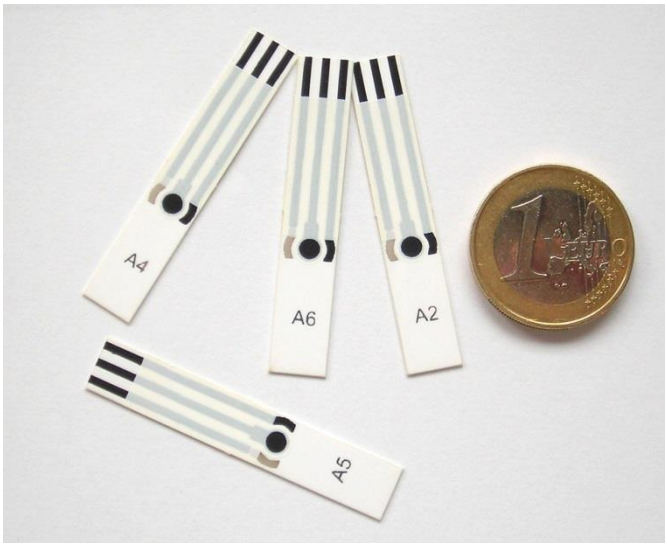
Test Procedure for ItalSens IS-1 Graphite Sensors

Using Naphthol Oxidation to Check the Electrode Stability or Detect Naphthol



PalmSens
Compact Electrochemical Interfaces

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1 Introduction

Conducting electrochemical experiments is sometimes a demanding task. While being usually easy to handle, simple to perform, miniaturized, quantitative and reliable, sometimes the results seem strange or the system seems to be defect. In these situations it is good to be able to check your device, solution and electrodes. The device can be self-diagnosed by running the tests measurements as described in the manual of your PalmSens product. For electrodes it is useful to have some standard procedure with a known substance to check the electrode. Common species used for this task are hexacyano ferrate ($K_3[Fe(CN)_6]$) or hexamine ruthenium ($[Ru(NH_3)_6]Cl_3$). We provide here a method based on naphthol. Naphthol is a common basic chemical and is used e.g. to synthetize pesticides or drugs. It is soluble in water to a certain extend and in organic solvents.

1.1 Goals of this application note

This application note is used to verify the IS-1 (graphite) sensors and their electrochemical stability.

1.2 Alternative use of this application note

The demonstrated detection of naphthol oxidation is a linear signal and thus can also be used for naphthol detection. Just use the standard addition method or prepare a calibration curve to detect naphthol.

1.3 Sensor used

The ItalSens graphite sensors (IS-1 aka IS-C) is based on a three-electrode system, with a graphite working electrode as well as a graphite counter electrode and a silver pseudo-reference electrode. 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 ItalSens flow cell or batch cell.

This application note shows how to measure naphthol in water with a graphite electrode.

2 Experimental part

For preparing the experiment you need: two stock solutions (see 2.3), a properly trimmed SPE and a potentiostat incl. the standard lab equipment

2.1 Equipment required:

- PalmSens, EmStat with PSTrace software (version 3.0 or higher) or PSTouch
- ItalSens IS-1 graphite sensors
- ItalSens sensor cable or another suitable connector
- Simple cell
- Distilled or ultra-pure water
- Plastic or glass containers for the standard and stock solutions

2.2 Reagents:

- Napthol
- Diethanolamine (DEA)
- Potassium chloride (KCl)

2.3 Solution

Prepare two seperate stock solutions of:

- 1 mM napthol solution
- buffer solution: 0.1M DEA and 0.1 M KCl

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 your bare hands. Cut away the access plastic around one the Screen Printed Electrode (SPE) and place it in the connector. You must trim the sensor narrow enough that it fits into the connector, but please take care neither to damage the electrodes nor the lines during cutting.

