

CHEMICAL FRACTIONATION OF CADMIUM IN NATURAL WATERS FROM PARANÁ RIVER AT CORRIENTES-ARGENTINA

Pellerano¹, R. G.; Romero¹, C. H.; Acevedo¹, H. A.; Vázquez¹, F. A. and
Marchevsky², E. J.

¹*LABQUIAM, Laboratorio de Química Ambiental, FACENA, UNNE, AV. Libertad 5450,
Corrientes (3400), Argentina.*

²*Universidad Nacional de San Luis, Facultad de Química Bioquímica y Farmacia,
Chacabuco y Pedernera, San Luis (5700) Argentina*

E-mail: marchev@unsl.edu.ar

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Abstract

Paraná River (Spanish Río Paraná), the second longest river in South America is a very important source of water in Argentina. The present paper proposes a technique that combines Solid Phase Extraction (SPE) with Solid Phase Spectrophotometry (SPS) for cadmium fractionation in natural water. The concentrations of cadmium bound to humic substances and of free metal ions were determined from their sorption-elution from chromatographic support resin (Silica C18). Cadmium determination is based on Solid Phase Spectrophotometry (SPS) with 1-(2-pyridylazo)-2-naphtol (PAN) sorbed on anionic resin. It was optimized using Response Surface Methodology (RSM) based on sequential experimental Doehlert design. Recoveries were obtained for all samples studied. The detection limit (DL) was $1.0 \mu\text{g L}^{-1}$ for Cd(II). The precision for 10 replicate determinations at $10 \mu\text{g L}^{-1}$ cadmium levels was 3.2% relative standard deviation (RSD).

Keywords: Cadmium, chemical fractionation, Paraná river, solid phase spectrophotometry.

Resumen

El río Paraná es el segundo río mas largo de Sudamérica (después del Amazonas) constituyendo así una de las fuentes más importantes de agua dulce para los países que recorre, entre ellos la Argentina. En el presente trabajo se propone una técnica

innovadora que combina a la extracción en fase sólida (con Silica C-18) y a la espectrofotometría en fase sólida con 1-(2-piridilazo)-2-naftol (PAN) sorbido sobre una resina aniónica Dowex 1X8, para lograr el fraccionamiento químico en aguas de este río. La metodología correspondiente a la medición de la concentración de cadmio se optimizó utilizando un modelo de superficie de respuesta, basado en el diseño de Doehlert. El método demuestra poseer una excelente performance y sencillez. El límite de detección fue de $1.0 \mu\text{g L}^{-1}$ y la precisión se cuantificó midiendo la desviación estándar relativa para 10 réplicas, el valor alcanzado fue de 3.2%.

Palabras clave: Cadmium, fraccionamiento químico, río Paraná, espectrofotometría en fase sólida.

Introduction

In order to understand the environmental chemistry of Cadmium it is necessary to characterize the proportions and forms of all its various species under the diverse range of possible conditions in a natural system. Cd(II) is present in natural waters in a wide range of species varying in particle size and chemical nature. Fractionation allows to identify the fractions (classes) of Cd(II) that exist in the distinct groups and to determine the sum of their concentrations in each class by the particular techniques used. However, the speciation process corresponds to a fractionation operation [1,2], namely, the classification of an analyte (metal) or a group of analytes (metals) from a certain sample according to physical or/and chemical properties.

Fractionation studies are based on the identification of operationally defined fractions of metal forms having similar chemical properties and reactivity. Solid Phase Extraction [3] (SPE) offers the possibility of performing a simultaneous enrichment step, and distinguishes different metal forms or groups with the same chemical characteristics in studies for elucidating metal bioavailability in water samples. This is due to the fact that different resins interact with different metal species [4]. The structural characteristics are the key of the preconcentrated natural substances [5]. For example, the structure of the humic substances and their complexes permits the extraction according to their hydrophobic characteristics (attributable to the aromatic groups) and allows the separation with adsorption onto polymeric resins [6], or by partition onto chromatographic supports as octadecyl groups bound to silica. It must be emphasized that the extraction with column defines a fraction of the species [7], but by no means this correspond to a unique chemical entity.

Silica C18 was chosen as the column filling, due easy elution with methanol, zero retention of cations, acceptable capacity and pre-concentration efficiency for humic acids [8]. The different fractions of Cd(II) were determined by Solid Phase Spectrophotometry [9] (SPS) sensor. The SPS methodology includes the analyte preconcentration onto a solid phase, whit a previous step of chemical reaction to produce a chromogenic compound, and the subsequent absorbance measurement on solid phase. Finally, the proposed method was applied to water samples from Paraná River in Argentina.

