



Review Compositional Analysis of Metal(IV) Phosphate and Phosphonate Materials—Pitfalls and Best Practices

Risto Koivula * D and Wenzhong Zhang

Department of Chemistry—Radiochemistry, University of Helsinki, 00540 Helsinki, Finland

* Correspondence: risto.koivula@helsinki.fi; Tel.: +358-29-4150130

Abstract: Metal(IV) phosphate and phosphonates materials have increasingly found their applications in water purification, heterogeneous catalysis, drug delivery, and proton-exchange membrane fuel cells. The strong linkage between tetravalent metal cations and phosphate/phosphonate groups offers a unique bottom-up design platform, resulting in chemically stable inorganics or hybrids. Task-specific physiochemical functionalities could be deposited by modifying the phosphate/phosphonate groups before the material synthesis. The high reactivity between the metal centre and the phosphorus-containing linker, on the other hand, often leads to obtaining unordered materials (amorphous solids or coordination polymers). The chemical composition of the prepared materials is a key parameter in guiding the synthetic approach and in governing their performances. This narrative review focuses on critically summarising the traditional and advanced analytical methods for probing the composition of these materials. The reader is introduced to and guided on the advances and restrictions of different analysis techniques when probing metal(IV) phosphates/phosphonates. Both solution-based and solid-state spectroscopic techniques are covered with a focus on understanding the quantity and the linkage status of the phosphorus-containing moieties. These techniques include atomic spectroscopy, mass spectroscopy, nuclear magnetic resonance spectroscopy, X-ray-based methods, and neutron activation analysis.

Keywords: metal phosphate; metal phosphonate; characterisation; composition analysis

1. Introduction

The chemistry of tetravalent metal phosphate and phosphonate materials has sparked a great deal of attention for more than half a century, ever since the pioneering work on crystalline zirconium phosphate conducted and reported by Alberti [1] and Clearfield [2]. These solid materials have been utilised as ion exchangers, heterogeneous catalysts, proton conductors, gas sensors, and drug carriers, amongst others. Zirconium seems to remain the most widely studied tetravalent metal centre element, followed closely by titanium. Sparse interests are also given to tetravalent hafnium, germanium, tin, and cerium. Most scholarly articles before the 1980s focused on purely inorganic metal phosphates, while the first report regarding the inorganic-organic hybrid zirconium phosphonate was dated in 1978. The widespread interest in such materials can be seen from the constantly increasing number of publications (Figure 1).

The rigid and stable inorganic polymeric structures are constructed by sharing oxygen atoms (located on the vertices of phosphate/phosphonate tetrahedra) with tetravalent metals in an octahedral configuration. This gives rise to the possibility of obtaining amorphous solids (coordination polymer) and a wide range of crystalline materials. The most prominent structural type of metal phosphate/phosphonate is the two-dimensional lamellar form composed by the stacking of layers. The somewhat tunable interlayer cavities are perfect hosts for guest molecules and ionic species. The chemistry of metal phosphates is almost entirely dependent on the hydroxyl groups attached to the phosphorus atoms, whereas advances in modern phosphonate chemistry allow various organic functionalities to be



Citation: Koivula, R.; Zhang, W. Compositional Analysis of Metal(IV) Phosphate and Phosphonate Materials—Pitfalls and Best Practices. *Separations* 2023, *10*, 600. https://doi.org/10.3390/ separations10120600

Academic Editors: Victoria Samanidou and Gavino Sanna

Received: 26 September 2023 Revised: 15 December 2023 Accepted: 16 December 2023 Published: 18 December 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). decorated onto the solid skeletons built upon this strong metal—oxygen—phosphorus bonds [3]. Many recent reviews have extensively summarised these materials from synthetic [4], structural [5], functional [6], and catalytical [7] aspects. However, there are currently no reviews dedicated to the compositional analysis methods with regard to metal(IV) phosphate/phosphonate materials and it has become clear that some analysis techniques have been adopted in 'general use' without proper consideration and precautions when analysing the structure of these materials in the recent literature.



