

# Determination of trace borohydride in basic solutions using differential pulse polarography

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Synthesis of borohydride is important because of its use as a hydrogen energy source. The objective of this study was to develop a new and simple method for the trace determination of borohydride so that it can be used during the investigation of a new reaction for its synthesis or in some kinetic studies.

A differential pulse polarographic method has been developed for this purpose since the results obtained with this method are very reproducible and the instrument used is not expensive. The optimum working condition was found to be as 0.05 M phosphate buffer (pH 9), containing 0.1 M KNO<sub>3</sub> electrolyte. It allows trace determination of borohydride in the range of 10<sup>-4</sup> – 10<sup>-6</sup> M using the oxidation peak at -0.06 V with high accuracy. The detection limit was 6 × 10<sup>-7</sup> M in phosphate buffer. The nature of the peak was evaluated using direct current polarography and it was found that this peak at -0.06 V was an oxidation peak.

There was no serious interference from some cations such as Cr(III), Cr(VI), Fe(III), Cd(II), Pb(II), Zn(II), Ni(II), and Se(IV) and anions such as chloride, bromide, nitrate, and sulfite when 2-14 times of borohydride was present. It was found that only copper (II) had an overlapping peak. This interference of copper was eliminated by the addition of EDTA. Using this procedure, in the presence of 5 × 10<sup>-5</sup> M copper, for 2 × 10<sup>-5</sup> M borohydride the result found was (1.9 ± 0.2)10<sup>-5</sup> M for N = 3 and 90% confidence interval.

**Key Words:** Trace borohydride, determination, differential pulse polarography, copper interference.

## Introduction

As a powerful reducing agent, borohydride is used in industry, it is a hydrogen source, and it is used in fuel cells. Although it is such an important substance there are only a few methods for its determination. In

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a volumetric method iodate has been used in the presence of iodide and the iodine formed is titrated with standard thiosulfate solution.<sup>1</sup> Titrimetric methods, including the iodate method, are less accurate and slow and not selective. Using cyclic voltammetry (CV) with a gold working electrode in basic solution (0.2 M NaOH) about  $10^{-4}$  M borohydride could be determined. With this method<sup>2</sup> it was possible to show the absence of borohydride during the electrochemical synthesis of  $\text{BH}_4^-$  from borate. Using square wave voltammetry,<sup>3</sup> about  $5 \times 10^{-5}$  M of borohydride ( $\text{BH}_4^-$ ) could be determined. The spectrophotometric determinations are based on the reaction of borohydride with the additive reagent giving a colored product. Using the reaction between acetone and borohydride an indirect spectrophotometric method has been developed,<sup>4</sup> the amount of acetone used up in the reaction with borohydride was calculated, and from the stoichiometry of this reaction the amount of borohydride could be determined. With the use of the reduction of  $\text{NAD}^+$  to NADH by borohydride it was possible to determine  $\text{BH}_4^-$  using a spectrophotometric method.<sup>5</sup> The absorption at 340 nm enabled the determination of borohydride in solution over the range 10-100 nmol with a molar extinction coefficient of  $12.2 \times 10^3$ . Decomposition of sodium borohydride ( $10^{-3}$  M) has been studied as a function of time and pH by using direct current polarography in 0.01 M pyrophosphate buffer and KCl.<sup>6</sup> It was found that the hydrolysis reaction was first order in borohydride concentration. The hydrolysis of tetrahydroborate ( $5 \times 10^{-2}$  M) has been studied also electrochemically in ammonia buffer between pH values of 9 and 12.5. A stepwise hydroborate hydrolysis with the formation of an electro-oxidizable intermediate was observed.<sup>7</sup>

Borohydride releases hydrogen in the presence of a suitable catalyst. This method is used in studies searching for a catalyst for hydrogen generation from borohydride under different conditions.<sup>8,9</sup>