Experimental

Reagents and chemicals

All reagents used were of the highest available purity and at least of analytical grade. Working standard solutions were prepared by stepwise dilution from 1000 mg L^{-1} Cd(II) stock standard solution immediately before use.

A solution of 1-(2-pyridylazo naphthol) (PAN, Aldrich) $10^{-3} \text{ mol L}^{-1}$ was prepared

by dissolution in ethanol.

A buffer solution was prepared by diluting 3.0 mol L⁻¹ ammonium hydroxide solution, adjusted to pH 9.5 with hydrochloric acid solution. Triton X-100 (Fluka) 5% v/v was used as non-ionic tensioactive solution.

SPS resin - *Dowex IX8 anionic resin (200 – 400 mesh)* was used in the chloride form, for the fixation of Cd-PAN complex on the SPS sensor. The resin was washed repeatedly with water, and then treated with 2 M HCl during 24 hours and finally with water until the waste was free from chloride. The resin was air-dried in a polyethylene container.

Reversed phase SPE resin - *Silica C-18 100 mesh* was used for retention of Cd-humic acid (Cd-HA) complexes. The sorbent (0.400 g) suspended in CH₃OH was slurry loaded into the columns, washed with 10 mL of CH₃OH, rinsed with 20-30 mL of bi-distilled water and then conditioned with buffer at the pH of the subsequent experiment.

Apparatus

A single-beam Metrolab® 1700 microprocessor-controlled UV-Vis spectrophotometer with 1-mm optical path length quartz cells from Hellma was used for all absorbance measurements. It was connected to a Pentium 586 personal computer by means of a serial port for data acquisition and data processing using Metrolab SF-170 program [10].

A home made rotating agitator and an Altronix® pH-meter fitted with a glass/saturated calomel electrode were also used. Data analysis was performed by employing the software UNSCRAMBLE version 6.0 [11] for the regression model, and the experimental design.

Fractionation of Cd(II) in river water

The water samples were filtered through 0.45 µm membrane filter, then the filtrates were passed through the adsorbent column packed with Silica C-18 for reversed phase SPE and the effluent was reserved for following analysis. Species retained on the resin were eluted with methanol for the determination with SPS. The negative charge of the humic substances and their complexes allows the extraction by ion exchange and their hydrophobic characteristics – attributable to the aromatic groups- permit the separation by partition onto chromatographic supports such as octodecyl groups bound to silica. The speciation scheme is illustrated in figure 1. The method was applied at natural pH (varying from 6.90 to 7.40) to these samples.

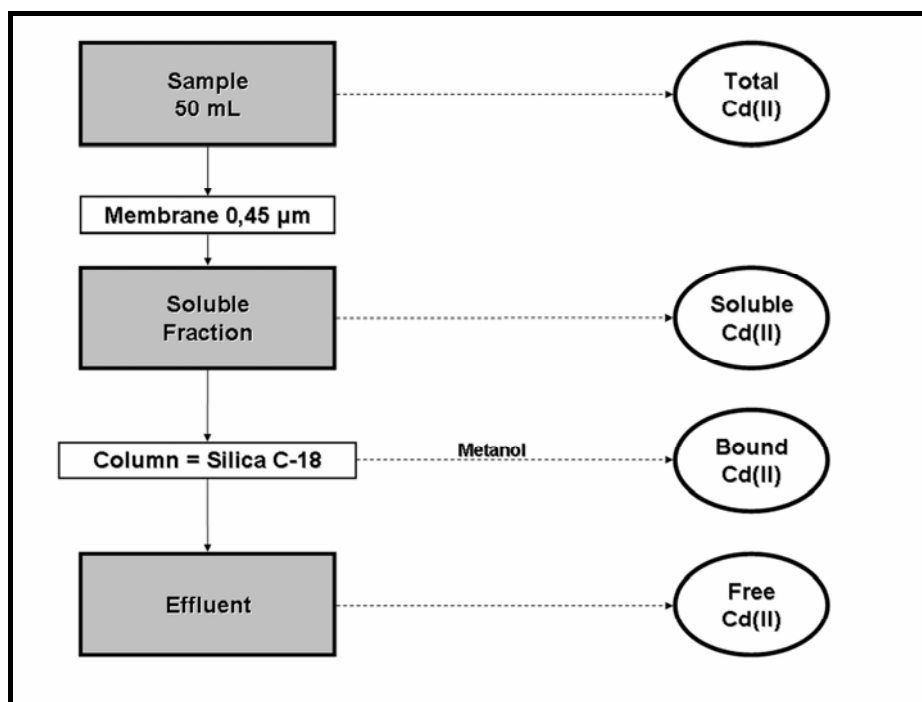


Figure 1. Flow scheme of fractionation analysis for water samples

Suspended particles

The water samples were filtered through a 0.45 μm membrane filter to separate the metal bound to suspended particles. The measurements were performed by difference between the total concentration of Cd(II) (Cd_T) and filtered cadmium (Cd_f)

