Aditest AP – User Manual

Determination of Antioxidants in Lubrication Oils

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1 Method

Lubrication oils, in industrial processes, are exposed to harsh conditions leading to their oxidative degradation. Antioxidants are added to extend the lifetimes of the oils. Using Aditest AP, the proportion of antioxidants in lubricating oils can be determined by the adsorption stripping linear sweep voltammetry method, according international standards ASTM D6971 and D6810.

During voltammetric analysis, a sample of oil is added to a vial containing a suitable electrolyte. The next step, is thorough mixing of the two phases in the vial – either by hand or using a bar-blender – in order to extract the additives from oil to the electrolyte. Then the electrode system is immersed into the electrolyte solution, where the additives are adsorbed onto the surface of the working electrode – a glassy carbon disc electrode. During the determination, anodic oxidation of electrochemically active substances adsorbed on the surface of the working electrode occurs. The measurement is conducted in a three electrode system with platinum reference electrode. The current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time with scan rate 0.1 V/s. The measured current in the order of A to mA is plotted as a function of applied potential. The results are derived from oxidation current peak surfaces proportional to the additive content.

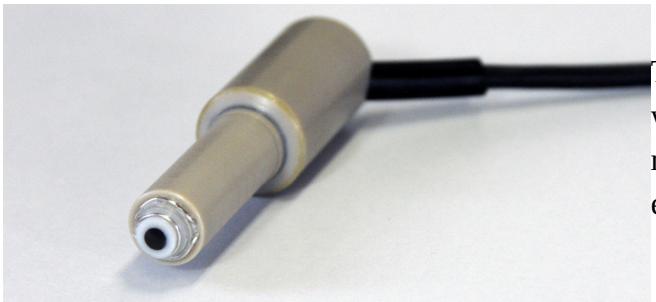
2 Instrument description

Aditest AP (Fig. 1) consists of a metal body and an electrode system.

Figure 1: Aditest AP

Connector (Fig.2 - 1) serves for the electrode system connection. The instrument is interconnected with a computer by USB cable (Fig 2 - 2).

Figure 2: Rear view



The electrode system (Fig. 3) consists of a working glass carbon electrode, a platinum wire reference electrode and a platinum auxiliary electrode.

Figure 3: Electrode system of Aditest AP

3 Solutions and Consumables

3.1 Electrolytes

Electrolyte for phenolic based antioxidant determination – <u>Fenstrip</u>: a mixture of ethanol and distilled water (10:1) containing diluted basic electrolyte.

Electrolyte for aromatic amine based antioxidant determination – <u>Amstrip</u>: a mixture of acetone and distilled water (10:1) containing diluted neutral electrolyte.

3.2 Glass vials

Volume at least 10 mL, diameter 22 mm, inner diameter of the neck 12 mm, to be able to insert the electrode system.

3.3 Pipettes

for sample 0.1 to 0.5 mL

for electrolyte 3 to 5 mL

3.4 Alcohol cleansing pads

for working electrode cleaning.

3.5 Aluminium sheets

Aluminium sheets covered by aluminium oxide layer (for use in thin film chromatography) for electrode system maintenance. See .

4 Example of determination

4.1 Situation

In a typical case of **Aditest AP** use, the additive content in in-service oil is compared to the antioxidant content in a fresh oil. The fresh oil is taken as a standard and the result is expressed as a proportion between an antioxidant content in in-service and fresh oil (calculation: **6 Calculations & Results**). In the following example an aromatic amine based antioxidant is determined.

4.2 Sample preparation

Blank: to a 10 mL vial add 5 mL of electrolyte **Amstrip**.

Standard: in a 10 mL vial mix 5 mL of electrolyte **Amstrip** and 0.4 mL of **fresh** oil. Shake vigorously.

Sample: in a 10 mL vial mix 5 mL of electrolyte **Amstrip** and 0.4 mL of **in-service** oil. Shake vigorously.

4.3 Measurement

1. Connect the electrode system through the connector in the rear panel of the instrument. Connect the computer with USB cable.
2. Launch *Diram Measure* program in the computer.
3. **Caution:** before every individual measurement – voltage scan, it is necessary to thoroughly wipe the surface of the glass carbon electrode by alcohol cleansing pad in order to remove the oxidation products.
4. Press *New calibration* button.
5. Choose *Blank*. Wipe the electrode. Immerse the electrode in the electrolyte to measure **blank**.
6. Measure blank pressing *Start* button. Dialog Voltammogram (Fig. 4) opens. Set maximum potential 1300 mV, scan rate 100 mV/s. Press *Start*.

