

Simulation of the determination of lead azide content in waste water from explosives manufacture

Lead azide ranks in the category of intensive explosives, which may, even in an insignificant amount, initiate other explosives. Consequently, lead azide is very suitable for detonator filling. Lead azide is manufactured industrially by the reaction of a diluted solution of sodium azide with lead nitrate in the presence of protective colloid. After the reaction and after filtering off the lead azide precipitate, waste water is left which always contains part of the lead azide due to its relatively high solubility and to the reaction conditions. The azide ions concentration in waste water is in the range of 400-550 mg.dm⁻³. Since an excessive amount of lead nitrate is used for lead azide precipitation during its manufacture, the waste water from the manufacture contains an excessive amount of lead ions.

The objective of this experiment is to determine the amount of azide and lead ions and the content ratio of lead nitrate and lead azide in waste water from the lead azide manufacture. The experiment is divided into two steps. In the first step the lead azide concentration in the waste water is to be determined. In the second step the total content of lead ions in this water is to be ascertained. You will conclude the experiment with a total balance of lead azide and lead nitrate in this waste water and with the calculation of the amount of chemicals needed for the liquidation of these dangerous substances. In order to avoid the danger posed by the liquidation of „real“ waste water from the lead azide manufacture, the whole experiment is based on the analysis of „model waste water“ with the risk lowered to the lowest possible level. This, however, does not mean that the applied chemicals are absolutely safe.

In an acidic solution, azide ions are oxidised by nitrite ions to nitrogen according to Eq.:



Nitrite ions are reduced to N₂O. The waste water from lead azide manufacture contains both dissolved lead azide and fine particles of undissolved lead azide. The latter decomposes by the addition of nitric acid while hydrogen azide and lead nitrate originate. However, the addition of nitric acid complicates azide liquidation in waste water. With only a small amount of nitric acid added, solid azide particles do not dissolve and the reaction halts due to the low concentration of hydroxonium ions. In contrast, significantly excessive amount of nitric acid leads to the release of hydrogen azide from the solution. Consequently, another purpose of the experiment is to determine the amount of sodium nitrite needed for the liquidation of azides in the waste water, and to establish the range of pH in which the course of decomposition would be optimal and toxic hydrogen azide would not develop.

TASK I

Determination of azide concentration in a waste water sample

I.1 Task:



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Oxidimetric determination of azide ions content from a waste water sample.

I.2. Course of determination:

Oxidimetric titration of azide ions in „model“ waste water by a nitrite solution in nitric acid. Iron (III) chloride is used as an indicator in this determination. It reacts with azide ions producing red iron (III) azide. The solution discolours after all azide ions have reacted.

I.3 Equipment:

- 3x titration flask 250 cm³
- burette 25 cm³
- Mohr (graduated) pipette 5 and 10 cm³, volumetric pipette 25 cm³
- 3x volumetric flask 50 cm³, 100 cm³ and 250 cm³
- graduated cylinder 10 cm³
- beaker 50 and 250 cm³
- funnel
- wash bottle with distilled water
- pH metre calibrated

I.4 Chemicals:

Chemicals	Relative molecular weight	R codes	S codes
NaNO ₂ solution ($c=0,04 \text{ mol.dm}^{-3}$)	69,00	8-22-50	1/2-45-61
NaN ₃ solution ($c = 0,04 \text{ mol.dm}^{-3}$)	65,00	28-32-50/53	1/2-28-45-60-61
FeCl ₃ solution 10%	162,21	22-34	26-27-36/37/39
HNO ₃ solution ($c = 4 \text{ mol.dm}^{-3}$)	63,01	8-35	1/2-23-26-36-45
NO ₂	46,01	20	1/2-9-26-28-36/37/39-45
Pb(N ₃) ₂	291,23	61-3-20/22-33-50/53-62	53-45-60-61
N ₂ O	44,01	8	38
HN ₃	43,03	28-32-50/53	1/2-28-45-60-61
Waste water sample	-		
Distilled water	18,02		

I.5 Safety regulations:

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Some of the used solutions and originating chemical substances are highly dangerous. It is therefore required that you read the RISK (R) and SAFETY (S) phrases of the used substances and that you observe the ensuing instructions. In the case of titration at a lower pH value, the release of highly toxic hydrogen azide may occur. It is therefore required that you use corresponding protective aids.

I.6 Working procedure:

I.6.1 Preparation of NaNO₂ standart solution

Prepare sodium nitrite standart solution of $c = 0,004 \text{ mol.dm}^{-3}$ from the sodium nitrite solution of $c = 0,04 \text{ mol.dm}^{-3}$.

I.6.2 Determination of azide ions concentration and a final value of pH

Pour 10 cm^3 waste water sample from the stock solution into a 250 cm^3 titration flask, dilute the solution by about 50 cm^3 distilled water and add 3 cm^3 HNO₃ solution of the concentration 4 mol.dm^{-3} . Place pH metre electrodes in the solution to monitor the changes in pH values. Add 1-2 drops of 10% FeCl₃ solution to indicate the end of titration. Determine the consumption of sodium nitrite solution of the molar concentration $0,004 \text{ mol.dm}^{-3}$ until the solution discolours (titration out of azide ions). Observe the growth of pH values and note the final value after the titration of azide ions. Carry out the determination three times.

