INNOVATIVE AND CLEANER INORGANIC TECHNOLOGIES
Module supervisor: dr hab. inz. Marcin Banach
Laboratory Instruction No 6
COMPARISION OF THE PRODUCTS AND SIDE-PRODUCTS FROM CLEANER AND CLASSICAL TECHNOLOGY OF PHOSPHORIC ACID PRODUCTION

REPORT:
ONE WEEK AFTER THE END OF THE CLASS

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Projekt „Międzynarodowy program kształcenia Innowacyjne Technologie Chemiczne”
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1. Subject of the exercise

The goal of the exercise is to analyze wet-process phosphoric acid (WPA) obtained on previous laboratory classes (Exercise 5) according to the quality requirements. By-products of the process (washings solution and phosphogypsum and hemihydrate) should be analyze as well in order to calculate extraction efficiency and mass balance. The analysis of WPA comprises phosphorus content determination using titration method with magnesium chloride and comparative analysis of sulphate content. The phosphorus concentration in washing is analyzed with titration method and phosphogypsum is subjected to the spectrophotometric analysis using method with yellow phosphoric-molybdeno-vanadate complex formation.

2. Equipment

- Magnetic stirrer
- Heating plate
- 3 Nessler cylinders or volumetric cylinders
- Spectrophotometer UV-Vis

3. Exercise content

PART A

a. Phosphoric acid analysis

Total phosphorus content analysis with magnesium chloride

Samples for analysis: phosphoric acid and washings from exercise 5, industrial phosphoric acid, thermal phosphoric acid

Principal of this method is titration of the phosphates present in the acid with nominated magnesium chloride solution in alkali environment at presence of thymolphtalexone as indicator. The interfering cations (Ca^{2+}, $Fe^{2+,3+}$, Al^{3+}) are eliminated by addition of Na_2EDTA solution (sodium salt of ethylenediaminetetraacetic acid) which forms stable complex with them.

Two parallel sample analysis should be conducted!

1) Weight ca. 2 g of the sample in the weighing bottle and transfer quantitatively to a 250mL volumetric flask. Fill with distilled water.
2) Take 25.0 mL of the diluted sample to a 250mL conical flask, add 5 mL of 0.05M Na_2EDTA, 10 mL of ammonium buffer and a bit of an indicator.
3) Titrate the sample with 0.05M $MgCl_2$ solution to remove excess of the added Na_2EDTA. The colour of the solution changes from greyish to blue (Titration no. 1).

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4) Add 35 mL of the acetone and place the sample on the magnetic stirrer. Add about 12 mL of the $MgCl_2$ solution from the burette (the amount added might be lower, observe the solution colour and stop addition when it changes into bluish).
5) Leave stirred sample for 5 min. Afterwards add additional small portion of the indicator and continue titration till the blue colour remains for at least 1 min (Titration no. 2).
6) Calculate phosphorus content (as H_3PO_4) according to the following equation:

$$\%H_3PO_4 = \frac{V \cdot 0.0049 \cdot 250 \cdot 100}{m \cdot 25}$$

where:

V- volume of the strictly 0.05M solution of the $MgCl_2$ from Titration no. 2 (**Attention! The volume should be calculated in the case when the nominated concentration of the solution is different from 0.05M**!)

0.0049 – the amount of the phosphoric acid (H_3PO_4) which is equivalent to 1mL of the 0.05M $MgCl_2$

m- weight of the sample, g

The **washings** from the WPA process should be analyzed similarly.

Bear in mind that final mass balance of phosphorus is expressed as P_2O_5, not in H_3PO_4. The results of phosphoric acid concentration analysis must be then recalculated.

Determination of sulphates content

Samples for analysis: phosphoric acid and washings from exercise 5, industrial phosphoric acid, thermal phosphoric acid

Principles of this method is comparison of the turbidity formed as a result of reaction between sulphate ions and barium chloride for sample and reference solution.

