

# Carbon Paste Electrode Modified with Organofunctionalized Mesoporous Silica for Electrochemical Detection and Quantitative Determination of Cadmium (II) Using Square Wave Anodic Stripping Voltammetry

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*A carbon paste electrode modified with mesoporous silica functionalized with acetyl-acetone (AcAcNH<sub>2</sub>-HMS) was prepared, characterized and used for cadmium (II) quantitative determination in aqueous media. The measurements were made using square wave anodic stripping voltammetry, which implies two steps: an open circuit analyte accumulation on the electrode and the electrolysis of the accumulated cadmium and its determination. The influence of some experimental variables such as carbon paste composition, working solution pH, the supporting electrolyte concentration, accumulation potential and accumulation time were studied. The prepared and characterized modified carbon paste electrode demonstrated a linear response over the concentration range between 80 and 2000 ppb cadmium, with an accumulation time of 120 s and an accumulation potential of -1.4 V vs. ESC. The effects of potential interfering ions were studied. The prepared electrode was used for cadmium determination in natural and residual water samples and spiked samples, with good results in accuracy and precision studies.*

*Keywords: modified carbon paste electrode, organofunctionalized silica, cadmium, square wave anodic stripping voltammetry*

Electrochemical stripping analysis is known as the most sensitive electroanalytical technique and proved to be adequate for toxic trace metal monitoring and determination.

This electroanalytical technique involves a variety of electrochemical approaches, being characterized by a step of preconcentration (accumulation) onto the electrode surface, prior to voltammetric, potentiometric or chronoamperometric measurement and quantification [1-6]. The electrochemical stripping analysis sensitivity is ascribed to the preconcentration step. This step is followed by measurement step, in which the accumulated metals are stripped off the electrode surface during scanning a suitable potential function.

The main advantage of electrochemical stripping analysis compared to other analytical techniques is the preconcentration factor. It can bring very useful information about total metal content, and also about their chemical forms in different media (labile fraction, speciation) [7-9].

Anodic stripping voltammetry, the most popular stripping voltammetric technique, is an effective technique for the determination of trace amounts of metal ions [2, 3, 5, 10]. Two basic electrode systems, the mercury-film electrode (MFE) and hanging mercury drop electrode (HMDE), were developed and gained wide acceptance in the stripping voltammetry [2-6]. Good properties of mercury, such as reproducibility and purity of the surface, high hydrogen overpotential and possibility of amalgam formation, make it an excellent electrode for anodic stripping voltammetry.

In spite all these advantages, because of the toxicity of mercury, future regulations and occupational health considerations may severely restrict the use of mercury as

an electrode material. In addition to toxicity, mercury has other limitations such as difficulties in the determination of metals with dissolution potentials that are more positive than that of mercury (Ag and Au) and problems with metals insoluble in mercury (As) [10, 11]. Another disadvantage of mercury electrode for anodic stripping voltammetry is the formation of intermetallic compounds in amalgams [10].

As a result, new alternative electrode materials with similar performances are highly desired. Different bare carbon, gold or iridium electrodes have been used as possible alternatives to mercury [12-15]. The basic problems that restrain the application of solid electrodes in ASV are low cathodic potential limit, multiple peaks and large backgrounds contributions [16].

Chemically modified electrodes (CME) are also widely used in analytical chemistry [17, 18]. Different approaches for working electrode modification, including adsorption [19, 20], covalent bonding [21, 22], coating the surface electrode with thin polymeric films [23-30] and embedding suitable functional ligands in a conductive porous matrix [31-34] have been developed to overcome the above-mentioned problem for solid electrodes. The number of functional groups on adsorbed films may be limited and the stability and durability of the adsorbed films may be poor. Polymeric films appeared in 1978 as an efficient possibility to obtain modified electrodes by coating their surface, independently, [35, 36]. There are many reasons for polymer films popularity as modifier agents, first of all their high stability towards adsorbed films and the films can be insoluble in the contact solution, their degradation not being a problem [37].

It has been shown that trace and ultra-trace amounts of various metals can be determined by means of anodic

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stripping voltammetry using chemically modified carbon paste electrodes [31-34, 38-47], screen printed electrodes [48-52] and nanotubes [53, 54].