Figure 1. Number of publications with a title containing zirconium/titanium phosphate/phosphonate sorted according to publication year (decade). Data obtained from Web of Science core collection, Clarivate Analytics.

The high reactivity and stable coordination of phosphate/phosphonate to tetravalent metal ions comes with a noticeable disadvantage—the high reactivity renders the preparation of crystalline ordered structure almost impossible at mild conditions. Rather harsh synthesis conditions and/or chemicals are needed to obtain crystalline materials, such as prolonged hydrothermal treatment (atmospheric pressure reflux or pressurised autoclave conditions) and the addition of mineralising agents (most typically fluoride or oxalate). Ordered porous materials are also produced via template-directed routes [8–10]; nevertheless, these materials typically lack long-range orientation and are usually seen as amorphous materials in the most typical crystal structure analysis, powder x-ray diffraction (XRD).

Following established or novel synthetic routes, the obtained metal phosphate/ phosphonates need to be systematically characterised so that the material's diverse and unique features could be rationalised and fully understood. For this, an array of structural and compositional characterisations is available thanks to the development of modern physics and analytical chemistry techniques. One of the most easily accessible structural characterisation methods is XRD, by which the long-range ordering in the analyte powder is evaluated. Any crystalline phases present in the material readily give constructive interference of the incoming X-ray beam at certain angular positions. However, it is impossible to identify the entirety of the metal phosphate/phosphonate materials by using structural characterisation methods alone. Unfortunately, powder XRD seems to have become the only characterisation method adopted in certain literature, and this is not an appropriate approach. If synthesis conditions are not carefully optimised, the resulting product often constitutes a mixture of crystalline and amorphous phases, the latter of which simply does not show up in certain structural characterisations (e.g., powder XRD). Understanding the true nature of the metal phosphate/phosphonate materials is a key prerequisite before further performance evaluations. It is also a quality control process to warrant repeatability and reproducibility, which sadly has suffered a depreciation in the current literature.

Compositional analysis of metal phosphate/phosphonate materials is far from a straightforward task. Standard characterisation methods, if not utilised properly, can pro-

vide erroneous information on the material's chemical compositions. The main challenges are associated with the low solubility of the four-valent metals and many phosphorous compounds, the quantification difficulties for the oxygen content (low-Z element), the uncertain protonation states of the phosphate/phosphonate ligands, and the presence of crystalline water. Elucidating the true composition is as important as figuring out characterising the structure of the materials, particularly when assessing the material's versatile properties. This principle applies also to amorphous or partially amorphous materials. In this mini-review, methods for compositional analysis of metal phosphate/phosphonate materials are discussed and compared, with the help of literature practice. Factors affecting the quantification by utilising different methods are illustrated, and some best-practice methods are recommended. This review could serve as a practical guide and a check-list when working with the compositional characterisation of metal(IV) phosphate and phosphonate materials.

2. Analysis of Metal and Phosphorus Contents

Since any metal phosphate/phosphonate materials are essentially built by metal centres and phosphorus-containing ligands, it is important to understand how many of the building blocks in the precursor actually translate into solid materials. Furthermore, the phosphorus-to-metal atomic (molar) ratio gives an indication of the possible presence of other components. For crystalline materials, the phosphorus-to-metal ratio should correspond to the chemical stoichiometry, as validated by any structural characterisations (i.e., single crystal diffraction methods). This composition of the materials needs to be characterised irrespective of the structural characterisations, and such is generally lacking in the literature, which leaves the possibility of, for example, the aforementioned amorphous metal oxide to be present in the material, which complicates the assessment of the material's functional results.