Separation of metal-humic complexes

A 50 mL aliquot of filtrated solution was passed through the column for humic complexes retention (with Silica C-18), to adsorb the metal bound to humic substances. The metals sorbed on the resin were eluted with 2 mL of methanol. Then each methanolic fraction was digested and determined by SPS sensor.

Free metal ions

Free cadmium ions were determined on the aqueous effluent, by SPS as stated above, without digestion.

Sampling and Handling

Paraná River is located in South America, with a length of 4,880 km, draining an area of roughly 2.8 million km^2 . Its width and depth are variable depending on the geological composition of its bed. It is formed at the junction of the Paranaíba and Grande rivers in south central Brazil, it follows Paraguay's borders with Brazil and then Argentina. It then flows generally southwards into the Río de la Plata estuary. The water samples were collected at the east coast of Paraná River at Corrientes ($27^\circ 46' \text{ S}$, $58^\circ 83' \text{ W}$) Argentina. The measuring station selection was based on the availability and facility of latest procedures. Water sampling was carried out from March 2005 to February 2006, at different year's seasons, at the same point at Corrientes, Argentina.

All samples were collected in a polyethylene container carefully cleaned with nitric acid and stored at 4 $^\circ\text{C}$ until analysis. Analyses were performed with the least

possible delay. Usual general precautions were taken to avoid contamination.

Results and Discussion

In order to determine the Cd(II) content in each fraction, we used solid phase Spectrophotometry, that was optimized by response surface methodology. A brief description of the sensor design is included.

Chemical variables Optimization and Sensor design

pH dependence and buffer selection

Previous experiments for complex formation indicate that the optimum pH interval is 8.8 to 10.5. The pH 9.4 was chosen for subsequent determinations and ammonia – chloride of ammonium solution (pH 9.2) was selected as the buffer solution [13].

Screening studies

A general procedure was applied using varying experimental conditions. The following factors were evaluated: PAN concentration, tensioactive concentration (Triton X-100 was chosen as tensioactive solution) and potassium iodide concentration. A two-level full factorial design of three factors (2^3) in duplicate was used. Maximum and minimum levels of each factor were chosen according to data from previous experiments. The significance of effects was checked by analysis of the variance (ANOVA) and using p-value significance levels. The ANOVA results are presented in Pareto chart of main effects, as shown in figure 2.

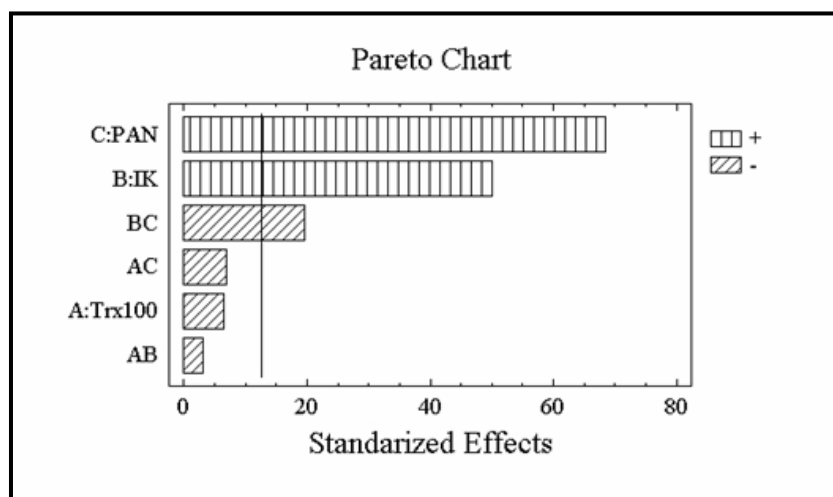


Figure 2. Pareto chart for net absorbance

The results demonstrate that the variation in PAN and KI concentration are significant. The interaction between PAN and KI concentrations is statistically significant too. The factor Tritón X-100 is not significant in this case.

PAN and KI concentrations

The Doehlert designs [14], which have already been used in optimization

processes [15 – 18], were applied for the optimization of chemical variables according to the screening analysis. (Potassium iodide and PAN concentration).