Despite the availability of a number of chemically modified carbon paste electrodes for the determination of trace amounts of metals from natural waters, there is still a need for the development of new electrodes for the metals determination that are superior in accuracy, precision and speed at the concentration levels commonly encountered in different natural samples. The above-mentioned methods surmounted some mentioned problems; however, some of these modified carbon paste electrodes require additional steps for their preparation [33, 46, 47], require a medium exchange [10, 44], need long accumulation time or renewal time [10, 47], have high detection limits and narrow working ranges [34, 45]. A drawback of organic ligand modified electrodes is that the ligands in these sensors are in contact by weak physical interactions or in loose association with the electrode. This may be easily degrade over time from depletion of ligand bearing material, especially in some solvents in which these ligands have a high degree of solubility.

Chemically modified electrodes involving organofunctionalized silica based materials have drawn much attention in the field of stripping voltammetry [55, 56]. These materials combine the rigid three dimensional structure of inorganic lattice with the intrinsic chemical properties or organic moieties [57-64].

In this paper, the realization, characterization and application of a carbon paste electrode modified with acetyl-acetone functionalized HMS mesoporous silica for Cd(II) quantitative determination from natural and residual water samples are presented.

## Experimental part

### Apparatus

All the voltammetric measurements were carried out with an voltammetric analyzer, Voltalab PST 050 Radiometer, controlled by VoltaMaster 4.0 software, in a 20 mL capacity thermostated glass cell at 25°C, using a carbon paste modified with HMS silica functionalized with AcAc as working electrode, a saturated calomel as reference electrode (SCE) and a platinum wire as auxiliary electrode. High purity argon (Linde Gas 5.0) was used for solutions deaeration. Square wave anodic stripping voltammetry was used for the stripping step.

### Reagents and solutions

All the necessary solutions were prepared with water purified in a Millipore Mili-Q system. All the chemicals were of analytical grade. The supporting electrolyte for voltammetric experiments was a Britton-Robinson buffer solution (pH 7.00). A "Certipur" (Merck) stock solution containing  $1000\mu\text{g}\cdot\text{L}^{-1}$  Cd(II) was used for daily preparation of working standard solutions by appropriate dilution.

Graphite powder (with particles diameter < 20  $\mu\text{m}$ ) (Fluka) and paraffin oil (Merck) were used for the preparation of carbon paste electrodes. Dodecylamine (Aldrich), tetraethoxysilane (TEOS) (Fluka), 3-aminopropyl-triethoxysilane (APTES) (Aldrich) and 3-bromo-2,4-pentandione were used to functionalize the HMS silica.

For modifying the carbon paste electrode, hexagonal mesoporous silica (HMS) was synthesised using dodecylamine ( $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$ ) as a template and TEOS as a silica precursor and ethanol as co-solvent by a procedure reported by the authors in a previous work [65]. For the acetyl-acetone functionalized HMS silica, the HMS silica was firstly silanized with APTES. Thereafter, the  $\text{NH}_2$ -

HMS solid was reacted with 3-bromo, 2,4-pentandione in order to obtain the  $\text{AcAcNH}_2$ -HMS mesoporous silica by a procedure reported in the above mentioned work [65].

### Preparation of the unmodified and modified carbon paste electrodes

Unmodified carbon paste electrodes were prepared by thoroughly mixing of graphite powder with a few drops of paraffin oil until a homogenous paste was obtained. The carbon paste electrode was finally obtained by packing the paste into a plastic tube (2 mm interior diameter) equipped with a piston. A copper wire served as an external electric contact. Carbon paste electrodes modified with organofunctionalized HMS silica were prepared in a similar manner: the HMS silica or  $\text{AcAcNH}_2$ -HMS, respectively (1:6 ratio of HMS or  $\text{AcAcNH}_2$ -HMS : graphite powder) were mixed with graphite powder and paraffin oil, until a homogenous paste was obtained.

The surface was smoothed on a bond paper. When necessary, a new surface was obtained by pushing an excess of paste out of the tube, removing this excess, and again mechanically polishing the electrode surface.

## Results and discussion

### Voltammetric behaviour of Cd(II) on unmodified and organofunctionalized silica modified carbon paste electrodes

Preliminary voltammetric experiments were carried out to identify the general features of Cd(II) behaviour on unmodified and modified electrodes with  $\text{AcAcNH}_2$  functionalized HMS silica, in Britton-Robinson buffer (pH 7.00) aqueous medium.

