

Isolation of KH_2PO_4 from crude glycerol purified using *Acromonia aculleata* charcoal as adsorbent

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Abstract

Activated charcoal was prepared from *Acrocomia aculeata* (macaúba) endocarp by ZnCl_2 activation. The charcoal was used for the adsorptive purification of pretreated crude glycerol (CG) and potassium dihydrogen phosphate (KH_2PO_4 or KDP) was formed by the addition of H_3PO_4 to the crude glycerol containing KOH, which was used as catalyst in the production of biodiesel and glycerol. The KH_2PO_4 was isolated and purified by recrystallization from aqueous solution. The KH_2PO_4 was characterized by X-Ray diffraction (XRD), thermal analysis (TGA/DTA) and spectrophotometry in the infrared region – FTIR. From 216.0 m of crude glycerol, 20.1038 g of purified KH_2PO_4 was obtained.

1. Introduction

Potassium dihydrogen phosphate (KH_2PO_4) is a salt commonly used in buffer solutions, as a food additive, and in fertilizer. Its crystal is also employed with lasers in fusion experiments [1]. Among the methods for KH_2PO_4 preparation found in the literature, the crystallization methods, such as the use of N-methyldiethanolamine (MDEA) as an extractant to produce KH_2PO_4 from KCl and H_3PO_4 , where MDEA presented good water solubility and extraction selectivity, large extraction capacity, low toxicity and moderate price, was described by Tang et al. [2] and others [3–5]. Other methods for the production of KH_2PO_4 involve neutralization technology based on the thermal-process reaction between H_3PO_4 and KOH or K_2CO_3 [6], the direct chemical conversion method, the ion exchange method, and extraction technology [7–10].

Tan et al. [11] increased water resistance of magnesium oxychloride cement (MOC) without gel-like P5 in the hydration product by mixing phosphoric acid in the $\text{MgO-MgCl}_2\text{-H}_2\text{O}$ system. According to Ying Li et al. [12], the incorporation of KH_2PO_4 increased the performance of MOC with respect to the long-term compressive strength, water resistance, thermal stability, qualitative and quantitative composition, micro morphology, and pore structure of MOC.

As the KH_2PO_4 is a material with several isomorphs, which are archetypal of hydrogen-bonded material. KH_2PO_4 possesses piezoelectric, ferro-electric, electro-optic, and nonlinear optical properties, to which many researchers from various fields are strongly attracted. Recently, Jayaprakash et al [13] described the effect of doping KH_2PO_4 with magnesium chloride crystal (MCKH_2PO_4) on structural, thermal, optical, nonlinear optical and electrical properties of KH_2PO_4 . Jayaprakash et al. employed the slow evaporation technique with millipore water as a solvent to grow single crystals of pure KH_2PO_4 and MCKH_2PO_4 at room temperature. The investigations were performed to determine the optical, mechanical nonlinear optical (NLO) and thermal behaviors of KH_2PO_4 and MCKH_2PO_4 . KH_2PO_4 is employed in various applications as a piezoelectric transducer in various sound reproduction systems, and it is the first material to possess the key property of nonlinearity, which has lead to a magnificent and trending era in the field of photonics [14].

Javani et al. [15] proposed the stepwise isolation of K_2HPO_4 and KH_2PO_4 as a means of compensating the cost of biodiesel production. Recently, we studied the "Preparation of activated charcoal from *Acrocomia aculeata* for purification of pretreated crude glycerol" [16]. We decided to study the isolation of KH_2PO_4 from the medium containing glycerol and KOH that results from the transesterification of waste cooking oil (WCO). This study sought to compensate for the cost of producing biodiesel and glycerol and decrease the environmental problems resulting from the storage of these residues (glycerol and KOH).

2. Experimental

2.1. Raw materials and chemicals

Crude glycerol was obtained from triacylglycerides (waste cooking oil) by the transesterification reaction. MeOH (analytical grade), H_3PO_4 , and KOH were supplied by Vetec, São Paulo, Brazil.

