

## Elemental Analysis of Egyptian Phosphate Fertilizer Components Samples by TGA, DTA and IR Methodes

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### Abstract:

The accumulation of certain elements in vitally important media such as water, soil, and food is undesirable from the medical point of view. It is clear that the fertilizers vary widely in their heavy metals and uranium content in the phosphate fertilizer and its components collected from Abu-Zaabal and Abu-Tartur fertilizers and chemical industries in Egypt and are elementally analyzed. The aim of this study was to determine the concentration of Cd, Cu, Cr, Ni, Pb, Zn (environmental pollutants i.e. toxic elements), and Co, K, Mg, Mn, Na (common elements) in phosphate rocks used for production of fertilizer. The data showed major concentrations of 17 elements (P, S, Ca, Ti, V, Mn, Fe, Zn, As, Sr, Y and Zr) and rare-earth elements (Rh, Pr, Gd, Tb and Tm). The results for the input raw material rock phosphate and the output product as final fertilizer are presented and discussed. Phosphate rock belongs mainly to sedimentary, slightly to igneous, and negligibly to metamorphic rocks. It is used for the production of phosphorous based fertilizers, acids, detergents and many products of common use. The rock is mainly composed of phosphorous and minutely of many other elements. Phosphate rock samples of local origin were collected from the geological rock formations around the New Valley Governorate were obtained from the Abu-Tartur fertilizer factories. Analysis of phosphate rock for all the elements of interest was carried out with IR Spectroscopy analysis Tanta University Model FT-IR Tensor 27 Bruker ( $5000\text{ cm}^{-1} - 200\text{ cm}^{-1}$ ). The results showed that heavy metal content was lower in Abu-Tartur phosphate than that in imported rock and were below the safe limits with the exception of lead whose concentration was found to be higher in local phosphate deposits than that in imported rock samples. Phosphate rock is a source of heavy metal pollution of air, soil, water, food chain etc, therefore requires removal of heavy metals (HMs) from the rock prior to its use. This work has shown that compounds with phosphate structures can be synthesized and characterized by TGA, DTA methods and IR spectroscopy.

**Keywords:** Phosphate rock / Pollutants / Heavy metals / Egypt Phosphate / IR.

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### I. Introduction

The dehydration of metal phosphate hydrates has not been extensively studied as compared to dehydration studies of metal sulphates. Since metal sulphate monohydrates exhibit certain acidic properties it was of interest to see whether the metal phosphate monohydrates exhibit similar characteristics, in view of the structural and configurational similarity between the sulphates and the phosphates of the alkali earth phosphates, the dehydration of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  was the most extensively studied by thermal means<sup>[1-4]</sup>. In all cases the anhydrous salt was first formed, followed by the pyrophosphate. The same was true of  $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ . The phosphates of sodium and potassium show step-dehydration and also condensation steps<sup>[5,6,7]</sup>. The dehydration of some transition-metal phosphates, although showing loss of water in more than one distinct step, does not show the formation of stable monohydrate intermediaries. Thermogravimetric analysis (TGA) is the most widely used thermal method. It is based on the measurement of mass loss of material as a function of temperature. In thermogravimetry a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. A plot of mass change versus temperature (T) is referred to as the thermogravimetric curve (TG curve). For the TG curve, we generally plot mass (m) decreasing downwards on the y axis (ordinate), and temperature (T) increasing to the right on the x axis abscissa as illustrated in Fig. 3. Sometime we may plot time (t) in place of T. TG curve helps in revealing the extent of purity of analytical samples and in determining the mode of their transformations within specified range of temperature. In thermogravimetry, the term 'decomposition temperature' is a complete misnomer. In a TG curve of a single stage decomposition, there are two characteristic temperatures; the initial  $T_i$  and the final temperature  $T_f$  (see Fig. 3).  $T_i$  is defined as the lowest temperature at which the onset of a mass change can be detected by thermobalance operating under particular conditions and  $T_f$  as the final temperature at which the particular decomposition appears to be complete. Although  $T_i$  has no fundamental significance, it can still be a useful characteristic of a TG curve and the term procedural decomposition temperature has been suggested. The

difference  $T_f - T_i$  is termed as reaction interval. In a dynamic thermogravimetry a sample is subjected to continuous increase in temperature usually linear with time whereas in isothermal or static thermogravimetry the sample is maintained at a constant temperature for a period of time during which any change in mass is noted. Now we will take up the instrumentation commonly used to obtain TG Curve. Infrared (IR) spectroscopy have been applied to hydrated phosphates. IR data for the hydrated phosphates<sup>[8-11]</sup> has been reported by various authors, although only few phosphates were studied, and gives complete detailed assignment for  $H_2PO_4^-$  and  $H_2O$  species, deals only with monocalcium phosphate monohydrate with no attempt at comparing the various hydrates.

