Heavy metal analysis of river water using the ItalSens HM1 sensor
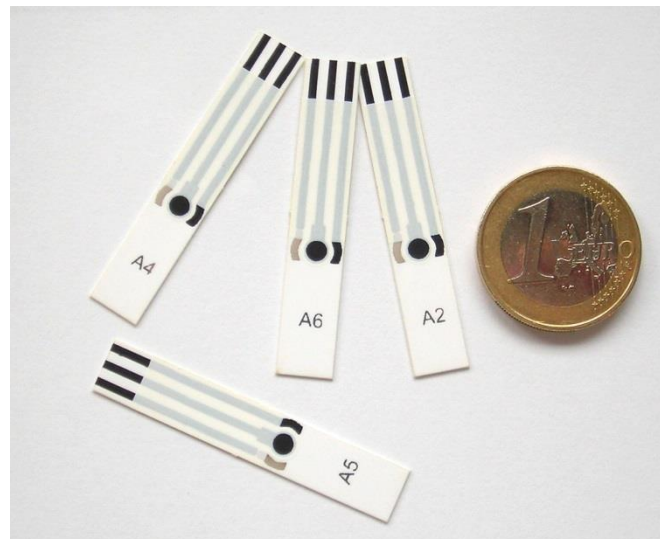
Quantification of copper, lead and cadmium in aqueous solutions

PalmSens
Compact Electrochemical Interfaces

www.palmsens.com

Contents

1   Introduction

Pollution is a known issue for decades. A focus of interest is, of course, unhealthy or outright toxic substances in resources we use for creating everyday goods or even consume ourselves. Spoiled water is the cause of many illnesses and other health issues. Due to this the monitoring of drinking water is an important task to keep people healthy. While for surface water bacteria are the main threat, in almost all urban areas water is consumed after flowing through pipelines. This or the direct pollution of ground water can lead to heavy metals in drinking water. Many heavy metals are biologically active and cause illnesses. A well-known example is lead poisoning. In this application note we will show how to detect different metals in aqueous solution with the IS-HM1 sensor.

1.1   Goals of this application note

This application note is intended to provide the user with a comprehensive set of instructions for use of the screen printed electrode (SPE) IS-HM1 in analysing Pb, Cd and Cu concentrations of a polluted river water sample.
Also by providing a step by step introduction for the Analytical Mode of PSTrace and PStouch the user is afterwards familiar with this convenient mode of PSTrace and PStouch.

1.2   Alternative use of this application note

The demonstrated technique works also for other heavy metals as long as they deposit properly on graphite surfaces or form mercury alloys. The detection of heavy metals that have very similar redox potentials will lead to overlapping peaks and thus will make an accurate analysis very difficult. We recommend performing test measurements to ensure a sufficient peak separation.

1.3   Sensor used

The HM1 sensor from ItalSens is an excellent electrode to quickly and cheaply measure the ppb levels of heavy-metals such as Pb, Cd and Cu in aqueous solutions. [1] The ItalSens mercury salt modified graphite sensors (IS-HM1) are three-electrode sensors, with a mercury salt graphite working as well as a graphite counter electrode and a silver pseudo-reference electrode. The sensors come printed on polyester stripes with 20 sensors per stripe and need to be cut to the right size prior to use.
The sensors can be used by placing a drop of the solution on the sensor surface, by using a simple cell or by using the ItalsSens flow cell or batch cell. For stripping voltammetrie and trace analysis we recommand a simple cell that allows stirring during the deposition step of the measurement.

This application note describes how to quantify Cu, Pb and Cd in aqueous solution by stripping voltammetry and the Analytical Mode of PSTrace.

2 Experimental part

For the Experiment you need a properly cut IS-HM1, a potentiostat with the usual equipment, a magnetic stirrer and the solutions from 2.2 and 2.3.