2.1. Dissolution and Digestion

As the first step in any solution-based analysis methods, the metal phosphate/ phosphonates must be completely solubilised into an aqueous solution. A combination of concentrated nitric acid, perchloric acid, and hydrofluoric acid (HF) is generally adopted for this purpose, among others [11,12]. Due to the slow and low dissolution process of typical tetravalent metal compounds oxo clusters, HF is added to form soluble complexes (e.g., ZrF_6^{2-}). Nitric acid and perchloric acid as strong oxidation agents are used to digest the organic components. The digestion process could be carried out on a heating plate (with plastic or Teflon beakers) or in any compatible high-pressure digestion system (microwave digester or autoclave). Literature recipes for digestions are rarely clearly mentioned and they vary greatly from one material to another. However, the overall goals for the digestion are (i) to transfer all the metal and phosphorus as soluble species into the solution; (ii) to decompose any remaining organic compounds; and (iii) to obtain a clean solution matrix that is suitable for subsequent measurement. The last goal usually requires the elimination of residual HF and perchloric acid. Depending on the material composition, different approaches need to be considered, particularly considering reprecipitation and possible polyatomic phosphorous species [13,14]. Quality control samples (e.g., stoichiometric metal oxides, non-volatile organophosphorus compounds, or highly crystalline metal phosphate phases) are highly recommended for any of these digestion processes since they may generate volatile (highly toxic) compounds.

2.2. Atomic and Mass Spectroscopy

Metal(IV) and phosphorus dissolved in a solution can be quantified by atomic or optical spectroscopic methods, or mass spectroscopic methods. However, it is crucial to ensure the complete dissolution of the compounds containing these elements as explained earlier. For atomic/optical spectroscopy, the analysis is based on the characteristic photon emission(s) or absorption(s) of different atoms. There are many available techniques for atomisation and excitation of the elements—chemical flame, graphite furnace heating, direct-current plasma, and inductively coupled plasma. They differ from one another mostly on the temperature of the flame/plasma, thus resulting in different atomisation and ionisation capabilities. Common techniques include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), microwave plasma atomic emission spectrometry (MP-AES), and inductively coupled plasma optical emission spectrometry (ICP-OES). The detection limits for common metal(IV) in solution are at the level of sub-mg/L, sometimes even possible for the level of μ g/L. The more sensitive analysis method is the inductively coupled plasma mass spectrometry (ICP-MS), where the detection limits could reach ng/L or pg/L. It should be noted that phosphorus content cannot be measured by AAS techniques since the atomisation condition provided is not enough to decompose phosphate into phosphorus atoms. The main challenge of obtaining an accurate result is associated with the efficiency of the sample disintegration and dissolution process.

Not only nebulised aerosol could be fed into the ICP torch but also the ablated solid materials. Laser ablation-ICP (LA-ICP) is a technique that utilises a laser to evaporate or sublimate solid samples. This allows the direct analysis of a solid without dissolution. To the best of our knowledge, LA-ICP-based techniques for compositional analysis of metal phosphate/phosphonate were not found in the literature. The LA-ICP-MS method gives direct isotopic information and quantification information (including for oxygen [15]), making it an ideal method when suitable standards are used.

The element-specific quantification analysis by atomic or mass spectroscopic techniques is recommended for the compositional analysis of metal phosphate/phosphonate materials. These methods produce accurate results both in terms of overall content and metal-to-phosphorus ratio. The shortcoming of these methods is the long sample preparation routes (referring to digestion).

2.3. X-ray Spectroscopy

X-ray-based analysis is non-destructive and as such a very attractive measurement technique. There are several X-ray-based techniques which could give quantitative compositional information of the sample, and they differ mainly in the type(s) of incoming radiation and measurable radiation after the interaction with the matter.

The most common technique is the energy-dispersive X-ray spectroscopy (EDX or EDS), which is sometimes also referred to as energy-dispersive electron probe microanalysis (ED-EPMA). For this purpose, an X-ray detector is usually fitted to a scanning electron microscope (SEM). EDX is an element-specific method because of the intrinsic differences in X-ray emission lines of different elements, and qualitative element identification is easily achieved. However, there are many issues associated with the quantification of elemental compositions by the EDX method: (i) the existence of a background continuum in the EDX spectrum, which comes mainly from bremsstrahlung X-rays and Compton scatterings; (ii) intrinsically overlapping emission peaks; (iii) insufficiency of the sample thickness.