### **Thermogravimetric analysis**

So far we have discussed the instauration of TG now we turn our attention to quantitative aspects of TG. As discussed earlier TG curves<sup>[12-20]</sup> represent the variation in the mass (m) of the sample with the temperature (T) or time (t). Normally, we plot mass loss downward on the ordinate (y) axis and mass gain upwards as shows a loss of mass at approximately 700°C, although this loss is very small (less than 2%). This is due to the fact that at this temperature the carbonates are transformed to carbon dioxide. The small size of this loss means that this phosphate is stable Figure 2. This behavior was reported too by D. Luna-Zaragoza (*Journal of Minerals & Materials Characterization & Engineering, Vol. 8, No. 8, pp 591-609, 2009*). Sometime we also record derivative thermogravimetric (DTG) Curves. A DTG curve represents the rate of mass change (dm/dt) as a function of temperature, or time t against T on the abscissa (x axis).

### **1.2- Interpretation of TG Curves**

TG curves of a pure compound are characteristic of that compound. Using TG curve we can relate the mass changes to the stoichiometry involved. This can often lead us directly to the quantitative analysis of samples whose quantitative composition is known. To further illustrate, let's consider the example of TGA curve of  $CaHPO_4 \cdot 2H_2O$ . This curve explained the chemistry of  $CaHPO_4 \cdot 2H_2O$  when it is heated the % mass lost by the sample between 800 and 950°C was indicated. This exactly corresponds to the mass changes. As in this case, percentage weight loss of  $CaHPO_4 \cdot 2H_2O$  will be We have seen above how TG Curves is related to stoichiometry (quantitative interpretation).

### **Factors affecting on TG curve 1.3-**

In the beginning we talked about the lowest temperature,  $T_i$  at which the onset of a mass change can be detected by the thermobalance operating under particular conditions and  $T_f$  is the final temperature at which the decomposition completed. We may like to call this as decomposition temperature, which is not correct. Actually in TGA techniques<sup>[21-28]</sup>, both  $T_i$  and  $T_f$  do not have fundamental significance, but they can still be a useful characteristic of a TG curve and the termed procedural decomposition temperature. It is often used for the temperature at which mass change appears to commence. This indicates us that procedural decomposition temperature does not have a fixed value, but depends on the experimental procedure employed to get it. Similar to this there are many factors which influence a TGA curve. These factors may be due to instrumentation or nature of sample. We have listed the main factors which affects the shape, precision and accuracy of the results in thermogravimetry as follows: a) Instrumental factors, this factors are furnace heating rate, Recording or chart speed, Furnace atmosphere Geometry of Sample holder, location of sensors, Sensitivity of recording mechanism and Composition of sample container. b) Sample Characteristics, The sample characteristics are amount of sample, Solubility of evolved gases in sample, Particle size, Heat of reaction, Sample packing, Nature of sample and thermal conductivity.

### **Application of Thermogravimetric Analysis 1.4-**

In the previous section we have seen how TGA can be used to understand the chemistry of decomposition of a particular compound. TGA also provides information about the temperature range over which a particular sample appears to be stable or unstable. We have also interpreted TG curves qualitatively<sup>[29-33]</sup>. Beside these there are many other applications of thermogravimetric analysis listed as: Purity and thermal stability, Solid state reactions, Decomposition of inorganic and organic compounds, Determining composition of the mixture, Corrosion of metals in various atmosphere, Pyrolysis of coal, petroleum and wood, Roasting and calcinations of minerals reaction kinetics studies, Evaluation of gravimetric precipitates, Oxidative and reductive stability, Determining moisture, volatile and ash contents and Desolvation, sublimation, vaporizations, sorption, desorption, chemisorptions.

