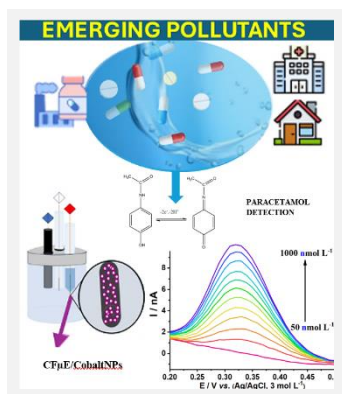


A. Alarcón-Vargas <sup>1</sup>, Patricio J. Espinoza-Montero <sup>1</sup>, (1) Escuela de Ciencias Químicas, Pontificia Universidad Católica del Ecuador, Avenida 12 de Octubre y Roca, Quito 170525, Ecuador, apalarconv@puce.edu.ec



Pollution of natural effluents by pollutants of emerging concern is a problem of great interest today. The development of an electrochemically modified carbon fiber microelectrode with cobalt nanoparticles is reported for the quantification of paracetamol at trace levels in tap water and river water, using differential pulse voltamperometry. We achieved a method of quantification of paracetamol and reproducible, which presents a linear range of 50.00 to 1000.00 nM with  $R^2 = 0.9981$ , a detection limit of 32.69 nM and quantification limit of 98.07 nM. The electrode is robust against real samples. This method is suitable for routine environmental control and evaluation of the quality of the treated water.

### Introduction

Paracetamol (N-acetyl-p-aminophenol, PCM) is an antipyretic and analgesic marketed without prescription and overdose of this medicine is one of the most common causes of poisoning worldwide (hepatotoxicity). High concentrations of this drug are common in natural effluents that pass through densely populated urban areas <sup>[1]</sup>. Currently, the development of sensors is one of the most efficient methods to detect drugs as they achieve high specificity, short response time, and low-cost analysis. In recent years, carbon-based nanomaterials such as carbon fibers have been tested as they have excellent conductivity, mechanical and thermal stability and achieve lower limits of detection (LD) <sup>[2]</sup> compared to traditional methods <sup>[3]</sup>. Therefore, in this work we report the development of a carbon fiber microelectrode (CFμE) modified electrochemically with cobalt nanoparticles (CFμE/Co) to detect PCM in complex matrices such as tap water and river water by differential pulse voltammetry (DPV).

### Material and Methods

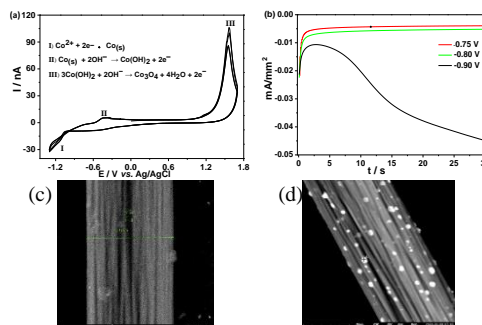
All electrochemical measurements (voltamperometric and electrochemical impedance spectroscopy (EIS)) were performed in a classic three-electrode cell. The working electrode a CFμE (PANEX 35), Ag/AgCl (3 M KCl) as the reference electrode and a graphite bar as a counter electrode. First, the working electrode was built with the methodology previously reported by our laboratory <sup>[2]</sup>. The modification of the surface of the working electrode was performed with chronoamperometry at different reduction potentials: -0.75, -0.80 and -0.90 for 30 s, in a solution of cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) of concentration 10 mmol  $\text{L}^{-1}$  in PBS (0.1 M) at pH 7.

### Results and Discussion

#### Electrodeposition of cobalt nanoparticles (CoNPs)

Fig. 1(a) shows the voltammetric behavior of CFμE during the growth of Co nanoparticles, where three peaks

are observed, related to the formation of different cobalt species and a cross-linking of the current that is indicative of the phenomenon of nucleation and growth of cobalt crystals. Based on the previous experiment, Co was electrodeposited on the CFμE surface by chronoamperometry at pH 7, Fig. 1(b).

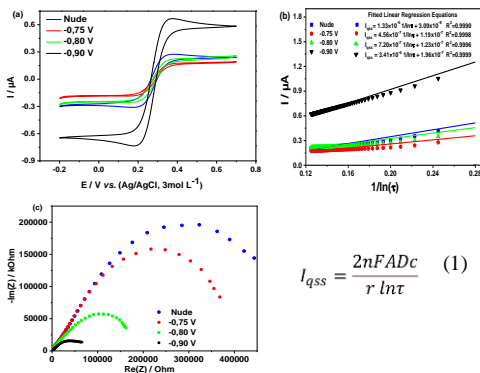


**Fig. 1.** (a) Voltamperometric behavior of CFμE at 10 mM  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and phosphate buffer 0.1 M pH 7,  $v = 50 \text{ mV/s}$ . (b) Electrodeposition of cobalt nanoparticles by chronoamperometry at different potentials. (c) Scanning electron microscope (SEM) micrographs of unmodified CFμE and (d) micrography of CFμE/Co at -0.90V.