2.2. Typical procedures

The crude mixture (216.0 mL) of glycerol, pH 9, and KOH resulting from the transesterification of WCO [16] was treated with phosphoric acid (20 mL) to pH 2. The precipitated KH_2PO_4 (20.1038 g) was filtered and purified by recrystallization. The procedure for the production and recrystallization of KH_2PO_4 was performed four times to produce four different samples.

2.3. Purification of KH_2PO_4 by recrystallization

The KH_2PO_4 (20.1038 g) resulting from the pretreatment of crude glycerol was washed with 6 x 25 mL of diethyl ether by stirring with a magnetic stirrer for 20 minutes to remove less polar impurities. The sample was filtered under reduced pressure, and the filtrate was analyzed by TLC to confirm the removal of non-polar impurities. The sample was dried in an oven at 120°C and weighed (13.6724 g). The KH_2PO_4 was dissolved in 130 mL of boiling distilled water containing 1% w/w (0.1367 g) of activated charcoal, filtered and allowed to crystallize. After recrystallization, the KH_2PO_4 was dried at 120°C to furnish 9.5081 g of purified salt.

2.3.1 Elemental analysis based on energy-dispersive X-Ray fluorescence (EDXRF) of KH_2PO_4 (Chemical or elemental composition of KH_2PO_4)

The energy-dispersive X-Ray fluorescence (EDXRF) of KH_2PO_4 was performed on an X-ray fluorescence spectrometer, model EDX 720 (Shimadzu®; Kyoto; Japan) equipped with an x-ray tube, and liquid nitrogen was used as the cooling agent. The software used was PCEDX (version 1.11 Shimadzu®).

2.3.2. Experimental X-ray diffraction of KH_2PO_4 . Characterization of the material by powder XRD

The measurements were accomplished using a Shimadzu model XRD-6000 diffractometer employing CuK α monochromatic radiation ($\lambda = 0.15406$ nm – 40 kV and 30 mA) at a scan rate of 2.0 degrees.s⁻¹ covering the 2 θ scale from 10–80°. KH₂PO₄ was dried at 120°C before analysis by X-ray diffraction.

2.3.3. Spectrophotometry in the infrared region – FTIR of KH₂PO₄.

Fourier transform infrared spectroscopic (FTIR) analyses were performed on an IRPrestige-21 spectrophotometer (Shimadzu) using the transmittance method. The samples were prepared with KBr oven dried at 120 °C for 3 h and crushed in a press. The resolution used was 2.0, and 20 scans were taken.

2.3.4. Thermal gravimetric (TG) analysis of KH₂PO₄.

KH₂PO₄ was dried at 120°C prior to thermogravimetric analysis (TG). Thermogravimetric analyses involving sample characterization were performed in the TA Instruments Q-600 – The KH₂PO₄ samples were placed in a platinum crucible and heat treated in a TA Instruments model Q-600 analyzer - simultaneous DTA/TGA/DSC thermal analysis module, operating under a synthetic air atmosphere, with a heating rate of 10°C min⁻¹ from room temperature to 1000°C. The pure KH₂PO₄ salt was used as a reference for the acquisition of thermogravimetric (TG) curves.

3. Results and Discussion

The KH₂PO₄ was obtained from pretreated crude glycerol (CG). Glycerol is a by-product of transesterification of triacylglycerides contained in WCO. FAME (Fatty Acid Methyl Esters; biodiesel) is the principal product. In the transesterification reaction, two phases were formed: the biodiesel phase and the glycerol phase (CG). CG contained glycerol along with many other materials such as soaps, remaining catalyst (in this case KOH used in excess), MeOH and esters (glycerides) formed during the process. The glycerol content was approximately 10 wt.%. In this study, the glycerol phase was treated with 85% H₃PO₄ to produce CG, a small organic phase containing a mixture of FAME, fatty acids and glycerides, and unpurified solid KH₂PO₄.