For obtaining quantitative elemental compositional results, care must be taken during sample preparation and the actual measurement. Standardless methods would most probably give erroneous results. Modern EDX softwares are equipped with complex computer algorithms for correcting the spectrum to achieve more accurate quantification, and the most used method is called the "ZAF" method. This method considers the atomic number ("Z"), absorption ("A"), and fluorescence ("F") between different elements in the sample and in the standards [16]. To achieve an EDX quantitative analysis, one needs carefully selected standard samples, an even sample surface coated with a homogenous conductive layer, a stable electron beam current, and lastly, adequate counting statistics for the peak-of-interest. Even if all the above-mentioned problems are taken into consideration, the spectral interferences still cannot be avoided.

For example, for the most widely studied zirconium phosphate/phosphonate materials, the K α 1 spectral line of P is completely overlapping with the L α 1 line of Zr (Table 1),

and the energy resolution (on the scale of 100 eV) of the X-ray detectors (typically silicon drifted detectors, SDD) cannot distinguish between these two peaks (for instance, see examples in [17,18]). With adequate precautions, the Zr quantification results would still be trustworthy by quantifying based on the K α lines (at 15.8 keV), but the mathematical peak deconvolution of the P K α lines from the Zr L α lines would introduce too much uncertainty to the results. This uncertainty has been seen in the literature where crystalline zirconium phosphate materials, whose stoichiometry could be deduced from single-crystal XRD measurement, gave inaccurate Zr and P quantification results in EDX measurement [19]. A similar situation applies to energy-dispersive X-ray fluorescence (ED-XRF) analysis, where an X-ray tube produces the incident beam. However, the quantification of Zr and P contents by EDX measurements is not rare in the literature and could lead to significant errors.

Element	Kα1 (keV)	Lα1 (keV)
Р	2.014	-
Ti	4.511	0.452
Ge	9.886	1.188
Zr	15.775	2.042
Sn	25.271	3.444
Hf	55.790	7.899

Table 1. Characteristic X-ray emission lines of selected elements.

Wavelength-dispersive (WD) X-ray analysis compensates the ED methods for spectral resolution and background reduction. Depending on the radiation source, both WD-EPMA and WD-XRF are essentially improving the corresponding ED methods. In the WD methods, the X-ray emission is monochromatised using crystal analysers before being counted on the detector. This could lead to a proper separation of the P K α lines from the Zr L α lines. WD methods with proper matrix corrections are better at achieving quantifiable results for the compositional analysis, especially for zirconium phosphate/phosphonate materials [20,21].

Another applicable type of X-ray-based analysis is X-ray photoelectron spectroscopy (XPS), traditionally named electron spectroscopy for chemical analysis (ESCA). This method differs from the ED or WD X-ray spectroscopy since it is the emitted photoelectrons that are being measured in XPS. The quantification by XPS provides accurate results for homogenous samples with adequate standards [22]. However, it should be noted that XPS is a surface analysis technique responsive only to a few-nm thickness layer, and the photoelectron generated deeper inside the materials will be attenuated and will not reach the detector. In addition, surface layer oxidation and contamination with adventitious carbon significantly impair the quantification results by XPS. Since both EDX and XPS would possibly result in erroneous results, it is common to obtain incoherent quantification data when comparing these two methods.

In ED methods, the oxygen content associated with the analysis is always a stoichiometric calculation of the other elements and it should not be taken seriously. The X-ray emission of O is too low to be accurately quantified due to the interference from the background spectrum. However, in WD methods and XPS, the obtained oxygen content is the actual measurement result.

X-ray-based spectroscopic methods are a group of well-documented and non-destructive analysis techniques that are useful for the compositional analysis of any metal phosphate/phosphonate materials. Both the metal and the phosphorus contents could be accurately measured when proper precautions have been taken. WD techniques are recommended over ED techniques, and it is not possible to obtain trustworthy quantification results of Zr and P by using ED methods alone. Electron sources are more destructive compared to X-ray sources. The heterogeneity of the sample must be examined especially when using XPS but also for other techniques.