As can be seen, in none of these studies was emphasis given to trace borohydride determination. In the present work a direct method was developed and it was possible to determine very low concentrations ( $10^{-6}$  M) of borohydride using differential pulse polarography (DPP). The determination of low concentrations is important for the investigation of some reactions in order to synthesize borohydride. In this case even a trace amount detected will be an indication that this reaction will work. Thus, the conditions for a better yield can be investigated. In studies of methods for the synthesis of borohydride, one needs a rapid, simple, and accurate method to control the borohydride concentration in the reaction medium. The aim of this work was to fill this gap. Electrochemical methods offer useful alternatives since they allow faster, cheaper, and safer analysis. They can be used for the determination of organic and inorganic substances without any extraction or separation procedure.<sup>10-12</sup> The results obtained with DPP are very reproducible since with the use of a dropping mercury electrode (DME) the behavior of the electrode is independent of its history.

## Experimental

### Reagents

All chemicals used were of analytical-reagent grade (proanalysis). Triply distilled water was used in the preparation of all solutions.  $\text{KNO}_3$ , KCl, and sodium acetate were prepared from reagent grade salts.

0.1 M EDTA solution (0.1 M) was prepared from  $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$  by diluting it into 50 mL. 0.05 M phosphate buffer (pH 9) solution was prepared by diluting 5 mL of 1.0 M phosphoric acid into 80 mL. After that 1.0 M NaOH was added dropwise, adjusting pH to 9 using a calibrated pH meter, and diluted into 100

mL. NaOH was washed first with distilled water in order to remove the carbonate formed on its surface.

Stock borohydride solution (0.1 M) was prepared from 0.192 g of NaBH<sub>4</sub> by diluting it into 50 mL using 1 M NaOH, since it decomposes in water at pH lower than 8 by the formation of NaBO<sub>2</sub> and hydrogen.

Solutions of 10<sup>-3</sup>-10<sup>-5</sup> M were prepared daily from 0.1 M solutions.

The mercury used in the dropping mercury electrode was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO<sub>3</sub> (3.0 M) and water columns in the form of fine droplets by using a platinum sieve. The collected mercury was dried between sheets of filter paper. Before use, a DPP polarogram of this mercury was recorded in order to confirm the absence of impurities.

## Apparatus

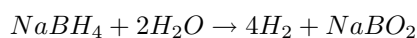
A polarographic analyzer (PAR 174 A) equipped with a PAR mercury drop timer was used. The natural drop time of the electrode was in the range 2 to 3 s (2.31 mg s<sup>-1</sup>). A Kalousek glass electrolytic cell with a saturated calomel reference electrode (SCE), separated by a liquid junction, was used in the 3-electrode configuration. The counter electrode was platinum wire. The polarograms were recorded with a Linseis (LY 1600) X-Y recorder under the conditions of a drop life of 1 s, a scan rate of 2-5 mV s<sup>-1</sup>, and a pulse amplitude of 50 mV.

## Results and discussion

Trace determination of borohydride is very important. Even trace quantities will show that the reaction under investigation will work when optimum conditions are fulfilled. The aim of this work was to develop a new method for the determination of trace borohydride using DPP since with this method very low concentrations can be determined and the results obtained are very reproducible.

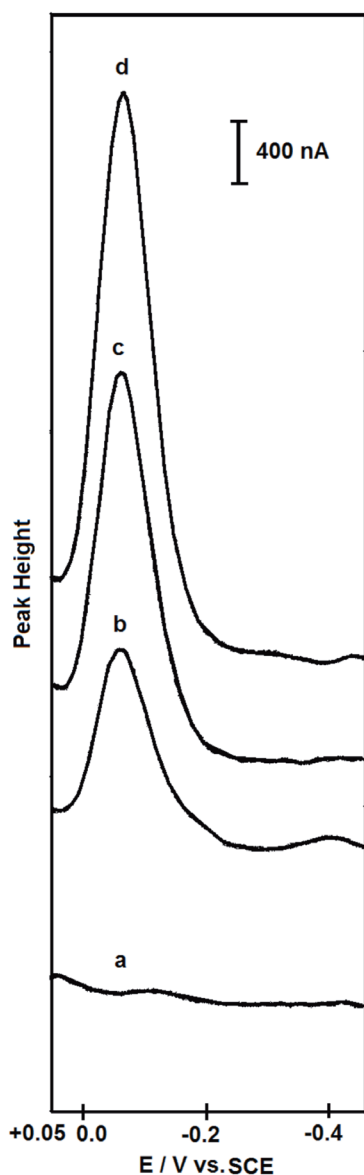
### Determination of borohydride (BH<sub>4</sub><sup>-</sup>) using DPP