3.1. Pretreatment of glycerol

Several methods are currently used for purification of glycerol. In this study, the crude glycerol was initially treated with H₃PO₄ until the glycerol solution reached pH 2. The KH₂PO₄ precipitate obtained in the acidification step was filtered through a Buchner funnel and recrystallized. The glycerol was purified and clarified using charcoal produced from *Acromonia aculleata* as the adsorbent, according to the method previously described by our research group [16].

3.2. Production of KH₂PO₄

In a previous work, Javani et al. [15] described the production of K_2HPO_4 by the stepwise acidification of glycerol, obtained from saponification of WCO, with H_3PO_4 to pH 9.67. The pH of the glycerol filtrate was lowered to 4.67 by the addition of H_3PO_4 , and the precipitated KH_2PO_4 was recovered by filtration. The salts were washed with isopropyl alcohol to eliminate traces of glycerol, fatty acids, and glycerides that remained and then recrystallized. In the present study, the crude glycerol was acidified with H_3PO_4 to pH 2, producing only KH_2PO_4 .



3.3. Recrystallization of KH_2PO_4

To produce pure KH_2PO_4 , a highly accurate knowledge of the solubility is necessary for the crystallization process [17–19].

3.4. EDXRF of the KH_2PO_4

The EDXRF is an apparatus used for the quantitative and quali-quantitative determination of chemical elements in a wide range of samples. The analyses performed involved qualitative and quantitative determinations, with only the pre-calibration of the equipment ($Al \geq 80\%$ and the detection of Sn and Cu), using only atmospheric air, and restricting the detection of metals between ^{13}Al and ^{92}U . The samples were placed in a sample holder made of polypropylene film, and the analysis conditions were as follows: 10 mm collimator, scans with voltages of 0–40 KeV (Ti-U) and 0–20 KeV (Na-Sc) with a time of 100 seconds for each sample.

In this method, the material to be analyzed is struck with an X-ray beam that interacts with the atoms of the sample, causing the ionization of the innermost layers of the atoms. The filling of the resulting vacancies by more peripheral electrons induces the emission of X-rays characteristic of the constituent elements of the sample.

Energy scattering X-ray fluorescence is a non-destructive multi-element analytical technique capable of identifying elements with atomic number Z equal to or higher than 12. When the electrons of the innermost layer of the atom (for example, K and L) interact with photons in the X-ray region, these electrons are ejected, creating a vacancy. To recover the stability, the electronic vacancies are immediately filled by electrons from the closest layers ($K\alpha$, $K\beta$ or $L\alpha$, $L\beta$), resulting in an excess of energy in the process, which is manifested in the form of the emission of X-rays characteristic of each atom present in the sample. EDXRF was used as a method for semi-quantitative elemental analysis, and the titanium derivatives were not quantified. Their concentrations were lower than the quantification limit. However, their presence was clearly observed in the XRD powder spectra. The XRD patterns of the KH_2PO_4 are shown in Fig. 1.

3.5 XRD patterns of the KH_2PO_4

On the basis of the XRD of KH_2PO_4 obtained from crude glycerol, the extraction/purification method was observed to be successful. In the highlighted XRD regions of $2\theta \sim 55^\circ$ and $70\text{-}75^\circ$, it can be seen that the principal impurities that were found in sample 1 had been removed in sample 4. The XRD pattern of sample 4 was very similar to that of the commercial sample, as well as that of a sample reported in the literature [20]. Small differences in intensity and position can occur because of the preferential orientation and the possible variations in the crystallization of KH_2PO_4 [21].

3.5. Spectrophotometry in the infrared region – FTIR of KH_2PO_4 .

The vibrational spectra in the infrared region of commercial KH_2PO_4 and the KH_2PO_4 samples (four) are shown in Fig. 2. The same transmission bands can be seen in the FTIR spectra of the KH_2PO_4 standard and the four samples. The band corresponding to the O-H stretching vibration of water can be observed in the 3468-cm^{-1} region, as well as the band for the POH stretching vibration at 1631 cm^{-1} , the band for the HO-P-OH bending vibration at 635 cm^{-1} , the band corresponding to P-OH deformation or KO stretching at 540 cm^{-1} , and a band for PO_4 stretching at 416 cm^{-1} (Table 1).

