Application Area: Analytical Electrochemistry

Metrohm 663 VA stand for Heavy Metal Ions detection in Water

Keywords

Heavy metal, analytes, solution, differential pulse voltammetry, analytical electrochemistry, voltammetry

Introduction

The determination of heavy metal ions in a solution is one of the most successful applications of electrochemistry. Many electrochemical techniques were developed for this scope.

In this application note, anodic stripping voltammetry is used to measure the presence of two analytes, Pb and Cd, in a sample of tap water.

Additionally, the standard addition method is used to quantify the concentration of the two above-mentioned elements.

Experimental setup

A PGSTAT302N, equipped with a Metrohm 663 VA stand was used (2.663.0020).

The working electrode (WE) was a Multi-Mode Electrode pro (6.1246.120)[1] in the dropping mercury electrode (DME) configuration.

The reference electrode was a double junction Ag/AgCl reference electrode (6.0728.120). All potential values mentioned in this document are referred to the potential of this electrode.

The electrolyte was composed of 10 mL H_2O + 0.5 mL of acetate buffer, made of 1 mol/L ammonium acetate + 1 mol/L acetic acid.

The experiment was divided in three parts. The first part was an anodic stripping voltammetry measurement of the sample. The second part was an anodic stripping voltammetry measurement with the first addition of standard solutions in the same vessel. The third part was an anodic stripping voltammetry measurement with a further addition of standard solutions in the same vessel.

For the first addition, the solution was composed as followed: 10 mL H_2O, 500 µL acetate buffer, 100 µL Pb standard solution (1 mg/L) and 100 µL Cd standard solution (1 mg/L).

For the second addition, the solution was composed as follows: 10 mL H_2O, 500 µL acetate buffer, 200 µL Pb standard solution (1 mg/L) and 200 µL Cd standard solution (1 mg/L).

Each measurement consisted of a section for preconditioning the Hg electrode, where nitrogen was purged in the stirring solution and a new drop was formed. Then, a reduction potential of -0.9 V was applied at the Hg drop, in order to reduce the Pb and Cd anions at the Hg drop surface under stirred conditions.

Afterwards, the stirrer was switched off and the differential pulse voltammetry (DPV) measurement was done. In Figure 1, the potential profile applied to the cell, is shown together with the specific parameters, which are used to define the applied signal.

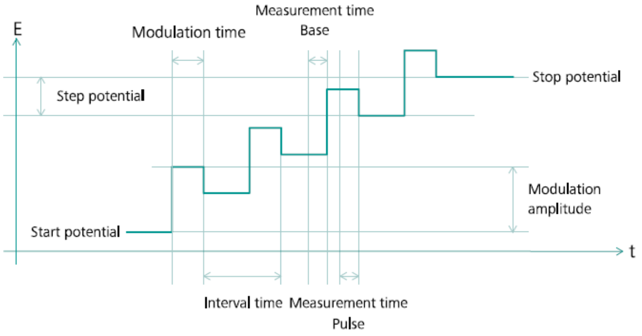

Figure 1 – Schematics of a potential signal for the differential pulse voltammetry applied to the cell.

- The potential was applied from -0.9 V (start potential) to -0.2 V (stop potential).
- The modulation amplitude was 50 mV, applied for 40 ms (modulation time).
- Finally, the interval time was set to 100 ms.

The resulting current was recorded at the end of the base, and at the end of the pulse.

The outcome of the differential pulse voltammetry is a differential current vs. applied potential plot, with peaks at the reduction potential of the analytes.

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[1] A description of use and maintenance of such an electrode is show in: http://va-electrodes.metrohm.com/#!/

The second and third steps of the experiment are similar to the first one (presented above), with the addition of standard solutions.

The peak heights were determined from the current vs. potential plot of the three sections of the experiment. Peak height vs. analyte concentration plots were built for both Pb and Cd. From the intersection of the regression line with the X–axis, the concentration of the analyte in the sample can be calculated.

Results and Discussion

In Figure 2, the voltammograms resulting from the differential pulse voltammetry of the three sections of the procedures are shown: no standard addition (blue line), first addition (in red) and second addition (in green).