2.5 Conducting the Experiment

Enter the *Scientific mode* of PSTrace or PStouch to start the analysis. This can be either done by selecting it in the *Tools* → *General Settings* menu of PSTrace or by using the dropdown box top left hand side of the PSTrace screen. In PStouch you can tap on the upper left logo to change the mode or choose in the upper right menu *Select app mode*
Load the method IS-1 ItalSens Graphite Sensor Naphthol.psmethod or enter the parameters manually (see. chapter 3.1.1). Fill the cell with buffer solution, fix the IS-1 SPE in the solution and make sure all three electrodes of the IS-1 are covered with solution. First a blank measurement is recorded to have a reference for a naphthol free solution. Start the measurement. Then using appropriate dilutions repeat the scans with naphthol concentrations of 10 µM , 20 µM and 30 µM. This can be achieved by simply adding the necessary amount of 1 mM napthol solution to the cells and mix the solution afterwards thoroughly. If you start your blank measurement with a 10 mL buffer solution you would need to add 100 µL to raise the concentration to 10 µM, another 100 µL to raise it to 20 µM and another 100 µL to raise it to 30 µM. The results should be as shown in figure 1.

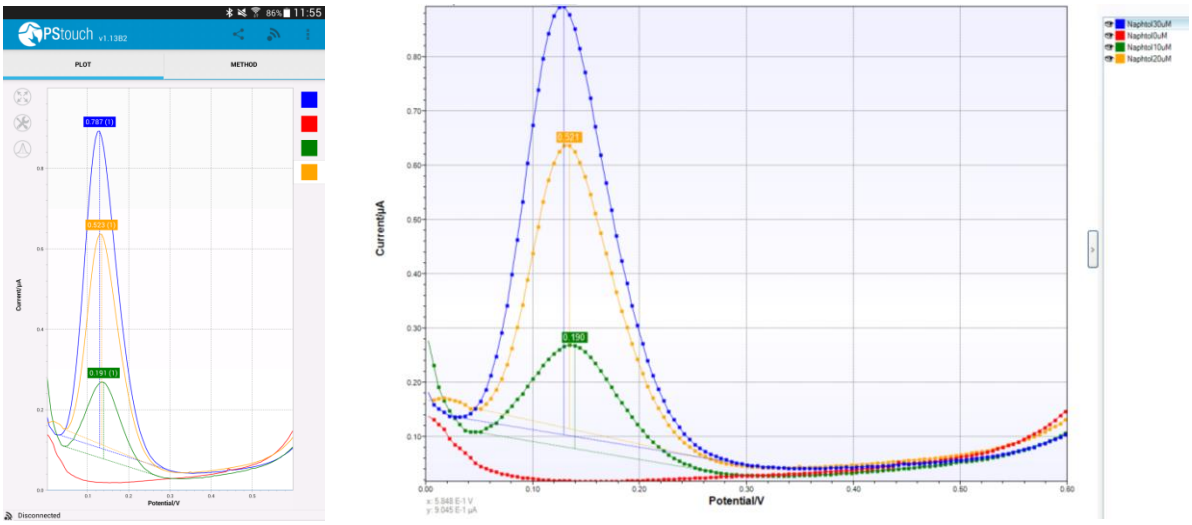

figure 1 The results of the 0, 10 uM , 20 uM and 30 uM naphthol in 0.1M DEA in PStouch (left) and PSTrace (right).

If the scans are significantly different try activating the electrode in a 0.1 M phosphate buffer saline (pH 7). By running Cyclic Voltammetrie (CV) with the parameters listed in 3.1.2. Than repeat the measurement.

Perform DPVs with the parameters from 3.1.1 or load the **IS-1 ItalSens Graphite Sensor Naphthol.psmethod** and perform a measurement in pure buffer and buffer with 10 µM, 20 µM and 30 µM naphthol. Compare your result to figure 1.

3 Additional information

3.1 Parameters for manual setting of the measurement

3.1.1 Measuring Naphthol

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

Parameter	Value
Technique	Differential Pulse
Current Range	10nA-100µA
E cond	0
t cond	0
E dep	0
t dep	0
t eq	8
E begin	0
E end	0.6
E step	0.007
E pulse	0.07
t pulse	0.02
Scan rate	0.07

3.1.2 Activation of a carbon surface

An Activation of a carbon surface removes adsorbed species and creates new surface groups. Perfect surfaces have usually a very low reaction rate. Creating new surface groups increases the reactivity of a carbon surface significantly. This has different reasons one prominent one is the increase of interactions between the surface and the species in solution. To activate a graphite electrode use 0.1 M phosphate buffer saline (pH 7) with at least 10 mM sodium chloride in it. Perform the following method and immediately use the activated electrode.