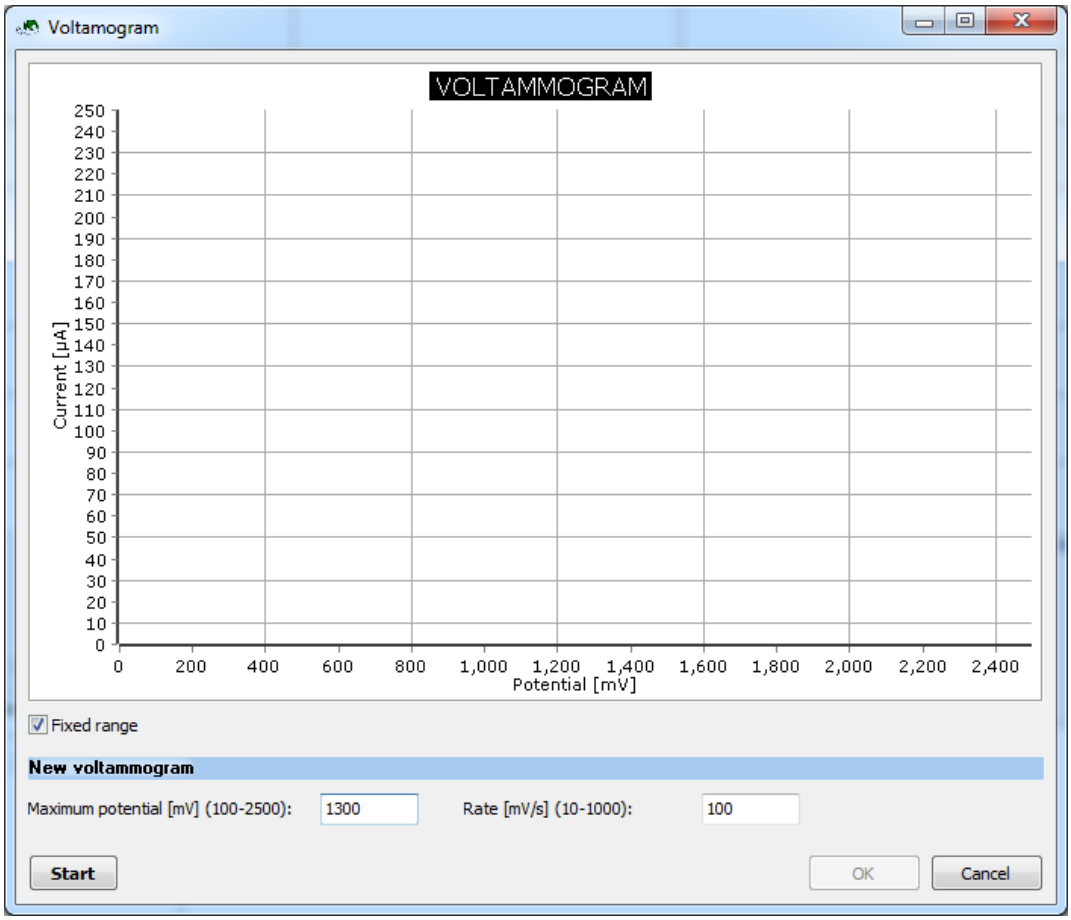


Figure 4: Dialog Voltammogram

7. The result is the black curve depicted in **Fig. 5**. Wipe the electrode. Repeat the measurement. (It is recommended to cancel the first measurement in situations when the electrode has been exposed to air for long periods.)

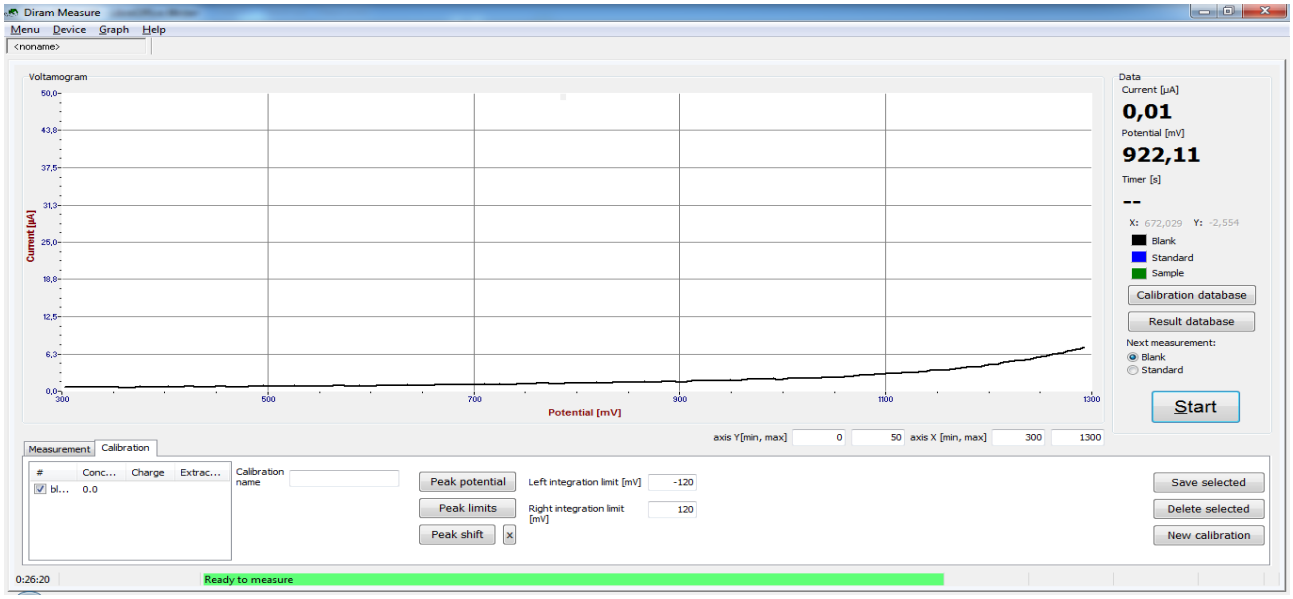


Figure 5: Result for electrolyte – **blank.**

8. Press *Standard* button.

9. Wipe the electrode. Immerse the electrode into the sample **Standard**.

10. Press *Start* button to measure the standard. The result is the blue curve in **Fig. 6**.

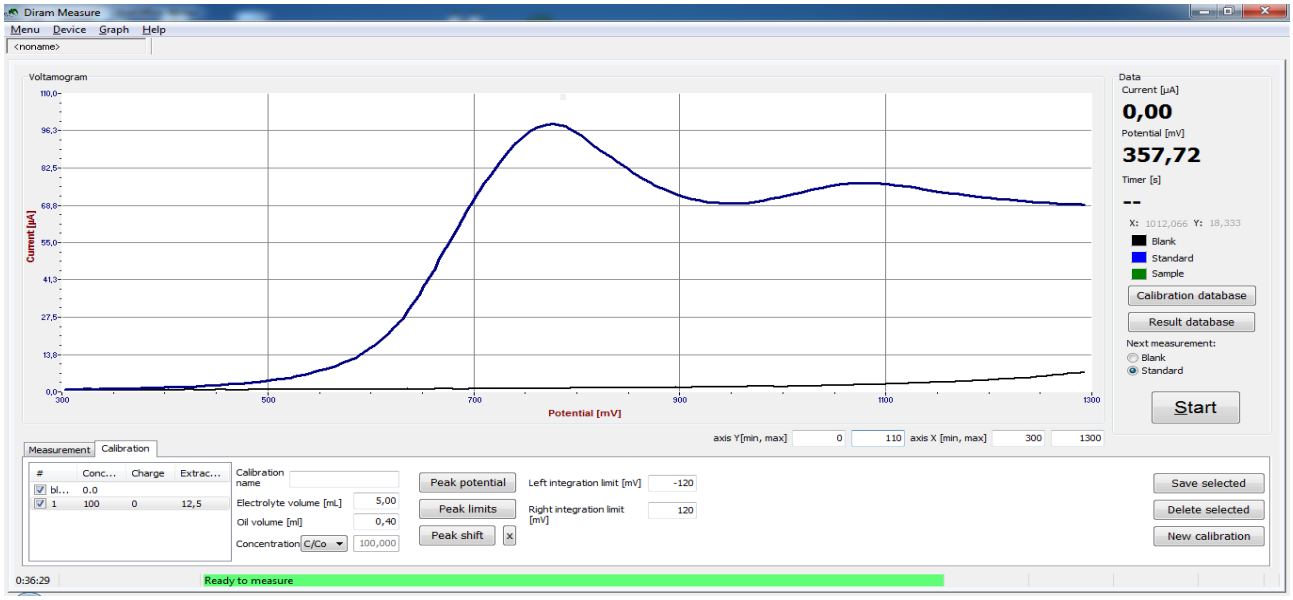


Figure 6: The results for **blank** (black curve) and **standard** (blue curve).