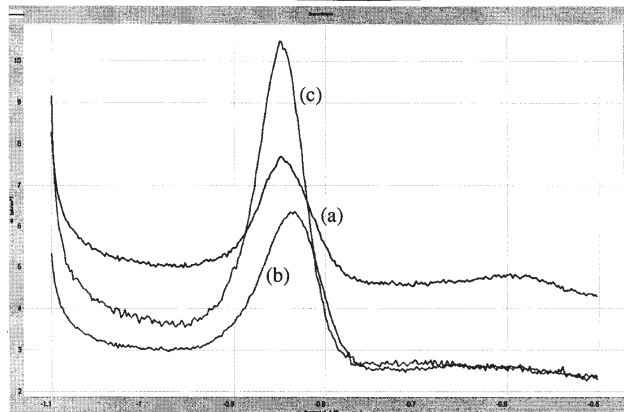


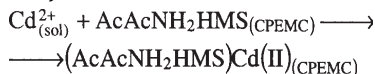
Fig. 1. Square wave anodic stripping voltammograms obtained for 1 ppm Cd(II), in Britton-Robinson solution (pH = 7.00): (a) carbon paste electrode; (b) HMS silica modified carbon paste electrode; (c)  $\text{AcAcNH}_2$ -HMS modified carbon paste electrode; accumulation potential, -1.4 V vs. ESC; accumulation time, 120 s

Figure 1 presents square wave anodic stripping voltammograms of Cd(II) on: carbon paste electrode (a), HMS modified carbon paste electrode (b) and  $\text{AcAcNH}_2$ -HMS modified carbon paste electrode (c). Anodic stripping voltammetric signals were obtained in all cases: (a) -0.846 V; (b) -0.836 V; (c) -0.848 V vs. SCE. Comparing the peak current intensity it can be seen that the one obtained in case (c) is 2.6 times higher than in case (a) and 2 times higher than in case (b). The peak from (c) voltammogram is much better defined, comparing to those from (a) and (b) voltammograms, which are wider.

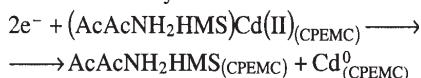
The increase in anodic current at the  $\text{AcAcNH}_2$ -HMS modified electrode demonstrated that organic moiety  $\text{AcAcNH}_2$  directly bonded on HMS plays an important role in the Cd(II) accumulation process on the electrode surface. In these conditions, the reaction mechanism at

the surface of AcAcNH<sub>2</sub>-HMS modified electrode could be assigned to the following steps:

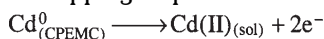
1. rapid preconcentration (accumulation) step (open circuit)



2. electroanalytical accumulation step



3. stripping step



#### Influence of carbon paste composition

The influence of the carbon paste composition on the voltammetric response of the organofunctionalized silica modified electrode was evaluated by square wave anodic stripping voltammetry. Electrodes with different percentage of modifier were prepared and their voltammetric signals were examined under the same conditions. The maximum peak current intensity and a well defined peak were obtained for an organofunctionalized silica: graphite powder ratio of 1:6. At higher modifier concentrations (> 17%) a decrease in the peak current intensity was observed. This is probably owed to the reduction of conductive area at the electrode surface.

#### Supporting electrolyte nature and concentration and pH influence

Voltammetric behaviour of Cd (II) was investigated in different supporting electrolytes: 0.1 mol·L<sup>-1</sup> HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, 0.1 mol·L<sup>-1</sup> KCl, KNO<sub>3</sub>, CH<sub>3</sub>COONa and Britton-Robinson buffer at different pH values. Anodic stripping voltammetric peaks observed in most of the supporting electrolytes were poorly defined and not sufficiently intense. pH influence on anodic stripping voltammetric signals was evaluated for 1 ppm Cd(II) concentration, in Britton-Robinson buffer solutions with pH values between 2.53 and 9.00.

Peak current intensity and peak potential dependences on pH variation are presented in figure 2. It can be observed that at pH range of 2.56 to 7.00 the peak current intensity increased with increasing pH; after that pH value, the peak current intensity decreased with increasing pH. Peak potential shifts almost linear towards more cathodic values with increasing pH. The optimal pH value founded and used for further studies was 7.00.