Borohydride solutions are not stable in acidic solutions (pH < 8); they decompose with the formation of hydrogen and sodium metaborate as given below:

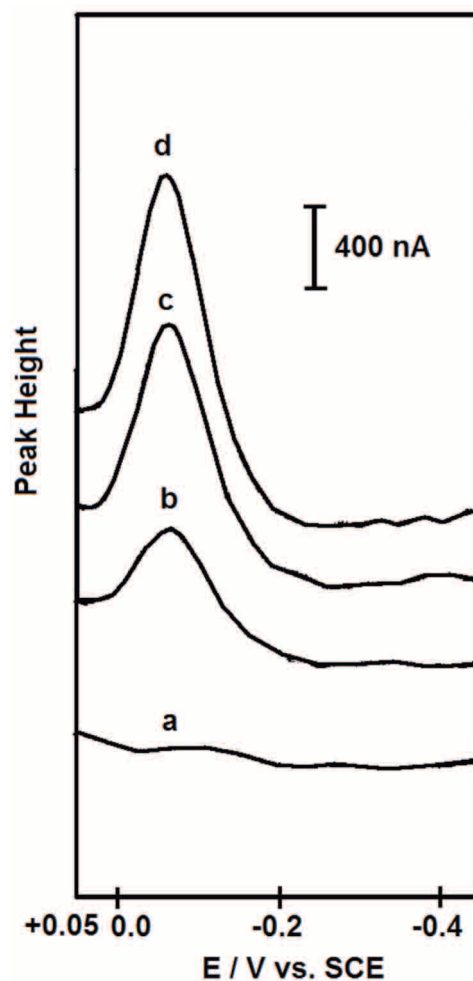


To protect it from decomposition, its polarographic determination was performed in basic solutions. The polarograms of borohydride were taken in several buffer solutions such as phosphate and acetate and in several electrolytes such as KCl and KNO<sub>3</sub> at various pH values. At pH values larger than 9, a mercury peak appeared and overlapped with the borohydride peak at about -0.05 V. It was found that phosphate was the most suitable buffer for borohydride determination. Phosphate buffer (0.05 M), pH 9, containing various electrolytes such as 0.1 M sodium acetate, 0.1 M KCl, and 0.1 M KNO<sub>3</sub> responded well to standard additions. However, the peak height of borohydride was largest in phosphate buffer in the presence of either 0.1 M KCl or 0.1 M KNO<sub>3</sub>. The response of standard additions in KNO<sub>3</sub> (in phosphate buffer) is given in Figure 1 for 1 × 10<sup>-5</sup> M borohydride. Although a mercury peak at about 0 V was observed in the presence of chloride ion (KCl), there was no such

peak in the presence of  $\text{KNO}_3$ . In this medium,  $3 \times 10^{-6}$  M borohydride could be determined with high accuracy,  $(3.1 \pm 0.3) \times 10^{-6}$  M, using standard additions as shown in Figure 2.



**Figure 1.** Differential pulse polarographic determination of  $1.0 \times 10^{-5}$  M  $\text{BH}_4^-$ , (a) 10 mL 0.05 M phosphate buffer (pH 9.0) + 0.1 M potassium nitrate, (b) a + 0.1 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (c) b + 0.1 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (d) c + 0.1 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ .



**Figure 2.** Differential pulse polarographic determination of  $3.0 \times 10^{-6}$  M  $\text{BH}_4^-$ , (a) 10 mL 0.05 M phosphate buffer (pH 9.0) + 0.1 M potassium nitrate, (b) a + 0.03 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (c) b + 0.03 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (d) c + 0.03 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ .

With the use of smaller current ranges much lower concentrations can be determined. The results obtained are summarized in Table 1. The detection limit was  $6.0 \times 10^{-7}$  M under the conditions given above.

**Table 1.** Determination of borohydride in pH 9.0, 0.05 M phosphate buffer, 0.1 M KNO<sub>3</sub>.

Borohydride present (M) BH <sub>4</sub> <sup>-</sup>	Calculated using standard additions (M)	% Error	$\bar{X}$	s	$\bar{X} \pm ts/\sqrt{N}^*$
$1.0 \times 10^{-5}$	$1.0 \times 10^{-5}$	0	$1.02 \times 10^{-5}$	$7.21 \times 10^{-7}$	$(1.02 \pm 0.12) \times 10^{-5}$
	$9.6 \times 10^{-6}$	-4			
	$1.1 \times 10^{-5}$	+10			
	$3.2 \times 10^{-6}$	+7	$3.1 \times 10^{-6}$	$2.0 \times 10^{-7}$	$(3.1 \pm 0.3) \times 10^{-6}$
	$3.1 \times 10^{-6}$	+3			
	$2.8 \times 10^{-6}$	-7			

\*N = 3, 90% confidence interval

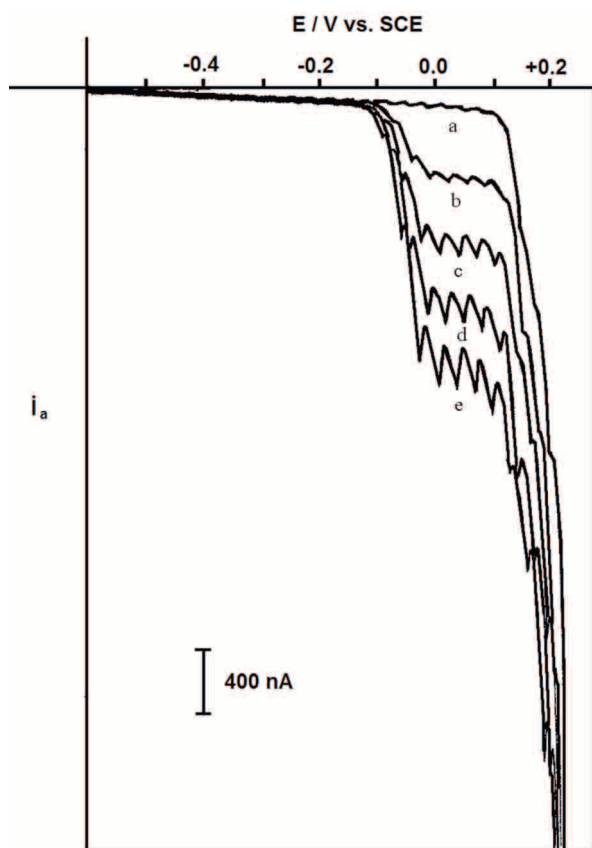
As known, the nature of a polarographic peak cannot be evaluated by DPP. For this purpose direct current (DC) polarography has to be used. The DC polarographic wave for  $2.0 \times 10^{-5}$  M borohydride is observed in pH 9 phosphate buffer containing 0.1 M KNO<sub>3</sub>. The polarogram was taken with a sweep in the positive direction. As can be seen in Figure 3, borohydride has an oxidation peak at -0.06 V and it responds well to standard additions.