11. Define the peak potential by pressing *Peak potential* button, move cursor to maximum and click the left button of the mouse. Peak potential appears as a solid blue line.

12. Define the peak limits clicking at *Peak limits* button and to the start and the finish as shown in **Fig. 7**. The integration area is given by integration limits depicted by blue dotted lines. The integration limits can be equal to the peak limits or defined in more narrow intervals.

Narrower intervals can lead to more precise results. Integration limits can be changed by inserting numbers to columns *Left integration limit* and *Right integration limit*, respectively. The correct setting of the limits is discused in Chapter 7 Determination of peak limits and integration limits .

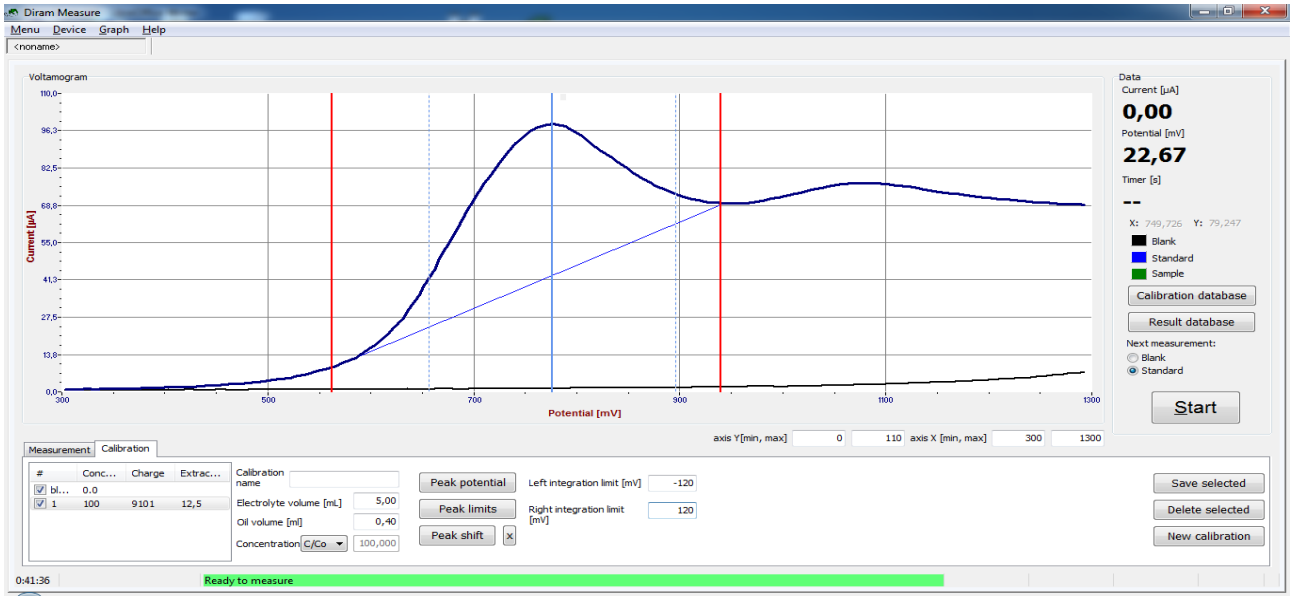


Figure 7: Peak potential - maximum (blue line), peak limits (red lines) and integration limits (blue dotted lines).

13. Wipe the electrode. Measure **Standard** for the second time. The result is another blue curve with maximum slightly shifted with respect to the preceding curve (**Fig. 8**).

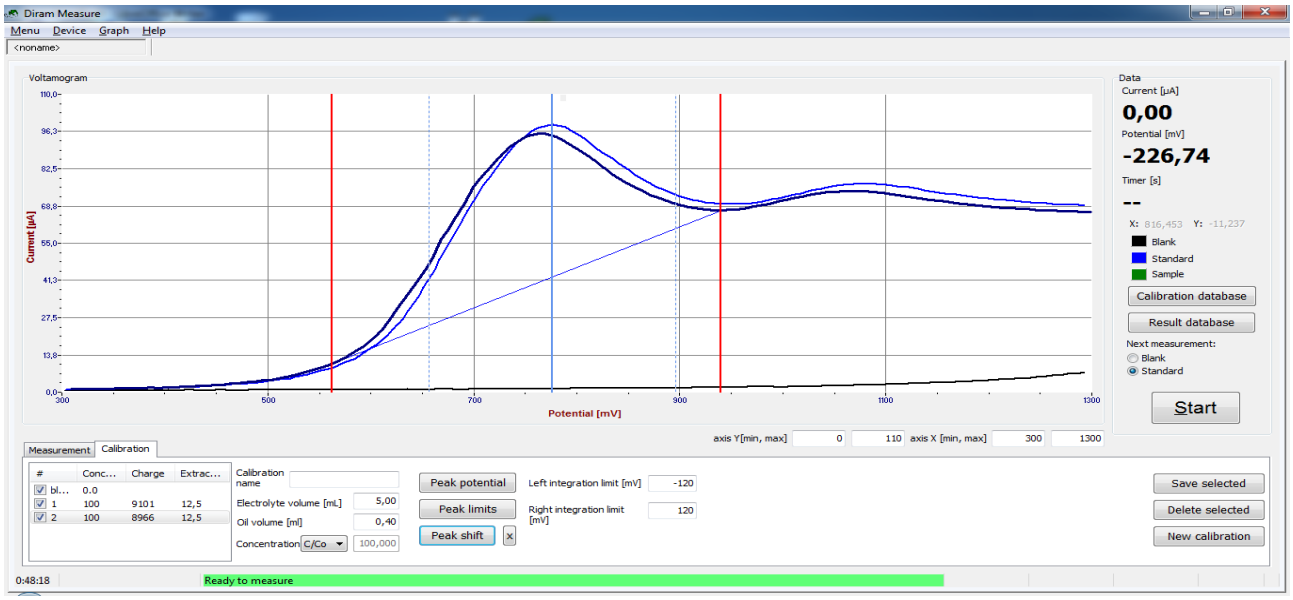


Figure 8: Second **Standard** measurement.

