Quantitation of Azide and Lead in Lead Azide by Voltammetric Method

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Summary: A voltammetric method for quantitative determinations of azide and lead in lead azide is presented. The determination of azide is based on oxidation of azide ions at a carbon paste electrode and that of lead on reduction at a dropping-mercury electrode in a 0.1 M acetate solution at pH 4.6.

This voltammetric method is also applied in determination of trace amounts of azide in evinronmental samples. The limit of detection is about 0.05 mg NaN_3 per m^3 of air, when 25 L of air is passed through 10 ml 0.2 M KOH for absorption of air.

Introduction

Lead azide (PbN_3) to a large extent has replaced mercury fulminate as initiating explosive in detonators and blasting caps. The sensitivity of lead azide to some degree can be manipulated by coating with crystals with dextrine during the precipitation process. Lead azide is less poisonous than sodium azide. In production facilities the concentration of sodium azide should not exceed 0.3 mg per m^3 and hence, for proper checking of the amount of sodium azide present, it is desirable to be able to quantitate the levels in concentrations as low as 0.1 mg per m^3.

Various analytical methods for the analysis of various types of azides are described in the Encyclopedia of Explosives and related items [1]. These methods are based on gas-volumetrical, titrimetrical and polarographic procedures for the simultaneous determinations of lead and azide [2,3] and of azide alone [4,5]. However, the reproducibility of these analytical methods is questionable. Besides, azide content in sodium azide has also been determined voltammetrically by oxidation at a carbon paste electrode [6].

The aim of the present study is to develop methods for the determinations of lead and azide content in lead azide as well as trace amounts of azide in environmental samples. Lead ions are reduced at a dropping mercury electrode where as azide ions are oxidized at a stationary carbon paste electrode. Voltammetry is used as a method of choice which has turned out to be a suitable method of analysis for the determination of both components.

Results and Discussion

Chemical and electro chemical reactions of azide ion

Becuase of its properties, the azide ion qualifies as a pseudohalide ion. It reacts with acids, oxidizing and reducing agents and forms salts.

Hydrogen azide is very soluble in water, forming stable solutions. It reacts as an acid (pK=4.6) and its acidic character has been utilized in analytical determination [7]. On the other hand, lead azide is only slightly soluble in pure water having a solubility product (pL) = 7.9 at an ionic strength of 0.1. The solubility of lead azide increases with decreasing pH due to reaction of the azide ions with hydrogen ions.

In Fig. 1, the conditional solubility product and the solubility of lead azide are shown as a function of pH in a 0.1 molar acetate solution. As shown in the figure, the solubility increases already at small changes in pH and pH value 4.4 as a consequence of the reaction of the azide ions with hydrogen ions.

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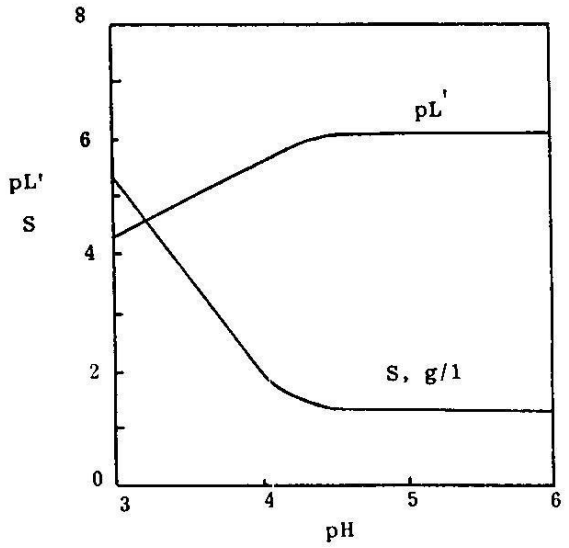

Fig. 1: The conditional solubility product, pL, and solubility, S/gL^{-1}, as a function of pH in 0.1 molar acetate.