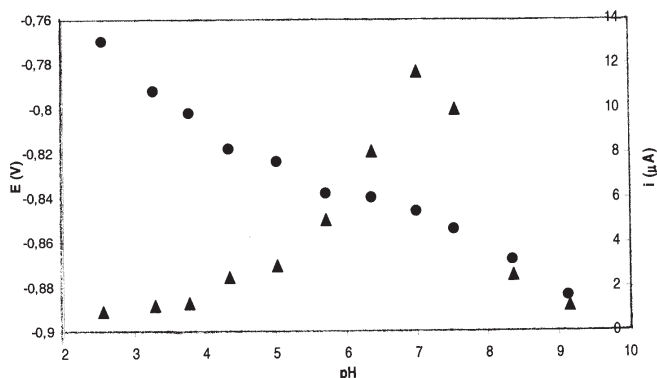


Fig. 2. Influence of pH on anodic peak current intensity (▲) and potential (●) of 1 ppm Cd<sup>2+</sup>, in Britton-Robinson buffer, -1.4 V vs. SCE accumulation potential and 120 s accumulation time

#### Accumulation potential influence

The influence of accumulation potential on the peak current intensity of Cd(II) was studied over the potential range between -0.800 and -1.600 V vs. SCE, in the same working conditions. When Cd(0) was oxidized, it was observed that for a -1.4 V vs. SCE accumulation potential was obtained the highest anodic peak current intensity (fig. 3 (●)); -1.4 V was the value chosen as accumulation potential in further studies.

#### Accumulation time influence

The influence of accumulation time on the anodic peak current intensity for 1 ppm Cd<sup>2+</sup> was also examined. Figure 3 (◆) shows that peak current intensity increased almost linearly with increasing accumulation time from 0 to 270 s and then remaining almost constant. For all subsequent measurements for the accumulation time a value of 120 s was used, as a compromise between measurements sensitivity and analysis time.

#### Calibration curve, linearity, detection and quantification limit, precision and accuracy

To verify the linear relationship between peak current intensity and cadmium concentration, a calibration curve was realized, using the optimal parameters previously established.

The homogeneity test, that verifies if there are significant differences at working range limits [66], was carried out to establish the working concentrations range. A preliminary working range was established (0.08 – 2 ppm Cd<sup>2+</sup>) and measurements of Cd(II) peak current intensity were done using 10 replicates for minimum concentration level and 10 for the maximum one. Testing value PG was calculated (5.19) and was compared with the tabled value of F function (5.35). As PG < F, subsequently the concentration range was correctly chosen.

To decide whether the method presents linearity or not the linearity statistical test was carried out. The current peak values for 10 standard solutions, whose concentrations were equidistant dispersed on the whole working range, there were measured. After that, the statistical parameters of the linear ( $y = a + bx$ ) and the nonlinear ( $y = a + bx + cx^2$ ) functions were calculated (table 1).

In the literature there are several calculation methods for detection limit (DL) and quantification limit (QL) determination [66]. Here the data from the linearity study were used. In this case  $DL = 3s_0/b = 52.5$  ppb and  $QL = 10s_0/b = 175.1$  ppb, where  $s_0$  is standard deviation of the intercept and  $b$  is the calibration curve slope.

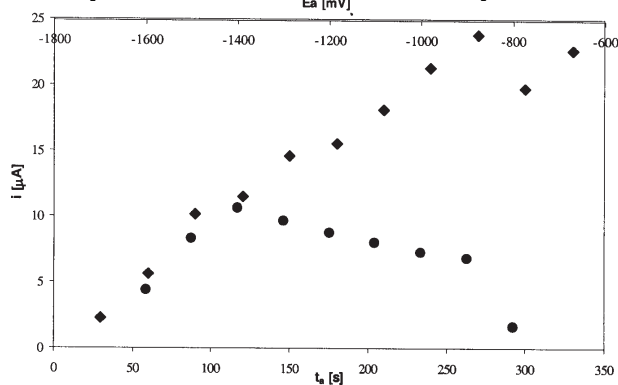


Fig. 3. Influence of accumulation potential (●) and accumulation time (◆) on stripping peak current intensity for 1 ppm Cd<sup>2+</sup>, pH 7.00 Britton-Robinson buffer