I.6.3 Determination of azide ions concentration (initial value of pH 1,3)

In the next step pour 10 cm^3 waste water into a 250 cm^3 flask and add such amount of nitric acid to set an initial value of pH in the solution would be 1,3. Determine once again the consumption of sodium nitrite standard solution needed for the liquidation of azide ions and determine the final value of pH in the solution. Carry out the determination three times.

I.6.4 Determination of azide ions concentration (constant value of pH)

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Carry out further waste water titration while preserving pH at a constant value during the whole course of titration by way of adding nitric acid by stages:

- titration at pH value = 0,5
- titration at pH value = 2
- titration at pH value = end pH value from titration I.6.3

Carry out the determination three times.

Calculate the average value from the all results obtained from the consumption of sodium nitrite standard solution and for pH values.

I.6.5 Verification of obtained results

Based on the obtained results determine the amount of azide ions in the waste water sample and the interval of pH values in which optimum decomposition of azides by sodium nitrite occurs, i.e. find out whether the redox reaction proceeds sufficiently quickly, reproducibly and without releasing toxic hydrogen azide.

Verify your conclusions by way of titration of a model waste water sample which you prepare from sodium azide of a known azide ions concentration with the addition of nitric acid ensuring optimum concentration of hydroxonium ions.

TASK II.

Determination of lead concentration in a waste water sample

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II.1 Task:

Complexometric determination of the Pb^{2+} content from a waste water sample

II.2 Course of determination:

Pb^{2+} ions form a complex with the sodium salt of ethylenediaminetetraacetic acid (Chelator 3). Xylenol orange is used as an indicator in this determination. The stability of the complex, which is used to determine the Pb^{2+} content, depends on the solution pH.

II.3 Equipment:

- 3 x titration flask 250 cm³
- burette 25 cm³
- graduated cylinder 100 cm³
- 2 x volumetric flask (100 cm³, 1 dm³)
- wash bottle with distilled water
- Mohr (graduated) pipette 10 cm³, volumetric pipette 20 cm³
- filtration funnel, small
- spoon
- 3 x beaker (250,150,100 cm³)
- weighing boat

II.4 Chemicals:

Reagent	Relative molecular weight	R codes	S codes
Chelator 3	372,24	22-36/37/38	26-36
$\text{Pb}(\text{NO}_3)_2$ (analytical grade)	331,2	20/22,33,50/53	17,45,60,61
Xylenol orange	-		
Hexamethylenetetramine (urotropin)	140,19	11, 42/43	2,16,22,24,37
HNO_3 solution 65%	63,01	8,35	1/2,23,26,36,45
Distilled water	18,02		

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II.6 Working procedure:

II.6.1 Preparation of chelatone 3 standard solution

Prepare chelatone 3 standard solution of $c = 0,005 \text{ mol.dm}^{-3}$. (c -molar concentration), (total volume of solution - 1 dm^3).

II.6.2 Preparation of $1 \text{ mol.dm}^{-3} \text{ HNO}_3$ solution

Prepare HNO_3 solution of $c = 1 \text{ mol.dm}^{-3}$ from HNO_3 solution of $w = 0,65$, $\rho = 1,3913 \text{ g.cm}^{-3}$. (w -mass fraction, ρ -density), (total volume of solution - 100 cm^3).

II.6.3 Determination of the titre of a $0,005 \text{ mol.dm}^{-3}$ solution of chelatone 3

Determine the titre of a $0,005 \text{ mol.dm}^{-3}$ solution of chelatone 3 in the following way: Weigh $0,02 \text{ g Pb(NO}_3)_2$ with an accuracy of four places of decimals. Dilute this amount in 100 cm^3 distilled water and acidify by several drops (about five) of a $1 \text{ mol.dm}^{-3} \text{ HNO}_3$ solution. Then add the indicator – xylenol orange (spoon tip), adjust the solution pH by solid hexamethylenetetramine up to violet colouring, and titrate by the pre-prepared chelatone 3 solution up to lemon-yellow colouring. Determine the consumption of the chelatone 3 solution. Carry out the determination six-times and calculate the concentration of the standard solution.

II.6.4 Determination of Pb^{2+} concentration in a waste water sample

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Obtain 20 cm³ waste water sample and pour it in the titration flask. Add distilled water from the wash bottle so as to have about one third of the flask filled with the solution and acidify by several drops (about five) of a 1 mol.dm⁻³ HNO₃ solution. Then add xylenol orange (spoon tip), and finally add hexamethylenetetramine by small doses up to the solution's evident violet colouring. Titrate the solution from the burette by the chelatone 3 solution up to purely yellow colour. Determine the consumption of the chelatone 3 solution. Carry out the determination six-times and calculate the Pb²⁺ concentration in the waste water sample.

Task III – summary Task I and Task II

Calculation of lead azide concentration and of lead nitrate concentration in waste water.

After determining the content of azide and lead ions in the waste water sample solve the following problem:

How many **grams** of lead azide and how many **grams** of lead nitrate are contained in 500 dm³ waste water from explosives manufacture?

How many **dm³** sodium nitrite ($c = 4 \text{ mol.dm}^{-3}$) will be needed for the liquidation of azide from this water given the assumption that you work with a 10% nitrite excess?

How many **grams** of potassium hydrogencarbonate will you need to precipitate lead ions from 500 dm³ waste water while assuming that lead carbonate originates and hydrogencarbonate is used in a 10% excess?