2.1 Equipment required

- PalmSens, EmStat or EmStat Blue with PSTrace software (version 3.0 or higher)[1] or PStouch (Android 4.3 (Ice Cream Sandwich) or higher)
- Stirrer switch box, magnetic stirrer and magnetic stirring bar
- Sensor: ItalSens IS-HM1 sensors
- PalmSens universal sensor connector or another suitable connector
- Simple cell or ItalSens flow through cell
- Distilled or ultra-pure water
- Plastic or glas containers for the standard solutions

2.2 Reagents

- 6 M HCl,
- 1 g/L solutions of AA/ICP metal standards for Pb
- 1 g/L solutions of AA/ICP metal standards for Cd
- 1 g/L solutions of AA/ICP metal standards for Cu

2.3 Solutions

Make up 10 mL solutions of 5 ppm of each metal by pipetting 10 µL of HCl, into a bottle. Then add 50 µL of stock metal solution and clean water, making a total volume of 10 mL.

2.4 Electrode Preparation

To attach the electrode to the sensor cable, take the strip of electrodes and hold it at the end with the writing. Since the electrodes are easily contaminated or destroyed , please take care not to touch it with bare hands. Cut away the access plastic around one SPE and place it in the connector. You must cut the sensor narrow enough that it fits into the connector, but please take care not to damage the electrodes nor the lines during cutting.

2.5 Conducting the Experiment

2.5.1 Conditioning the sensor

Perform repeatedly a LSW with the sensor until the prominent peaks are almost gone and the curves of each scan are stable and overlap. All necessary files can be downloaded in the **HM1conditioning bundle**.

Enter the *Scientific mode* of PSTrace or PStouch to start the analysis. In PSTrace this can be either done by selecting it in the *General Settings* from the *Tools* menu of PSTrace or by using the dropdown box top left hand side of the PSTrace screen. In PStouch the app mode selection is found if you touch the Pstouch logo in the upper left corner or in the menu in the top right corner. Furthermore you need to tell the software, that you intend to use a magnetic stirrer. Open in PSTrace the Tools – General Settings menu. Then check the "stirrer present"box and choose the stirrer you use. Open in PStouch in the right upper right corner the menu and choose *Settings*. There you can set the stirrer *ON*.

---

[1] It is also possible to use the Android App PStouch to control your potentiostat, but the App does not offer the Analytical Mode.

The electrode requires conditioning before use and this is done by running a standard method in 20mM HCl (~ 33 µL of 6 M HCl in 10 mL). The most convenient way to do this is using a script. This is a convenient tool to perform more complex processes automatically. This time we want to perform repeatetly the same measurement, to condition the sensor. Open the script window in the *Script – Open Script window* menu and load the script entitled **HM1condition** (figure 1). You can download this script including the needed procedures at palmsens.com with the **HM1conditioning bundle.** The default data and method path is the PSData folder in "My Documents". Check the paths of the two method files of the script and the data output ensuring that they are all correct. If they are not correct the blocks of that method will be red instead of blue. The names of the two needed Methods is HM1cond.psmethod (first block) and HM1prescans.psmethod (block connected to the repeat block). Unfortunately is scripting not possible with PStouch yet. The conditioning needs to be done manually by starting the methods over and over again. Fill the cell with the 20 mM HCl, insert the magnetic stirring bar, put the cell on the magnetic stirrer, connect the sensor to the potentiostat, immerse the sensor and make sure the three electrodes of the sensors are covered with solution. If you made changes in the script save it and then press Run. The conditioning takes ca. 15 min. For manual setting of the parameters, these are listed in 3.1.1.
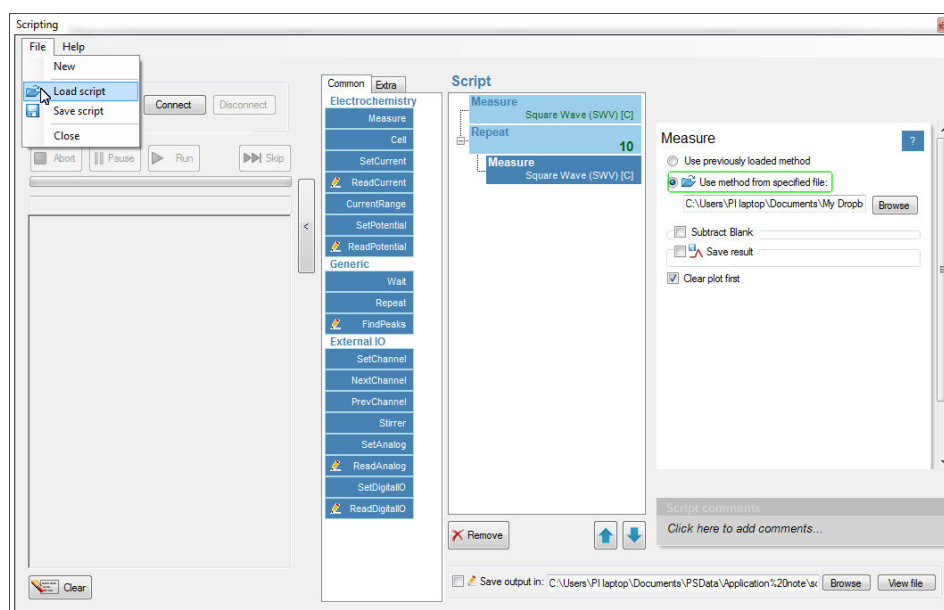

