Application Note AN-SENS-002

采用差分脉冲伏安法重金属

A voltammetric approach for the quantitative analysis of heavy metal ions with INTELLO and NOVA

Heavy metal contamination poses significant environmental and health concerns, necessitating reliable analytical techniques for detection. Differential pulse voltammetry (DPV) is a widely used electrochemical method for the sensitive and selective quantification of heavy metal ions.

This Application Note describes the principles of DPV, its advantages over other electroanalytical techniques, and its implementation for detecting heavy metals in aqueous samples. Experimental parameters, electrode selection, and standard addition procedures are discussed, along with representative results demonstrating the method's effectiveness.

INTRODUCTION

DPV, alongside square wave voltammetry (SWV), already discussed in AN-SENS-001, is another example of a pulsed voltammetric technique. DPV was actually developed first and is often linked to the field of polarography. This pulsed voltammetric technique is typically used with a dropping mercury electrode, although the general principle can be applied to static electrodes as well. In the case of DPV, a short pulse with constant height is superimposed at the end of every step of a staircase linear sweep voltammetry (LSV) determination (**Figure 1**). During the experiment, the current is sampled at two points: before (i_1) and after (i_2) the pulse. The difference (i_1-i_2) vs. the potential is the signal which is plotted in DPV. Sometimes i_1 is referred to as the base current and i_2 as the pulse current.

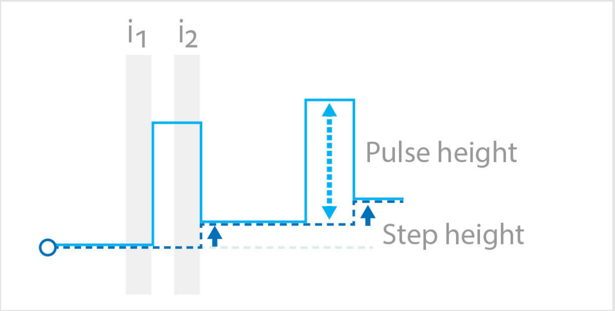

Figure 1. Typical DPV waveform for the forward direction (e.g., from 0 to 1 V).

Like SWV, this approach allows the separation of faradaic and capacitive current, boosting the sensitivity of the technique compared to normal staircase voltammetry. In INTELLO, the i_1 and i_2 signals can optionally be sampled in the signals tab of the DPV command. In NOVA, custom plots of either signal can be produced in the same tab. The waveform is characterized by the height of the pulse (ΔE) and the step height (ΔE_s). The scan rate is determined only by step height and step duration of the underlying LSV. The pulse duration should not be set longer than the step duration in order to avoid artifacts, with typical values for the step being around 100–500 ms, and around 50 ms for the pulse. In comparison to SWV, DPV is considered less applicable to a wider range of systems due to the interference of oxygen and the slower scan rates required for DPV. In some cases it can produce better separation of closely positioned peaks and sharper peaks in general. The following is an example of a typical DPV measurement made with a PGSTAT302N and the Metrohm 663 VA stand, with the same measurement also possible with the next-generation VIONIC powered by INTELLO.

SAMPLE AND EXPERIMENTAL DETAILS

A PGSTAT302N equipped with a Metrohm 663 VA stand (2.663.0020) was used for this study. The working electrode (WE) was a Multi-Mode Electrode pro (6.1246.120) in the dropping mercury electrode (DME) configuration. The reference electrode (RE) was a double junction Ag/AgCl reference electrode (6.0728.120). All potential values mentioned in this Application Note 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 concentration of heavy metal ions was quantified by making two standard additions. For the first addition, the solution was composed as follows: 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 step to precondition the Hg electrode, where nitrogen was purged in the stirring solution and a new Hg 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 stirring conditions. Afterwards, the stirrer was switched off and the DPV measurement was performed. The DPV measurement was repeated twice.

The peak heights were determined from the current vs. potential plot of the three experimental iterations (i.e., sample, sample with first standard addition, and sample with second standard addition). Peak height vs. analyte concentration plots were created for both Pb and Cd. The analyte concentration in the sample can be calculated from the intersection of the regression line with the x-axis.

