

## DETERMINATION OF Pt(IV) BY ADSORPTIVE STRIPPING VOLTAMMETRY

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### Abstract

Adsorptive stripping voltammetric procedure for the determination of the traces of Pt(IV) in the presence of dimethylglyoxime has been evaluated with respect to different parameters. The sensitivity of the method and the linearity between the peak current and the concentration of Pt(IV) in the solution depends on the electrode area, the addition of surfactants and the pulse height. The most appropriate supporting electrolyte was 0.1 mol/L acetate buffer between pH 4.0 and 5. All experimental parameters were discussed and optimized to yield a highly linear response and good precision. Using 2 min of preconcentration at a 0.029 cm<sup>2</sup> electrode and the differential pulse mode, a detection limit of 50 ng/g Pt(IV) was achieved for the analysed solid samples.

**Keywords:** Platinum, Adsorptive stripping voltammetry, Dimethylglyoxime, Determination

### Introduction

Many electrochemical active complexes of platinum group metals (PGM) can be adsorbed on the mercury electrode surface to cause a catalytic hydrogen current. Mostly based on this principle, several electroanalytical methods for the trace determination of PGM have been reported in the last few years [1-5].

This study considering our previous investigations [6-7] is an optimization approach for some parameters of importance for the analytical application of the method proposed. Dimethylglyoxime (DMG) as a chelating ligand has been used for the adsorptive preconcentration of platinum(IV) on the stationary mercury electrode.

### Material and Methods

All reagents were of analytical reagent grade. Deionized water was additionally purified using the Milli - Q system. Acetate buffer of pH 4.6 was used as a supporting electrolyte. This was prepared by mixing the appropriate amounts of 0.1 M acetic acid and 0.1 M sodium acetate. A stock solution of 0.1 M DMG (butane-2,3 dione dioxime, Merck) was prepared by dissolution of the pure substance in absolute ethanol. A platinum standard stock solution (1.00 mg/ml) was prepared by dissolving platinum wire (99.99%) in aqua regia. The residue was then dissolved in a few drops of 1 M HCl and the solution obtained was diluted to 50 ml with 0.1 M HCl. The platinum(IV) solution was standardized gravimetrically (precipitation with DMG). Working standards were prepared by serial dilution with 0.1 M HCl. A combined glass electrode and a pH meter were used for the pH measurement.

Voltammetric measurement were performed with an EG&G PAR model 264A stripping voltammeter in connection to the EG&G 303 stationary mercury electrode (SMDE). An Ag/AgCl electrode filled with a saturated KCl solution was used as a reference electrode and a platinum wire as an auxiliary. The voltammograms were

recorded on an Omnigraphic 100 X-Y recorder Model RE 00 89. Measurements were made by applying a differential pulse (DPP) mode with scan rate of 10 mV/s in the negative (cathodic) direction.

### Results and discussion

Various experimental parameters affecting the stripping response of the metal chelate, such as the electrode area, the addition of surfactants and the pulse height were assessed. The effect of electrode area on the peak height for the reduction of platinum-dimethylglyoxime (Pt-DMG) and platinum-nioxime(cyclohexane-1,2-dione dioxime) complexes shows that with an increase of the electrode area the sensitivity increases, especially by the DMG ligand. A lower change can be noticed by the reduction of the adsorbed platinum-nioxime complex. A good compromise between the sensitivity and the mechanical properties of the stationary mercury drop electrode is a medium drop size of 0.029 cm<sup>2</sup> surface area. Also, in the observed range and stated conditions DMG ligand gives a higher peak than the other ligand.

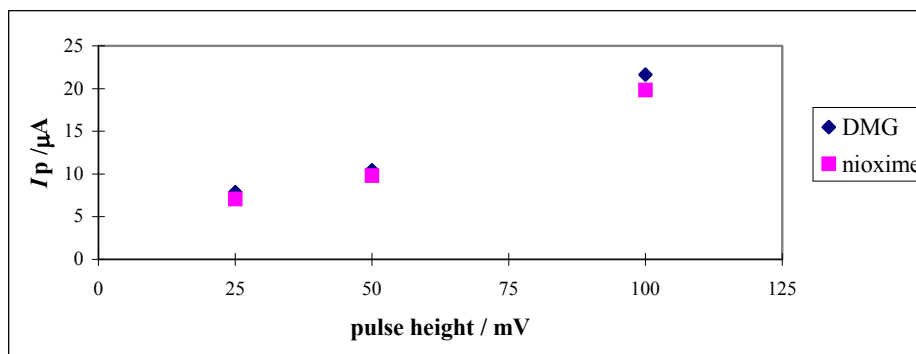
It might be expected that different surface active substances and anions, which are specifically adsorbed on mercury electrode, inhibit the adsorption of Pt-DMG complex, and suppress the stripping response. Because the adsorption of iodide is stronger with a higher excess of positive charge on the mercury electrode the inhibition of the platinum complex will be stronger at greater positive potentials. As we expected with iodide a further peak height decrease is owing to the competitive complexation of the platinum. In the presence of the nonionic surfactant Triton X-100 the peak height was completely suppressed by the addition of 1 mg/L of this surface active substance.

An increase in the pulse height up to 50 mV causes an increase in the peak current for two complexes (Fig.1). When the pulse height is higher than approximately 65 mV the peak current starts to broaden and it split occurs when the pulse height reaches 100 mV. The optimization of the experimental parameters indicated that the pulse height of 50 mV was the optimal.

Under constant experimental conditions quite well reproducible results were obtained with a relative standard deviation (RSD) of 2.5 %. The accuracy of the analytical results obtained with this method depends on the control of all experimental parameters and the presence of surfactants. Depending on the complexity of the sample, destruction of surfactants, e.g. through UV irradiation [8] is therefore required and an evaluation based on multiple standard addition is recommended.

### Conclusion

The results of our investigations showed that the sensitivity of the method proposed and the linearity between the peak current and the concentration of Pt(IV) in the solution depends on different parameters. The optimum concentration of the supporting electrolyte (acetate buffer) is 0.1 mol/L and the optimum pH value is 4.6. The preconcentration time of 2 min at the electrode area of 0.029 cm<sup>2</sup> and a pulse height of 50 mV were the most favorable for the adsorptive stripping voltammetric measurements of platinum(IV).



**Figure 1.** Dependence of pulse height on the peak current in the presence of different ligands; 0.1 mol/L acetate buffer of pH 4.6;  $1 \times 10^{-4}$  M DMG;  $1 \times 10^{-4}$  M nioxime; deposition time 2 min at  $-0.4$  V; electro electrode area  $0.029 \text{ cm}^2$ .

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