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Investigation on a Small Oscillogram

Hong Fang ZHANG, Jian Bin ZHENG*, Hong Gang NI, Hung KAO

Institute of Analytical Science/Shaanxi Provincial Key Lab of Electroanalytical Chemistry, Northwest University, Xi'an 710069

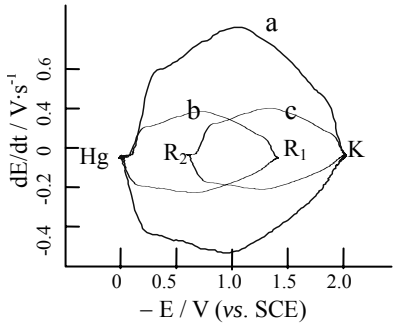
Abstract: A small oscillogram, one end of which was substituted by a bright point caused by the redox of an appropriate depolarizer and the other end of which was the redox of Hg or the redox of supporting electrolyte cation, was investigated in this paper. Experimental results of application of the small oscillogram to oscillographic determination of cefoperazone showed that the small oscillogram was more stable, sensitive, and less interference than classical oscillogram.

Keywords: Electroanalysis, oscillographic analysis, oscillogram.

Oscillographic chronopotentiometry is a type of current-controlled electroanalytical technique founded by J. Heyrovsky in 1941[1] and developed by Hung Kao after 1963[2-5]. In this technique, a constant-amplitude of alternating current $j=j_0\sin(\omega t)$ as well as a less direct current, passed through the electrolytic cell and the change of potential of the polarizable electrode exhibited on the oscillograph directly as a function of time during a continuous potential scan from zero to –2V. Generally, quantitative analysis of micro-components is implemented by the incision depth on dE/dt-E curve or the peak height on d^2E/dt^2-E curve. When substance was Na^+ or K^+, the incision located at more negative potential than -2V, quaternary ammonium salts often were used as the supporting electrolyte solution because of an oscillogram extended from zero to -3V in quaternary ammonium salts. For most metal ions and drugs, the oscillographic determination often is carried out in HAc-NaAc, NH_3-NH_4Cl or NaOH solution, and the oscillogram extended from zero to -2V[5,6]. However, three disadvantages are discovered. Firstly, the interferences of other substances are serious. Secondly, the sensitivity is low since the alternating current is bigger for getting a satisfied oscillogram. Thirdly, the determination of the substances, which the incision produced near the end of dE/dt-E curve was difficult. In order to overcome these shortcomings, a smaller oscillogram, one end of which was substituted by an appropriate depolarizer (R_1 or R_2) and the other end caused by the redox of Hg or supporting electrolyte cation (K^+) , was investigated (**Figure 1b, 1c**). To demonstrate the advantages of the small oscillogram, cefoperazone was determined in 0.5 mol/L HAc-NaAc + Cd^{2+} (selected as R_2 in **Figure 1c**) and 0.5 mol/L HAc-NaAc solution, respectively, with the small and classical oscillogram.

* E-mail: zhengjb@nwu.edu.cn

Figure 1 Classical (a) and small oscillograms (b, c)



Effect of concentration of Cd^{2+} on the stability of the oscillogram and determination of cefoperazone

The concentration of Cd^{2+} definitely affects the stability of the small oscillogram (-0.7V end is caused by the redox of Cd^{2+} and -2V end is caused by the redox of Na^{+} in the supporting electrolyte), and influences the determination of cefoperazone. Alternating current and direct current were adjusted accord to the demands of oscillographic determination, that is, making up and down time lag on *E-t* curve be equal ($\tau_{min}=\tau_{max}=\tau$), and the time lag percent ($\tau/\pi\%$) is about 75% [7]. The experimental results showed that more than 4×10^{-3} mol/L Cd^{2+} in the supporting electrolyte not only could enhance the stability of the oscillogram, but also ensured higher sensitivity and the linearity of determination of cefoperazone.

Comparison of determination results of cefoperazone by small oscillogram and classical oscillogram

The results of determination of cefoperazone by the small oscillogram and classical oscillogram were compared, and some influences on the shape and the stability of oscillograms parameters were measured. The experimental results showed that the potential range of the small oscillogram was between -0.7V and -2.0V, and that of the classical oscillogram was between -0.1V and -1.9V; alternating current needed in the small oscillogram was 0.216 mA, and that for the classical oscillogram was 0.380 mA; the small oscillogram was more stable and detection limit was six times lower than that of the classical oscillogram. The good stability of the small oscillogram was because of the needed alternating current was less than that for the classical oscillogram; the vibration of the small oscillogram caused by redox reaction at two ends was less than that of the classical oscillogram. The high sensitivity of the small oscillogram was due to the alternating current was small, in the result led to the small capacity current caused by the supporting electrolyte.

The effect of interference of some ions on the determination of cefoperazone in 0.5 mol/L HAc-NaAc + 4×10^{-3} mol/L Cd^{2+} was investigated by the small and classical

oscillogram. When the relative error of the analytical results was 5% for the determination of 1.200×10^{-5} mol/L cefoperazone, with the classical oscillogram, 5-fold excess of Cu^{2+}, Tl^{+}, Cd^{2+}, $Pb^{2+}$and In^{3+}, 1-fold excess of Zn^{2+} did not interfere the results; and with the small oscillogram, the experimental results showed that 50-fold excess of Cu^{2+}, 30-fold excess of Tl^{+}, 20-fold excess of Cd^{2+}, Pb^{2+} and In^{3+}, 1-fold excess of Zn^{2+} did not interfere. In conclusion, oscillographic determination of cefoperazone with the small oscillogram has less interference than the classical oscillogram.

Conclusion

The small oscillogram is more stable, sensitive and less interference than the classical oscillogram, thus the small oscillogram has important theory significance and applied value.

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