2.4. Neutron Activation Analysis

Neutron activation analysis (NAA) is by far the most accurate method for quantitative compositional analysis [23]. The NAA analysis usually does not require any chemical pre-treatment, and it utilises characteristic nuclear reactions of different isotopes when the sample is irradiated by a neutron source. The produced radioisotopes and/or their daughters are subsequently measured conveniently on a gamma detector. NAA suffers much less from matrix effects since light elements (H, C, N, O) in the samples do not produce significant interferences for the determination of heavier elements. It is a multi-element technique; therefore, quantification for many elements could be carried out simultaneously. Essentially, it is the neutron cross-section of each nuclear reaction that governs the analysis and is therefore device specific depending on the energy of the produced neutrons.

Concerning zirconium phosphate/phosphonate materials, Table 2 lists the nuclear reactions relevant for quantification with a simple comparator method by the fast neutron (14 MeV) activation [24]. The measurement methodologies for other elements are also found in the literature: Ti [25], Hf [26], Ge [27], Sn [28], and Pb [29]. NAA measures accurately the oxygen content, which is important for compositional analysis. The problematic part of NAA is the potentially radioactive sample handling and waste management that makes the facilities heavily regulated and not so easily accessible.

Table 2. Nuclear reactions used for elemental quantification by NAA for zirconium phosphate/phosphonate materials.

Element	Reaction	Half-Life	Gamma Energy (MeV)
О	¹⁶ O(n,p) ¹⁶ N	7.13 s	6.13, 7.12
Ν	¹⁴ N(n,2n) ¹³ N	9.97 min	0.511 (annihilation)
Р	$^{31}P(n,\alpha)^{28}Al$	2.25 min	1.78
Zr	90 Zr(n,2n) 89m Zr	4.18 min	0.588

2.5. Gravimetry and Colourimetry

With the lack of modern and highly sensitive spectroscopic methods, traditional gravimetric and colourimetric are also viable methods for tetravalent metal and phosphorus (mainly as phosphate) analysis. These methods are still useful and well accessible due to their relative simplicity and robustness of the analysis when large sample quantities are available, making the science more equal. The main drawbacks of them are the large amount of sample requirements as well as lower sensitivity compared to modern methods. For example, zirconium could be precipitated as zirconium cupferron (ammonium salt of N-nitroso-N-phenylhydroxylamine) and later calcined to form zirconium dioxide (ZrO₂) for gravimetric analysis [2,30]. This method suffers from specificity, i.e., titanium produces a positive interference. Colourimetric methods are more unique for a distinctive element, and the detection limit is much lower when utilising a UV/visible spectrophotometer (compared to gravimetry). Titanium, as an example, is quantifiable through the violet titanium-hydrogen peroxide complexes, whose maximum photon absorption is at 420 nm [1].

The measurement of phosphorus is almost entirely based on the phosphate species and therefore any organophosphorus would significantly impair the results. Calcination of metal phosphate with the addition of soluble magnesium salts results in the formation of insoluble (water) magnesium pyrophosphate for gravimetric analysis [31]. For colourimetric determination of phosphate, there are also a number of methods, and the most classic one is based on a blue-coloured phosphomolybdate complex $(NH_4)_3[PO_4(MoO_3)_{12}]$ [32].

In general, the traditional methods are still valid and serve their purpose well via simple chemical reactions and processes. The methods produce good sufficiently reliable results when there are no known interferents present and when the sample quantity is adequate for such analysis.

3. Speciation of the Phosphorus-Containing Moieties

Metal phosphate/phosphonate materials are constructed via covalent linkages between the tetravalent metal centres and the ligands. The phosphoric acid molecule harbours three hydroxyl groups while phosphonic acids contain two. The protonation and deprotonation states of the phosphorus-containing moieties determine the connectivity among the building blocks as well as the chemical properties of the solid materials. Apart from understanding the accurate content of metal and phosphorus, the speciation of the phosphorus-containing ligand must be separately examined. This helps identify the overall crystallinity of the materials since pure crystalline materials usually contain one or a few distinctive specie(s) of the ligand. It is also relevant when preparing a mixed phosphate/phosphonate material, whereby the ratio between phosphate and phosphonate in the precursor does not directly translate into the solid phase because of the differences in their reactivity. The current section focuses only on the quantifiable characterisation techniques, thus infrared spectroscopy and Raman spectroscopy are excluded—these two techniques can provide diagnostic functional group information identification on solid materials [11,33,34].

