3.4± 1.1 nM; limit of detection of Co(II) is 1.6± 0.9 nM. For the determination of Ni(II) and Co(II) in natural waters we used standard addition method.

Determination of copper and lead

For determination of Cu(II) and Pb(II) we used 8-hydroxyquiniline(oxine) as a surface-active lingand. For AdCSV the buffer has important rol for pre-concentration process as well as stripping process. After earring out a series experiments using different buffers we found that HEPES-Na (sodium 4-(2-hydroxyethyl)-l-piperazinethan sunfonate) was the best buffer. The optimal and suitable conditions for the determination of Cu(II) and Pb(II) are given in tab. 2.

Tab. 2. Optimal conditions for the determination of Cu(II) and Co(ll) by DP-AdCSV.

1	Concentration of HEPES-Na buffer	10-2 for Cu(II); 10^{-3}M for Pb(II)
2	pH of the solution	7.0 – 8.0 for Cu(II) ; 7.5 – 8.5 for Pb(II)
3	Concentration of oxine	10^{-3}M for both metals
4	Removing dissolved oxygen by	bubbling nitrogen for 10 min
5	Potential for adsorptive pre-concentration	-300mV for both metals
6	The time for pre-concentration	60 - 120 s
7	The rest time	10 s
8	Velocity of rotating disc electrode	HMDE
9	Technical parameters:	
	Amplitude	50mV
	Duration of a pulse	50ms
	Scan rate	20mV/s
	Potential range	from - 450 mV to - 800 mV
10	Volume of analysed solution	10 or 20 ml
11	Temperature	20°C - 30°C

In the optimal conditions given over Cu gave stripping peak at -450 mV and Pb gave peak at -580 mV. The reproducibility of measurements was very high. Limit of detection was 3.0 – 1.2 nM (for Cu) and 5.2– 0.8nM (for Pb).

In Fig.1 there are AdCSV curves of Ni and Co (in the concentration 30 nM) when measurements of one solution using one mercury film electrode were repeated in 10 times. In Fig. 2 there are AdCSV curves of Pb(II) in the concentration range of 10^{-8}M – 10^{-7}M using a HMDE.
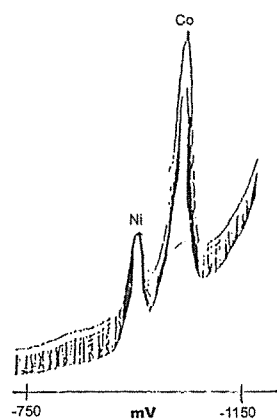

Fig.1. Reproducibility of AdCSV measurement of Ni(II) and Co(II) in the concentration of 30nM in the Optimal conditions
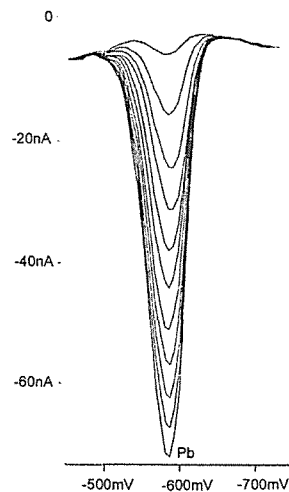
Fig. 2. AdCSV curves of Pb(II) in range of concentration 10^{-8}-10^{-7} M in the optimal conditions

Practical application

Determination of Ni and Co in natural waters [6]

In order to achieve the optimal procedure for the determination of traces of Ni(II) and Co(II) in natural waters we have treated the water samples (river water, sea water and lagoon water) by different ways: a)

without filtration of samples; b) filtration through 0.45μm filters; c) after filtration, the samples were treated by the mixture of HNO_3 and HC1 (Suprapure, MERCK); d) after adding H_2O_2 samples were treated by UV radiation at 90^0C for 90 min.