figure 1 The scripting window

Typical scans from the conditioning stage are shown in figure 2. Notice please that the peaks are decreasing with each scan, until they almost vanish completely. When finished rinse the cell and electrode with some 20 mM HCl solution and clean water.
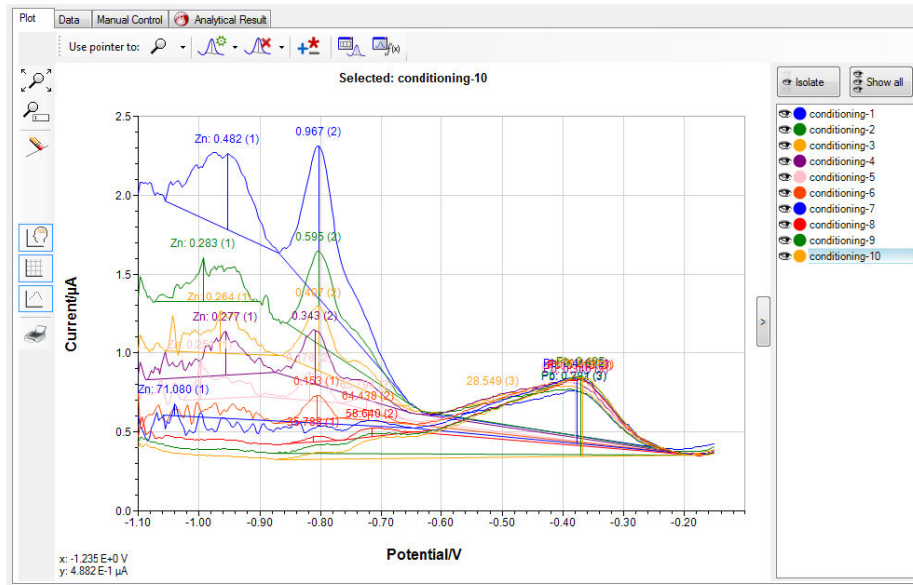
figure 2 The scans of the conditioning step

2.5.2 Preparing the Analysis in the Analytical Mode

figure 3: Analysis settings for PSTrace (left) and PStouch (right)

This analysis will be performed with the standard addition method. The standard addition method starts by measuring the sample and than measure the sample again after a known amount of the anlyte(s) have been added. If a linear realtionship between signal (peak current) and analyte (heavy metal) concentration is given, the concentration of the original sample can be calculated. PSTrace will be used in the Analytical Mode to auto-calculate sample metal concentrations from the standard additions.

Load the analysis file **HM1 standard addition river water.psmethod** from our website. To load a complete example including all curves in PSTrace click in the Analytical mode in the menu on Analysis – Load Analysis and load the **HM1 standard addition river water.pds** file from our website. In the method box click on the Analysis tab as shown in figure 3. Here all the settings for the standard additions will be filled out for you. The magnitude of the additions might need to be adjusted depending on your river water sample. In this example the Cd has a forced left and right peak to help on low Cd measurements. This can be changed back to Auto. If peaks are clearly visible, the Auto option is a good choice, but if peaks are very small and/or broad it is difficult for the software to find the peak. A forced peak border is then the mean of choice. The parameters of the measurement are again listed in 3.1.2.