## **2. Geological Origin**

Phosphates in mineralogy and geology, refers to a rock or ore containing phosphate ions. Inorganic phosphates are mined to obtain phosphorus for use in agriculture Phosphates are the naturally occurring form of the element phosphorus<sup>[34]</sup>. The largest phosphorite or rock phosphate deposits in Egypt, are found as beds, layers and as lenses intercalated with limestones, chert, claystones and marl beds. The geological studies of Allam and

Shamah, (1986)<sup>[21]</sup> on the Duwi (Phosphate) Formation ( Late Cretaceous ) at the coastal plain of Quseir-Safagadistrict along the Red Sea coast. , Eastern Desert, Egypt, showed that the main rock types are: phosphorite, organic rich shale, siliceous claystone, glauconitic sandstone, chert, dolomite, and oyster limestone Some phosphate rock deposits are notable for their inclusion of significant quantities of radioactive uranium isotopes. This syndrome is noteworthy because radioactivity can be released into surface waters inthe process ofapplication of the resultant phosphate fertilizer (e.g. in many tobacco farming operations in the southeast USA).Phosphates are the naturally occurring form of the element phosphorus). Many phosphates are not soluble in water at standard temperature and pressure. The sodium, potassium, rubidium, caesium and ammonium phosphates are all water soluble. Most other phosphates are only slightly soluble or are insoluble in water.The study of the impacts of phosphate mining activities on the groundwater quality in WadiQueh area ( Port Safaga) suggest that the groundwater in the area grades from fresh to brackish water (961–1,580 mg/l), and is characterized by sodium–calcium–sulphate–chloride and sodium–magnesium–sulphate–chloride chemical types. The results showed high concentrations of the heavy metals. Generally, phosphate deposits can contain significant amounts of naturally occurring heavy metals. Mining operations processing phosphate rock can leave tailings piles containing elevated levels of cadmium, lead, nickel, copper, chromium, and uranium. Unless carefully managed, these waste products can leach heavy metals into groundwateror nearby estuaries<sup>[35,36,37 and38]</sup>. Uptake of these substances by plants and marine life can lead to concentration of toxic heavy metals in food products.

### **III. Materials and Experimental methods**

#### **3.1. Sample collection and preparation**

The samples of the present study is collected from Safaga Phosphate mines at Longitude 26 43 N and Latitude 33 57 E., 30 km south west Safaga city and from Abu-Zaabal and Abu-Tartur fertilizers and chemical industries in Egypt. The samples were transferred to cloth bags from the destination sites and brought to the mineral processing laboratory of Tanta University Egypt. The rock samples were washed to remove dust and dried in the sun. Rock was crushed, ground to powder, homogenized, and kept in an oven at 110 °C for 10 h to remove moisture.

The phosphate rock is coarse grained, yellowish brown in colour and has some pyrite crystals (golden yellow and cubic crystal form), clasts of quartz and chert. The rock effervesces with dilute HCl acid, suggesting carbonate cement. Allam (1988) suggested that the Late Cretaceous phosphate of Duwi and Hamrawein (Quseir) area is of elastic origin indicated by the dominance of detrital phosphate and quartz clasts with cement of carbonate and little silica. Part of phosphatic deposits were diagenetically as evidenced from apatite mineral formed by replacement of some carbonate materials. Also some of phosphatic deposits are formed authigenically as evidenced by the present of euhedral prismatic crystals of apatite mineral formed by direct precipitation from sea water.

### **IV. Results and discussion**

Elemental analysis of 10 samples was carried out to determine the concentration of elements of interest in them and to compare the concentrations in local samples with those of the imported samples, and analytical results are summarized in Table 1. Comparative study was done to check relative quality of resources through heavy metal content and nutrient amount in the samples under study and those measured worldwide (Table 1). Heavy metal content is one of the deciding factors for the quality of phosphate resources, which does not have any standard permissible limit because the maximum allowable content depends on soil characteristics, irrigation water quality, crop type, etc.

#### **4.1. Environmental pollutants (toxic elements):**

The elements analyzed in the present study have been classified and elaborated as follows:

##### **4.1.1. Zinc (Zn)**

Zinc (Zn), a minor nutrient content in Egypt ore. The ms% 0.0469 of zinc is considered as adequate for most field-grown crops<sup>[39]</sup>, and lies within the global range of Zn in phosphate rock.

