



Evaluation of Sudanese Phosphate Rocks by Two Rapid Methods for Determination of Total and Available Phosphorus: Comparative Study

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ABSTRACT

The present work was carried out to study effectiveness of phosphate rocks decomposing by using two rapid digestion methods (single and mixed acids). A rapid method for determining P_2O_5 of phosphate rocks based on colorimetry has been determined. The loss on ignition (L.O.I) method's values is ranging between 8.80% to 25.25% for Jebel Kurun and between 13.84% to 18.78 % for Uro. The comparison between determination total and available phosphorus with single digestion ($HClO_4$) and "mixed acids" (HCl , HNO_3 , and $HClO_4$) showed that the total phosphorus measured by single digestion ranged between 31.51% and 44.62% of Krurn and between 27.60% and 28.52% of Uro areas. By the mixed acids method it was found to range from 19.32, to 48.30% P_2O_5 and 21.85% to 33.20% of Kurun and Uro respectively. The available P_2O_5 was ranged between 14.3 to 23.90% P_2O_5 of Nuba Mountains Jebel Kurun and between 11.10% to 18.60% for Uro area. A comparison of methods used for colorimetric determination of total P_2O_5 indicated that the results by mixed digestion method is the highest. The production its make appear to have very promising practical application.

Keywords: phosphate rocks, mixed digestion method, total phosphorus.

INTRODUCTION

Phosphate rock is a general term used for rocks that contain a high concentration of phosphate minerals, which commonly belong to the apatite group. Phosphate rock minerals are the significant global Resources of phosphorus. Phosphorus is one of the major nutrients limiting plant growth, it's the

second most important plant nutrient after nitrogen.^{1,2} Phosphorus from rock phosphate is used in the production of phosphate fertilizers.³ Fertilization is as necessary for the improvement of the Soil as nutrient substrate and can make a good replacement of the removed nutrients by harvesting and other processes.⁴ The use of the fertilizers in Sudan is often limited to irrigated agriculture and rarely practiced

under rained areas. This may be due mainly to the financial handicaps of the farmers and unawareness about the importance of chemical fertilizers.⁵ In the Sudan, and because it is a big agricultural country, there is a great need to obtain cheap and safe resources of phosphate ores for phosphoric acid and phosphate fertilizer industry.⁶ The use of indigenous natural phosphate rocks had been recognized as available low-cost alternative for the conventional water-soluble phosphorus fertilizers though they show large differences in their suitability for direct application and many factors influence their capacity to supply phosphorus to crops.⁷ Since deficiency of phosphorus is the most important chemical factor restricting plant growth, chemical phosphate fertilizers are widely used to achieve optimum yields.⁸ The main uses of this acid are for dissolving metals (oxides, hydroxides, carbonates, sulphides and arsenide's ores). HClO_4 : about 72%, when hot is an extremely powerful oxidizing agent and as such will dissolve almost all metals and convert them into ions having their highest oxidation states in solution.⁹ A sample solution was prepared by dissolving of rock sample in an aqueous mixture of perchloric and nitric acids; the perchloric acid digestion of PRs is effective on most phosphorus minerals such as apatites. There is variety of methodologies used for determination of different forms of phosphorus from phosphate rocks. In this study a reliable methods is needed which allows to increase the phosphorus availability, and to assess the relative importance of PRs as source of phosphorus fertilizer.

Statistical analysis

The significance of differences in contents of total and available P_2O_5 percent in different phosphate rock was determined by analysis of variance (ANOVA test).

MATERIALS AND METHODS

When we come to look at actual procedures for dissolving inorganic samples (such as PR) by using hot concentrated mineral acids, we find that rather than just using a single acid, a mixture of acids is used. On the other occasions samples are treated with a mixture of acids, and then "fumed to dryness". HNO_3 oxidizes HCl to give various reactive oxidation products such as chlorine and nitrosyl chloride. Several acids decompose under

these conditions to yield decomposing products even more reactive than the acid itself; the acids will oxidize all metals except the noble ones. The molybdophosphovanadate procedure described below was used to determine of P_2O_5 in phosphate rock. The reduced-molybdophosphate method is accepted as one of the most sensitive means of determining phosphorus. Twenty four composite surface phosphate rocks samples, collected from Jebel Kurun and Jebel Uro areas these two locations lie in the center of eastern part of the Nuba Mountains in the state of southern Kordofan (Sudan) $11^\circ 54' \text{N}$ and $31^\circ 22' \text{E}$ between Abu Giubiha and El Rashad towns.¹⁰ The samples were prepared at the Laboratory of the Geological Research Authority of Sudan (GRAS), Ministry of Minerals. The samples mixed, homogenized, _crushed in a jar crushers and powdered to a fineness (200 mesh), then dried in an electric oven at 110°C for 2 hours, then cooled and kept in desiccators for analysis.¹¹ Loss On Ignition, total P_2O_5 determined by two rapid digestion methods (Single acid and Mixed acids), available phosphorus determined by using Olsen Method.¹² One gram of PRs sample was accurately weighted into 50 mL beaker, 10 mL of concentrated HCl , 5 mL of concentrated HNO_3 , and few anti-bombing granules, was added. The mixture was heated to evaporate off the oxides. The solution was heated till the residue was about 5 mL. Then 5 mL of perchloric acid 70% added, the mixture was maintained at the boiling-point until the fumes were driven off suddenly. Then cold to the room temperature and 50 mL of distilled water was added, boil for three minutes, cold again and filtered into conical flask by using Whitman No.42. A 5 mL of stock standard solution 0, 5, 10, 20, 25 and 5 mL of a portion of an aliquot samples, and 20 mL of reagent were added into 100 mL volumetric flask, fill with distilled water, shakes and the blank of standard potassium di-hydrogen phosphate were used to calculate total phosphorus as P_2O_5 after 20 minutes wavelength was set at 640 nm.