3.1. Potentiometric Titration

All metal phosphate/phosphonate materials containing protonated P—OH groups are essentially solid-phase weak acids, i.e., the acidic groups can be neutralised via acidbase reactions. Potentiometric titration is the most classic method for speciation of the phosphorus-containing moieties in metal phosphate/phosphonate materials. During the titration, an increasing amount of base solution is added in a stepwise fashion to a suspension of solids, and the equilibrium pH values after every addition interval are recorded. The pH values are then plotted against the total amount of base added, yielding the titration curve.

The main takeaway information from a titration curve is the total ion exchange capacity but also the nature of the acidic sites. The ion exchange capacity is one of the key performance parameters if the metal phosphate/phosphonate materials are used as ion exchangers for separation and purification purposes. However, the nature of the acidic sites can shed light on the crystallinity of the material. Amorphous materials usually show a gradually rising titration curve without clear features, whereas sharp, stepwise inflexion points and clear plateaus are typical for crystalline materials [2]. The plateaus are caused by the fact that, in crystalline materials, certain P—OH groups are identical to each other, resulting in the same dissociation constant.

There are also several drawbacks regarding the potentiometric titration: (i) other organic acidic groups (on the phosphonate ligand) will interfere with the neutralisation process; (ii) certain types of metal phosphate/phosphonate materials start to decompose already at the neutral pH range; and (iii) the structure of the materials has an impact on the titration by different bases, larger titrants (e.g., Cs^+) might not be accessible to the acidic sites. Care must be taken when designing the titration study since the kinetics of certain ion-exchange reactions are extremely slow (i.e., when there is lattice diffusion involved and when the materials are composed of large crystals). Particularly, the effect of carbon dioxide is often neglected when the pH of the system reaches 5 or more. It is worthwhile to monitor the P content in the solution due to the possible detachment of phosphate/phosphonate groups throughout the titration should be performed if the conditions allow. Nevertheless, potentiometric titration provides necessary information regarding the acidity of the material and helps elucidate the nature of the phosphorus-containing ligands in the solid materials.

3.2. Liquid 31P Nuclear Magnetic Resonance Spectroscopy

Accommodating $\frac{1}{2}$ spin nuclei, 31 P atoms are of 100% natural isotopic abundance. The high sensitivity of 31 P NMR makes it a reliable tool for qualitative and quantitative

analyses, comparable to ¹⁹F and ¹H NMR. The chemical shifts between phosphate and phosphonates are separated to a satisfactory level, thereby warranting the identification and quantification of individual molecules [35]. This is particularly useful when analysing a mixed phosphate-phosphonate material or a phosphonate material with more than one type of ligand [36]. During the synthesis of mixed metal phosphate/phosphonate materials, both phosphate and phosphonate are introduced into the precursor. However, due to the differences in reactivity, the organic-to-inorganic phosphorus ratio in the precursor does not translate directly into the obtained solid materials. By re-dissolving the solids into liquid, the amount of different phosphorus ligands could be quantified by liquid ³¹P NMR spectroscopy. Possible oxidation or degradation product of the phosphonate ligands (as a result of harsh synthesis conditions) would also be shown from the same spectrum.

There are two main methods for solubilising solid metal phosphate/phosphonate materials for ^{31}P NMR analysis. One could either dissolve the materials in an HF/D₂O mixture or treat the solid with an excess amount of base (e.g., NaOH in D₂O) and filter away the insoluble hydrated zirconia particles [37]. The main goal is to transfer the phosphorus-containing ligand into a solution phase. Since either acid or base needs to be added to accomplish the dissolution, the protonation state(s) of the phosphorus-containing ligands cannot be elucidated. The quantification analysis of phosphorus species is carried out by routine ¹H-decoupled ³¹P NMR with the internal standard method, with settings that could suppress the nuclear Overhauser effect and long-enough relaxation delay to ensure the complete relaxation of phosphorus atoms [35]. Some organosoluble metal(IV) phosphonate materials can be dispersed in deuterated organic solvents for direct quantification analysis [38,39].