All experiments were carried out using 50 ml of standard solution containing 5 μg of cadmium. Two variables (PAN concentration and potassium iodide concentration) were regarded as factors, and the experimental data were processed using the Unscramble program. Lagrange's criterion [19] was used for determination of the critical point of the second-order equation.

Doehlert matrix

Table 1 shows the proposed Doehlert design and the experimental results obtained for the net absorbance. The equation which fits the experimental values is

$$A_{net} = 0.695 + 0.0333[PAN] - 0.0090[KI] - 0.0067[PAN][KI] - 0.0156[PAN]^2 - 0.139[KI]^2$$

that illustrates the relation between net absorbance and the molar concentrations of PAN (multiplied by 10^{-6}) and of KI (multiplied by 10^{-2}) (see Figure 3).

Table 1. – Doehlert design

Experiment	PAN x 10^{-6} M	KI x 10^{-2} M	Net absorbance
1	2 (-1)	2 (0)	0,331
2	4 (- 0.5)	3 (+1)	0,421
3	4 (- 0.5)	1 (-1)	0,412
4	6 (0)	2 (0)	0,695
5	8 (+ 0.5)	3 (+1)	0,551
6	8 (+ 0.5)	1 (-1)	0,596
7	10 (+ 1)	2 (0)	0,574

The software indicates the presence of a maximum which corresponds to 7.113×10^{-6} in PAN and 1.941×10^{-2} in KI. These coordinates correspond to the stationary point, i.e. in the center of an optimum field response, therefore the PAN and KI concentrations were chosen as optimum.

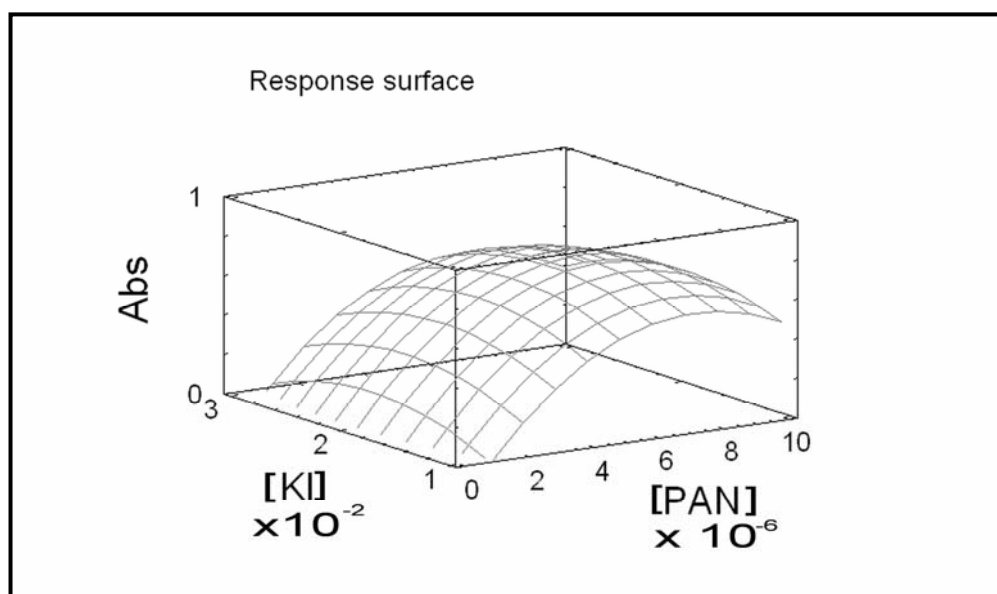


Figure 3. Response Surface

Other experimental conditions

The optimum stirring time was 20 min for the 50 mL sample volume. The fixed complex is stable for at least two days after equilibration. The addition sequence of reagents did not affect the results and the sequence used here was: Triton X-100 – KI – PAN – Buffer – Resin. The solid support level in the cell is a very important variable [20, 21]. This level has to be sufficiently high to allow the light beam to pass through the resin (and not the homogeneous solution), since if it is too high it lowers the absorbance value, as usual. In this case, the optimum height of the resin in the cell was 20 mm from the bottom cells.

General procedure for Cd(II) determination

The mixture solution was diluted to 50 mL with bi-distilled water. Finally 70 mg of resin were added and the solution was mechanically shaken for 20 min. The colored resin was transferred into a 1 mm quartz cell and the absorbance was measured at 555 nm (the absorption maximum of the Cd(II)-PAN complex species in the resin phase) and 800 nm (the absorption of the resin is proportional to the resin packed in the cell). A blank of bi-distilled water as a reference was utilized.