## Interference studies

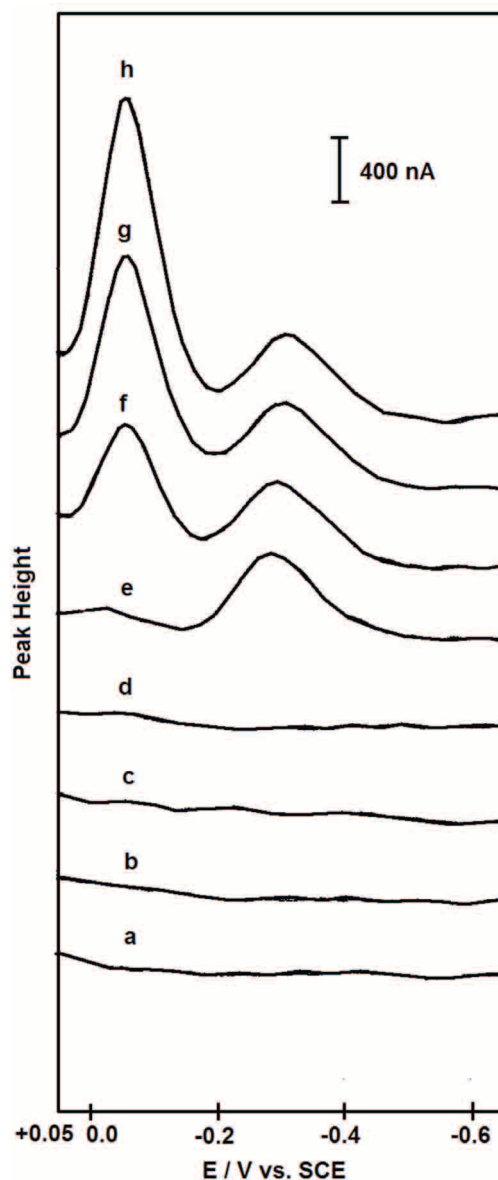
Since the borohydride peak, which appeared at -0.06 V, is very near to the mercury peak, there may be some interference because of some substances and anions present such as chloride, phosphate, and iodide, by facilitating the oxidation of mercury. This new mercury peak may overlap with borohydride peak. Although in the presence of 0.1 M chloride there was a peak on the positive side of the borohydride peak, there was no peak overlap.

Because of the large current at about 0 V with 0.1 M phosphate buffer, 0.05 M phosphate at pH 9 has been used in the presence of 0.1 M KNO<sub>3</sub> throughout the experiments.

The most probable ions that would be found in the presence of borohydride may be iron, chromium, or copper. During the synthesis of borohydride the reactor walls may contain iron and/or chromium, if they are made of steel. Thus during the determination of its production yield using polarography it will be important to see whether there is any interference from these ions. A polarogram of a phosphate buffer (pH 9) solution containing Fe(III) was taken and as can be seen from Figure 4 there was no peak for  $1.4 \times 10^{-4}$  M iron in this medium. Chromium(VI) had a peak at about -0.3 V (curve e, Figure 4), which will also not overlap with borohydride. Since chromium(III) has a peak at much more negative potential there will be no interference from it either. When borohydride was added to this medium the peak at -0.06 V responded well to standard additions (Figure 4).