##### **4.1.2. Manganese (Mn)**

Manganese (Mn) is the basic macronutrient for plants. It was found to be enriched in Egypt phosphate rock with an average value of ms% 0.2185. It shows that Egypt phosphate resources for fertilizer manufacturing have compatible quality<sup>[40,41]</sup>.

#### **4.2. Heavy metal contamination**

The concentration of heavy metals measured in the Egypt rock phosphate samples of present study is comparably lower than that in the other phosphate rock deposits. There is a possible risk of contaminants

accumulating in soils and crops due to impurities in agricultural fertilizers and soil which needs to be addressed. The concentration may be safe from an agricultural point of view, as far as human beings are concerned they are exposed to heavy metals from various pathways: inhalation and ingestion of heavy metals from phosphate rock dust, drinking of heavy metal contaminated water as a result of mining, milling, manufacturing and disposal processes and eating of heavy metal affected food etc. Heavy metals can become toxic if accumulated in excessive amounts than those naturally required. Heavy Metals (HMs) can exert detrimental effects on human health and on the environment<sup>[42,43,44,45, and 46]</sup>. Since metals are widely distributed in environmental matrices, humans are exposed to them by either anthropogenic activities or inadvertently by necessity.

Exposure to heavy metals occurs in occupational settings and in the general environment. The environment is contaminated by heavy metals<sup>[18,19,20]</sup> in phosphate rock through various sources:

a) Dry milling of phosphate rock is a major source of air pollution. Also heavy metals as effluents are released to the environment during manufacturing of phosphate fertilizers. Mining activities of phosphate rock have been reported to cause heavy metal contamination to the soil in a localized area<sup>[47]</sup>. Heavy metals such as chromium in mining and milling dust damage the nasal and lung cells.

b) Dry and wet deposition of mining and milling dust contribute variable amounts of metals to the soil, depending on the nature and distance of sources<sup>[22]</sup>. Heavy metal contamination of soil has markedly increased in the past few decades. Application of phosphate fertilizers are among the other sources of heavy metal (like Mn, Fe, Zn, As, Pr, Sr, Ti, Ca, S, V and Zn) input into the agricultural system. Repeated use of these fertilizers may result in the accumulation of these metals and increase the contamination potential in soil<sup>[48]</sup>.

c) Increased anthropogenic input of heavy metals in soils may result in transport of an increased content of heavy metals in the groundwater or surface water. Heavy metals input include those from commercial fertilizers, phosphate industry waste, and mining and processing water. Toxic metals commonly released by mining are As, Fe, Mn, Gd, Tb, Tm and Zn. These metals (Rare Earth Element) when present in mining or milling dust are washed out from air through wet deposition but then enter the surface waters through run off. Also erosion of phosphate rock through rain can be a major cause of addition of these metals to a water body. Individually, these metals may be toxic to aquatic biota, or they may exhibit a combined toxicity greater than that of the individual elements<sup>[49]</sup>. Also heavy metals can enter into food chain through the food contaminated by heavy metals dust or through the contaminated crops. The increase in removal of heavy metals from phosphate rock results in the increase in the quality of the fertilizer made from it. It is important that we understand and utilize all our management options in taking the necessary steps to protect public health and the environment. Phytoremediation is a natural remediation of soil or water by growing plants that can efficiently take up metals from the contaminated system and then removing the metals from the system by harvesting the plant biomass<sup>[50]</sup>. The technique of electrokinetics may be effective for the removal of heavy metals from phosphate rock.

#### **4.3. X-Ray Fluorescence (XRF) Technique (Elemental analysis)**

X-ray fluorescence is created from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. Table (1) and Fig. (1) represents the analysis of the phosphate samples using the XRF technique. The data showed major elements Ca, Mn, Fe, Zn, Sr, Rh, Ba, and La (Qualitative Analysis), Fitting Coefficient: 0.1327.

Table (1): Results of analysis of the phosphatesamples using XRF-technique (Quantitative Analysis).