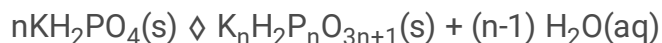
Table 1
FTIR assignments for KH_2PO_4 [19].

$\text{KH}_2\text{PO}_4\text{ (cm}^{-1}\text{)}$	Assignments
3468	O-H stretching, H-bonded
2900	O-H stretching
2810	Intermolecular H-bonded –OH stretching
2443	O-H stretching
1631	O-P -OH symmetric stretching
1463	O-H stretching
1290	CH_2 bending, $\text{P}=\text{O}$ symmetric stretching
1091	P -O-H symmetric stretching
920	$\text{O}=\text{P-OH}$ bending
635	HO-P-OH bending
540	P -OH deformation/K-O stretching
416	P-O_4 stretching

3.5. Thermal gravimetric (TG) analysis of KH_2PO_4 .

The same percentage of mass loss, depending on temperature, was observed in the TG curve of the pure salt sample (Fig. 3) and those of the four samples of KH_2PO_4 salts (Fig. 4). The formation of potassium polyphosphate was also indicated.

A loss of 12% in mass in the region of 200 °C and 400 °C, which corresponds to the loss of a water molecule in the salt polymerization process, can be observed because, when KH_2PO_4 is heated continuously to higher temperatures, constitutional water is released to form long-chain potassium polyphosphate, known as Kurrol's salt. Kurrol Potassium Polyphosphate is easily obtained by further heating of KH_2PO_4 [22].



4. Conclusions

The production and isolation of KH_2PO_4 are simple and environmentally friendly processes because no special chemicals or equipment are required. Overall, the isolation process reported in this work can be scaled up to commercial levels without any significant changes in its parameters. Acidification of the soap in the crude glycerol to free fatty acids and KH_2PO_4 was accomplished with the addition of H_3PO_4 to a pH of 2. The KH_2PO_4 FTIR data helped us to analyze the vibrational functional groups. The thermal analysis by TG/DTA techniques reveals the thermal stability of the KH_2PO_4 . The product KH_2PO_4 can be used as potash-phosphate fertilizer, in addition to more refined applications. KH_2PO_4 is a source of two nutrients, potassium and phosphorus. The KH_2PO_4 obtained satisfies the industrial grade standard. This process of production and isolation furnished a product of high purity in high yield and contributed to the removal of industrial waste from the environment. The KH_2PO_4 salt is usually applied in medical, food and industrial fields [6].

Declarations

Acknowledgements

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Data availability

The paper entitled "Isolation of KH_2PO_4 from crude glycerol purified using *Acromonia aculleata* charcoal as adsorbent" is submitted for your kind considerations. The research data policy and data availability are not shared with anyone before publication.

Conflict of interest

This paper does not have any competing interests.

Ethical approval

This paper does not have any ethical statement, and this work does not involve any conflict of interest.

Author Contribution

Author Contributions Milton de Souza Freitas The author confirms sole responsibility for the following: data collection, and manuscript preparation. João Victor Godinho The author confirms sole responsibility for the following: analysis and interpretation of results, and manuscript preparation. David Lee Nelson The author confirms sole responsibility for the following: analysis and interpretation of results, and manuscript preparation. Alexandre P. Wentz The author confirms sole responsibility for the following: analysis and interpretation of results, and manuscript preparation. Claudio Roberto Neri The author confirms sole responsibility for the following: analysis and interpretation of results, and manuscript preparation. Lucas D. Zanatta The author confirms sole responsibility for the following: analysis and interpretation of results, and manuscript preparation. Fernando L. P. Pessoa The author confirms sole responsibility for the following: analysis and interpretation of results, and manuscript preparation. Sandro L. Barbosa The author confirms sole responsibility for the following: study conception and design, data collection, analysis and interpretation of results, and