Analytical parameters

The precision for 10 replicate determinations was 3.2% relative standard deviation (RSD) calculated from the net absorbance obtained. The calibration graph results linear, with a correlation coefficient of 0.9995, at levels near the detection limits, up to at least 100 $\mu\text{g L}^{-1}$. The detection limit calculated by using 3σ recommendations [22], was established from the absorbance measurements from five different determinations on the blank solution. The value of DL obtained for 50 mL of sample volume was 1.0 $\mu\text{g L}^{-1}$.

Effect of foreign ions

A study of the potential interferences in Cd(II) determinations was performed. A relative error of less than 5% was considered to be within the range of experimental error, so the tolerated level was taken as the highest amount of the tested ion with a signal variation of less than 5%. The results are summarized in table 2.

Table 2. Effect of foreign ions on the determination of $20 \mu\text{g L}^{-1}$ of Cd (II) ($V = 50 \text{ mL}$)

Foreign ions	Tolerance level $\mu\text{g L}^{-1}$
Cl^- , NO_3^- , NO_2^- , SiO_3^- , PO_4^{3-} , CO_3^{2-} , HCO_3^- Ca(II), Mg(II)	> 10000
SO_4^{2-}	5000
F^-	2000
Al(III)	1000
Cr(III), Pb(II)	100
Fe(III)	50
Bi(III)	25
Zn(II)	10
Ni(II) Cu(II)	5
Co(II)	< 2

Analytical applications

The proposed method has been applied with good results to Cd(II) fractionation in natural waters during a time spanning the period from March 2005 to February 2006. Analysis of each water sample was made in triplicate. Total concentrations of Cd(II) were very low or undetectable in some cases, therefore it was necessary to process a larger sample volume in the fractionation scheme (300 mL) in order to improve the detection limit of the method in each fraction. The enrichment factor was 6. The results are shown in table 3. Periodical variations in the proportion of bound and free Cd(II) in the samples can be observed according to the sampling date.

Table 3. Determination of Cd(II) on river samples collected from Paraná River with proposed method and reference method (ICP-AES)

Sample	Proposed Method						Reference Method
	Cd(II) concentration found in each fraction * ($\mu\text{g} \cdot \text{L}^{-1}$)						
	Amount added	Particulate	Bound	Free	Total found	Recovery (%)	Total Cd(II) found
Mar-2005	--	1.5 ± 0.4	0.8 ± 0.1	0.2 ± 0.1	2.6 ± 0.2	101.9	2.55 ± 0.13
May-2005	--	1.1 ± 0.2	0.2 ± 0.1	< 0.1	1.4 ± 0.1	96.5	1.45 ± 0.15
Ago-2005	--	0.3 ± 0.2	0.2 ± 0.1	< 0.1	0.5 ± 0.1	90.9	0.55 ± 0.10
Oct-2005	--	0.4 ± 0.2	< 0.1	< 0.1	0.4 ± 0.2	88.8	0.45 ± 0.13
Dic-2005	--	2.1 ± 0.2	1.1 ± 0.1	0.4 ± 0.1	3.9 ± 0.1	100.0	3.90 ± 0.12
Feb-2006	--	2.0 ± 0.3	0.9 ± 0.1	0.4 ± 0.1	3.4 ± 0.2	98.5	3.45 ± 0.03

^a mean (n = 3)

Since certified reference materials (CRM) for Cd(II) fractionation are not available at the moment, an internal validation of the proposed method was established. The validation consists of a comparison of results obtained with the proposed method with those obtained by means of a reference technique. To check the trueness of the proposed SPS method, the analytical procedures were applied to the determination of total Cd(II) in different samples from the Paraná River. The results are in excellent agreement with those found by a reference technique for Cd(II) (ICP-AES) (Table 3).

The Cd(II) total content was determined in drinking water from Corrientes city (Argentina), the result was lower than the detection limit. Therefore, a recovery study was performed by adding three different amounts of Cd(II) (Table 4). The average percentage of recovery (mean of three determinations) was acceptable.

Table 4. Recovery study.

Sample	Cd added [$\mu\text{g} \text{L}^{-1}$]	Cd found [$\mu\text{g} \text{L}^{-1}$]	Recovery [%] ^a
Dinking water	0	< 1.0	--
from	2.5	2.6	104.0
Corrientes	5.0	4.9	98.0
	10.0	10.2	102.0

^aAverage values from three determinations

Conclusions

The technique was successfully applied to the determination of trace levels of Cd(II) in this region of Argentina. It has been shown that accurate and reliable results can be obtained. The method showed advantages of simplicity, high sensitivity in detection and a lower cost than other instrumental techniques. The results are strongly related to the values obtained with the reference method in all cases.

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