

Photoelectrochemical detection of toxic heavy metals

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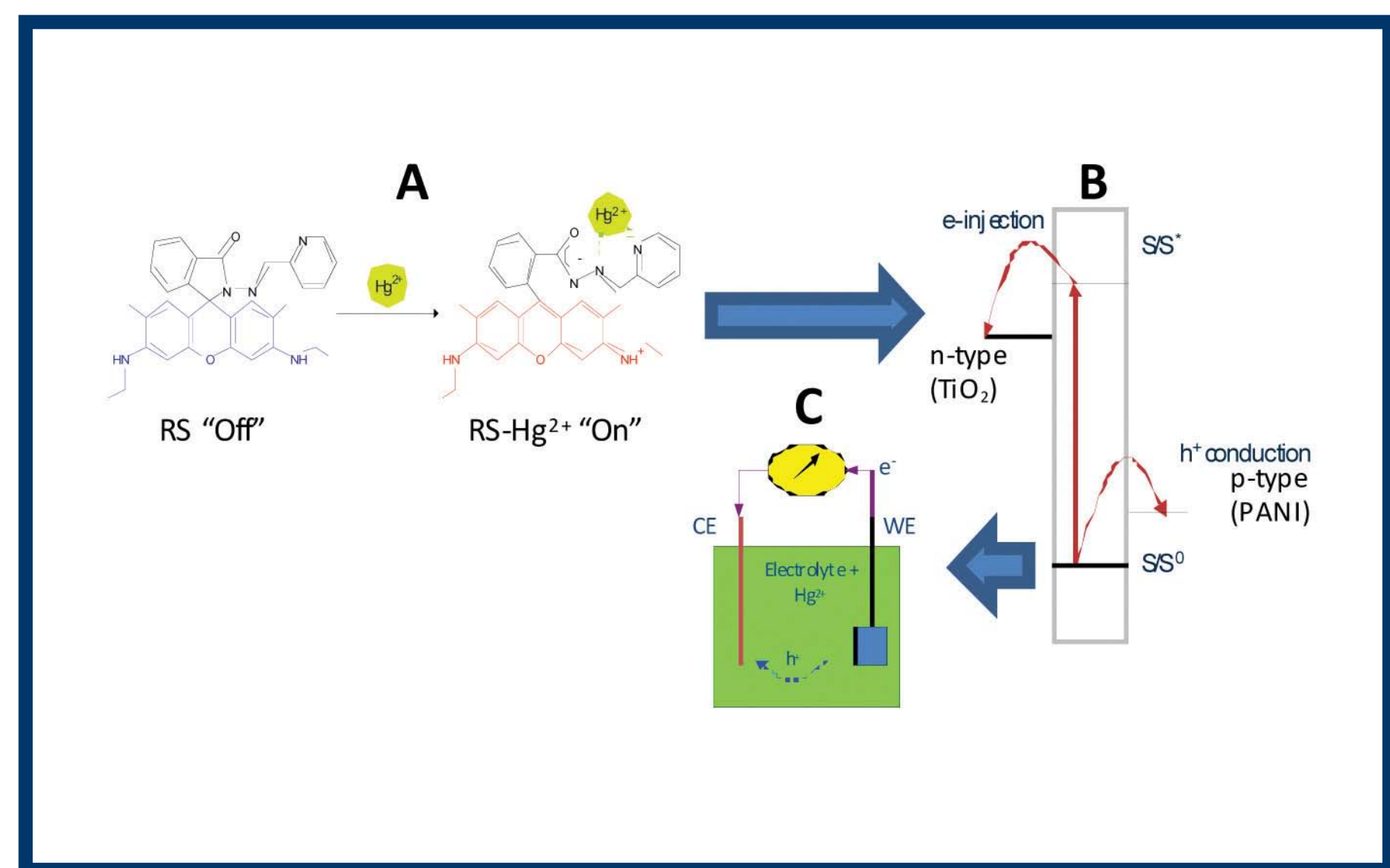
INTRODUCTION

Toxic heavy metals in air, soil, and water are global problems that are a growing threat to the environment. Trace metal determination is currently done by expensive separation techniques which include inductively coupled plasma (ICP) and cold vapor atomic fluorescence spectroscopy (CVAFS). These techniques are sensitive and accurate in their detection of metals in the environment but are expensive to maintain, immobile and require sample preparation.

