Determination of Vitamin H1 by the Potentiometric Titration

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Abstract

Cerium (IV) sulphate solution in sulphuric acid was used for the determination of vitamin H1 (p-aminobenzoic acid) in sulphuric acid solution by potentiometric titration. The optimal working conditions were set up for the quantitative determination of p-aminobenzoic acid. The method is simple, rapid and reliable. The effects of the reaction medium pH and of the titrant concentration were investigated. The apparent redox standard potential of the p-aminobenzoic acid first oxidised form/p-aminobenzoic acid first reduced form, $\varepsilon^0_{ox/red}$ is 0.900 ± 0.100 V; the number of electrons required for quantitative determination of p-aminobenzoic is n = 4; the redox standard apparent potential of the Ce^{4+} / Ce^{3+}, $\varepsilon^0_{Ce^{4+}/Ce^{3+}}$ = 1.175 ± 0.175 V was also determined.

Keywords: p-aminobenzoic acid, potentiometric titration, Ce(IV) solution

Introduction

Para-aminobenzoic acid (PABA) is also known as vitamin H1 of group B, a very potent natural antimutagen.[1] Large intake has been shown to counteract the antimetabolite effect of sulphonamides in bacterial culture. PABA is a colorless to yellow crystalline powder, water soluble. When it is expose to light and air the color is changed, but it is heat and light stable in aqueous and mild alkaline solution. The kinetic behavior of aqueous solutions of PABA,[2] the partition of it between organic solvents and water, the influence of the electrophilicity and/or nucleophilicity[3] and pH of the solvent[4] were studied. Various methods used for determination of p-aminobenzoic acid such as: colorimetric,[5,6] spectrometric,[7-15] chromatographic (HPLC, CZE, GC, TLC) [16-18] and electrometric[29-32] methods were presented in the literature. There are few titrimetric methods for direct determination of PABA [33-34], the most of them are based on back-titration of the analyte.[35]

This paper presents a simple, rapid and reliable method for assay of p-aminobenzoic acid by direct titration. The optimal working conditions for the direct quantitative determination of PABA by redox potentiometric titration with Ce (IV) solution were established.

Materials and Methods

Reagents and Equipment

All the reagents used were of analytical grade. p-aminobenzoic acid was provided by Sigma, 1x 10^{-1}mol L^{-1} cerium (IV) sulphate standard solution in sulphuric acid 1 mol L^{-1} and the concentrate sulphuric acid d = 1.84 g x cm^{-3} were provided by Merck. 1x 10^{-1} mol L^{-1}, 2 x 10^{-2} mol L^{-1} sulphuric acid solutions were obtained by successive dilution of the concentrate sulphuric acid with distilled water. 5 x 10^{-3} mol L^{-1} cerium (IV) sulphate solution in 2 x 10^{-1} mol L^{-1} sulphuric acid, 1 x 10^{-2} mol L^{-1} cerium (IV) sulphate solution in 1 mol L^{-1} sulphuric acid and respectively p-aminobenzoic 1x 10^{-2}mol L^{-1} in sulphuric acid 1M were prepared by dilution of stock solutions. The buffer solutions were prepared according to standard method,[36] 2 x10^{-1}mol L^{-1} hydrochloric acid solution, 2 x10^{-1}mol L^{-1} potasium chloride solution and 2 x10^{-1}mol L^{-1} kalium hydrogen ftalate solution were used.

All the potentiometric measurements were made with a Consort P901 pH/mV-meter.

A platinum redox electrode was used as indicative electrode for titration. A saturated calomel electrode was used as reference.

Procedure

The two electrodes were immersed into Berzelius beaker containing accurately measured volumes of PABA solutions with various concentration of sulphuric acid and respectively buffers solutions added in aliquots.

The electromotive force of the system was recorded after each addition of the titrant solution (cerium (IV) sulphate solution).

Results and discussion

The influence of the acidity of the reaction medium and of the titrant solution (cerium (IV) sulphate solution) as well as the influence of Ce^{4+} concentration in titrant solution were studied in order to establish the optima working conditions.

An exemple of the titration curve of PABA with 1x10^{-1} mol.L^{-1} cerium (IV) sulphate solution in H_2SO_4 1 mol.L^{-1} is presented in (**Figure 1**). From each titration curve the equivalence volume, the apparent redox standard potential of the PABA first oxidized form / PABA first reduced form ($\varepsilon^0_{ox/red}$), the apparent redox standard potential of the Ce^{4+} / Ce^{3+} ($\varepsilon^0_{Ce^{4+}/Ce^{3+}}$), and the number of electrons exchanged during the redox reaction (n) were determined. The equivalence volume was determined also by the first and the second derivative of the titration curve.