Element	ms%	mol%	Sigma	Intensity	K ratio Line	Type
P	8.6534	16.7662	0.9054	3002	0.0306193	K
S	13.0305	16.7662	0.9054	3002	0.0306193	K
Ca	53.0381	54.5949	0.1397	122630	0.1632133	K
Ti	0.4649	0.4004	0.0867	1238	0.0008871	K
V	0.0523	0.0424	0.0680	185	0.0001051	K
Mn	0.2185	0.1641	0.0489	1390	0.0005386	K
Fe	20.8260	15.3850	0.0398	158922	0.0547812	K
Zn	0.0469	0.0296	0.0271	570	0.0001401	K
As	0.0338	0.0186	0.0212	646	0.0001345	K
Sr	0.4660	0.2194	0.0157	16820	0.0032092	K
Y	0.0907	0.0421	0.0147	3571	0.0006858	K
Zr	0.0388	0.0175	0.0149	1624	0.0003233	K
Rh	-	-	-	39427	0.0280056	K
Pr	0.1624	0.0475	0.1467	472	0.0007129	L
Gd	0.7349	0.1928	0.1158	3526	0.0036495	L
Tb	1.9574	0.5081	0.1018	10970	0.0104669	L
Tm	0.1856	0.0453	0.0871	1202	0.0009638	L

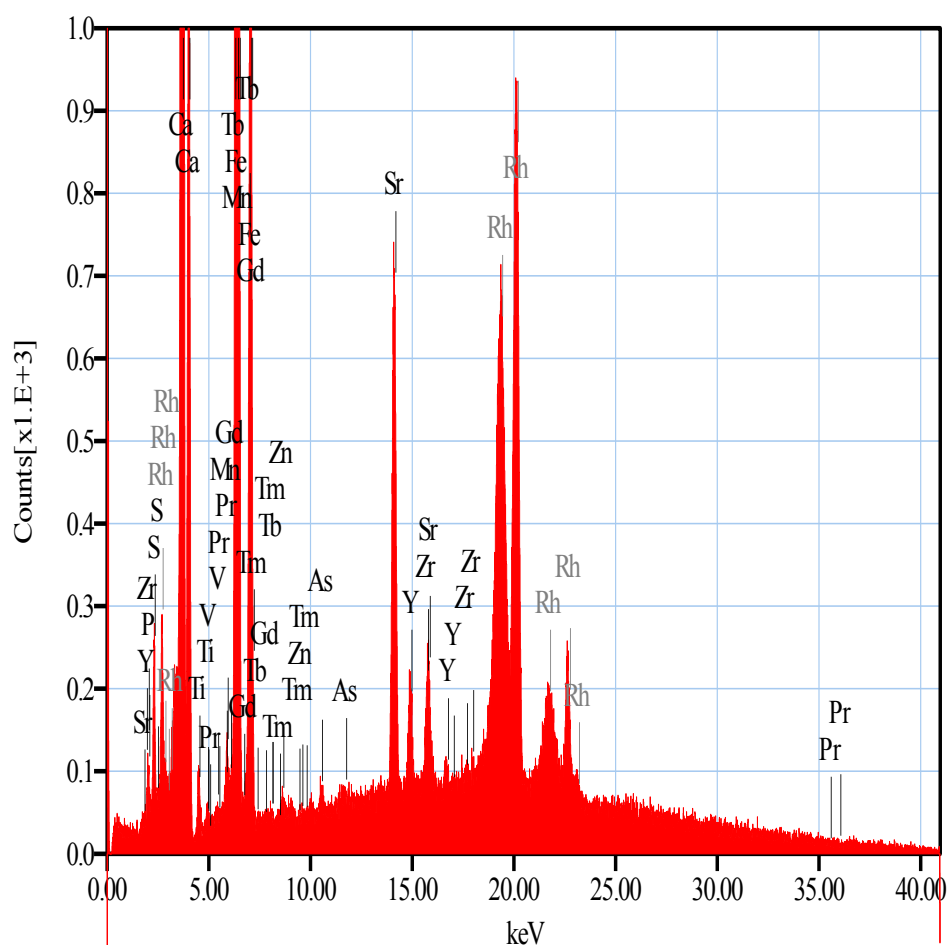


Fig.(1): Illustrates the analysis in one of the phosphatesample by XRF Technique.