Immobilisation of cation-selective fluorophores on various substrates introduced the possibility for portable and on-site instant verification of heavy metal pollutants. In this work, the favorable properties of the mercury-sensitive fluorescent molecule, Rhodamine 6G hydrozone derivative (RS), were combined with titanium dioxide (TiO₂) and polyaniline (PANI) to construct an electrochemical cell that is capable of conducting a current in the presence of white light and inorganic mercury (Hg²⁺). A prototype photoelectrochemical mercury detector (PEMD) was constructed and investigated as a possible inexpensive tool for on-site prescreening of Hg²⁺ in surface water.

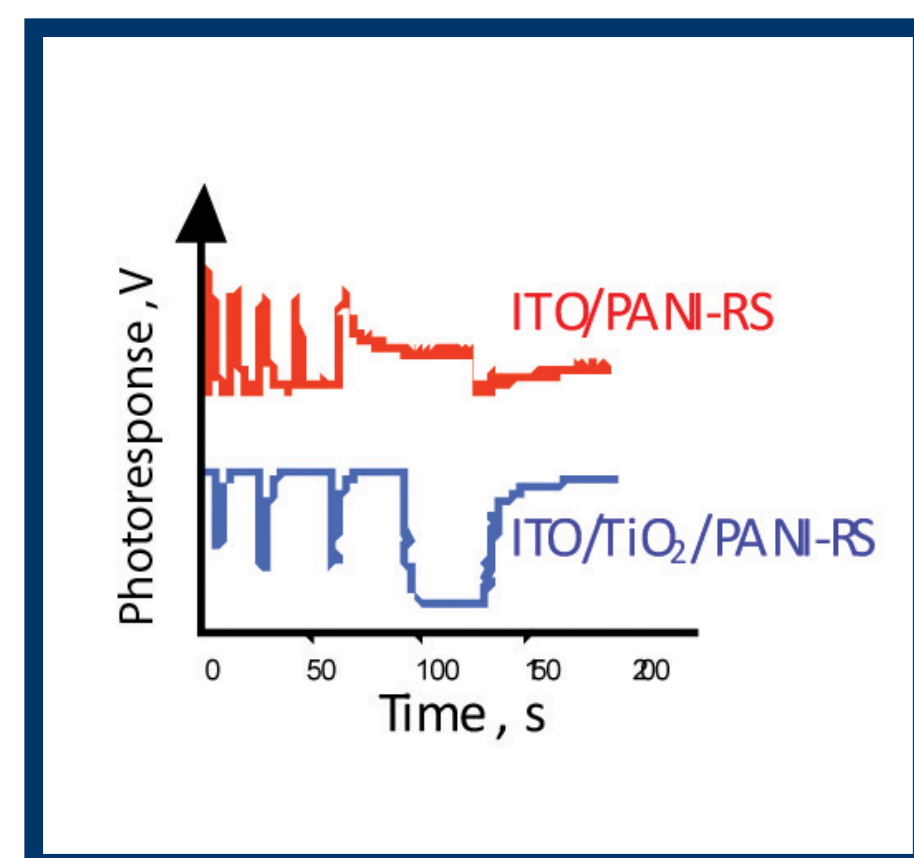
METHODOLOGY

A novel method for Hg²⁺ determination is illustrated in scheme 1. A Hg²⁺ selective chemosensor will “switch on” or fluoresce in contact with Hg²⁺ (A). In the presence of suitable charge separators (B), the photon-excitation will be converted into an electron injection. In a closed electrical circuit (C), the charge separation will result in an electron current, equivalent to the amount of Hg²⁺ in solution.



Scheme 1: The principle of photoelectrochemical detection of Hg²⁺ in water

RESULTS AND DISCUSSION



ITO and ITO/ TiO₂ substrates were coated with a composite of PANI and RS (PANI-RS) and had a photocathodic and photoanodic response towards Hg²⁺ in aqueous solutions respectively (Figure 1).

Figure 1: The photoresponses of the photoelectrodes in aqueous Hg²⁺ solutions under illumination.

Sensitivity and range of working electrodes

The working photoelectrodes photoresponse increased with increasing Hg²⁺ concentration.