14. Adjust the potential of the peak by pressing *Potential peak* button and by clicking on the peak maximum so that both maxima are on the same potential (Fig**. 9**).

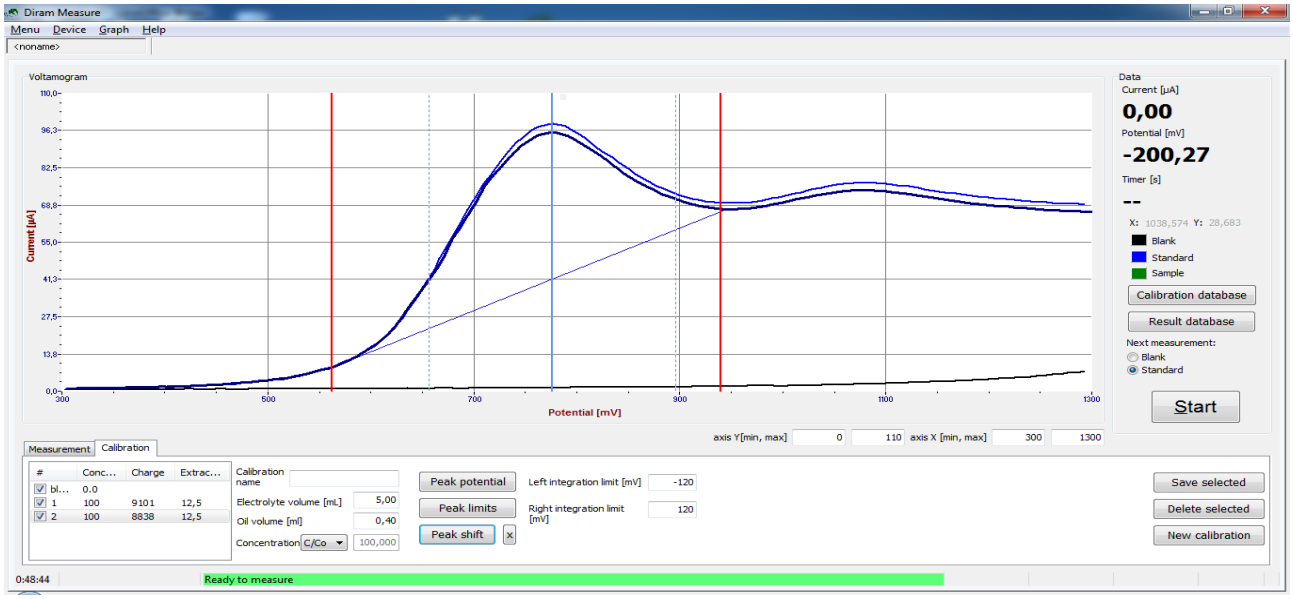


Figure 9: Peak adjustment

15. Wipe the electrode. Measure Standard the third time, adjust potential if necessary. The results should be stable and reproducible.
16. Insert name of calibration i.e. CAL1 to the field *Calibration name* and save by pressing *Save selected* button.
17. Go to the *Calibration database* and choose the calibration by pressing *Use* button.
18. The name of the calibration appears in the main screen: *Used calibration* 57/CAL1. Go to the bookmark *Calibration* and select blank and one of the standard measurements by checkbox in the left part of the main screen. They appear on the screen.
19. Input the sample name to the column *Sample name* (sample 1).
20. Wipe the electrode. Insert the electrode into **Sample**. Measure **Sample** by pressing *Start* button. The result is the green curve (**Fig. 10**).

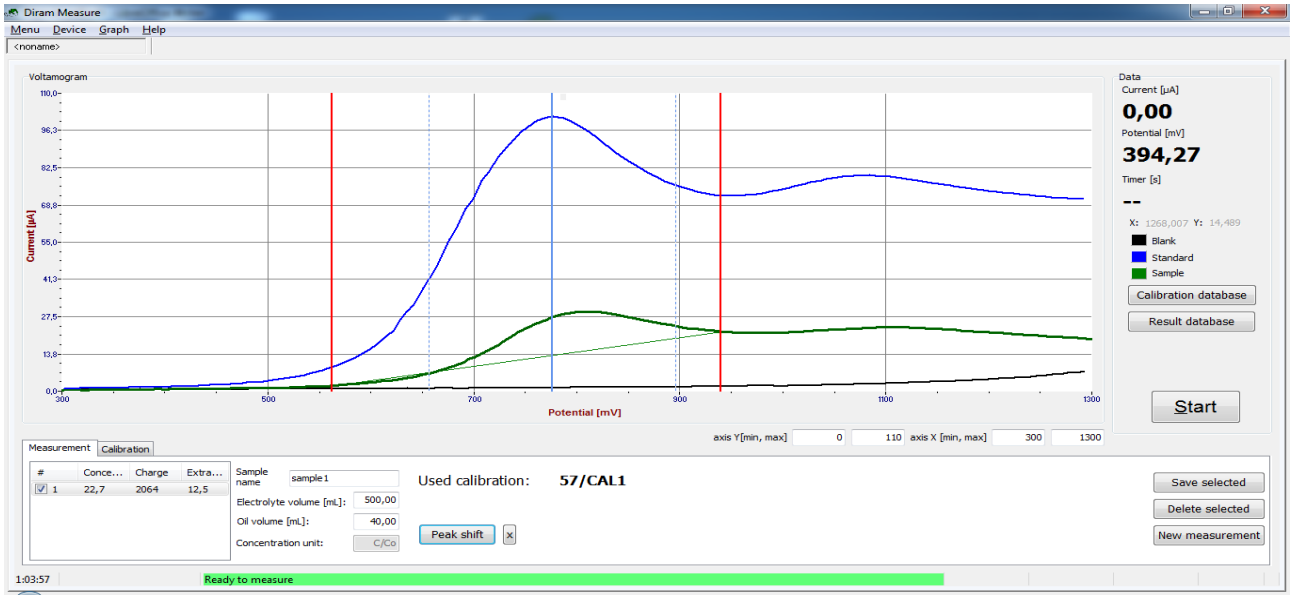


Figure 10: The results for the electrolyte - **Blank** (black curve), **Standard** (blue curve) and **Sample** (green curve).

21. Shift peak position clicking *Peak shift* and then on the peak maximum so that the peak maximum is the same as in Standard (**Fig. 11**).