2.5.3 Performing the measurement

The pH of your sample should be around 2.5. This can be achieved be adding 10 µL of 6 M HCl to 10 mL of your sample. Usually the volume change that is caused by this addition can be neglected. Fill the cell with your sample and after immersing the connected sensor, make sure the three electrodes are covered with sample solution. Insert the magnetic stirring bar and position everything on the stirrer. Press the green play button to start the analysis of the sample. Repeat scans by selecting **Overlay** from the dropdown box (PSTrace) or in the pop-up menu (PStouch) and pressing run again until you get a stable peak height (<10 % peak height difference to the former scan). The stirrer should be on and stirring during the deposition and off during the square wave voltammetry. Then select the replicate that you wish to keep and right click on it in the curve legend and then designate the curve use, i.e. sample, Standard_n. An example for the sample measurement can be seen in figure 4

Add an amount of metal that roughly resembles the amount of metal you expect in your sample. Make your addition as specified in the analysis table. This can be done by adjusting your table or your measurement. Perform the measurement, select for this curve **Standard_1** from the dropdown box (PSTrace) or pop-up menu (PStouch) seen in figure 4. Repeat the measurement. Once you are getting a stable Standard_1 curve, add your second amount of metals and record the **Standard_2** as described for Standard_1. Add metals and repeat the he measurements of Standard_n curves until you have a satisfiying amount of standard additions. A typical number is three additions. It is also possible to assign the curves to the different curve types after they have been recorded. Just select them in the legend window and change the curve assignement in the drop down menu or pop-up menu.

Perform SWV with the parameters from the file HM1 standard addition river water.psmethod or from chapter 3.1.2. Repeat the measurement after each standard addtion and declare for each curve if it is the sample or standard addition. Afterwards read your results in the Analysis Results tab.
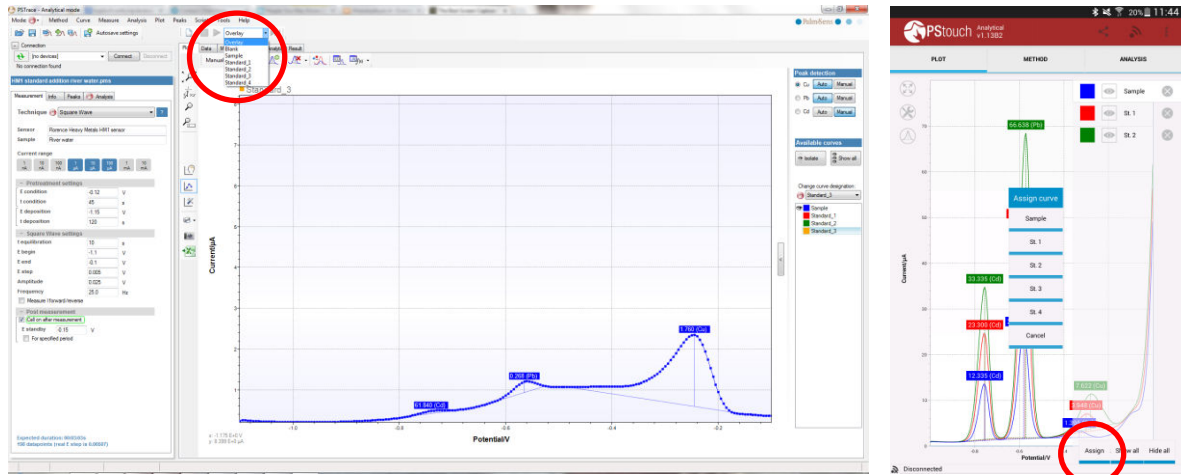
figure 4 The first scan of the sample and selection of additions for PSTrace (left) and the assignement of curves for PStouch (right).