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Figures

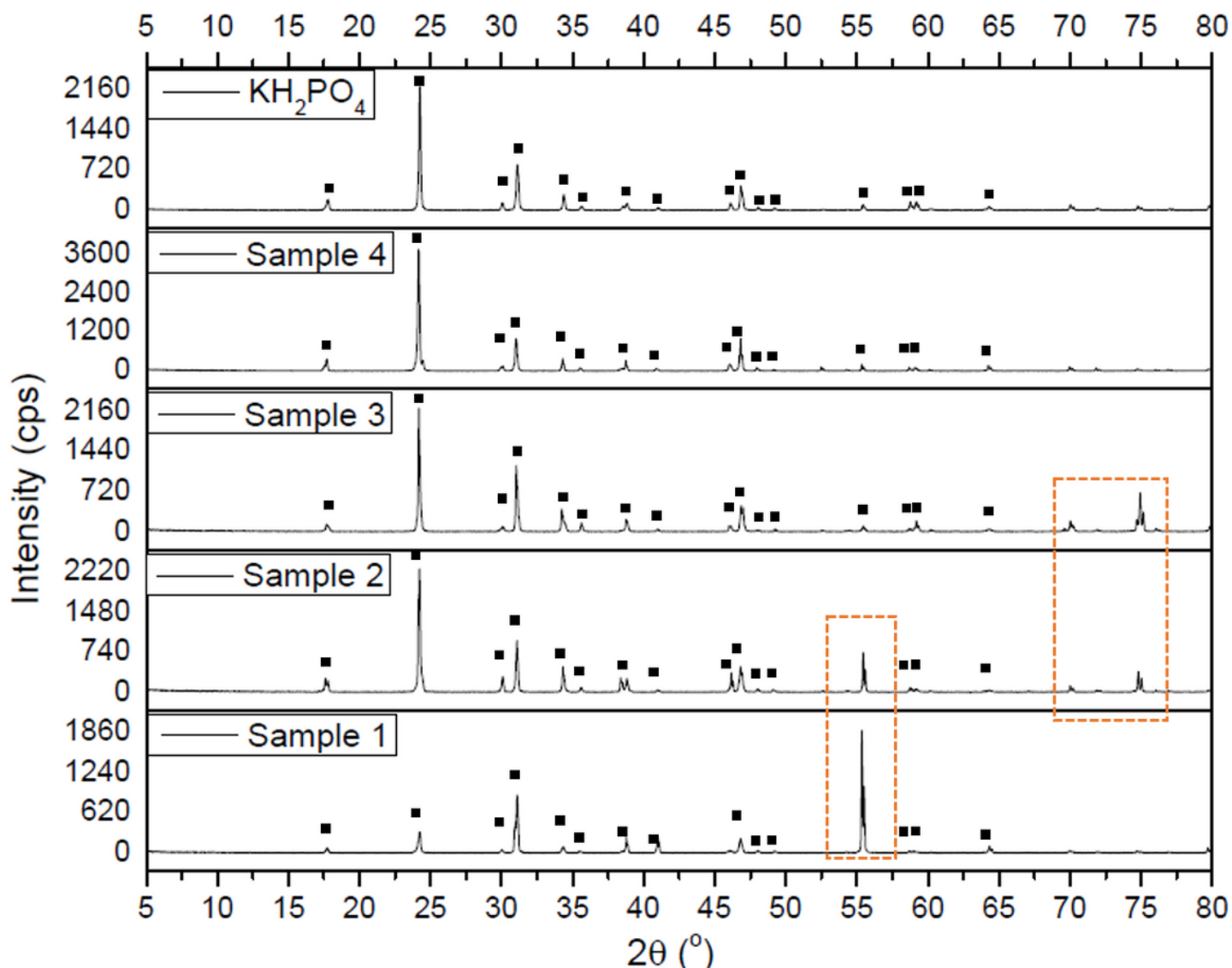


Figure 1

XRD patterns of KH_2PO_4 (prepared dry solid samples 1, 2, 3 and 4) and commercial standard KH_2PO_4 (top). Identification of the main diffraction planes of KH_2PO_4 .

