Detection of Multiple Heavy Metals by Stripping Voltammetry

PSAPP-008 Electrochemical Experiment

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1 Instructions

The following instructions will guide you to perform the experiment. The theory on which these experiments are based, can easily be checked online at palmsens.com, then search for “Introduction of the detection of multiple heavy metals”. The material needed for the experiments can be ordered via https://www.palmsens.com/product/educational-kit/#contents

2 Devices and Equipment

- EmStat / EmStat Blue
- sensor cable
- sensor connector
- maybe a USB cable
- computing unit (PC, Laptop, notebook, tablet PC (Android), smartphone (Android))
- potentiostat software (PStrace, PStouch)
- ItalSens IS-HM
- retort stand
- retort clamp
- beaker (electrochemical cell)
- stirrer
- optional: switchbox (increases the convenience)

3 Chemicals

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

Note: The higher the quality and accuracy of the metal salt solutions the higher the accuracy of the analysis. If a high accuracy is not necessary cheaper solutions or solutions made from solid metal salts can be used.

4 Instructions

4.1 Standard Metal Solution

For each metal make 10 mL solutions of 5 mg/L 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.
It is also possible to make one mixed solution of Cu and Pb; this makes an analysis of a sample with similar Cu and Pb a bit more convenient, but it makes it less flexible for unknown samples. A mixed solution is created by adding 50 µL of Pb solution to 50 µL of Cu and 10 µL HCl as well as pure water to a total volume of 10 mL.

4.2 Electrode Preparation

1. To attach the electrode (IS-HM) to the sensor cable, take the strip of electrodes and hold it at the end with the single letter (A to D) and a number (1 to 20). 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 for fitting it into the connector, but please take care not to damage the electrodes or the lines during cutting.
2. Enter the *Scientific mode* of PSTrace to start the preparation, if it is not already selected. This can be done either 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. If you have the switchbox for your stirrer, you need to tell the software that you intend to use a magnetic stirrer. Open in PSTrace the *Tools – General Settings* menu. Then select the check the "*stirrer present*" box and choose the stirrer you use.

3. The electrode requires conditioning before use and this is done by running a standard method in 100 mM HCl (667 µL of 6 M HCl in 40 mL). The most convenient way to do this is using a script. This is a tool to perform more complex processes automatically. This time we want to perform the same measurement repeatedly to condition the sensor. The methods that will be used in the script need to be created first. First a conditioning method is created. In the *Technique drop* down list Square *Wave* is selected. Choose the current ranges *1 µA, 10 µA* and *100 µA*. The fields *Sample* and *Sensor* are for your own notes. Set the parameters to:
    a. *E condition = -0.18 V*
    b. *t condition = 30 s*
    c. *E deposition = -1.1 V*
    d. *t deposition = 300 s*
    e. *t equilibrium* = 10 s
    f. *E begin* = -1.1 V
    g. *E end* = -0.15 V
    h. *E step* = 0.005 V
    i. *Amplitude* = 0.025 V
    j. *Frequency* = 15 Hz
    k. The *Cell on after measurement* should be checked and E *standby* set to *-0.2 V*

   Go to the *Methods* menu and choose *Save method* and save the method under a name that is unambiguous for you. Maybe this method was already prepared for you.
4. For the second method only one parameter needs to be changed:
    a. *t deposition* = 0 s

   Save this method under an unambiguous name too. Maybe this method was already prepared for you.
5. Open the script window in the *Script – Open Script window* menu. Remove existing building blocks from the *Script* column by clicking on the block and click *Remove*. Choose the *Measure* block from the list of building blocks. It is added to the *Script* column. Click on the added Measure block and choose in the right window the option to use a specific file. Choose the method you created under step 3. Next add a *Repeat* block and increase the number of repeats to 10. Add another *Measure* block while the added *Repeat* block is still selected. The *Measure* block will be added inside the *Repeat* block. Choose again for the *Measure* block that a specific file should be used and choose the method created under step 4. The script should look like Figure 4.1. It is also possible to save the entire script under *File – Save script* in the script window.