#### 4.4. Differential thermal analysis (DTA) and Thermo gravimetric analysis(TGA):

DTA as a method of material investigation and its curve Fig. (2) can record the transformations where the heat is either absorbed or released. It used as a finger print for identification purposes. It was made for the examination of different materials and helpful for better understanding of given results by x-ray diffraction, chemical analysis and microscopy. DTA can also be used for quantitative measurements (enthalpy measurements). The area under a DTA peak can be to the enthalpy change and is not a detected by the heat capacity of the sample. The obtained sample was analyzed by differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) using analyzer (Shimadzu TGA- 50H) in Physics Department Faculty of Science Cairo University was carried out in the temperature range 30 – 850°C at a heating rate of 10°C/min in N<sub>2</sub> atmosphere, which provides both mass losses Fig. (2) and thermal information . For this testing, a small powder sample of the manganese ore ( 3.047mg) is being heated continuously up to 850°C, and during this process the samples relative loss in weight (weight change sensitivity of 0.01 mg) is being measured over the time Fig. (2). In Fig. (2) there are two endothermic peaks at temperatures of 50°C and 235°C. The first one corresponds to decomposition of OH and the second correspond to decomposition of O. time Fig. (2). In Fig. (2) there are two endothermic peaks at temperatures of 50° C and 235° C. The first one corresponds to decomposition of OH and the second correspond to decomposition of O.

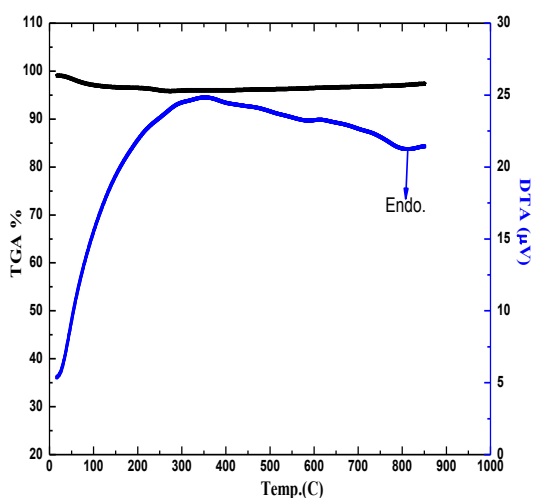


Fig.(2):TGA and DTA curves of phosphate ore sample under  $N_2$  atmosphere which shows the endo thermic peaks

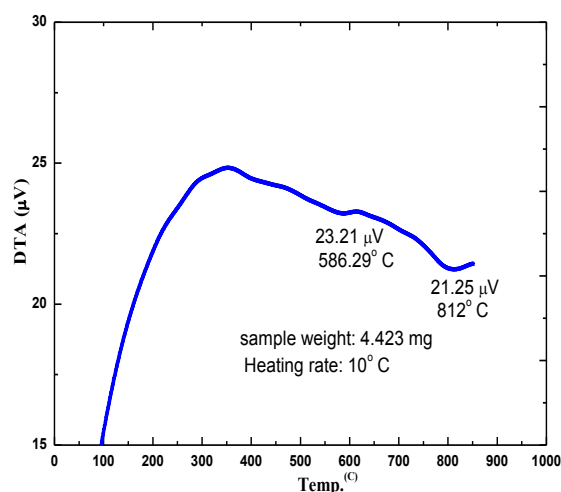


Fig.(3): DTA analysis shows the endothermic peaks with the phosphate ore sample under  $N_2$  atmosphere

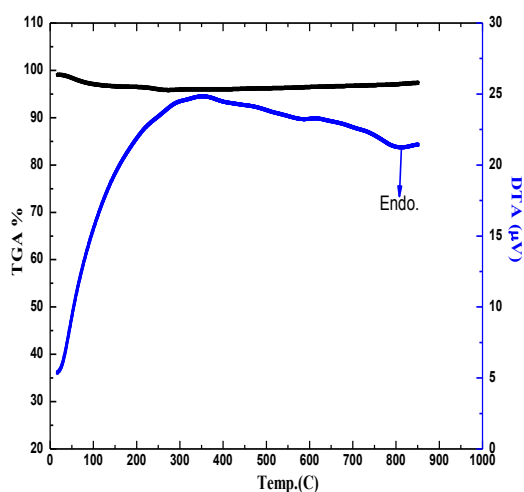


Fig.(4):TGA and DTA curves of phosphate ore sample under  $N_2$  atmosphere which shows the endo thermic peaks