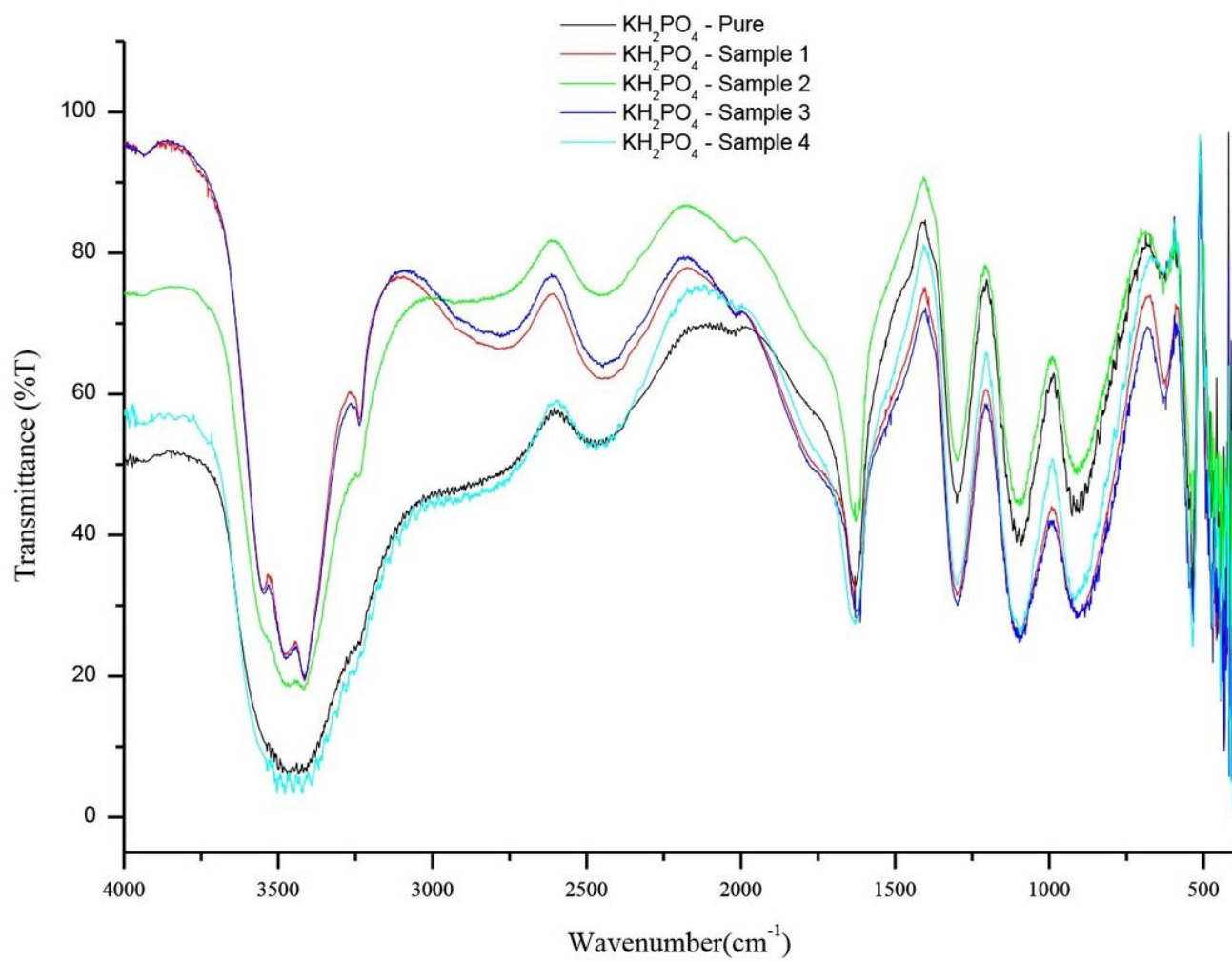


Figure 2

FTIR on KBr pellet of the commercial standard and samples 1, 2, 3 and 4 of KH_2PO_4 .

