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Differential pulse polarographic determination of trace levels of iron(III) by using the catalytic current

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Abstract. Trace of iron(III) are determined by differential pulse polarography in a medium of sodium hydroxide and sodium bromate using the catalytic current. Various cations do not interfere. The relative standard deviation is 2%.

Introduction

Catalytic regeneration of the analyte on the electrode surface in the presence of oxidizing agents can give rise to enhanced sensitivity for some elements in polarography. Thus catalytic currents have been observed for iron(III) in the presence of hydrogen peroxide [1–5] and bromate [6–9]. In the former case, the wave shapes were not satisfactory due to a large maximum. Zarebski [8] has reported a polarographic method for the determination of iron using alkaline triethanolaminebromate as supporting electrolyte. Later Ferri and Buldini [9] employed the same medium to achieve a 60 times enhancement in sensitivity. We found that the sensitivity of the catalytic current could be further improved in a medium of sodium hydroxide and sodium bromate. The method is ideally suited for the determination of trace levels of impurity iron in alkaline solutions. The characterization of the electrode process was done using Birke's diagnostic criteria.

Experimental

The polarography with the cell assembly had been described earlier [10]. The rate of flow of mercury was 1.862 mg s^{-1}. For DPP measurements, the pulse duration was 0.04 s and the pulse amplitude was 50 mV. The droptime was mechanically controlled. All reagents were of analytical reagent grade. A 1000 ppm iron(III) stock solution was prepared by dissolving high-purity iron powder in a mixture of hydrochloric and nitric acid and diluting to volume with distilled water.

Procedure. Transfer an aliquot of the sample into a polarographic cell containing 4.0 ml 1 mol/L sodium hydroxide and 4.0 ml 1 mol/L sodium bromate and dilute to 20 mL. Deaerate the solution by bubbling pure nitrogen for 10 min and record the polarogram from −0.80 V to −1.40 V vs. SCE. Repeat the procedure after a standard addition of Fe(III).

Results and discussion

It was observed that the peak current of Fe(III) in a supporting electrolyte (S.E.) of sodium hydroxide was enhanced by the addition of sodium bromate. The enhancement factors were 75 and 120 for 0.1 mol/L and 0.2 mol/L sodium bromate, respectively. The peak potential was at −1.135 V vs. SCE. The effect of variation of S.E. on the peak current was investigated. When the sodium hydroxide concentration was varied from 0.1 mol/L to 0.5 mol/L in a S.E. containing 0.1 mol/L sodium bromate, the peak current remained almost constant. The peak potential shifted slightly into the negative direction. The dependence of the peak current on the concentration of sodium bromate was studied: it increased with increasing sodium bromate concentration in a non-linear manner. The peak current was found to be a linear function of the square root of the bromate concentration. This is characteristic for catalytic electrode processes.

Catalytic currents are known to have a higher temperature coefficient than diffusion controlled currents. The peak currents were measured at various temperatures in the range of 25 to 50°C. It was found that i_p initially increased with temperature from 25 to 30°C, remained almost constant from 30 to 40°C and again increased sharply in the range of 40 to 50°C. The temperature coefficient at 25°C was approximately 10%/°C. Thus a 67% increase in sensitivity could be obtained by recording the polarograms at 35°C.

The DPP diagnostic criteria of Birke et al. [11, 12] were used to characterize the mechanism of the electrode process. The ratio of anodic to cathodic peak current was 1.0 and the difference in peak potentials was equal to the pulse amplitude. This indicated that the electron transfer step was reversible. The half-peak width value at ΔE = 50 mV was found to be 99 mV, which was nearly equal to the theoretical value (98.2 mV) corresponding to a reversible electrode process with n = 1 and ΔE = 50 mV. A logarithmic analysis of the d.c. polarogram of iron(III) in this medium also showed that the electrode process was reversible. The enhancement of the current in the presence of bromate confirmed the catalytic nature. Hence, the electrode process is an EC (catalytic) mechanism with reversible electron transfer.

The catalytic rate constant (k) was calculated using the expression $i_c/i_d = (\pi\ \delta\ k\ c_z)^{1/2}$, where i_c/i_d is the enhancement in DP peak current in the presence of an oxidant, c_z is the concentration of the oxidant and δ is the pulse duration [12]. Substituting the experimental values, the second order rate constant k was found to be 5.76×10^5 s^{-1} L mol^{-1}.