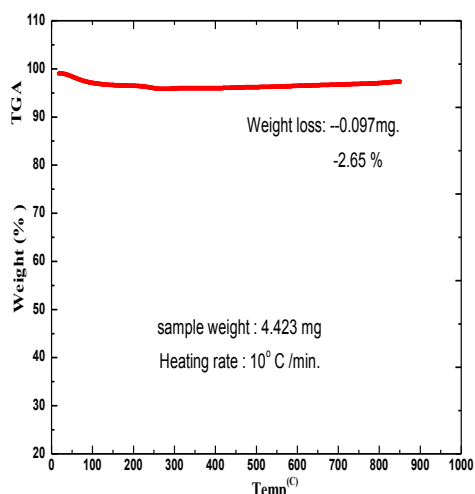


Fig.(5):TGA curve is displayed from left to right. The descending TGA thermal curve indicates a weight loss occurred by  $-0.097\text{mg}$ .

phosphate rock underwent phase transformation twice at 50 and 235°C, accompanying endothermic reactions. No sharp variation in the TGA graph indicates the absence of sudden phase changes due to material weight loss. 4.5. Infrared spectra IR spectra ( $5000\text{ cm}^{-1} - 200\text{ cm}^{-1}$ ) were recorded as FT-IR Tensor 27 Bruker system spectrophotometer Tanta University Egypt. The IR spectra provide information regarding the coordination mode in the complexes and were analyzed is shown in Fig.6. The dehydration of the hydrated phosphates (normal and acid) of sodium, potassium and calcium and also those of iron, nickel, copper and zinc were studied by infrared spectrometry, thermal gravimetry and differential thermal analysis. In most cases a gradual dehydration was found from the phosphate polyhydrate to the anhydride (sometimes to the pyrophosphate) without the formation of an extra-energetically stable monohydrate phase. monohydrate intermediaries. Infrared data for the hydrated phosphates has been reported by various authors, although only few phosphates were studied, and gives complete detailed assignment for  $\text{H}_2\text{PO}_4^-$  and  $\text{H}_2\text{O}$  species, deals only with monocalcium phosphate monohydrate with no attempt at comparing the various hydrates<sup>[51,52]</sup>. The IR spectrum of phosphate salts are

hydrolysed comparatively easily even on grinding in air, so that besides the  $H_2O$  and  $PO_4^{3-}$  vibrations other vibrations such as those due to  $H_2PO_4^-$  and  $HPO_4^{2-}$  appear. These latter species are characterized by P-O symmetrical stretching at  $870\text{ cm}^{-1}$  and P-O antisymmetrical stretching at  $930\text{ cm}^{-1}$  and  $995\text{ cm}^{-1}$ . The ligand shows bands at  $2500$  and  $3500\text{ cm}^{-1}$  which may be assigned to the  $-OH$  and  $H_2O$  groups, respectively. complexes, the presence of band in the region  $2900\text{ cm}^{-1}$  corresponding to free primary amine and the shifted of CN group towards lower side. In the ligand there are three strong intensity bands at  $1638$ ,  $1456$  and  $1429\text{ cm}^{-1}$  attributable to P-O and  $CO_3^{2-}$ , respectively. On complexation the band corresponding to  $\nu(C-N)$  is shifted towards lower side suggest that the ligand acts as bidentate chelating agent coordinating through nitrogen atoms of (C-N) group. Bands appearing at  $1044$ ,  $1098$ ,  $800$ ,  $867$ ,  $569$ ,  $605$ , and  $674\text{ cm}^{-1}$  attributable to  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$ ,  $CO_3^{2-}$  and  $SO_4^{2-}$  respectively. wavenumber. Absorbance measurements were taken at this wavelength in accordance with the mole ratio see Fig ( 6 ).