**Table 1**  
LINEAR AND NONLINEAR REGRESSION DATA FOR Cd(II) QUANTITATIVE DETERMINATION BY SWASV

Linear function $y = 12.839x - 1,6085$		
$b = 12,8394; s_b = 0,18320$	$a = -1,60848; s_a = 0,2248$	$R = 0,9976; R^2 = 0,9951$
$S_{y1} = 0,5541$	$S_{x0} = 0,0432$	$V_{x0} = 4,02 \%$
Nonlinear function $y = 1.3336x^2 + 10.079x - 0.6513$		
$a = -0.6513; s_a = 0.2188$	$b = 10.0790; s_b = 0.4859$	$c = 1.3336; s_c = 0.2277$
$E = 12.9442$		$R = 0.999; R^2 = 0.998$
$S_{y2} = 0.3586$	$S_{x0} = 0.0277$	$V_{x0} = 2.58 \%$

$s_a, s_b, s_c$  - standard deviation of  $a, b, c$  coefficients,  $R$  - correlation coefficient,  $S_{y1}$  - residual standard deviation for the  $y$  estimate in the linear regression,  $S_{x0}$  - method standard deviation,  $V_{x0}$  - method variation coefficient,  $E$  - sensitivity at the center of the working range,  $S_{y2}$  - residual standard deviation for the  $y$  estimate in the nonlinear regression

The method *accuracy* was evaluated from the recovery degree of the added analyte from spiked samples. For recovery calculation the equation:  $r\% = [(C_f - C_u)/C_A] * 100$ , ( $C_f$  - analyte concentration in spiked sample,  $C_u$  - analyte concentration in unspiked sample and  $C_A$  - spike concentration) was used. Recovery values lied between 90.70% and 100.69%, with a recovery average of 96.92% and a standard deviation of 1.89% (3 additions of 0.5 ppm Cd(II) for each of the 3 identical standard solutions of 0.5 ppm Cd(II)).

In this study, the method *precision* was evaluated only on repeatability level. Repeatability is expressed as percentage relative standard deviation (RSD %) and the value obtained after realizing the experiments and the calculations was 1.90 %.

#### Interferences

Possible interference from different metallic species (Cu(II), Co(II), Mn(II), Pb(II), Sn(II), Tl(I), Zn(II)) on 1 ppm Cd(II) anodic peak current intensity was investigated. The obtained results are presented in table 2.

In the presence of Cu(II) and Co(II), severe decreasing and even suppression of Cd(II) current peak were observed, the influence being constant at every investigated concentration.

Mn(II), Pb(II) and Zn(II) did not interfered in analyte determination at the same concentrations as Cd(II) (1

ppm) due to a facile accumulation of the analyte. At these ions concentrations of 10, respectively 100 times bigger than that of Cd(II), a significant decrease of Cd(II) signal was observed, presumably due to the competition with Cd(II) for active sites.

The presence of Sn(II) and Tl(I) at concentrations much higher than that of Cd(II) led to huge increase of Cd(II) signals, due to signals overlap.

The observed effects could be related with the interactions of the metal ions with the silica modifier. In some cases, the separation of the peaks suggested that a simultaneous analysis of some of these ions can be performed. The interference may be bypassed using standard addition procedures.

#### Analysis of cadmium in natural and residual water samples

The proposed modified electrode was applied for SWASV determination of Cd(II) in natural surface water samples from Arges river and in residual water samples from a Bucuresti plant.

The water samples were mixed with the same volume of a Britton-Robinson buffer solution (pH 7.00) before analysis. The previously optimized parameters for Cd(II) determination are presented in table 3.