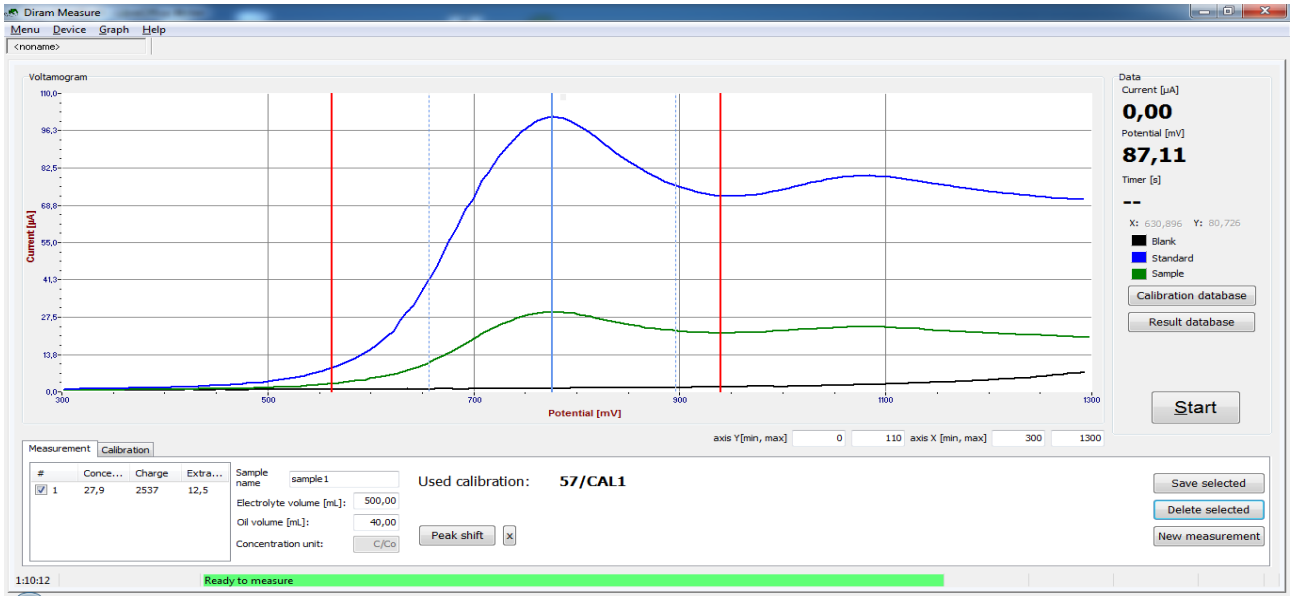


Figure 11: Adjustment of Sample potential.

22. The concentration is displayed (**Fig. 11,** 27.9 %).

23. Use the same procedure to measure Sample at least three times until stable and reproducible results are obtained. (**Fig. 12**). Average of measured values (27.9 %, 28.8 % and 28.0 %) gives resulting 28.2 %. The sample oil contains 28.2 % of original antioxidant level.

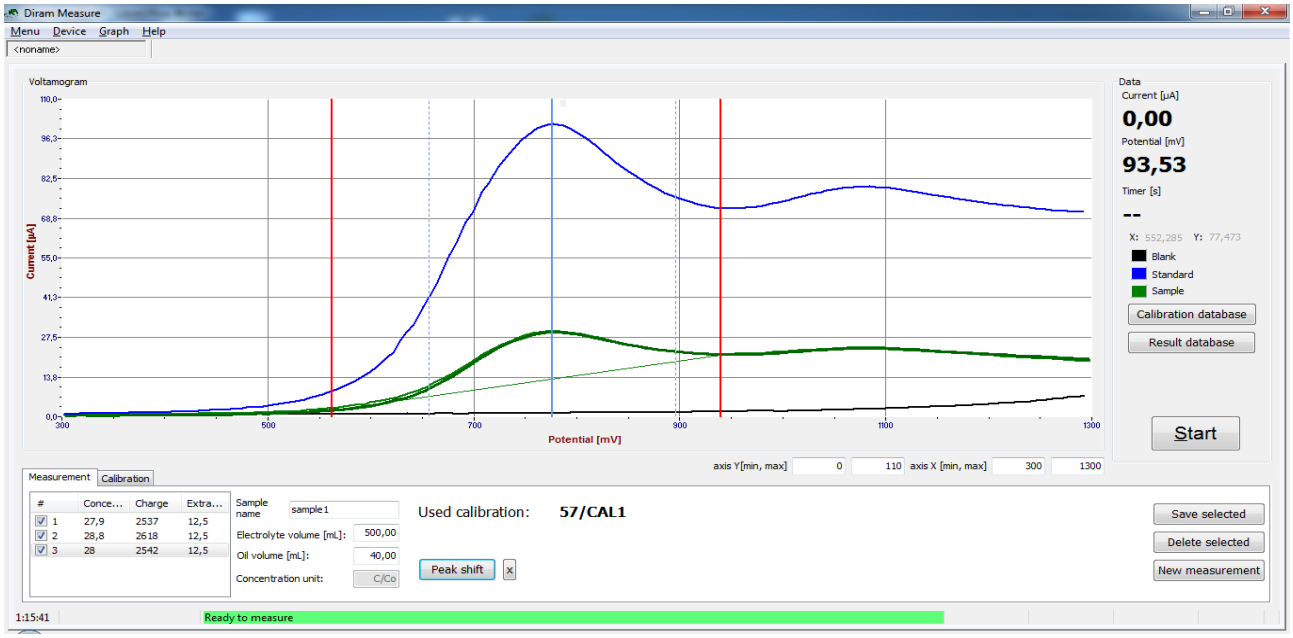


Figure 12: Results for the electrolyte - **Blank** (black curve), **Standard** (blue curve) and three times measured **Sample** (green curves).

5 Calibration database and Result database

5.1 Using calibration database

Calibrations are stored in the Calibration database. Each calibration record has to be started by pressing *New calibration* button on the main screen. When blank and standard are measured (see also Chapter 4.3 Measurement), the peak maximum, peak limits and integration limits are defined, the calibration can be saved under user name by clicking *Save selected* button on the main screen. To perform a measurement it is necessary to go to the Calibration database, select a calibration from the list and click on *Use* button. Then a new measurement can be started by pressing *New measurement* button.

It is possible to modify an existing calibration in the Calibration database by clicking *Modify* button. After changes are made it is possible to save the modified calibration as a new calibration in the database.