The oxidation of azide ions has been known for a long time and takes place according to:

$$2N_3^- = 3N_2 + 2e \quad (1)$$

The oxidation of hydrogen azide and azide ions in aqueous solution at platinum electrode has been studied previously [8] where the authors have shown that the oxidation potential is a function of pH which is to be expected since hydrogen azide is a weak acid. It is also known that azide ions yield an anodic wave at a dropping-mercury electrode with a half-wave potential $E_{1/2}$ = 0.25 V in consequence with the formation of slightly soluble mercury azide [2-5]. The following reaction occur:

$$Hg = Hg^+ + e \quad (2)$$

$$Hg^+ + N_3^- = HgN_3 \quad (3)$$

Linear scan voltammetry at a stationary electrode

In linear scan voltammetry, the potential is varied linearly with time whereupon a peak-shaped current-potential curve (voltammogram) is obtained for a stationary electrode in a non-stirred solution. The peak current (i_p) for a diffusion-controlled reversible reaction is proportional to the concentration (c). It is further proportional to the square root of the scan rate (v) according to;

$$i_p = 2.687.\ 10^5.\ n^{3/2}.\ A.\ D^{1/2}.\ v^{1/2}.\ c \quad (4)$$

where n=number of participating electrons
A= surface area of the electrode in cm^2
D= diffusion coeffient

If D, A and v do not change during the measurement, the peak current is linearly dependent on concentration (equation 4).

Various materials can be used as indicator electrodes. Mercury is used mainly in procedures based on reduction in the negative potential range from O V to -2 V (see figure 2), i.e. in determinations of metal ions, nitro compounds, nitrate ester, etc.

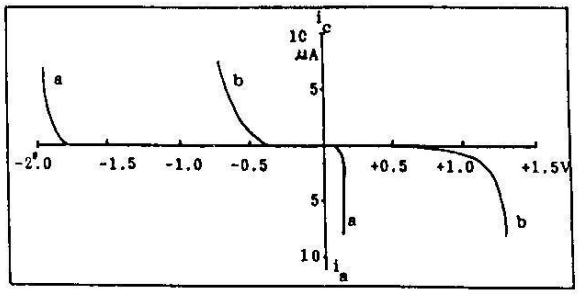

Fig. 2: Current/potential curve for a) a dropping mercury electrode in 0.1 molar acetate, and b) a carbon paste electrode in 0.1 molar acetate.

The greatest advantage of the carbon electrode is that the residual current is quite small within the positive potential range upto + 1 V (see figure 2). Carbon electrodes are for the most part used in methods based on oxidation and mainly for the determinations of organic compounds but also in determination of azide, which is oxidized at a relatively positive potential.

Voltammetric determination of Azide

The differential pulse technique was used in determination of azide partly to obtained high sensitivity but also to achieve good separation of the analytical peak from the back-ground current. Since azide ions react with hydrogen ions (pK=4.6), the voltammetric determination should be carried out at pH 4.6. To facilitate the determination of both lead and azide in the same solution acetate-buffered solutions with pH = 4.6 have been used. Figure 3 shows a differential pulse vol-

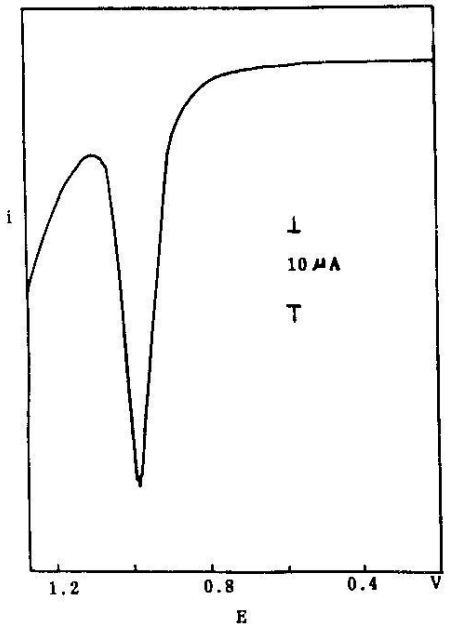

Fig. 3: Differential pulse voltammogram from the determination of 0.065 mmolar NaN_3.

tammogram from the determination of 0.065 mmolar azide. As indicated in the figure a sharp peak is obtained and even though oxidation occurs at a relatively positive potential an unambiguous baseline can be drawn. The peak potential is at + 0.97 V under our experimental conditions.