#### Morphological and electrochemical characterization:

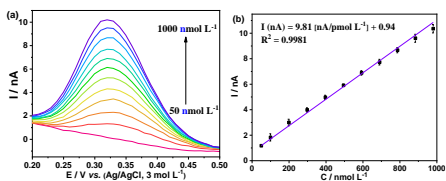
Scanning electron microscopy characterization reveals that CFμE/Co Fig. 1(d) presents spherical nanoparticles uniformly dispersed on the surface of the CFμE. Fig. 2(a) presents the electrochemical evaluation of the CFμE and CFμE/Co of -0.75, -0.80, -0.90 V against the redox pair  $\text{K}_4[\text{Fe}(\text{CN})_6]/\text{K}_3[\text{Fe}(\text{CN})_6]$  5 mmol  $\text{L}^{-1}$  en KCl 1 mol  $\text{L}^{-1}$  and present sinusoid symmetric voltametric responses of a microelectrode, confirming that the CFμE/Co at -0.90 V has a better electrochemical response. The effective electrochemical area was also calculated according to equation (1) <sup>[4]</sup>. Fig. 2(b) shows the curves of the linear fit of the  $I_{\text{qss}}$  as a function of  $1/\text{Inr}$ , and it was obtained that the effective area of the unmodified CFμE was  $7.44 \times 10^{-5}$

cm<sup>2</sup>, while the CFμE/Co constructed at -0.90 V had a significantly larger area of 1.91×10<sup>-4</sup> cm<sup>2</sup> increasing the sensitivity of the CFμE/Co to the PCM. In the Nyquist diagram, it was verified that the CFμE/Co built at -0.90 V presents a lower resistance to load transfer, Fig. 2(c).



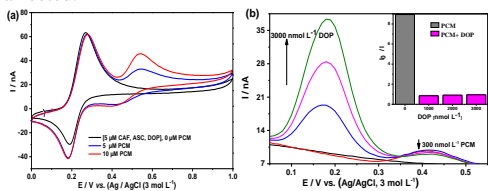
**Fig. 2.** (a) Voltamperometric response of CFμE and CFμE/Co; (b) curves of the chronoamperometric responses  $I_{qss}$  vs.  $1/\ln(t)$  of the CFμE and CFμE/Co modified to -0.75 V, -0.8 V, -0.9 V; (c). EIS of CFμE and CFμE/Co. All measurements were made at 5.0 mM K<sub>4</sub>Fe(CN)<sub>6</sub> (at 1.0 M KCl).

**Calibration Curve:** Fig. 3(a) and 3(b) show the responses of CFμE/Co against PCM between 50 -1000 nmol L<sup>-1</sup> and the calibration curve respectively, with a Limit of Detection (LOD) of 32.69 nM and a Limit of Quantification (LOQ) of 98.07 nM.



**Fig. 3.** (a) Differential pulse voltammogram of paracetamol response in a modified microelectrode and (b) calibration curve.

**Interferers Study:** The study was conducted with caffeine (CAF), ascorbic acid (ASC), and dopamine (DOP). Fig. 4(a) shows that CFμE/Co has only electrocatalytic activity for PCM and DOP, so the maximum current in the absence ( $I_0$ ) and presence ( $I$ ) of dopamine Fig. 4(b) was compared and it is observed that despite the fact that there is an electrocatalysis of dopamine, the paracetamol signal is not significantly affected.



**Fig. 4.** (a) DPV response of paracetamol and (b) paracetamol current in the presence of dopamine in CFμE/Co

To assess the accuracy of the method, the percentage of recovery was determined for drinking water and river

water samples. (Table 1).

**Table 1.** Precision and interday accuracy parameters applied to real tap water and river samples.

Parameters	Tap Water	River Water		
<b>Spiked concentration (nM)</b>	150	250	100	250
<b>Concentration Found</b>	159.36	265.13	86.98	277.52
	164.19	251.04	97.88	269.02
	137.92	262.57	110.54	271.39
<b>Average</b>	153.82	259.58	98.47	272.65
<b>SD nM</b>	13.98	7.51	11.79	4.38
<b>% Recovery</b>	102.55	103.84	98.47	109.06
<b>RSD</b>	9.09	2.89	11.97	1.61
<b>%Error</b>	2.55	3.83	1.53	9.06

### Conclusion

The CFμE/Co modified to -0.9 V allows the detection of paracetamol with an LOD of 32.69 nM and LOQ of 98.07 nM with a sensitivity of 9.81 nA nmol L<sup>-1</sup>. The performance of CFμE/Co in real matrices was evaluated and it is evident that it is sensitive and robust, with the capacity to perform environmental monitoring.

### Acknowledgments

The authors thank the Pontificia Universidad Católica del Ecuador.

### References

- [1] Peralta-Hernández, J. M., & Brillas, E. (2023). A critical review over the removal of paracetamol (acetaminophen) from synthetic waters and real wastewaters by direct, hybrid catalytic, and sequential ozonation processes. *Chemosphere*, 313, 137411. <https://doi.org/10.1016/j.chemosphere.2022.137411>.
- [2] Bolaños-Méndez, D., Alvarez-Paguay, J., Fernández, L., Saavedra-Alulema, P. F., Veloz-Romero, M. S., & Espinoza-Montero, P. J. (2024). An inexpensive paracetamol sensor based on an acid-activated carbon fiber microelectrode. *Chemosphere*, 346. <https://doi.org/10.1016/j.chemosphere.2023.140586>
- [3]. Attimadar, M. (2011). Simultaneous determination of paracetamol and lornoxicam by RP-HPLC in bulk and tablet formulation. *Pharmaceutical Methods*, 2(1), 61–66. <https://doi.org/10.4103/2229-4708.81084>.
- [4]. Szabo, A., Cope, D. K., Tallman, D. E., Kovach, P. M., & Wightman, R. M. (1987). Short communication chronoamperometric current at hemicylinder and band microelectrodes: theory and experiment. In *I. Electroanal. Chem* (Vol. 217). Elsevier Sequoia S.A.