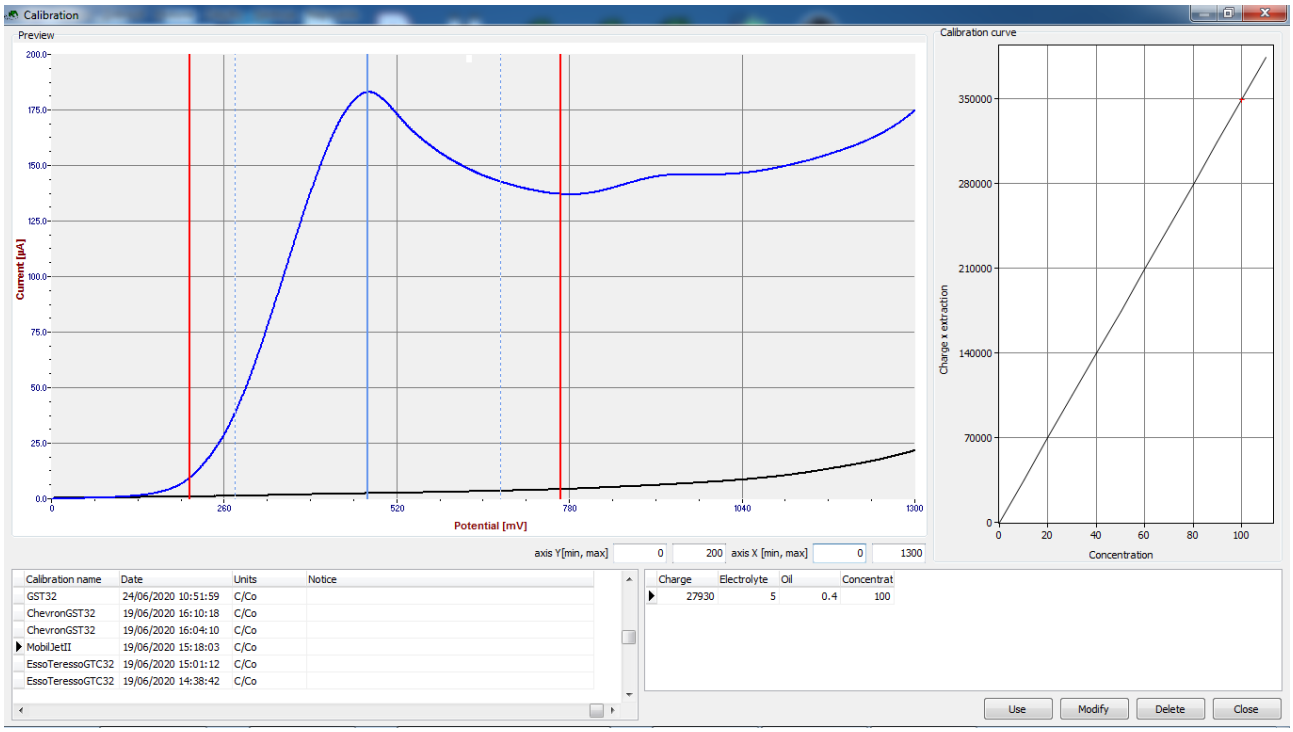


Figure 13: Calibration database

5.2 Using result database

To start a new measurement it is necessary to first select a calibration from the calibration database and click on *Use*. Than *New measurement* in the main screen should be pressed. Each measurement is connected to the pre-selected calibration: the peak position, peak and integration limits are defined by the calibration. Only *Peak shift* is allowed for measurement. When after a new measurement it is realized that another limits are required it is necessary to modify the calibration

accordingly and then repeat the measurement with the modified calibration. The measurement is saved to the Result database by pressing *Save selected* button.

6 Calculations & Results

In example in Chapter 4 the standard was fresh oil and the results were given in percents as a ratio of the remaining antioxidant in the in-service oil and in the fresh oil:

$$\text{remaining antioxidant [\%]} = \frac{\text{Sample peak area}}{\text{Standard peak area}} * 100\,\%$$

where the peak area is from above restricted by the measured curve and from bottom by the line connecting intersections of measured curve and red lines of peak limits. Left and right integration limits are given by blue dotted lines. Prior to the integration, the Blank is automatically subtracted from the measured curve.

If the antioxidant content in Standard is known, the content in in-service sample can be calculated as percentage or in mmol/L:

$$\text{antioxidant content [\%]} = \frac{\text{Sample peak area}}{\text{Standard peak area}} * \text{ antioxidant content in standard [\%]}$$

$$\text{antioxidant content [mmol/L]} = \frac{\text{Sample peak area}}{\text{Standard peak area}} * \text{antioxidant content in standard [mmol/L]}$$

If the additive and the lubrication oil are available, it is possible to perform the calibration using a set of standards with known additive concentration. The **Diram Measure** program then automatically returns concentration of additives in sample.

7 Determination of peak limits and integration limits

7.1 Peak limits

For correct determination of the peak, it is essential to set correct peak limits both in calibration and measurement mode. An example of a correct setting of a peak limits is shown in Fig.14. where the peak limits are red vertical lines and the peak area is in light blue. The upper limit is selected as a “valley” between two neighboring peaks. The lower limit is carefully selected to maximize the peak area while avoiding a negative area. An example of incorrect peak limit setting is given in Fig.15. In this example the lower peak limit is too low creating a negative peak area (in red).