2.5.4 Auto-Analysis

After completion of all measurements for this analysis click on the **Analytical result** tab (PSTrace) or the **Analysis** tab (PStouch) (figure 5) to view the calculated data. Points can be included or excluded from individual metal calibration curves by toggling the check box next to that addition as seen in figure 6. If a mistake was made in the settings of the additions table, they can be corrected and the data recalculated by pressing the Recalculate button. The values from each calibration or standard addition are summarised in the box **All results** at the top of the analysis window.
On completion of the measurements you can save all the data and curves in one file for use later by clicking Save Analysis within the Analysis menu.
All the data (raw or calculated) can be exported or printed for further manipulation using the All to clipboard and the Print buttons at the top of the data screen (figure 6).
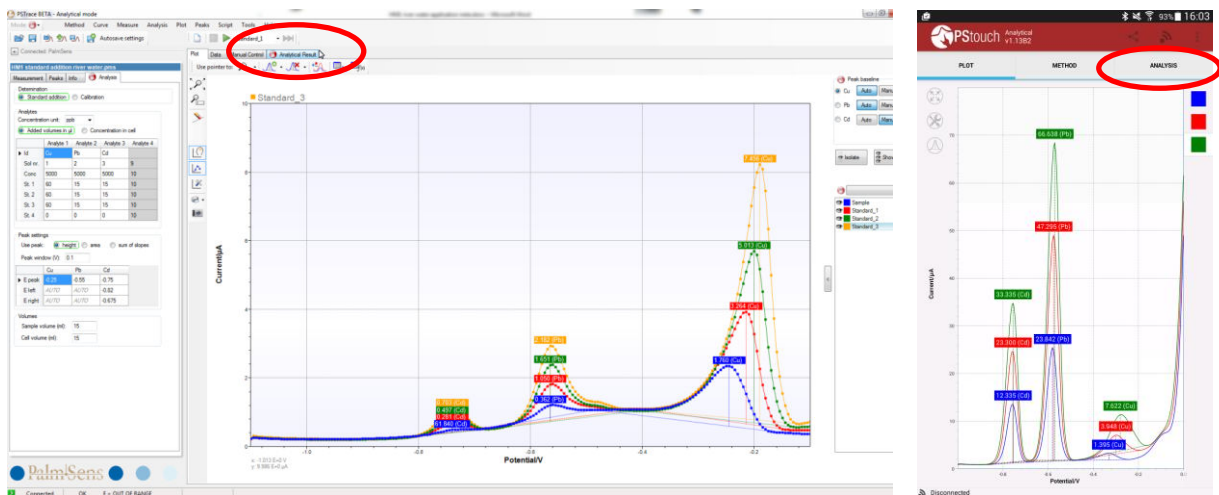

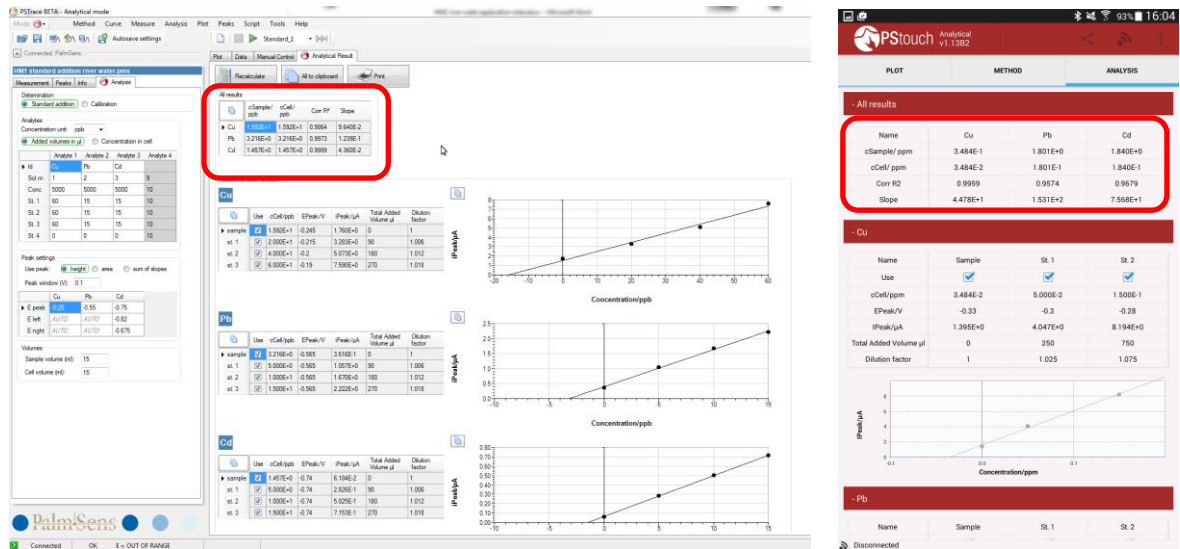figure 5 The final analytical scans and where to find the analytical results

figure 6 The calculated results for each analyte and summarized (red box)

3 Additional Information

3.1 Parameters for manual setting of the measurement

3.1.1 Conditioning the electrode

If the corresponding method file is not available, you can just enter the following parameters by hand. The script used to perform the conditioning is comprised of two methods. First the following method with a long period for deposition is performed.