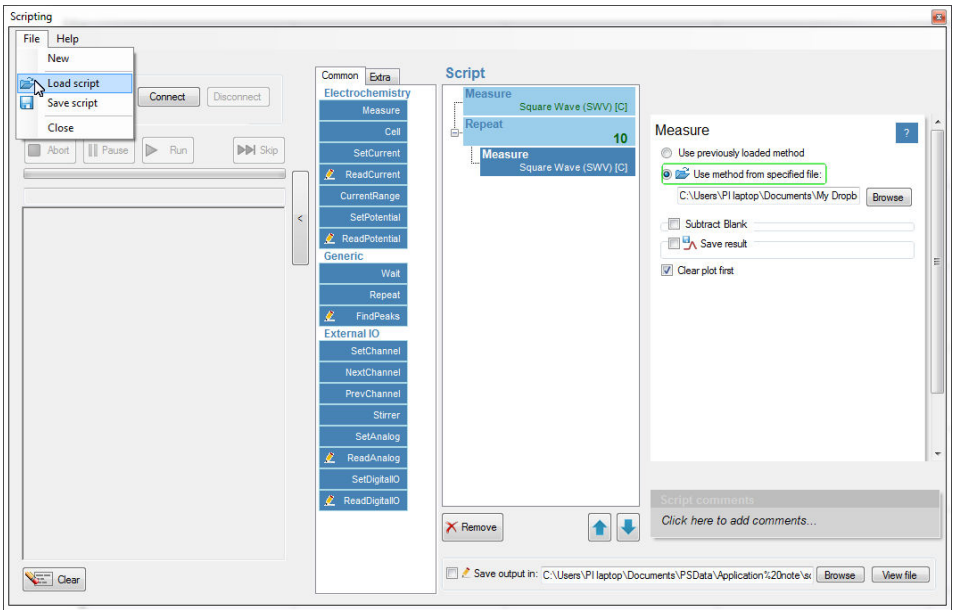

Figure 4.1: the script window

6. Fill the cell with the 100 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. The exact volume is not important. If you don't have the switch box, switch on the stirrer manually. Set the stirring to gentle stir (first black bar on the stirrer knob's scale). Press *Run* in the scripting window. The conditioning takes ca. 15 min. If you don't have a switchbox, manually switch the stirrer off during every *Equilibration* phase and on during the conditioning phase. So after the first 330 s off, on after each measurement and then off after 30 s, but the step of the measurement is indicated by PSTrace on the bottom left. With a switchboc this happens automated.
7. Typical scans from the conditioning stage are shown in Figure 4.2. Please, notice 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. The electrode is now ready to use. The polymer containing a mercury salt covering the electrode at the beginning of the preparation is now turned into a mercury film. This is also the reason why the potential should be kept below -0.1 V, otherwise the mercury film might be destroyed.

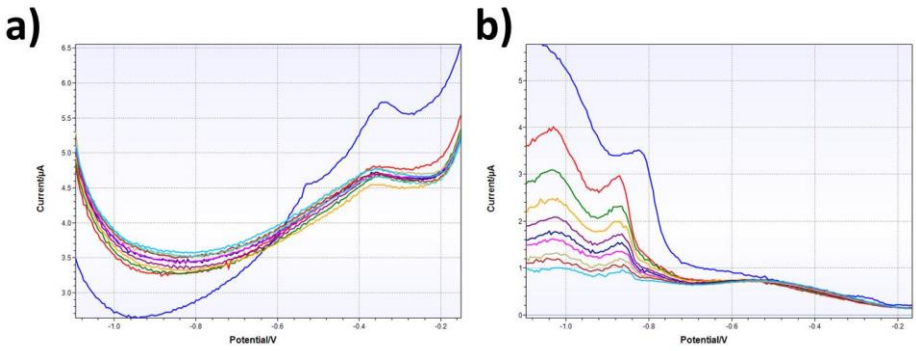

Figure 4.2: typical preparation scans for a IS-HM electrode, curves with shapes of a) and b) have both been observed and lead to functioning mercury films