After water samples were treated by the way given above the concentration of Ni(II) and Co (II) was determinated by standard addition method with 3 times of adding standard solution. The results are given in Tab. 3.
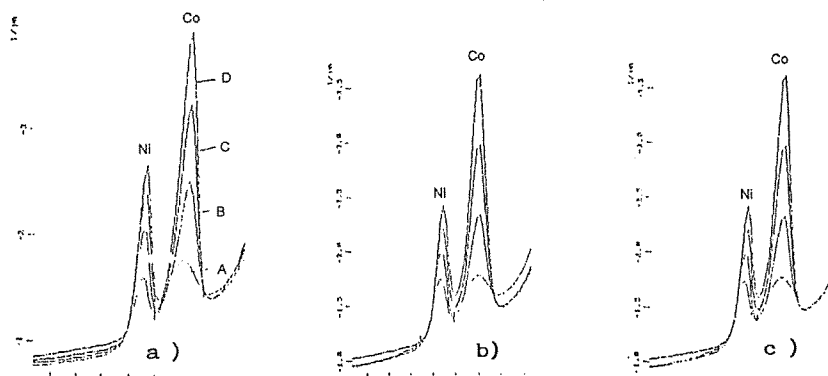

Fig. 3. AdCSV curves of Ni(II) and Co(II) when analysis of sample HR-1.
a) Without filtration; b) Sample was filtrated and then was treated by mixture HNO_3 and HC1; c) Sample was treated by adding H_2O_2 and then was treated by UV radiation at 90°C for 90 min.

Results in Tab. 3 show that concentration of Ni(II) and Co(II) in 3 types of water was practically same (because for storage of samples a suitable of HNO3 or HC1 was added, pH of samples got 2.0). Concentration of both metals in 3 types of water when samples were treated by mixture of acids and by UV radiation were practically same. Therefore we can choose one of ways for treatment of samples . The results given above show that the treatment of samples is indispensable .

Tab. 3. Results of determination of Ni(II) and Co(II) in natural waters
when samples were treated by different ways

No.	Samples	Salinity (o/oo)	Concentration of Ni(II) in ppb				Concentration of Co(II) in ppb			
			a)	b)	c)	d)	a)	b)	c)	d)
1	HR-1	0.03	0.82	0.73	1.30	1.25	0.20	0.15	0.28	0.30
2	HR-2	0.03	0.48	0.37	0.87	1.05	0.09	0.09	0.18	0.15
3	HR-3	0.04	0.55	0.60	1.16	0.94	0.12	0.10	0.22	0.18
4	HR-4	0.14	0.49	0.75	1.25	1.12	0.18	0.20	0.25	0.28
5	HR-5	0.35	0.96	0.95	1.34	1.30	0.10	0.14	0.22	0.19
6	LW-1	7.20	1.05	1.02	1.20	1.16	0.17	0.17	0.20	0.24
7	LW-2	20.4	1.21	1.15	1.32	1.38	0.15	0.13	0.18	0.20
8	LW-3	23.4	0.98	1.08	1.25	1.36	0.09	0.09	0.12	0.09
9	LW-4	20.2	1.02	0.95	1.12	1.20	0.12	0.10	0.12	0.15
10	LW-5	12.9	1.20	0.98	1.38	1.42	0.14	0.12	0.18	0.16
11	SW-1	30.8	0.68	0.75	0.88	0.92	0.10	0.12	0.16	0.10
12	SW-2	31.4	0.45	0.40	0.68	0.76	0.12	0.09	0.12	0.14
13	SW-3	32.0	0.52	0.63	0.82	0.70	0.09	0.10	0.14	0.10
14	SW-4	32.4	0.70	0.50	0.79	0.88	0.12	0.10	0.10	0.09
15	SW-5	32.6	0.56	0.62	0.75	0.79	0.09	0.12	0.12	0.10

a) samples without filtration; b) samples after filtration through 0,45μm filters; c) samples filtrated and then were treated by the mixture concern, HNO_3 and HCl; d) after adding H_2O_2, samples were treated by UV radiation at 90°C for 90 min.

Note: HR: Huong river water (in Hue City); LW: Lagoon water; SW: Sea water.

The procedure for the determination of Cu(II) and Pb(II) in natural waters is studying.

Conclusion

Adsorptive stripping analysis using MFE is the suitable method for the determination of traces and ultra traces of heavy metals as Co and Ni in natural waters in the conditions of laboratories of our country. We are continue to study in this field to determine heavy metals in different environmental samples.

Acknowledgement

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