3.3. Solid-State 31P Nuclear Magnetic Resonance Spectroscopy

Liquid-state ³¹P NMR allows the quantification of each kind of phosphorus-containing ligand, while the protonation information was lost owing to the acid/base pre-treatment. However, as stated in Section 3.1, the protonation state of a phosphorus-containing ligand gives valuable information regarding the properties of the materials and the structural linkage between the metal(IV) centre and the ligand. For highly crystalline materials, the protonation states of the ligands could be determined via crystallography methods, ideally by neutron diffraction. Nevertheless, the determination of hydrogen position comes with relatively large uncertainties because of the extremely small hydrogen nucleus.

For metal(IV) phosphate or phosphonate materials with only one type of ligand, a complete picture of the protonation states of the ligand can usually be acquired using solidstate ³¹P Magic Angle Spinning (MAS) NMR. For mixed ligand materials, the differences between the intrinsic isotropic chemical shifts of the ligands determine whether or not their signal separation might be possible. Crystallinity affects the full width at half-maximum (FWHM) of the resonance peaks, thus it is usually easier to resolve the protonation states of crystalline materials. Note that for layered materials, the phosphate or phosphonate groups on the exterior surfaces might give different resonance peaks due to the slightly altered chemical environments [40].

Here, we consider inorganic phosphate materials as an example. The protonation states of inorganic ortho-phosphate groups could be H_2PO_{4-} , HPO_4^{2-} , and PO_4^{3-} . A decent separation exists between the isotropic chemical shifts of the three protonation states. They are at ca. -10, -20 and -30 ppm, correspondingly. In addition, the assignment could be further validated through a $^{1}H^{-31}P$ cross-polarisation (CP) experiment. The CP here is not used for signal enhancement because the natural abundance of 31P is already 100%. The strength of dipolar interaction between ^{31}P and ^{1}H could be probed by CP measurements and therefore signals if there is any H atom(s) bound to the phosphorus. By running ^{31}P MAS NMR with and without high-power ^{1}H decoupling, the ^{31}P resonance signal increases as the number of protons bound to the PO₄ group is increased [41]. Accurate designation and assignment of the resonance peaks therefore are possible in inorganic metal(IV) phosphates [42–45], and mixed tin(IV) phosphate-phosphonate [20]. Organic

ligand degradation is possibly observed, also. For quantification, an extra-long relaxation delay time should be employed, and the spinning rate of the MAS probe needs to be high enough so that the resonance peaks are not overlapping with the spinning side bands. The deconvolution of resonance peaks by mathematical modelling provides certain insights into the quantifiable speciation, and this is especially useful in the case of a poorly crystalline material [11,33,46,47]. However, protonation states cannot always be solved in the case of amorphous materials since both metal(IV) coordination and protonation states affect the electron cloud distribution around the P atoms, and subsequently affect the ³¹P chemical shifts [48]. More complex information could be acquired by performing certain 2D NMR measurements [34].

3.4. CHN Elemental Analysis

In many cases, phosphorous is used as an anchor for different organic moieties when synthesising hybrids based on an M(IV) oxide backbone. A CHN elemental analyser is most commonly used in organic chemistry for compositional determinations. A small amount of samples (a few mg) are oxidised under an oxygen atmosphere, and the produced CO_2 , H_2O , and N_2 are quantified after a chromatographic gas separation. Such a technique is useful when organic phosphonate is involved in the materials. The analysis condition should differ from the common approach since the presence of P would interfere with the mineralisation of organic materials, forming glassy $P_2O_5 \times H_2O_y$ C materials. Some metal oxides (e.g., CeO₂, V₂O₅) should be added to the mixture to catalyse the oxidation process [49]. The elemental analysis could be approached by both CHN analysis and WD X-ray analysis for cross-validation. The quantification of phosphonate groups should not be based entirely on the carbon content since partial degradation can occur during the synthesis process.