RESULTS AND DISCUSSION

Figure 2 shows the voltammograms resulting from the DPV of the sample and the two standard additions.

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

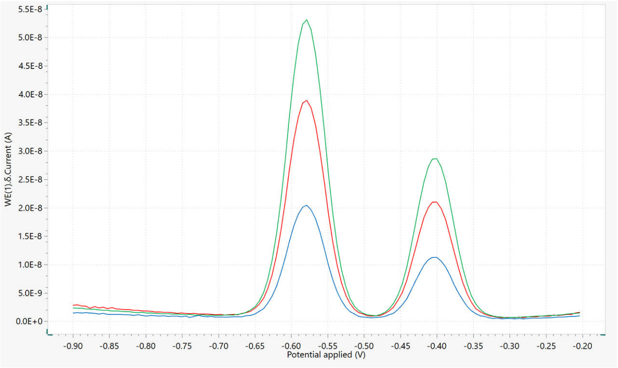

Figure 2. Differential pulse voltammetry plot with no standard addition (in blue), with the first standard addition (in red), and with the second standard addition (in green).

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

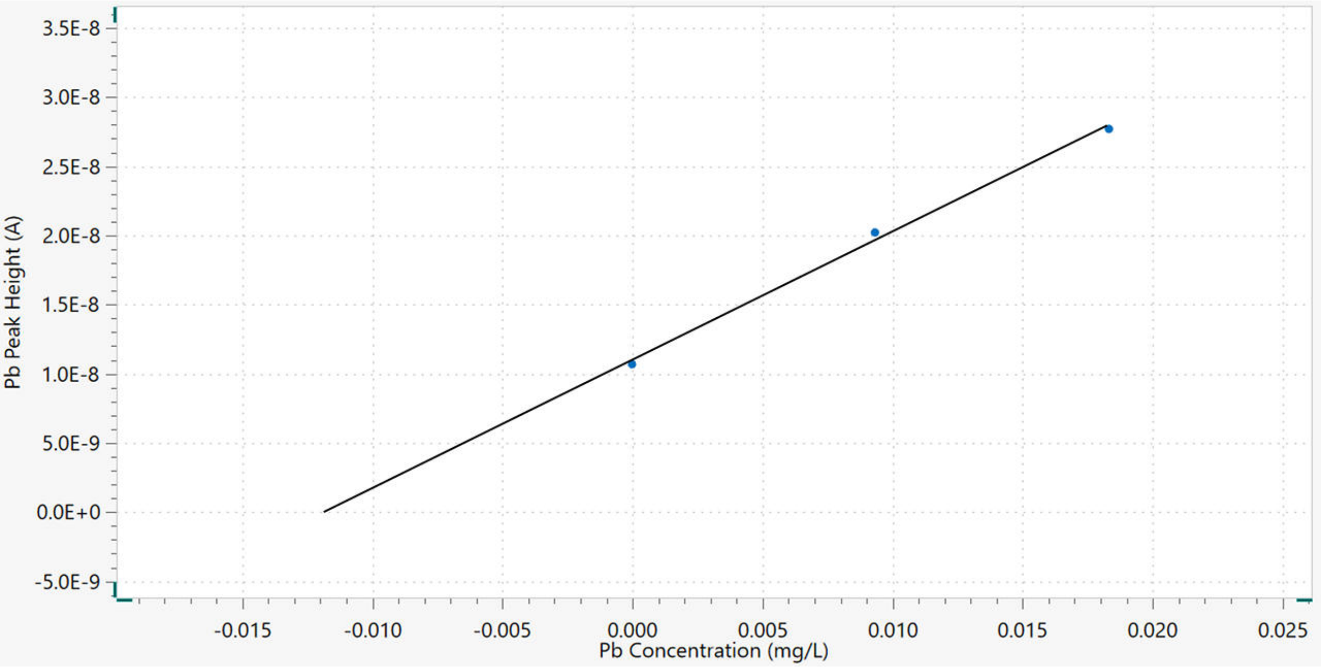

Figure 3. Pb peak height vs. Pb concentration. The regression line is also shown in black.

