



Development of an Electrochemical Immunosensor Based on Specific Antibodies Labelled with CdS Nanoparticles for In-Situ Paraquat Monitoring in Spiked Potato Samples

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Introduction

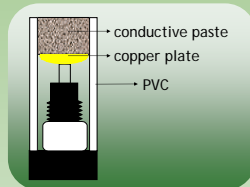
In this work, a new coulombimetric immunosensor to detect residual amounts of paraquat (PQ) in a complex matrix, such as potatoes, is presented. The immunosensor is based on graphite composite electrodes (GECs), immunoreagents specifically developed to detect paraquat, magnetic μ -particles, and CdS nanoparticles labelled to the specific antibodies. In this approach, CdS nanoparticles will be used as specific non-interfering labels and selective amplifiers. By means of the well-known anodic stripping techniques, CdS nanoparticles are read, and the amounts of its metal ions are expressed as a signal of current or charge.

Due to the high sensitivity of the immunosensor, the results obtained showed that after the extraction and dilution of the matrix, PQ can be determined in potato samples achieving limits of detection below 0.001 mg Kg^{-1} , and therefore, far below the MRL required by EC for paraquat (0.02 mg Kg^{-1}). Hence, the results obtained open the door to commercial sensors of simple manipulation, transportable and economics.

Coulombimetric PQ detection system

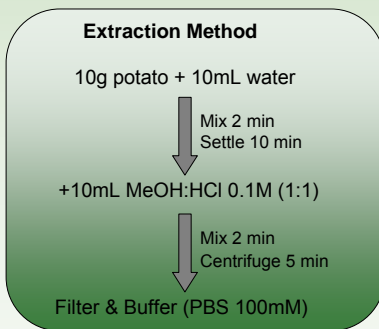
1. Graphite-epoxy composite (GEC) electrode

- The electrode paste is obtained by mixing graphite powder and epoxy resin.
- GEC electrode is used as working electrode.



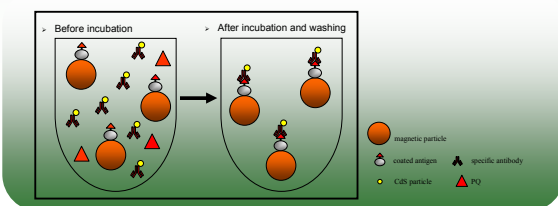
2. Blank potato samples extraction method

- Blank potato samples were supplied by The Food and Environment Research Agency (FERA), York, UK. The extract protocol was supplied by Chemisches und Veterinäruntersuchungsamt (CVUA), Stuttgart, Germany. The protocol is as follow:



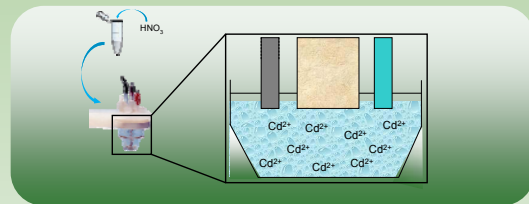
3. Immunochemical competitive assay

- The pesticide present in the sample and a specific antigen coated on the surface of MPs compete for a limited amount of antibodies labelled with the CdS nanoparticles.
- After the incubation and washing, an amount of the specific antibodies are bounded on the coated antigens. The others antibodies, captured by the analyte, are evacuated of the sensor.

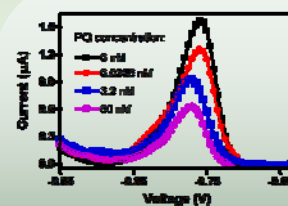


4. Electrochemical measurements

- After incubation, the magnetic particles could be magnetically separated from the assay solution.
- Then, HNO_3 is used in order to release to Cd^{2+} ions from the CdS particles.
- Afterwards, these ions are transferred to the electrochemical cell.

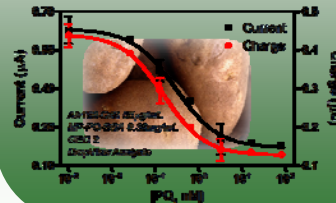


5. Paraquat detection.



- The amplitude of the current peak is inversely related to the PQ concentration.
- The current peak clearly appears to the Cd^{2+} oxidation voltage.
- The current value (μA) is obtained from the amplitude of the peak, while means the charge value (μC) is obtained from the area under the curve.

SWV. PQ detection. Potato samples (1/100).



Features of the paraquat assays	Potato sample extract (1%)	
	Current	Charge
Slope	-0.8785	-0.9175
IC_{50} , nM	0.2877 ± 0.21	0.1528 ± 0.15
LOD, nM	0.025	0.015
LOD ^a , mg Kg^{-1}	0.7×10^{-3}	0.4×10^{-3}
R ²	0.94	0.96

^a LOD taking into account the PQ molecular weight, the dilution of the sample performed, the amount of potato used, and the final volume of the extract.

Conclusions

- An electrochemical immunosensor for the quantification of paraquat residues in potato samples has been developed.
- This immunosensor, which is based on specific antibodies labelled with CdS nanoparticles, has already shown high sensibility to PQ residues, detecting this pesticide in concentrations far below the MRL required by EC.
- The sensor presented offers the possibility of detecting paraquat in sub-ppb concentrations, but using simple and inexpensive SWV measurements, that open the door to commercial sensors of very easy use, transportable and cost effective.

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