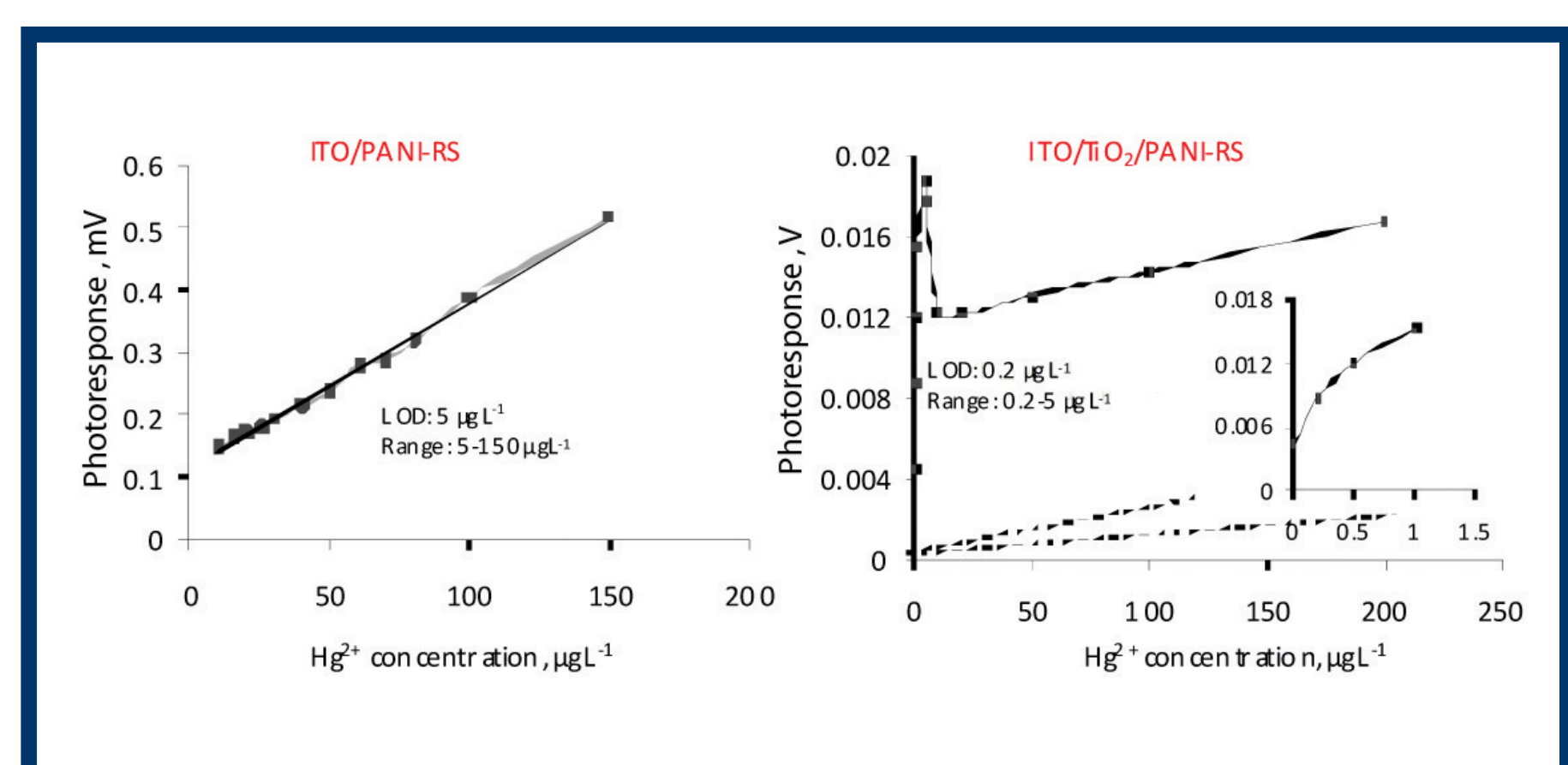


Figure 2: The range and sensitivity of the ITO coated electrodes towards Hg²⁺ in aqueous solutions

Selectivity of working electrodes towards Hg²⁺

The selectivity of the working electrodes towards Hg²⁺ in the presence of 1 mg L⁻¹ of background ions was determined. Figure 3 illustrates that ITO/TiO₂/PANI-RS had significantly higher selectivity for Hg²⁺ due to improved charge separation and reduced surface charge effects. The electrodes were also measured after evaluation to determine residual effects (named after in Figure 3).