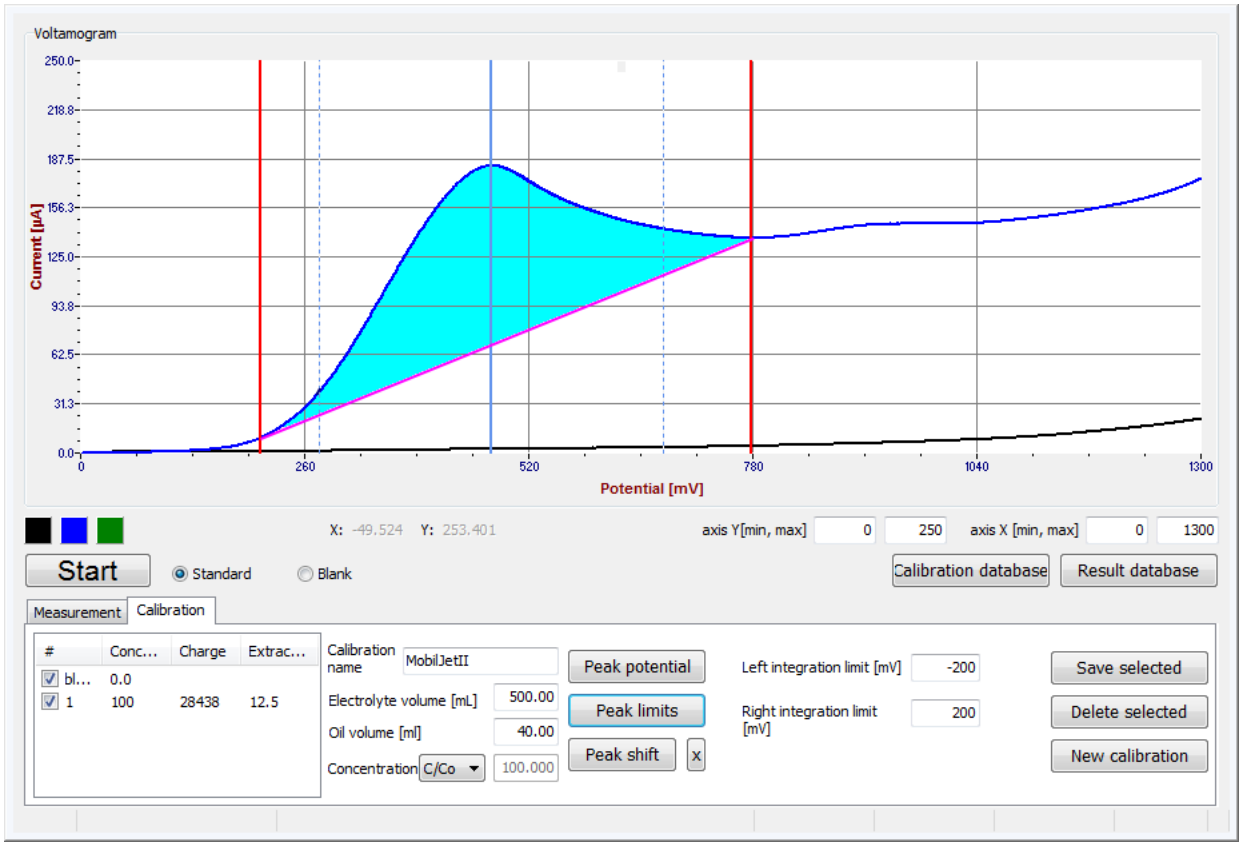


Figure 14: Correct determination of the peak area

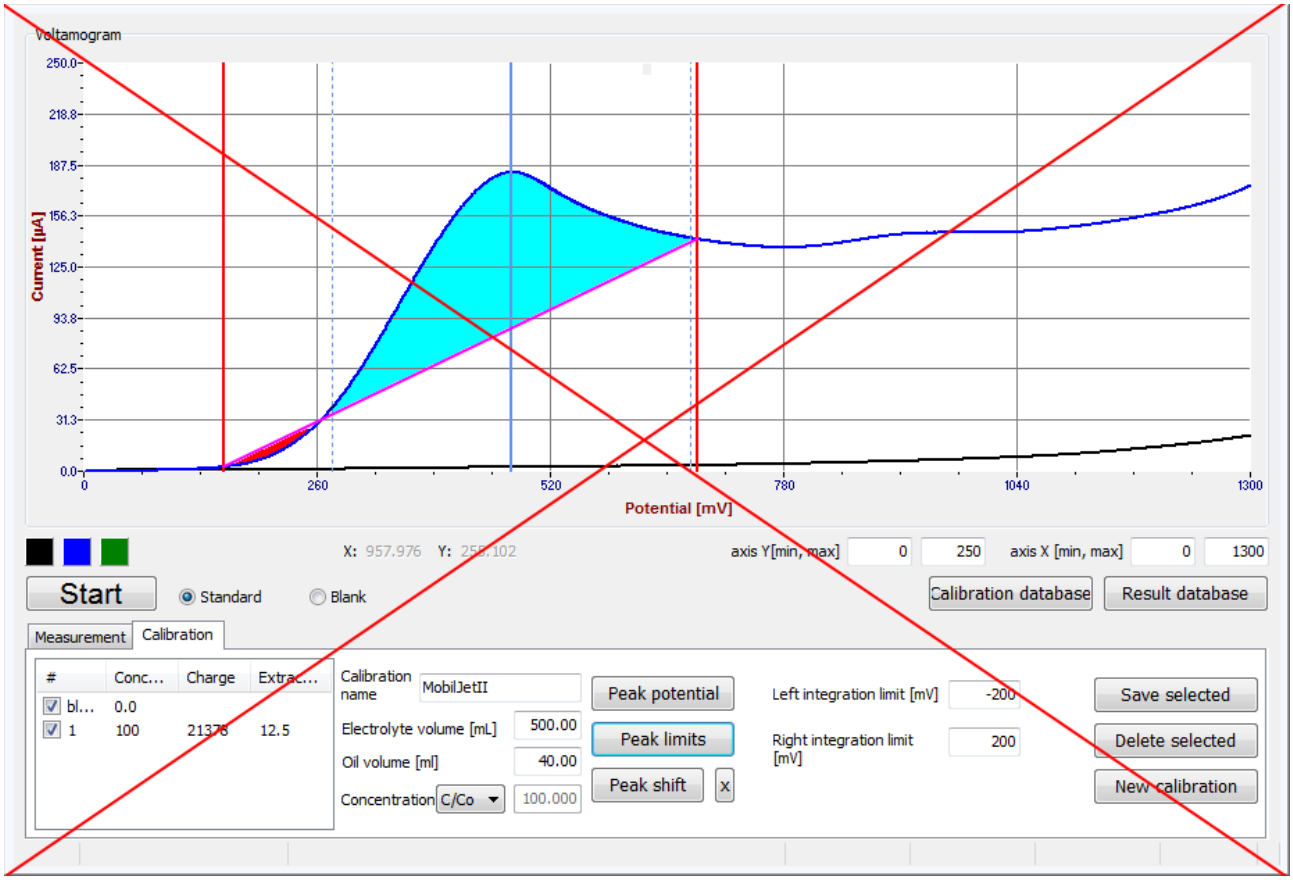


Figure 15: An example of incorrect setting of the peak limits

7.2 Integration limits

When the peak limits are correctly defined it is necessary to set the integration limits. In the *Diram Measure* program they are marked with blue dotted lines. The area that is used for calculations (yellow area in Fig. 15) is defined by the voltammetric curve, the magenta line connecting the intersections of the voltammetric curve and peak limits and the integration limits on the right and on the left. This area is proportional to the antioxidant concentration and is expressed numerically in a column in the left bottom part of the screen as “Charge”.