A considerable advantage of voltammetric methods is that a linear relationship exists between measurement signal (current) and concentration over a wide range of concentration. This relationship is shown in figure 4 for azide ion where the limit of detection is at about 0.001 mmolar.

For the analysis of lead azide about 100 mg of sample were dissolved in 50 ml of 10% ammonium acetate solution. The total amount of solution was determined by weighing in order to obtained the best accuracy. For the determination of azide and lead contents, about 1 g of the solution was carefully weighed and diluted to 100 ml exactly with 0.1 molar acetate buffer. The determination of both azide and lead contents was done using the same portion of sample.

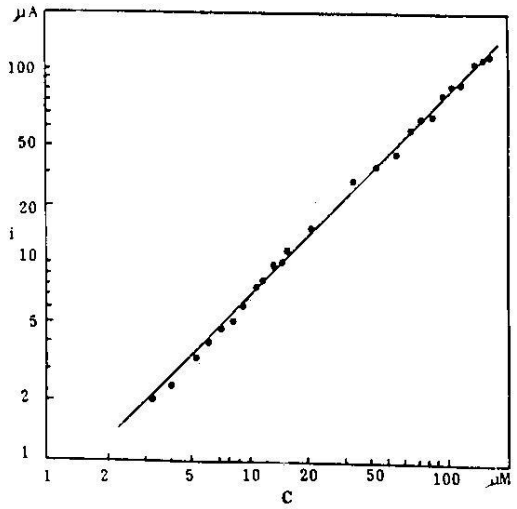

Fig. 4: Calibration curve for the differential pulse voltammetric determination of azide.

Table 1: Results from the determination of lead and azide contents in dextrinated and nondextrinated lead azide respectively.

Type	Lead (%)	Azide (%)	Total (%)
Dextrinated	68.54	29.54	98.08
	68.31	27.79	96.10
	69.84	28.75	98.59
	69.62	29.83	99.45
	66.45	28.30	94.75
Mean	68.61	28.62	97.23
Nondextrinated	70.78	27.83	98.61
	71.56	28.84	100.40
	71.17	30.37	101.54
	69.54	28.24	97.78
	71.57	29.11	100.68
Mean	70.78	28.39	99.17

Application of the analytical method

Two different types of lead azide, type I (dextrinated) and type II (nondextrinated) were analyzed. The results are summarized in Table 1. From the result, it is seen that the accuracy obtained was quite satisfactory. As was to be expected, the total content of lead azide was lower in the dextrinated sample.

The sodium azide content in the air of the room used for preparing sodium azide solutions

was determined after passing 25 L of the air through 10 mL of 0.2 molar KOH solution. After finishing the adsorption, the soluton was transferred to a 50 mL of 0.5 molar acetic acid were added. The solution was diluted to 50 mL with distilled water and a voltammogram recorded. The sodium azide content in samples representative for the average type air in the room were all below the detection limit of the method, i.e. proportional to 0.01 mg NaN_3 per m^3. Higher concentrations of sodium azide were recorded in the samples taken from the area where its preparationing was performed in some cases it was as high as 2 mg NaN_3 per m^3.

Experimental

The polarographic determinations were performed with a Metrohm Polarecord E 506 (obtained from Metrohm Ltd., Herisau, Switzerland). All potentials were measured and reported vs. Ag/AgCl electrode (Metrohm EA 427). Indicator electrode used was Metrohm EA 267 filled with a paste made from ultrapure carbon powder and liquid paraffin (UVASOL, E. Merck). During the measurements based on differential pulse, the pulse amplitude was kept at + 40 mV and the scan rate of 10 mV/s was used throughout the experiments.

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