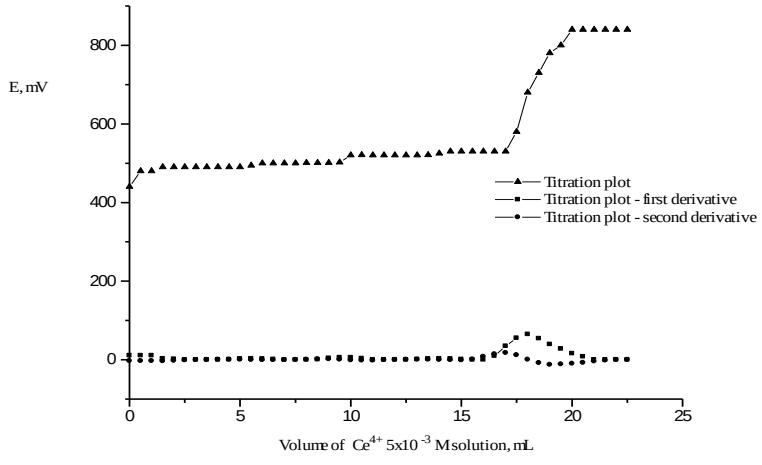

Figure 1. Titration curves of PABA with 1x 10^{-1}mol L^{-1}cerium (IV) sulphate solution in H_2SO_4 1.0 mol L^{-1}

The results obtained when the influence of the cerium (IV) sulphate solution was studied are presented in (**Table 1)**. The data reported showed that the titrant solution concentration influences the apparent standard potential of the two redox couples and the number of the electrons exchanged during the redox reaction. The redox reaction occurs harder when the titrant concentration decreases. In that case the redox standard potential of the Ce^{4+} / Ce^{3+} is lower and the number of electrons exchanged during the redox reaction is modified. For the assay of PABA were used 1x 10^{-1}mol L^{-1} or 1x 10^{-2}mol L^{-1}cerium (IV) sulphate solution made in sulphuric acid 1mol L^{-1}. In these conditions the reaction ratio between PABA: Ce (IV) is 1:4.

Table 1. The influence of the cerium (IV) sulphate solution concentration (in H_2SO_4 1.0M)

PABA Solution 10^{-2} mol.L^{-1}	Cerium (IV) sulphate solution		$\varepsilon^o_{OX/RED}$	$\varepsilon^o_{Ce4+/Ce3+}$	n
Volume in sample, mL	V_e mL	Conc M	mV	mV	e^-
2.0	22	$5x10^{-3}$	836	1046	5.5
5.0	19.7	10^{-2}	926	1246	4
5.0	20	10^{-2}	926	1250	4
1.0	4.2	10^{-2}	946	1236	4
10.0	3.8	10^{-1}	1054	1346	4

The reaction mole ratio between PABA and Ce (IV) is also influences by the acidity (pH) of the reaction medium (**Figure 2**).