2.5 grams of PRs samples were accurately weighted in 250 mL conical flask, 30 mL of concentrated HClO_4 (70%) and few pumice stones was added, pre-heated the flask to about 100°C , temperature was increased gradually to 180°C and digest the samples till dense white fumes of oxides appeared. Extra little HClO_4 was used to wash down the sides of the digestion flask; the heating was

continued boiling temperature for 20 minutes. At this stage the insoluble materials become like white sand. The total digestion with HClO_4 acid usually requires about 40 minutes,¹³ the mixture was cooled, diluted with distilled water to the volume mark, mixed well filtrated through filter paper Whitman No.42. 10 mL of aliquot samples of PRs was pipetted into 100 mL volumetric flask, 20 mL of reagent was added, the absorbance of total phosphorus was measured after 20 min. at wavelength 460 nm using blank and standard solutions.

RESULTS AND DISCUSSION

A calibration curves (Figures 1 and 2) was constructed and used to calculate the concentration of P_2O_5 . Organic matters is an important component

when determined by Loss On Ignition (L.O.I) techniques because it tends to either form soluble or insoluble materials (the heavy metals), as a result it can be migrate or retained in the soil.¹⁴ Tables (1) showed the average content of (L.O.I), the values was relatively low to moderate of all samples which suggested that these samples have a slightly lower organic materials calcite or gypsum content. The L.O.I was ranged between 8.80% to 25.25% for Jebel Kurun, and was found to be ranged between 13.84% to 18.78 % for Jebel Uro area table (2). Table.1 shows that the total P_2O_5 determined by mixed digestion method was ranged between 19.32% to 46.00% for Jebel Kurun area, and by another digestion method have been found that between 27.60% to 44.62%, from these two mentioned methods the mixed one was gave highest values of total P_2O_5

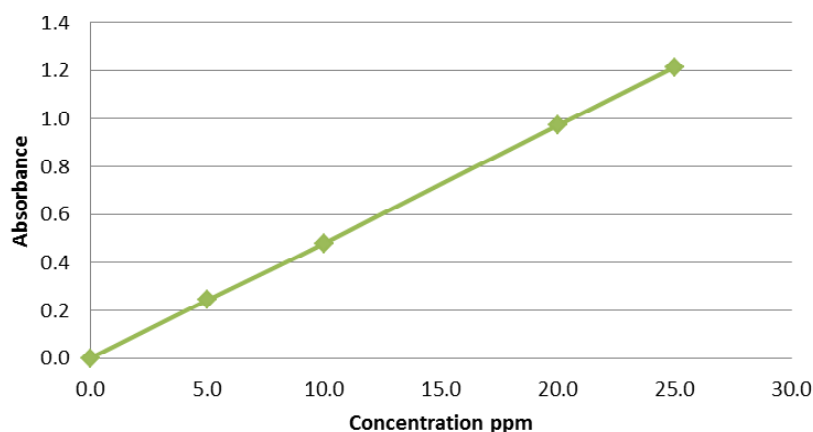


Fig. 1: A calibration curve of absorbance of standard solutions calculate the concentration of P_2O_5 % by mixed acids

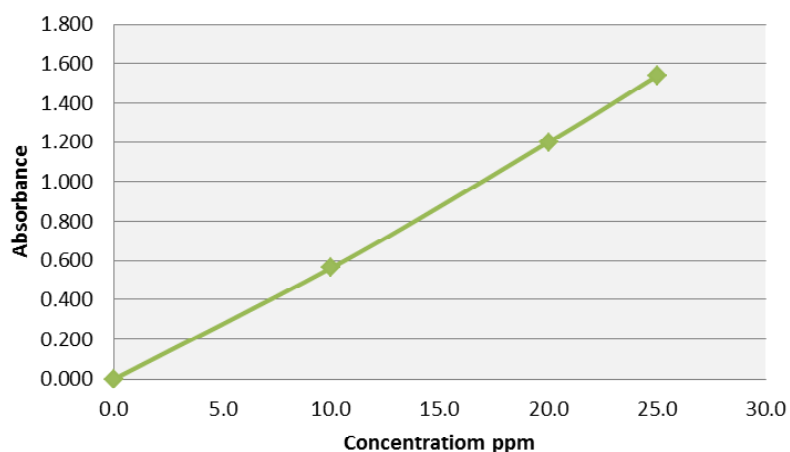


Fig. 2: A calibration curve of the absorbance of standard solutions of KH_2PO_4 calculate the concentration of P_2O_5 in the samples solutions by single acid digestion method