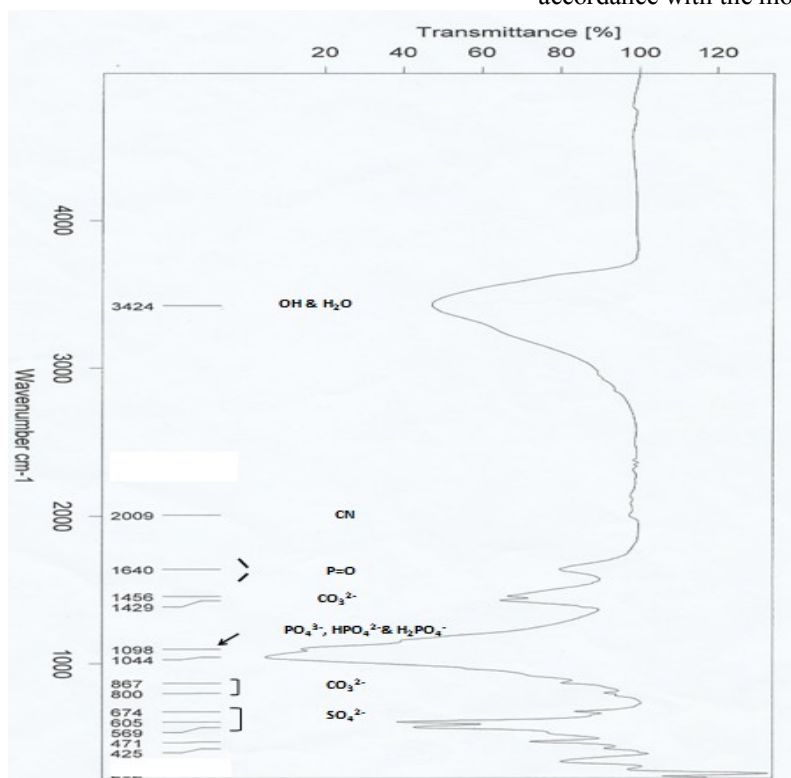
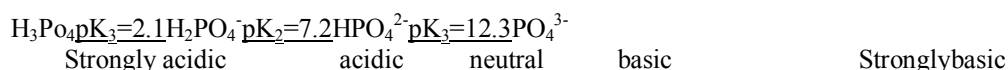


Fig.(6) . I.R. spectrum of  $Zn_3(PO_4)_2 \cdot z$ . A: polyhydrate; B: monohydrate.

In solution there exist a series of coupled pH-dependent equilibria between  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$ , and eventually  $H_3PO_4$  (Fig. 6). A quantitative measure of each equilibrium is provided by the law of mass action and expressed by the equilibrium constants,  $K_i$ , or the negative decadic logarithm thereof,  $pK_i = -\lg K_i$ . At a neutral pH of 7, the concentration of  $PO_4^{3-}$  in aqueous solution can thus be calculated to approximately 0.01% or  $10^{-4}$  mol/L out of a total phosphate concentration of 1.0 mmol/L. A distribution of the phosphate species is available as follows:



### V. Conclusion

Phosphate rock samples of local origin were analyzed for some toxic, major and minor elements. Concentrations of the elements under investigation in local phosphate rock were relatively smaller than that in the imported phosphate rock samples. The concentrations of the elements determined in the present study lay within the worldwide range of these elements. Egyptian phosphate rock resources can safely be used as raw material in fertilizer manufacturing plants. Heavy metals in phosphate rock pollute the environment by accumulation in air, soil, water bodies, food chain, etc. DTA, TG and IR studies carried out for a number of phosphate hydrates showed that although dehydration is usually stepwise, on the whole there is no intermediate richly-energetic monohydrate species.  $Zn_3(PO_4)_2 \cdot H_2O$  loses its water of hydration in a sharp step appearing in both TG and DTA curves. Infrared spectroscopy will be a very valuable tool in inorganic and solid state chemistry research also in



the next century. Thus, vibrational spectroscopy methods are valid for determination of: 1) the structure of molecular units in solids, 2) a lot physical properties, as free carrier concentrations. In the IR spectrum there is a shift in the bending vibration of  $\text{H}_2\text{O}$ .  $\text{Cu}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  loses its water in a more gradual step, but its IR spectrum indicates both a shift in strong  $\text{H}_2\text{O}$  and the librational modes of  $\text{H}_2\text{O}$ ,  $815\text{ cm}^{-1}$ , which characterizes a lowering of symmetry of the molecule.  $\text{NaPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{PO} \cdot \text{H}_2\text{O}$  show very similar behaviour in general. However, there is one main point of difference: whereas the sodium salt is formed during the dehydration of the polyhydrate, it is impossible to obtain the potassium salt in a similar manner, although in itself it is a stable well defined compound showing all the expected bands in its IR spectrum. In the hydrogen phosphates the dehydration step is followed by condensation step(s) all well shown in the DTA and TG curves. Their IR spectra, except for the  $\text{H}_2\text{O}$  vibrations, are different from those of the normal phosphates, as is expected from their different symmetry.

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