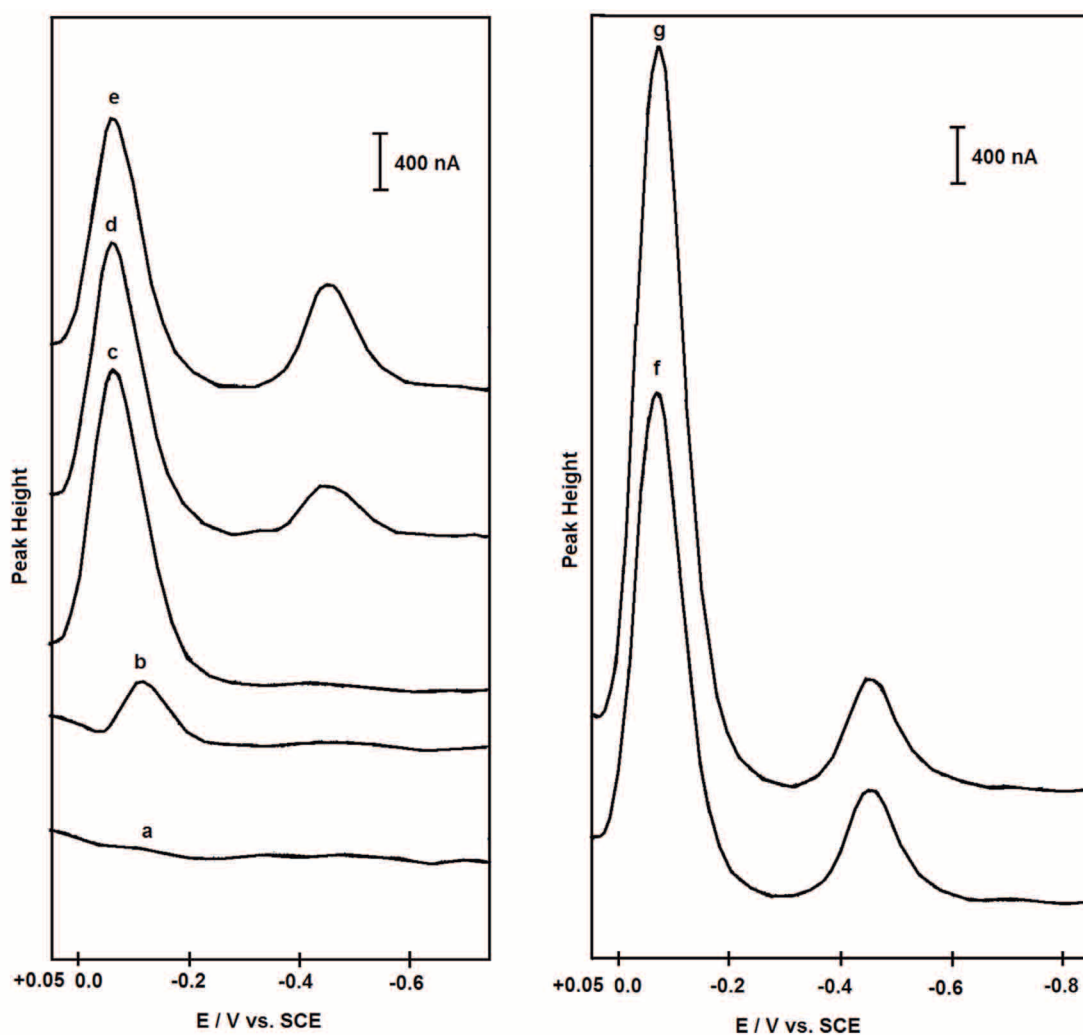
**Figure 3.** Direct current (DC) polarogram of  $2 \times 10^{-5}$  M  $\text{BH}_4^-$ , (a) 10 mL 0.05 M phosphate buffer (pH 9.0) + 0.1 M potassium nitrate, (b) a + 0.2 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (c) b + 0.2 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (d) c + 0.2 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (e) d + 0.2 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ .



**Figure 4.** Determination of  $\text{BH}_4^-$  in the presence of iron(III) and chromium(VI), (a) 10 mL 0.05 M phosphate buffer (pH 9.0) + 0.1 M potassium nitrate, (b) a + 0.2 mL  $1.0 \times 10^{-3}$  M Fe (III), (c) b + 0.2 mL  $1.0 \times 10^{-3}$  M Fe (III), (d) c + 0.1 mL  $1.0 \times 10^{-2}$  M Fe (III), (e) d + 0.1 mL  $1.0 \times 10^{-3}$  M Cr(VI), (f) e + 0.1 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (g) f + 0.1 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (h) g + 0.1 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ .

In the presence of Fe(III) and Cr(VI) the result found for  $1.0 \times 10^{-5}$  M borohydride was  $(1.1 \pm 0.1) \times 10^{-5}$  M. The result obtained with high accuracy is an indication that no redox reaction takes place between borohydride and either Fe(III) or Cr(VI). In another experiment first a polarogram of borohydride solution was taken, then Fe(III) and Cr(VI) were added at about 14 times larger concentration and there was no change in borohydride peak height.