1) **Two** parallel sample analysis should be conducted!
2) Weight 25 g of the sample in a 400 mL beaker.
3) Dilute the sample to 200 mL with distilled water and neutralize with NaOH solution (25%wt.), use indicator paper.
4) Transfer the solution to a 500 mL volumetric flask and fill with distilled water.
5) Filter the solution through a filter paper, discharge first part of the supernatant (ca. 30 mL).
6) Take 20.0 mL of the supernatant to the volumetric cylinder (or Nessler cylinder).
7) Dilute the sample to the 25 mL volume, add 1.0 mL of 10% hydrochloric acid, 3.0 mL of 1% starch solution and 3 ml of $BaCl_2$ solution and homogenize the mixture (e.g. with glass rod).

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8) Prepare the reference solution as well: take 1.0 mL of primary standard solution at concentration of 1mgSO_4^{2-}/1mL to a 100 mL volumetric flask and fill with distilled water. 1 mL of the obtained secondary standard solution contains 0.01 mg of SO_4^{2-}.
9) Take 10.0 ml of the secondary standard solution and follow the instruction described in **point 7).**
10) The intensity of the turbidity of analyzed phosphoric acid sample should be compared to the reference solution. The result of the analysis should be given as a concentration of sulphates greater, smaller or equal to the concentration of reference.

PART B

b. Phosphogypsum (hemihydrate) analysis

Samples for analysis: hemihydrate from exercise 5, phosphogypsum form classical method

Total phosphorus content determination

For the phosphorus content analysis the spectrophotometric method with yellow phosphoric-molybdeno-vanadate complex formation is used.

1) Calibration curve preparation

To the 5 volumetric flask of 50 mL add 20 mL of the "D" solution (mixture of equal volumes of ammonium metavanadate, ammonium molybdenate and nitric acid (1:2)) and the standard solution of KH_2PO_4, that contains 0.2 mg of P_2O_5 in 1 mL. Fill with distilled water. The proper volumes of standard are given in the table 1.

Table 1. Calibration curve

No.	Volume of the standard solution, mL	Phosphorus content in the flask, mg P_2O_5
0	0.0	0
1	5.0	1.0
2	7.5	1.5
3	10.0	2.0
4	12.5	2.5

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The complex with phosphate is formed within 15 min and is stable for 60 min.

Using the spectrophotometer with the wavelength 430 nm do the calibration curve and save the data in the memory of the device.

2) Weight ca. 1g of the sample (precision 0.0001g) into a 150 mL beaker. Pour 20 mL of the acids mixture ($HCl:HNO_3$ 1:3). Cover it with watch glass and heat gently to the boil on the heating plate for 30 min. Afterwards, add 30 mL of distilled water and boil for further 15 min. After cooling the sample, transfer it quantitatively into a 100 mL volumetric flask, fill with distilled water and filter it through filter paper.

There must be conducted two parallel mineralization of the phosphogypsum/ hemihydrate.

3) Take 1.5 mL of the supernatant to a 50 mL volumetric flask, add 20 mL of "D – solution fill with distilled water and wait 15 min for the molybdenum-vanadate-phosphate complex to form. Use the spectrophotometer with the wavelength 430 nm with previously stored calibration data.

AAS analysis of Ca, Mg, Fe, Cu

1) Weight ca. 1g of the sample (precision 0.0001g) into a 150 mL beaker. Pour 20 mL of the acids mixture ($HCl:HNO_3$ 1:3). Cover it with watch glass and heat gently to the boil on the heating plate for 30 min. Afterwards, add 30 mL of distilled water and boil for further 15 min. After cooling the sample, transfer it quantitatively into a 100 mL volumetric flask, fill with distilled water and filter it through filter paper.

There must be conducted two parallel mineralization of the phosphogypsum/ hemihydrate.

Solution is ready for AAS analysis, in case of Mg and Ca in must be diluted

4. Report requirements

The final report should summarize Exercise 1a and 1b and comprise:

- Initial Calculations
- Descriptions of the experimental part
- Results of the products analysis with analytical methods description
- Mass balance for materials and phosphorus (calculated as P_2O_5)
- Comment about the result of the XRD analysis of the solid by-product
- Conclusions, reference to the cleaner production

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