Table 1: Chemical analysis of L.O.I total and available P₂O₅ using two rapid methods (single & mixed digestion acids) of Jebel Kurun area

Sample No.	L.O.I %	Mixed acids	HClO ₄	Available
K1	16.78	44.16	43.24	16.3
K2	16.99	46	44.62	20.91
K3	18.73	33.81	43.01	15.6
K4	19.29	42.32	34.04	16.3
K5	14.06	43.7	33.81	19.3
K6	10.22	46	33.12	20.2
K7	12.91	43.97	35.65	23
K8	19.39	43.97	36.34	14.3
K9	17.83	42.59	36.8	22.5
K10	25.25	48.3	34.73	21.2
K11	16.3	33.35	35.65	23.9
K12	19.41	40.02	34.27	22.5
K13	9.48	38.18	35.19	20.9
K14	18.67	34.96	34.04	23
K15	14.74	34.5	35.88	22.5
K16	9.14	33.59	34.5	16.3
K17	8.94	23.46	27.6	15.9
K18	10.41	33.35	36.57	20.5
K19	8.84	29.44	34.96	23.9
K20	8.8	19.32	33.12	21.2
Mean	15.52	37.53	35.86	20.01
Median	18.69	39.1	35.08	20.9
CV%	6.89	20.76	10.79	15.49
Std. Dev	1.07	7.79	3.87	3.1
SE Mean	2.53	1.74	0.87	0.69

content than the single method, indication to the highest apatite content. However, Table (2) shows the total phosphorus for Jebel Uro area was found to be ranged between 21.82% to 33.20% by mixed method, but by another digestion method ranged between 28.52% to 31.15% of total phosphorus. However, total phosphorus content is not indication of phosphate rock, agronomic effectiveness, till the available phosphorus was determined.¹⁵ The available P₂O₅ of Jebel Kurun was found to be ranged between 19.90% to 23.90%, this result indicated to enrich of these phosphate rocks ores with phosphate minerals such as: Hydroxyl-Fluor-apatite, Ca₁₀(PO₄)₆F₂, Carbonate-apatite Ca₁₀(PO₄CO₃)₆(OH,F), Hydroxyl apatite Ca₁₀(PO₄)₆(OH)₂, Chlor-apatite Ca₁₀(PO₄)₆Cl₂. Based on data which obtained from the analyzed

Table 2: A chemical analysis of L.O.I total and available P₂O₅, using two rapid methods (single and mixed digestion acids) of Jebel Uro

Sample No.	L.O.I	Mixed acids	HClO ₄	Available
U1	18.78	21.85	28.52	18.6
U2	13.84	31.85	29.44	16.1
U3	14	23.46	30.13	11
U4	14.59	33.2	31.51	16.7
Mean	32.8	29.12	29.21	15.85
Median	17.18	31.22	29.9	16.4
CV%	9.76	16.83	4.31	20.89
Std. Dev	3.2	4.9	1.26	3.2
SE Mean	1.6	2.45	0.63	1.6

total and available phosphorus contents of PRs with digestion technique by using mixed acids (HNO₃, HCl and H₂SO₄) and single acid (HClO₄), extraction procedure it can be concluded that the digestion with mixed acids technique can be useful in determination of total phosphorus. Table (1 & 2) comparing the results of two extraction methods mixed and single acid showed highest value of both total and available phosphorus of Phosphate Rocks for the mixed acid digestion due to the strength of mixed acids than single acid. In comparing between two distinct areas for value of available phosphorus from Sudanese phosphate rock, found that Jebel Kurun area ranged between 14.30% to 23.90%, and between 11.10% to A comparison of two methods used for determination of dissolved total phosphorus of phosphate rocks was showed in table (1). The methods compared different approaches to oxidizing organic phosphorus compounds, and destroying polyphosphates to give forms total and available to standard colorimetric methods. The mixed acids (HCl, HNO₃ and HClO₄) reflux fuming was a techniques to evaporated PRs samples with this strong acids in covered beaker it gave a highest total P content of Jebel Kurun deposits phosphate and the lowest in Uro. The methods are rapid and have proved very useful in quickly evaluating the phosphate rock potentialities of an area economically.

CONCLUSION

Based on the results obtained from this study on comparison between two digestion methods

determination of phosphorus from phosphate rock can be draw attention to the following salient points as concluding remarks. Raw phosphate rocks represent an alternative for currently used phosphate fertilizers due to costs and energy limitations. To

prove suitability and adequacy of phosphate rock of Nuba Mountains (Jebel Kurun) and other parts of Sudan for fertilizers industry further detailed investigations are required.

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