Parameter	Value
Technique	Cyclic Voltammetry
Current Range	10nA-100µA
E cond	0
t cond	0
E dep	0
t dep	0
t eq	8
E begin	-0.6
E vertex1	1.6
E vertex2	-0.6
E step	0.007
Scan rate	0.1
Number of Scans	40

3.2 Quantifying an unknown naphthol sample

3.2.1 Calibration Curve

With the method used in this application note an unknown amount of naphthol in solution can also be quantified. For this you can either create a calibration curve or perform a standard addition. How to perform the latter one is described thoroughly in the heavy metal detection application note and briefly in chapter 3.2.2. The calibration curve can be done by just measuring as described in this paper and plot the height of the current peak versus the concentration of naphthol in the solution. The result should be a line. Measure now the current of your unknown sample and read from the graph the concentration of naphthol or calculate it with the linear equation.

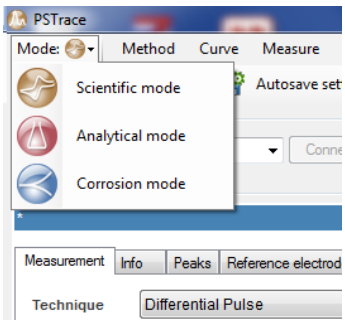

figure 2 Selecting the mode for PSTrace

This method can be automatically plotted and proceed by the Analytical mode of PSTrace. If you have measured your curves for the calibration curve (solutions with known naphthol concentrations) and sample solutions (solutions with unknown naphthol concentration), switch to the analytical mode by selecting the analytical mode from the top left drop down menu (PSTRace, figure 2) or the top right menu (PStouch, figure 3).
Afterwards the curves for the calibration curve and the sample are loaded into the plot window. This is done by choosing in the menu *Curve → Load curve(s)…* and load all the needed curves or choose *Add curve(s)…* to add curves to the plot in PSTrace. In PStouch the first curve is loaded with *Load curve(s)* and the rest is added with *Overlay curve*. Once all the curves are visible in the plot window, assign to each curve its function. This is done by marking the curve in the legend and declaring its designation with the drop down list beneath *Change curve designation* (PSTrace) or the button at the bottom of the curve legend *Assign* (PStouch). The curves for the calibration curves will be declared as *Standard_1* to *Standard_4*. The sample is assigned as *Sample*.
Go to the *Analysis* tab in the method editor (figure 4). Choose *Calibration* as Determination and *µM* as concentration. Check *Concentration in cell* and enter as *Id* for *Analyte 1* an abbreviation for naphthol (e.g. Naphth). Enter for each standard solution the concentration. Enter the volume of the sample (*Sample volume*) put into the cell and the volume after dilution of the sample (*Cell volume*). For the Peak settings choose *height* and as *E peak* the value of one Naphthol solution's peak, e.g. 0.1295 V and 0.1 V for the *Auto peak window*. Afterwards make sure all the peaks of the curve are found be the *Autodetect peaks* button (peak with green cog) by adjusting the values in the *Peaks* tab of the method editor.
After all is set just go to the *Analytical Result* tab of the plot window. After pressing the *Recalculate* button your results and calibration curve are displayed.

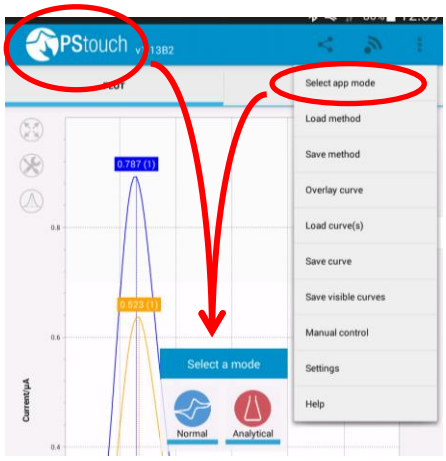

figure 3 Selecting the mode for PStouch

3.2.2 Standard Addition Method

Perform the measurement as described in chapter 2.5, but replace the blank buffer with your sample solution. Instead of just adding 100 µL, try to add an amount of naphthol that is roughly the amount you expect to be in your sample. After you added a few times the 1 mM naphthol solution and performed the measurement, you plot the peak height versus the known concentration of naphthol added. The intersection of the curve and the x-axis is the concentration of naphthol in the unknown sample.
This method can be automatically plotted and processed by the Analytical mode of PSTrace. The protocol is described more detailed in the heavy metal detection application note.