The molecular solubility of ferric hydroxide is not negligible in alkaline solutions because iron(III) may form soluble complexes of the type $Fe(OH)_4^-$. Hence the probable mechanism for the catalytic reaction can be expressed as follows:

$$Fe^{III}(OH)_4^- + e \rightleftharpoons Fe^{II}(OH)_3^- + OH^- , \quad (1)$$

$$6\ Fe^{II}(OH)_3^- + BrO_3^- + 3\ H_2O \rightleftharpoons 6\ Fe^{III}(OH)_4^- + Br^- . \quad (2)$$

The sensitivity for the determination of iron(III) by the catalytic current in a S.E. of 0.2 mol/L sodium hydroxide and 0.2 mol/L sodium bromate was 24.0 nA L μg^{-1} under the DPP conditions, t = 2.0 s and ΔE = 50 mV. The enhancement in sensitivity was about 120 times that of the diffusion current. This enhancement factor was two times higher than that reported earlier by Ferri and Buldini [9]. The linearity of the calibration graph was checked. The catalytic current was proportional to the iron(III) concentration in the range 0.001 to 0.5 ppm in a S.E. of 0.2 mol/L sodium hydroxide and 0.2 mol/L sodium bromate. A least square fit of the data was done by y-residual minimization. The slope of the calibration was 8 nA L μg^{-1} (t = 0.5 s; ΔE = 50 mV) and the correlation coefficient was 0.9994.

Furthermore, the effect of cations on the catalytic current of iron(III) was studied. Cations like Cu(II), Pb(II), Cd(II), Ni(II), Co(II), Cr(III), Mn(II) and Sn(II) did not interfere when present

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in about 100-fold weight ratio to Fe(III). 1000-fold amounts of Al(III), Zn(II) and Mg(II) did not interfere, too. The catalytic current was not affected by 10-fold amounts of Cr(VI), but higher concentrations interfered by broadening the peak.

Since the method is highly sensitive as well as selective, it can be used for the determination of trace levels of iron in various samples, such as natural fresh water samples and reagent chemicals like sodium hydroxide and potassium hydroxide. It can be applied for the evaluation of iron in any alkaline solution. No sample pretreatment is required. This is one of the advantages of this procedure. The standard addition method was used to evaluate the concentration of iron in the samples. The precision was estimated by six replicate measurements of 0.1 ppm iron(III) in a synthetic sample solution. The relative standard deviation was found to be 2%. Thus the method can serve as an alternative to the more commonly used photometric methods for the determination of trace levels of iron in aqueous samples and alkaline solutions.

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Extraction-spectrophotometric determination of nickel as Ni-$(PAR)_2$-$(CTAB)_2$ complex in polymetallic sea-bed nodules and steels

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Abstract. A red, water-soluble complex of nickel with PAR can be extracted into chloroform with CTAB at pH 7.0. The system obeys Beer's law upto 0.5 μg/ml with a molar absorptivity of 45 200 $L \cdot mol^{-1} \cdot cm^{-1}$ at 540 nm. Job's method of continuous variations revealed that the composition of the extracting species is 1:2:2 for nickel:PAR:CTAB. Based on this extraction, a highly sensitive and selective spectrophotometric method for the determination of nickel in polymetallic sea-bed nodules and in steels, after prior separation of iron and manganese, was developed. The standard deviation was 0.04–0.127 μg for 5–25 μg of nickel.

Introduction

Deep-sea nodules are concretions that are roughly spherical in shape and vary in size from a few millimeters to several centimeters. They are found on the ocean floor at depths anywhere from several hundred to several thousand meters and their abundance and composition vary considerably from one location to another [1].

Chemical analysis of sea nodules has evoked constant scientific interest since their discovery. Atomic absorption spectrometry (AAS) is regularly used in our laboratory for the determination of Cu, Co and Ni in such samples [2]. In view of their complex matrix, interelement interferences play a crucial role for reliability of the analytical results. The problem is further complicated by the absence of a sufficient number of reference sea nodule standards [3].

Computational identification and elimination of interelemental interference has received popular attention and different theoretical models have been proposed [3–5]. But in all these models the total effect of interferents is approximated as the sum of the effects of individual interferents on the analyte signal. This is not always accurate.

In spite of the widespread use of AAS, spectrophotometry remains widely employed in routine analysis because of its simplicity. In recent years, ion-pair metal complexes containing the analyte, an organic chromophore reagent and a surfactant have been used widely and effectively for the spectrophotometric determination of trace amounts of metal ions [6].

Nickel combines with 4-(2-pyridyl azo)resorcinol (PAR) in the ratio 1:2 to form a water-soluble, red coloured complex with an absorbance maximum at 520 nm (pH 3.3, ε = 37 200) and at 496 nm (pH 8, ε = 79 400) [7]. An attempt has been made in our present study to selectively extract this Ni-PAR complex with cetyltrimethyl ammonium bromide (CTAB) into chloroform. A method is proposed for the determination of nickel in polymetallic sea-bed nodules and steels and the results are presented.

Experimental

Apparatus

Absorbance measurements were made with a Shimadzu 2100 S double-beam UV-VIS spectrophotometer. pH-measurements were made on a Unitech UI-11P pH meter.

Reagents

All reagents were of analytical reagent grade unless specified otherwise.

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