4.3 Preparing the Analysis in the Analytical Mode

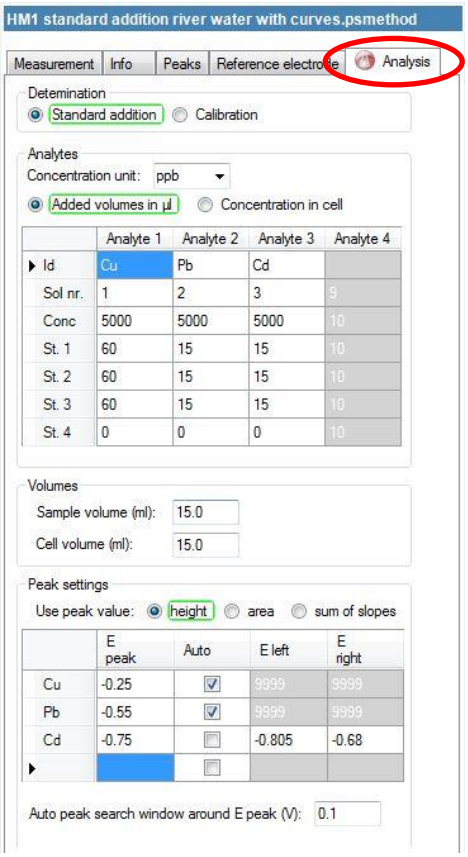

Figure 4.3: Analysis tab in the method editor in the Analysis mode.

This analysis will be performed with the standard addition method. The standard addition method starts by measuring the sample and then measures the sample again after a known amount of the analyte(s) has been added. If a linear relationship 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 after the measurements have been performed.
Switch PSTrace into the *Analytical Mode* by either selecting it in the dropdown menu in the upper left or in the *Tools* menu under *General settings*. In the method box click on the *Analysis* tab as shown in Figure 4.43. Here all the settings for the standard additions need to be inserted. The *Determination* should be set to *Standard addition*. The *Concentration unit* should be set to *µg/L*. The *Added volumes in µL* is selected. In the table all the information for the measurement series is entered. The *Id* is the name of the analyte. Enter here Cu for copper and Pb for lead. If the Cu solution and the Pb solution are separate solutions enter in *Sol nr.* 1 and 2, if it is a mixed Cu and Pb standard solution enter 1 and 1. The *Conc* row is for the concentration of the standard solutions in the concentration unit selected above, that is 5000 (µg/L) in this experiment. The magnitude of the additions might need to be adjusted depending on your sample. During this example an addition of 50 µL per step for Cu and Pb should be fine. The volumes section is used to consider any dilution of the sample. In tap water the Cu amount can be rather high and addition of 100 or even 200 µL might be appropriate. The *Sample volume* is the volume of the sample used and the *Cell volume* is the volume in the cell after the sample has been diluted. The *Peak settings* section defines how the measurements are transformed into values for the analysis. The peak height is proportional to the concentration, so *height* is chosen. The peaks for copper and lead are expected to be clearly visible. In this case the *Auto* option will be okay. But if peaks are very small and/or broad it is difficult for the software to find the peak and then a forced peak border is the mean of choice. The Cu peak is expected around -0.25 V and the Pb peak around -0.55 V. The last parameter *Auto peak search window around E peak (V)* defines how far a peak can differ from the set potential and still be detected. Set it to 0.1 V. All the parameters for the analysis can also be set or changed after the measurement.

4.4 Performing the measurement

Various different water samples are possible for analysis. A good sample to start with is a sample prepared by your instructor. The lack of interference and the possibility to know the true value allows an easy training for this analysis. Interesting samples are river, lake, ocean, and tap water. Waste water might be interesting too, but the possibility for hazard is higher if the source is unknown.

1. The pH of your sample should be around 2.5. This can be achieved by adding 33 µL of 6 M HCl per 10 mL of your sample.
2. Fill the cell with your sample and after immersing the connected sensor again, make sure the three electrodes are covered with sample solution. Insert the magnetic stirring bar and position everything on the stirrer.
3. In the *Technique drop* down list Square *Wave* is selected. Choose the current ranges *1 µA, 10 µA* and *100 µA*. The fields *Sample* and *Sensor* are for your own notes. Set the parameters to:
    a. *E condition = -0.12 V*
    b. *t condition = 45 s*
    c. *E deposition = -1.15 V*
    d. *t deposition = 120 s*

e. *t equilibrium* = 10 s
f. *E begin* = -1.1 V
g. *E end* = -0.1 V
h. *E step* = 0.005 V
i. *Amplitude* = 0.025 V
j. *Frequency* = 25 Hz
k. The *Cell on after measurement* should be checked and E *standby* set to *-0.15 V*