3.3 Why do we need chloride in the solution?

The reference electrode of the IS-1 is a pseudo reference electrode made out of silver. A concentration of at least 10 mM chloride stabilizes the potential of the elctorde by creating a silver chloride layer on top of the electrode.

3.4 Technical specifications of the IS-1

- Dimensions: 0.8 x 4.5 cm
- Working electrode diameter: 3 mm
- Thickness: 450 µm
- Coefficient of variation (CV) (n=10): 5 %
- Storage at room temperature
- Shelf-life time is approximately one year

Applicable in water with 2 < pH < 12 and in solutions with up to 5 % organic solvents like acetonitrile, alcohol etc. **not applicable in chlorinated solvents**.

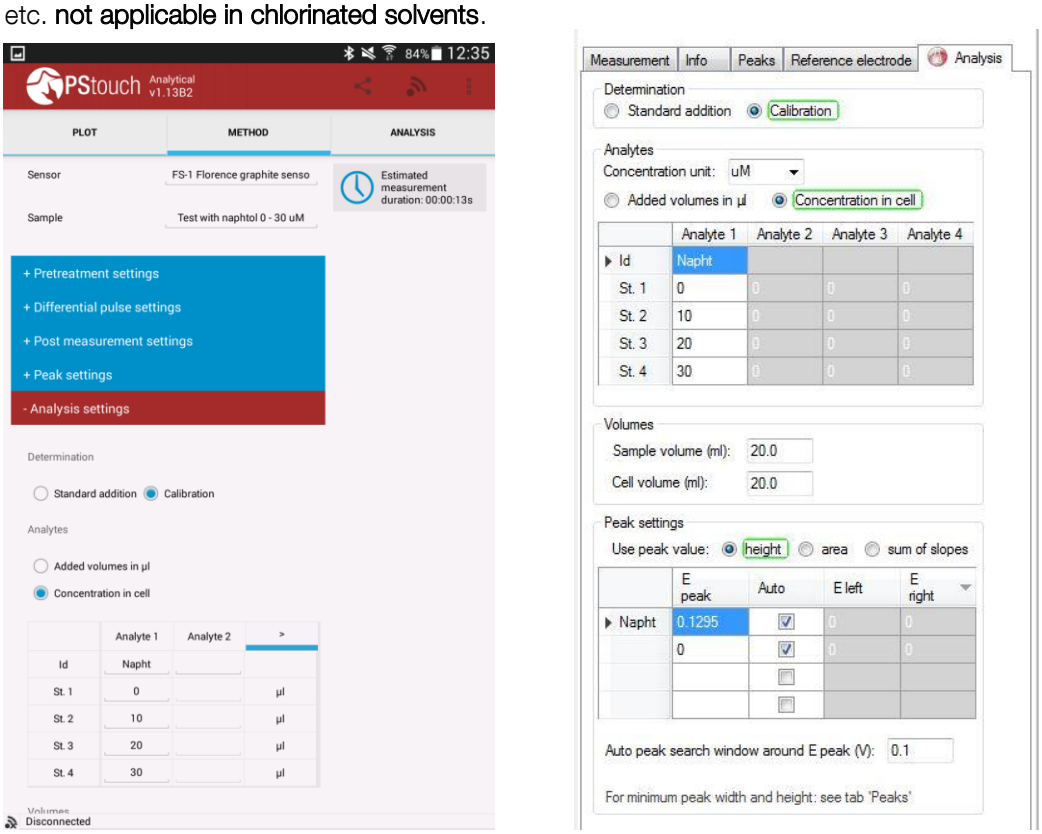

figure 4: The Analysis settings in PStouch (left) and PSTrace (right)