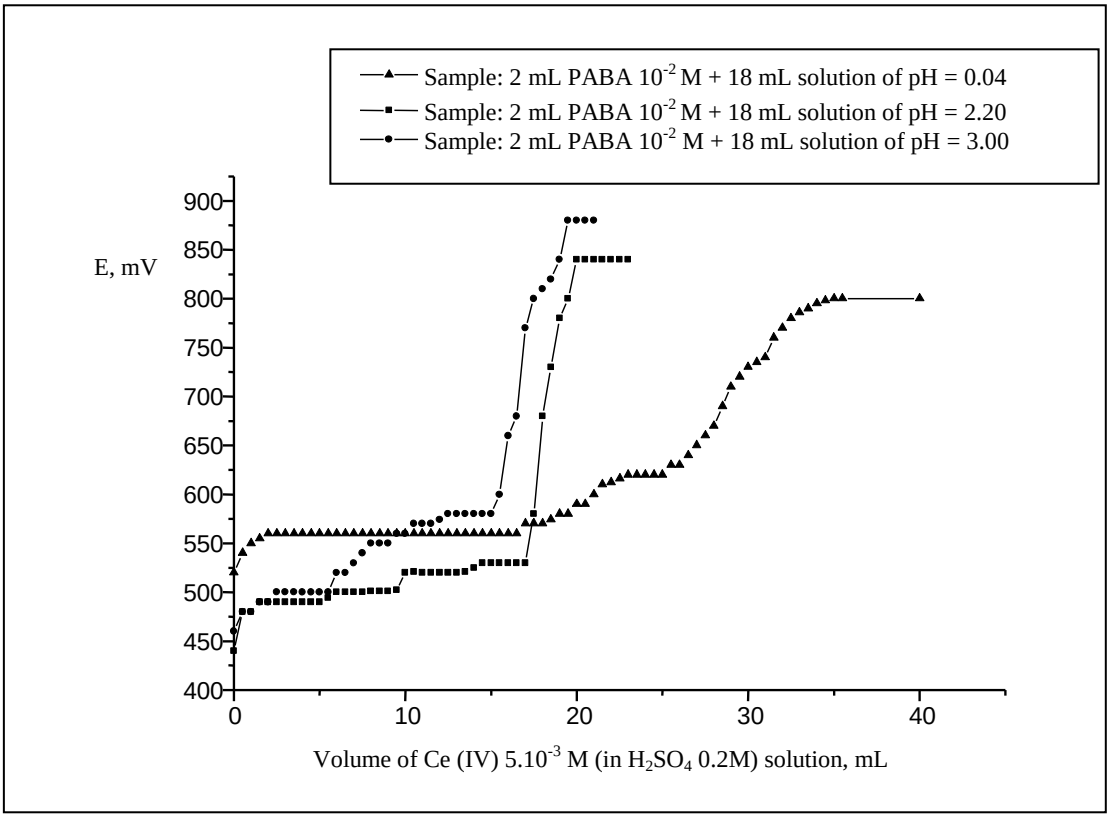

Figure 2 – Titration curves of PABA solution with different acidities, using 5x 10^{-3}mol L^{-1}cerium (IV) sulphate solution (in H_2SO_4 0.2 M).

As it can be seen in the (**Table 2**), at a titrant concentration of 5 x 10^{-3} mol L^{-1} (in H_2SO_4 2 x 10^{-1} mol L^{-1}) the oxidation rate decreased with the increase of the titration medium acidity.

Table 2. The influence of the pH of the reaction medium

Sample of PABA solution		Cerium (IV) sulphate solution in H_2SO_4 0.2 M				
Volume of 10^{-2}M solution in sample mL	Titration medium	V_e mL	Conc M	$\varepsilon^o_{OX/RED}$ mV	$\varepsilon^o_{Ce4+/Ce3+}$ mV	n e^-
2.0	H_2SO_4 1 M	28.24	$5x10^{-3}$	836	1046	7.0
2.0	buffer solution pH = 2.2	17.92	$5x10^{-3}$	922	1086	4.5
2.0	buffer solution pH = 3.0	16.50	$5x10^{-3}$	928	1126	4.1

Where: $\varepsilon^0_{ox/red}$ = the apparent redox standard potential of the PABA first oxidised form / PABA first reduced form;

$\varepsilon^0_{Ce^{4+}/Ce^{3+}}$ = the apparent redox standard potential of the Ce^{4+}/Ce^{3+};

V_e = the equivalence volume, (cerium (IV) sulphate solution, mL);

n= the number of electrons exchanged during the redox reaction;

The reaction is influenced by the medium acidity. When the acidity is high (pH=0.04), an advanced oxidation of PABA occurs and a number of 7 electrons are exchange during the redox reaction. The titration curve present man leap of potential but just one can be used to determine the equivalence volume. The number of electrons exchanged during the titratiom is 4 at pH ≈ 3.00.

PABA can be quantitatively determined in solution having a weak acidity (pH ≈ 3.00). by titration with a cerium (IV) sulphate solution 1x 10^{-2} – 10^{-1}mol L^{-1}in H_2SO_4 10^{-2} mol L^{-1}. The quantitative oxidation of PABA requires a number of 4 electrons during the redox reaction.

Analytical application

The proposed method was applied for the assay of PABA in solution containing known amounts of PABA. The assay was determinated also spectrometrically with reference at a standard solution. The results obtained by the two methods proved the method precision.

Table3. Results of PABA determination in synthetic samples

Amount (mg)		
Taken	Found by:	
	Proposed method	Spectrometric method[11]
2.80	2.40 ± 0.05	2.60 ± 0.06
6.50	6.80 ± 0.08	6.60 ± 0.09
13.80	13.60 ± 0.70	13.50 ± 0.30
20.60	20.40 ± 0.10	20.70 ± 0.40
24.50	24.30 ±0.20	24.20 ± 0.50

Note: each results represent the mean of three determinations ± s

Conclusions

The optimal working conditions for the assay of p-aminobenzoic acid by potentiometric titration with cerium (IV) sulphate solution were determined.

From the titration plot the apparent redox standard potential of the p-aminobenzoic acid first oxidised form /p-aminobenzoic acid first reduced form, $\varepsilon^0_{ox/red}$ = 0.900 ± 0.100 V; the number of electrons exchanged during the redox reaction, n = 4 and the apparent redox standard potential of the Ce^{4+} / Ce^{3+}, $\varepsilon^0_{Ce^{4+}/Ce^{3+}}$ = 1.175 ± 0.175 V were determined.

The concentration of cerium (IV) sulphate solution influence the apparent redox standard potential values and the raport ratio between PABA and Ce (IV).

The optimal working conditions for the assay of PABA implies the use of a titrant having the concentration of 1x 10^{-1}mol L^{-1} or 1x 10^{-2}mol L^{-1}, solutions in sulfuric acid 2.10^{-2} –1 mol.L^{-1}. The reaction ratio PABA: Ce (IV) is 1:4 in the condition stated above.

The potential values rise at higher concentration, so the redox procces occurs harder. The oxidation rate decreased with the increase of the acidity of the sample. This method was applied on syntethic samples. The results obtained prooves that the method proposed can be used for quantitative determination of p-aminobenzoic acid when the optima working conditions are applied.

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