The results obtained for Cd(II) quantitative determination using standard addition method from natural, respective

**Table 2**  
EFFECT OF SOME METALLIC CATIONS ON 1 ppm Cd(II) SIGNAL UNDER OPTIMIZED SWASV CONDITIONS, COMPARED WITH SOLUTION THAT DID NOT CONTAIN THE INTERFERENTS

Interferent	$C_M^{z+}/C_{Cd}^{2+}$	% of Cd(II) signal*
Cu <sup>2+</sup>	1	7,4
	10	-
	100	-
Co <sup>2+</sup>	1	18,9
	10	-
	100	-
Mn <sup>2+</sup>	1	112,0
	10	72,0
	100	32,9
Pb <sup>2+</sup>	1	106,2
	10	17,7
	100	34,6
Sn <sup>2+</sup>	1	70,3
	10	122,9
	100	223,6
Tl <sup>+</sup>	1	140,3
	10	379,6
	100	672,6
Zn <sup>2+</sup>	1	93,4
	10	14,5
	100	5,3

\*in relation to a 1 ppm Cd(II) in pH 7.00 Britton-Robinson buffer solution, without interferent

**Table 3**  
THE OPTIMIZED PARAMETERS FOR Cd(II) QUANTITATIVE DETERMINATION USING SWASV AND AcAcNH<sub>2</sub>-HMS MODIFIED CARBON PASTE ELECTRODE

Parameter	Optimized value
Accumulation potential	-1.4 V vs. ESC
Accumulation time	120 s
Scan rate	50 mV/s
Pulse amplitude	50 mV
Ramp step amplitude	1 mV
Ramp step duration	0.02 s
Supporting electrolyte and pH	Britton-Robinson buffer, pH 7.00

**Table 4**  
Cd(II) QUANTITATIVE DETERMINATION FROM NATURAL WATER SAMPLES

Replicate	Addition number	C <sub>Cd<sup>2+</sup></sub> (ppm)		R (%)
		Added	Found	
1	0	-	0.213	-
	1	0.291	0.430	85.4
	2	0.566	0.716	91.9
	3	0.826	0.978	94.1
	4	1.071	1.049	81.7
2	0	-	0.252	-
	1	0.291	0.412	75.9
	2	0.566	0.679	82.9
	3	0.826	0.869	80.6
	4	1.071	1.387	104.8

**Table 5**  
Cd(II) QUANTITATIVE DETERMINATION FROM RESIDUAL WATER SAMPLES

Replicate	Addition number	C <sub>Cd<sup>2+</sup></sub> (ppm)		R (%)
		Added	Found	
1	0	0	0.138	-
	1	0.291	0.433	100.89
	2	0.566	0.733	104.05
	3	0.826	0.956	99.14
	4	1.071	1.167	96.48
2	0	0	0.137	-
	1	0.291	0.424	99.21
	2	0.566	0.696	99.11
	3	0.826	0.923	95.90
	4	1.071	1.150	95.26
3	0	0	0.137	-
	1	0.291	0.418	97.54
	2	0.566	0.703	99.97
	3	0.826	0.943	97.88
	4	1.071	1.150	95.19
4	0	0	0.137	-
	1	0.291	0.414	96.79
	2	0.566	0.719	102.28
	3	0.826	0.891	92.49
	4	1.071	1.093	90.47

residual water samples, are presented in table 4 and table 5.

For the natural surface water sample an average concentration of 0.2325 ppm (11.86 % RSD) and an average recovery of 87.16 % (10.65 % RSD) were obtained. In the case of the residual water sample the average obtained concentration was 0.13725 ppm (0.36 % RSD), with an average recovery of 97.67 % (3.55 % RSD).

These results indicate that the proposed electrode can be used for quantitative determination of Cd(II) from water samples, under the optimized conditions and using calibration curve and standard addition approach (in order to eliminate the interferences and the matrix effect).

### Conclusions

In this paper the authors emphasize that AcAcNH<sub>2</sub> functionalised silica can be used in the preparation of

modified carbon paste electrodes and that these electrodes can be used for Cd(II) determination in water samples using SWASV procedure. The Cd(II) oxidation peak was obtained at -0.85 V vs. SCE, in Britton-Robinson buffer (pH 7.00). The best results were obtained in the following optimised conditions: -1.4 V vs. SCE accumulation potential, 120 s accumulation time, 50 mV/s scan rate, 50 mV pulse amplitude, 1 mV ramp step amplitude, 0.02 s ramp step duration. A linear range between 80 and 2000 ppb ( $7.12 \cdot 10^{-7} - 1.78 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) Cd(II) was obtained, with a 52.5 ppb detection limit.

An accurate and reproducible Cd(II) SWASV determination from natural and residual water samples can be done using standard addition method, taking into account the sample matrix and the concentration level of potential interfering ions.

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