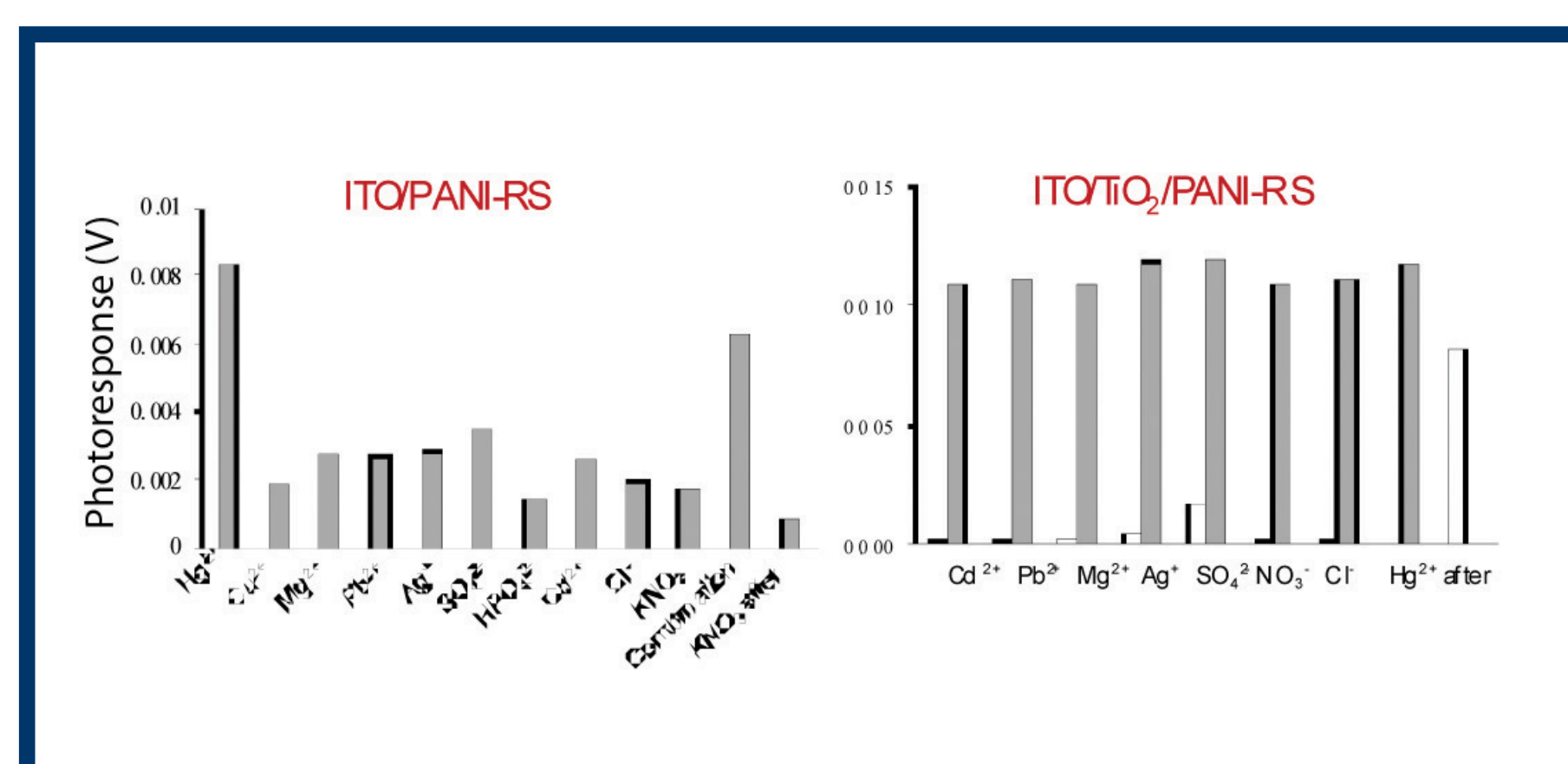


Figure 3: The photoresponses of ITO coated with PANI-RS and TiO₂/PANI-RS in the presence of background ions

The Prototype

A custom photoelectrochemical mercury detector (PEMD) was build using PANI-RS as a working electrode (Figure 4). The TiO₂/PANI-RS electrode could not be evaluated as its responses fell outside the range of the PEMD voltmeter. Environmental samples were evaluated from the Eersterivier in Kuilsriver (33°57'12"S; 18°39'52.0"E) and the prototype Hg concentration estimations were compared to those determined with a Direct Mercury Analyser (DMA) at the CSIR, Stellenbosch. The results are summarised in Table 1:

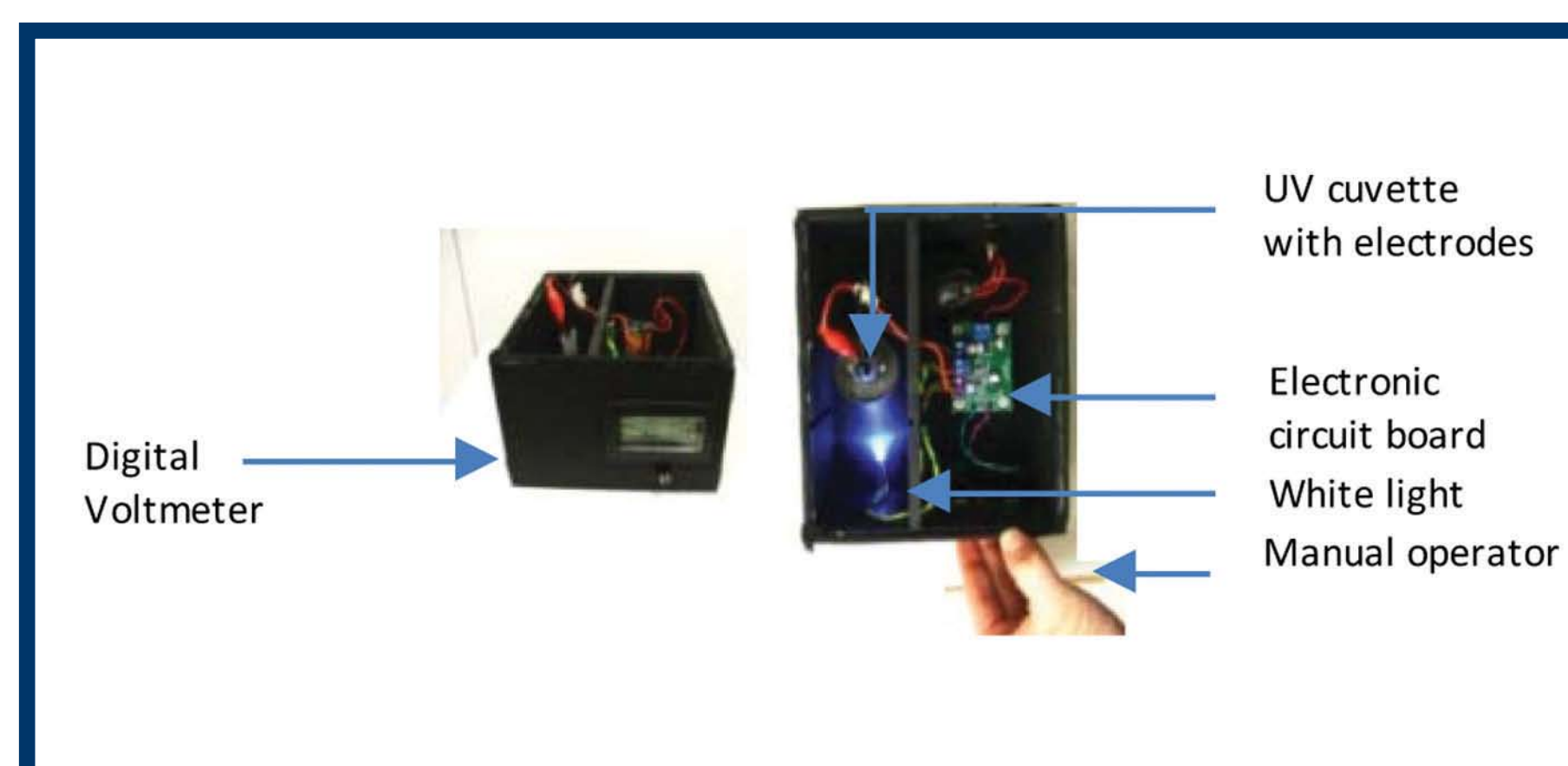


Figure 4: The photoelectrochemical Hg²⁺ detector (PEMD)

Table 1: Photovoltage responses for environmental samples compared to DMA results

Sample	Photovoltage, 100 µV		[Hg ²⁺], µg L ⁻¹			
	PANI-RS	*PANI-RS	Prototype	*Prototype	DMA	*DMA
Sample 1	0.8	1.2	> 0.2	> 2	4.04	6.09
Sample 2	1	1.1	> 0.2	> 2	4.01	6.62
Sample 3	0.8	1.1	> 0.2	> 2	5.71	7.78

* Photovoltage responses for environmental samples spiked with 2 µg L⁻¹

PANI-RS electrodes could only be used as prescreening method due to

- Quick saturation of the electrode surfaces;
- False positive responses due to matrix affects; and
- Challenges in getting accurate background responses.

CONCLUSIONS

A novel method for on-site prescreening Hg²⁺ has been developed and evaluated. The method can be extended to other heavy metals by replacing the Hg²⁺ selective chemosensor.

BIBLIOGRAPHY

- Chamier, J., Leaner, J.J. and Crouch, A.M. 2009. *Analytica Chimica Acta*, 661: 91-96.
- Chamier, J. and Crouch, A.M. *Materials Chemistry and Physics*. To be submitted 2010.

A prototype photoelectrochemical mercury detector can serve as an on-site and inexpensive tool to test for heavy metals in surface water.