Parameter	Value
Technique	Square Wave Voltammetry
Current Range	1µA-100µA
E cond	-0.18
t cond	30
E dep	-1.1
t dep	300
t eq	10
E begin	-1.1
E end	-0.15
E step	0.005
Amplitude	0.025
Frequency	15.0

Afterwards the following method is repeated **ten times**.

Parameter	Value
Technique	Square Wave Voltammetry
Current Range	1µA-100µA
E cond	-0.18
t cond	30
E dep	-1.1
t dep	0
t eq	10
E begin	-1.1
E end	-0.15
E step	0.005
Amplitude	0.025
Frequency	15.0

3.1.2 Stripping Square Wave Voltammetry

If the corresponding method file is not available, you can just enter the following parameters by hand.

Parameter	Value
Technique	Square Wave Voltammetry
Current Range	1µA-100µA
E cond	-0.12
t cond	45
E dep	-1.15
t dep	120
t eq	10
E begin	-1.1
E end	-0.1
E step	0.005
Amplitude	0.025
Frequency	25.0

3.2 Measuring range

Table 1 the typical LOD for 120s deposition. Calculated using 3*standard deviation of repeat measurements of 1ppb of each metal

Metal	LOD (ppb)	~Slope (nA/ppb)	Linear range (ppb)
Cu	<1	30	1-1000
Pb	<1	115	1-1000
Cd	<1	60	1-1000

This example is set for a typical river water sample but concentrations of metals can vary massively from location to location. The electrodes do have a large linear range but if the electrode is saturating then the deposition time needs to be lowered. This is done from the method editor and change t_{dep}. Set it to 60 s and the LOD will be 2 times larger (less sensitive).

As good working practice the first addition should double the peak height of the sample peak height. So the magnitude of the additions in Fig 4 might need to be changed. Keep standard addition volumes as small as possible (<50 µL/10 mL), so the standard solutions might need adjusting.

3.3 Electrode stability

In between measurements when in solution the sensor is held at a standby potential. This is to maintain the life of the electrode. The electrode can be repeatedly taken out and the sample changed without any effect on the electrode performance. Care must be taken to not run the electrode in a solution without acid or no salt. The stability of results is excellent throughout a typical day and will also work the following day. The best way to monitor electrode stability/performance is by using the gradient of the calibration slopes which are shown in the table as a guide. To store overnight, store dry but repeat the conditioning steps.

Be aware that applying potentials more positive than -0.1V will destroy the electrode!

And please always turn off the cell from the Manual Control tab before removing the electrode from the sample, if the cell is still on after the measurement.

The electrode is sufficiently stable to calibrate in the morning, obtain the sensitivity (S) and use the same S for all measurements (concentration of metal in the sample = I_{peak}/S). One point standard additions are also acceptable if you are happy with the electrode stability.

3.4 Interferences

The IS-HM1 sensor is best suited to aqueous environments but the results can be seriously impacted by surfactants (soaps) and oils. Oils can be overcome by only sampling below the water surface. Surfactants are best dealt with by diluting the sample.

3.5 Synthetic river water

It is sometimes desirable or easier to work with synthetic water. Smith et al describes how to replicate a typical river water sample. [2] For the purpose of this application note it is sufficient to use clean water acidified with HCl.

3.6 Literature

[1]   Palchetti, I.; Laschi, S.; Mascini, M.; *Miniaturised stripping-based carbon modified sensor for in field analysis of heavy metals*; Analytica Chimica Acta 530, **2005**, 61-67

[2]   Smith, E.J.; Davison, W.; Hamilton-Taylor, J.; *Methods for preparing synthetic freshwaters. Water Res.*; 36; **2002**; 1286–1296