4. Switch on the stirrer and set it to a gentle stir (first black line). If you do not have a switch box, make sure you set the same stirring velocity for every measurement. The stirrer should be on and stirring during the deposition and off during the square wave voltammetry. An easy way to achieve this is to pull the power plug. Press the green *Run* button to start the analysis of the sample. Repeat scans by selecting *Overlay* from the dropdown box and pressing run again until you get a stable peak height (<10 % peak height difference to the former scan). Then select the replicate that you wish to keep and right click on it in the curve legend and then designate the curve as sample.
5. Add an amount of metal that roughly resembles the amount of metal you expect in your sample. Your addition has to be as specified in the analysis table. This can be done by adjusting your table or added volume. In this experiment 50 µL from each standard solution should suffice. Perform the measurement, select for this curve *Standard_1* from the dropdown box (see Figure 4.4). Repeat scans by selecting *Overlay* from the dropdown box and pressing run again until you get a stable peak height (<10 % peak height difference to the former scan). Assign the curve you want to keep as *Standard_1* as *Standard_1*.
6. Add the next amount of metal standard solutions and perform the measurement for Standard_2. And afterwards add metal solution again for measuring Standard_3.

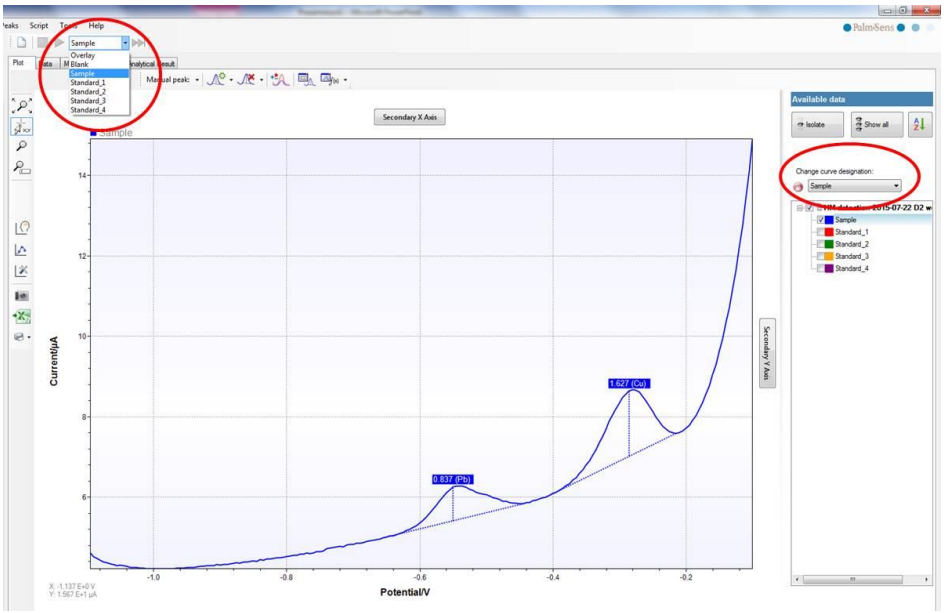

Figure 4.4: The first scan of the sample and the selection of a curve designation.

4.5 Auto-Analysis

After completing all measurements (Sample, Standard_1, Standard_2 and Standard_3) for this analysis click on the *Analytical result* tab to view the calculated data. If you need to adjust the parameters of the analysis in the method editor tab *Analysis*, press the *Recalculate* button in the *Analytical Results* tab after you have made the changes.
The values of the copper and lead analyses are summarized in the box *All results* at the top of the analysis window. Below that you will find the values and plots for copper and lead separately. Single points of the analysis can be included or excluded from individual metal calibration curves by toggling the check box next to that addition.

On completion of the measurements you can save all the data and curves in one file for later use by clicking *Save Analysis* within the *Analysis* menu.

4.6 Alternative Samples

As mentioned in the beginning of chapter 4.4 a wide range of water samples is possible. Depending on the time schedule of the lab course, you can choose multiple samples to determine the copper and lead content. You need to research the legal regulations, if these exist, for the maximum amount of metal in the samples.

In this experiment you detected heavy metals using Square Wave Voltammetry and Stripping Analysis.

Please note that teachers can request the answers to the question in the instructions, using https://www.palmsens.com/contact/