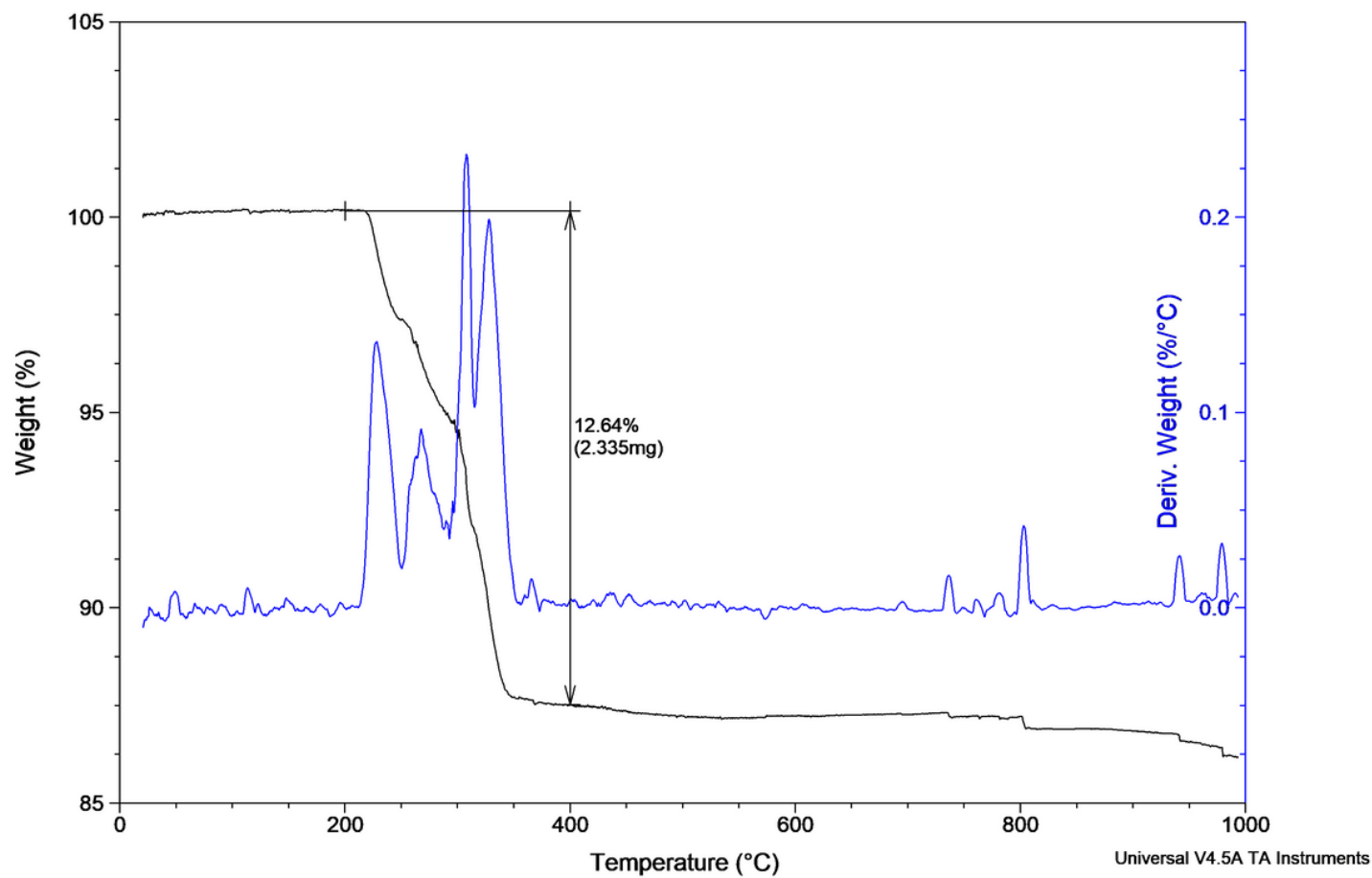
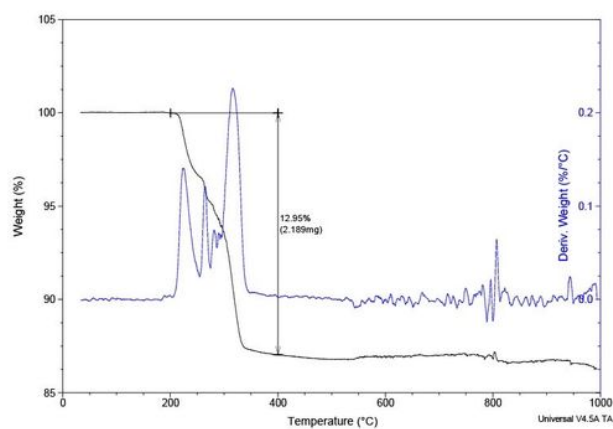