A copper reactor can also be used for borohydride production; in this case interference from copper has to be investigated. Using the same method given above for iron and chromium, it was shown that there was no redox reaction between copper and borohydride under the conditions where the borohydride determination was performed.



**Figure 5.** Elimination of copper interference using EDTA, (a) 10 mL 0.05 M phosphate buffer (pH=9.0) + 0.1 M potassium nitrate, (b) a + 0.2 mL  $1.0 \times 10^{-3}$  M Cu (II), (c) b + 0.2 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (d) c + 0.1 mL  $1.0 \times 10^{-3}$  M EDTA, (e) d + 0.1 mL  $1.0 \times 10^{-3}$  M EDTA, (f) e + 0.2 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ , (g) f + 0.2 mL  $1.0 \times 10^{-3}$  M  $\text{BH}_4^-$ .

However, since the copper(II) ion peak appears at about the same potential of borohydride, there will be a peak overlap. In this case, if there is a peak in the polarogram at about  $-0.06$  V of an unknown sample, it may belong either to copper or borohydride. If the peak belongs to copper, we have shown that with the addition of EDTA the Cu-EDTA complex ion peak will appear at about  $-0.45$  V. If only borohydride is present no peak at  $-0.45$  V will appear with the addition of EDTA. In the case of the presence of both ions, for the determination of borohydride, EDTA in small quantities will be added until the Cu-EDTA complex ion peak at  $-0.45$  V becomes constant. The peak at  $-0.06$  V will belong to borohydride, which can be determined by standard additions. As can be seen from Figure 5 under these conditions borohydride could be determined with high accuracy.

In the presence of  $5 \times 10^{-5}$  M Cu(II) ion the result found for  $2 \times 10^{-5}$  M borohydride was  $(1.9 \pm 0.2)10^{-5}$  M for  $N = 3$  and 90% confidence interval. Thus addition of EDTA will enable the determination of borohydride in the presence of Cu(II) ion. The results obtained in the presence of Cu(II) ion are given in Table 2.

**Table 2.** Determination of  $BH_4^-$  in the presence of  $5 \times 10^{-5}$  M Cu(II) ion (0.05 M phosphate buffer, pH 9.0, 0.1 M  $KNO_3$ ).

Borohydride present (M) $BH_4^-$	Calculated using standard additions (M)	% Error	$\bar{X}$	s	$\bar{X} \pm ts/\sqrt{N}^*$
$2 \times 10^{-5}$	$1.8 \times 10^{-5}$	-10	$1.9 \times 10^{-5}$	$1.5 \times 10^{-6}$	$(1.9 \pm 0.2) \times 10^{-5}$
	$1.9 \times 10^{-5}$	-5			
	$2.1 \times 10^{-5}$	+5			

\*N = 3, 90% confidence interval

There was no remarkable interference from some cations such as Cr(III), Cd(II), Pb(II), Zn(II), Ni(II), and Se(IV) and anions such as chloride, bromide, nitrate, and sulfite when 2-5 times of borohydride was present.

## Conclusions

Borohydride is a very important substance because of its use as hydrogen energy source. Thus, it is also very important to determine low concentrations of borohydride, since it may allow detection of the production of borohydride in a newly established reaction for its synthesis.

In this work we developed a new method where it was possible to determine very low concentrations of borohydride in 0.05 M phosphate buffer (pH 9) and 0.1 M  $KNO_3$ , using DPP. The detection limit found was  $6 \times 10^{-7}$  M.

It was found that there was no interference from Fe, Cr, Cd, Pb, Ni, and Zn ions. Only copper had an overlapping peak with borohydride. This interaction could be eliminated by the addition of EDTA, because of the shift in the Cu(II) ion peak to more negative potentials, thus enabling the determination of borohydride.

The results obtained are very reproducible since with the use of a dropping mercury electrode the electrode surface is always new and the behavior of the electrode is independent of its history. This proposed method is simple, rapid, sensitive, inexpensive, and highly reproducible.



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