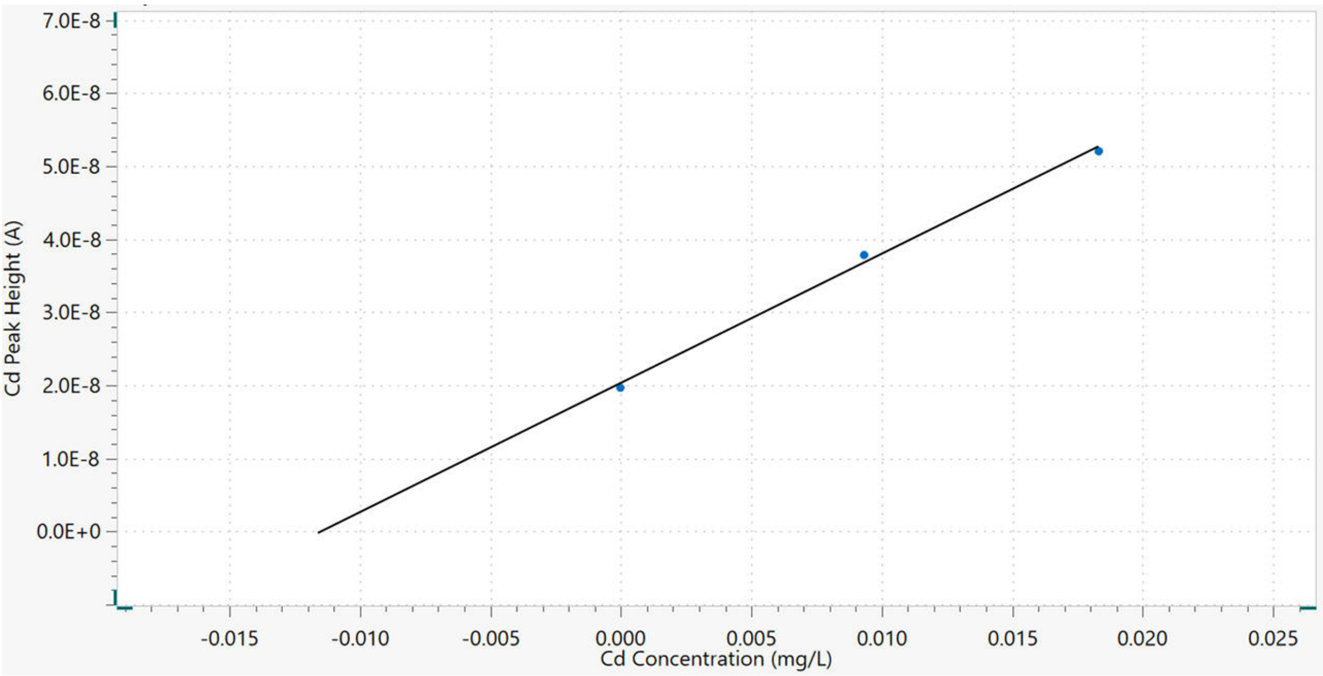

Figure 4. Cd peak height vs. Cd concentration. The regression line is also shown in black.

A regression line is drawn on the plots of **Figure 3** and **Figure 4**. The intercept value with the x-axis (i.e., at zero peak height) is the analyte concentration -C_s (µg/L) in the measuring vessel. The concentration C (µg/L) of the analyte in the sample is given by the following formula:

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

Equation 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 $C_{s,Pb}$ (μg/L) = 11.83 for Pb and $C_{s,Cd}$ (μg/L) = 11.46 for Cd.

According to **Equation 1**, this results in a Pb concentration of 12.41 μg/L and a Cd concentration of 12.04 μg/L.

When 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 may differ slightly.

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 it can be significant at higher volumes. Please contact us if you need assistance when choosing the instrumentation that best fits your application.

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