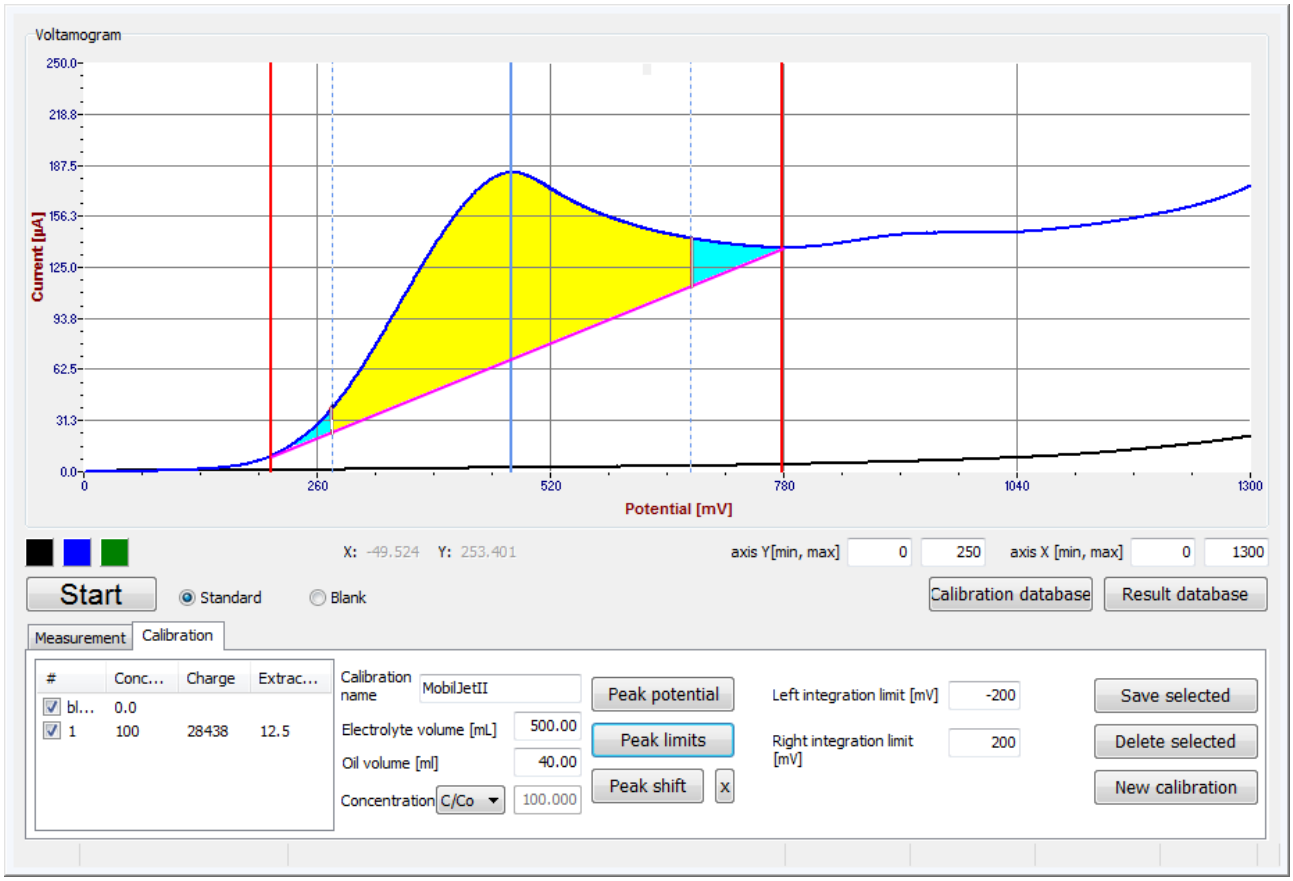


Figure 16: Definition of the integration area

The integration limits can be simply set equal to the peak limits. It is easy to do in the *Diram Measure* program by typing some large number to the columns **Left integration limit [mV]** and **Right integration limit [mV]**. When the inserted number exceeds the peak limit it is automatically set equal to the peak limit as the integration limit cannot be larger than the peak limit by definition. However, in some cases (i. e. close peaks partially overlapping) it can be advantageous to use more narrow integration interval. Using narrower integration interval does not introduce any additional errors to the calculation.

8 Maintenance of electrode system

The surface of the glassy carbon electrode is essential for correct measurement. It should always be maintained mirror glossy. Any scratching of the glassy carbon surface by contact with hard objects should be avoided.

Between individual measurements, the surface of the glass carbon electrode is wiped by alcohol cleansing pad in order to remove the oxidation products as described in Chapter 4.3 Measurement. Between and after measurements, the electrode system can be rinsed by acetone or ethanol and gently dried by a soft paper. Do not leave the electrode system dipped in the working electrolyte longer then necessary for measurement.

When the surface of the electrode becomes dim or scratched, it can be polished using aluminium sheets covered by fine aluminium oxide (these sheets are produced for thin film chromatography application). Move the glassy carbon electrode surface gently in a circular motion on the white side of the aluminum sheet until the prefect glossy surface is achieved.

9 Types of samples

9.1 Hindered phenol based antioxidants

Hindered phenol antioxidants include, but are not limited to 2,6-di-*tert*-butyl-4-methylphenol, 2,6-di-*tert*-butyl-4-butylphenol, 4,4´-methylenebis (2,6-di-*tert*-butyl-4-butylphenol).

In basic electrolyte (**Fenstrip**), phenol based antioxidants are detected at lower potentials compared to the situation in neutral electrolyte. When determining only phenols, it is therefore more convenient to use basic electrolyte **Fenstrip** as it is better to perform analysis at lower potentials because of lower bias. Aromatic amine based additives are oxidized at higher potentials and do not disturb the determination. Measurement of hindered phenolic antioxidants in non-zinc turbine oils is standardized by ASTM D6810.

9.2 Aromatic amine antioxidants

Aromatic amine antioxidants include, but are not limited to, alpha-naphtylamines and alkylated diphenylamines.

When analyzing only amines the elctrolyte of choice is **Amstrip**. In neutral electrolyte (**Amstrip**), aromatic amines are detected at lower potentials compared to phenol based antioxidants. Samples containing both phenols and amines can be analyzed in neutral electrolyte **Amstrip**, where separated peaks of amines and phenols are obtained. Measurement of hindered phenolic and aromatic amine antioxidants in non-zinc turbine oils is standardized by ASTM D6971.