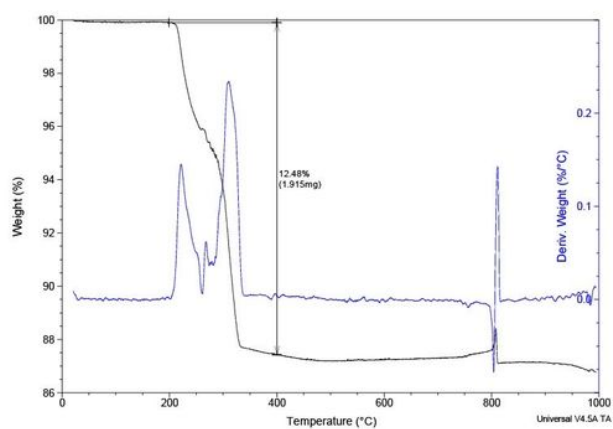
Figure 3

Thermogravimetric analysis of KH_2PO_4 Pure.

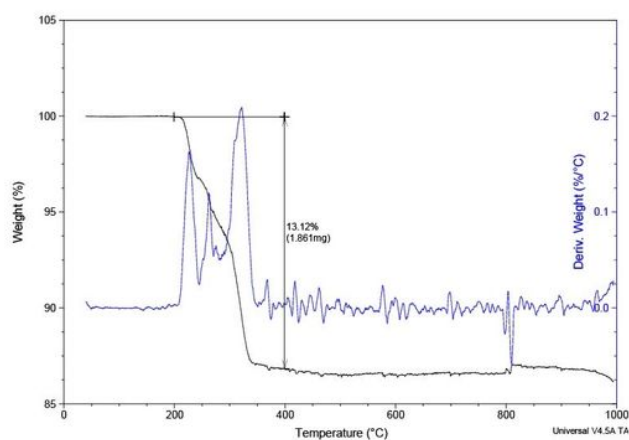
Sample 1



Sample 2



Sample 3



Sample 4

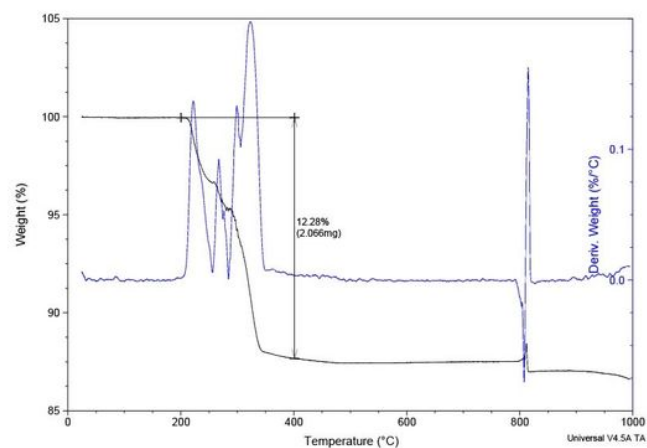


Figure 4

Thermogravimetric analysis of KH_2PO_4 .

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