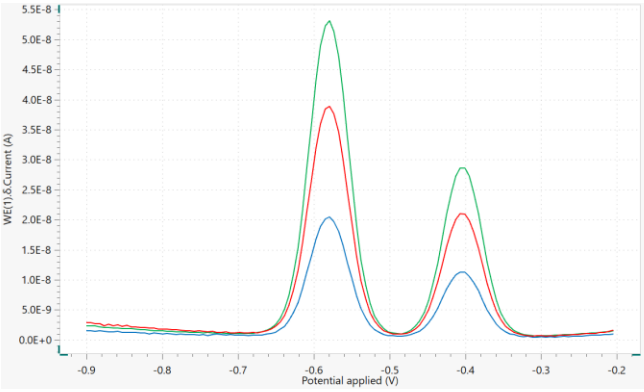

Figure 2 – Differential pulse voltammetry plot with no standard addition (in blue), with the first addition (in red) and with the second addition (in green).

The peak related to Pb^{2+} reduction appears at -0.40 V, and the due to the reduction of Cd^{2+} appears at -0.58 V. As expected, the peak height increases after each addition.

Figure 3 and Figure 4 shows the height of the Pb and Cd peaks plotted vs the concentration of Pb and Cd, respectively.

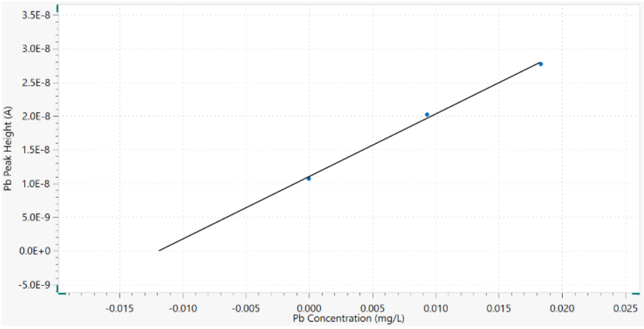

Figure 3 – Pb peak heights vs. Pb concentration. The regression line is also shown (in black).

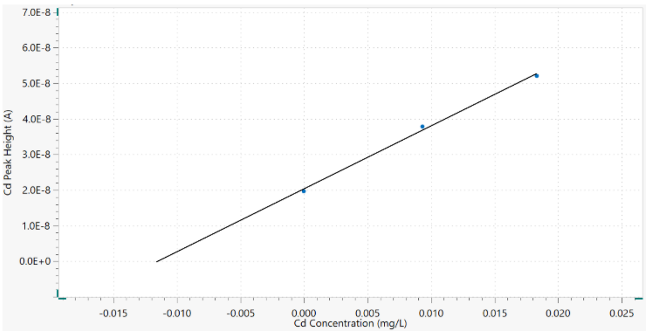

Figure 4 – Cd peak heights vs. Cd concentration. The regression line is also shown (in black).

A regression line is drawn on the plots of Figure 3 and Figure 4. The intercept value with the X–axis (i.e., at peak height equal zero) is the analyte concentration $-C_s\ (\mu g/L)$ in the measuring vessel.

The concentration $C\ (\mu g/L)$ of the analyte in the sample is given by the following formula:

$$C = \left| -C_s \cdot \frac{V_{cell}}{V_{sample}} \right| \qquad 1$$

Where $V_{cell}\ (L)$ is the total volume, composed of sample, electrolyte and water, and $V_{sample}\ (L)$ is the volume of the sample.

In the example above, the sample volume was $V_{sample}\ (mL) = 10.2$ and the cell volume was $V_{cell}\ (mL) = 10.7$. The analyte concentration in the measuring vessel was $-C_{s,Pb}\ (\mu g/L) = -11.83$ for Pb and $-C_{s,Cd}\ (\mu g/L) = -11.46$ for Cd.

According to Equation 1, this results in a Pb concentration of $12.41\ \mu g/L$ and a Cd concentration of $12.04\ \mu g/L$.

Conclusions

The combination of the Metrohm 663 VA stand and Metrohm Autolab PGSTATs allows performance of a complete range of electroanalytical experiments.

In this application note, differential pulse voltammetry (DPV) was used, to determine the concentration of lead and cadmium, in tap water. The technique of standard additions was used, and the concentration was calculated with the aid of the NOVA software.

Remarks

When the results obtained with other Metrohm instruments (e.g., VA Computrace, VIVA, Portable VA Analyzer) are compared with results obtained with the Metrohm 663 VA in combination with NOVA, slight differences can occur. The reason is that the calculations embedded in the Metrohm software tools are complex and might be slightly different. For example, Metrohm VA Computrace software can correct for the additional dilution due to every standard addition. When the volume of the added standard is small, the difference is negligible, but for higher volumes, it makes a significant difference. Please contact us in case you need any help in choosing the instrumentation which best fits your application.

Date

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For more information: Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**.

Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry**.