4. Crystalline and Absorbed Water Content

The amount of crystalline and absorbed water is not a crucial parameter in determining the properties of the metal(IV) phosphate/phosphonate materials. However, the content of water is highly changeable with regard to drying approaches, drying temperature, storage conditions, and so on. Without proper handling and measuring of the water content, the overall compositional calculation might be erroneous.

The measurement of water content is usually conducted by thermogravimetric (TG) methods. The weight profile, thermal history, as well as evolved gasses are monitored (if possible) when a sample is heated under a dynamic condition. The crystalline and absorbed water usually evaporates completely before 100–200 °C, and this could be evidenced by a weight loss and endothermic stage. For crystalline materials, the loss of crystalline water usually results in a clear and stable weight-loss step [46,50], but the same is not true for amorphous materials [47]. In the literature, the water content for amorphous materials is usually "decided" by assuming a complete elimination of water before a certain temperature [21]. Ideally, the point should be chosen with the help of the evolved gas analysis (TG-MS). All samples before compositional analysis should be treated in the same manner and kept in a controlled environment (e.g., desiccator, controlled humidity chamber) to prevent the alternation of the absorbed water contents.

5. Concluding Remarks

Growing demands for advanced materials have fuelled the interest in further development of metal(IV) phosphate and phosphonate materials. Whatever the crystallinity, morphology, or functionality, the composition of such materials must be accurately determined and documented. Certain practices in the literature are not carefully utilised and have led to erroneous results and interpretations. This review summarises the most common approaches for the compositional analysis of metal(IV) phosphate and phosphonate materials, with an emphasis on providing a "best-practice" approach. The core composition determination relies on a multitude of modern analytical approaches, which are generally available internationally. There is not a single method that would provide the whole picture of the composition, whereas each technique provides a piece of the puzzle that ultimately leads to a full understanding. Although instrumental availability and conditions vary, the most important compositional characteristics to be understood are metal content, phosphorus content and speciation, and water content. The most straightforward methods for metal and phosphorus content determinations are (i) digestion followed by concentration determination in solution (i.e., ICP-OES), and (ii) WD X-ray methods. For phosphorus speciation, solid-state ³¹P MAS NMR is the ideal choice. For water content determination, thermogravimetry methods with evolved gas analyser are recommended. Through the combination of chemical compositional analysis and structural analysis, the nature of the metal(IV) phosphate and phosphonate materials is unveiled. This is especially beneficial for future reproducibility and repeatability purposes.

Funding: This work was funded by Academy of Finland (316091).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of this study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

- 1. Alberti, G.; Cardini-Galli, P.; Costantino, U.; Torracca, E. Crystalline Insoluble Salts of Polybasic Metals—I Ion-Exchange Properties of Crystalline Titanium Phosphate. J. Inorg. Nucl. Chem. 1967, 29, 571–578. [CrossRef]
- 2. Clearfield, A.; Stynes, J.A. The Preparation of Crystalline Zirconium Phosphate and Some Observations on Its Ion Exchange Behaviour. *J. Inorg. Nucl. Chem.* **1964**, *26*, 117–129. [CrossRef]
- Dines, M.B.; DiGiacomo, P.M. Derivatized Lamellar Phosphates and Phosphonates of M(IV) Ions. *Inorg. Chem.* 1981, 20, 92–97.
 [CrossRef]
- 4. Pica, M.; Donnadio, A.; Casciola, M. From Microcrystalline to Nanosized α-Zirconium Phosphate: Synthetic Approaches and Applications of an Old Material with a Bright Future. *Coord. Chem. Rev.* **2018**, *374*, 218–235. [CrossRef]
- 5. Vivani, R.; Alberti, G.; Costantino, F.; Nocchetti, M. New Advances in Zirconium Phosphate and Phosphonate Chemistry: Structural Archetypes. *Workshop Innov. Appl. Layer. Mater. Catal. Nanotechnol.* **2008**, *107*, 58–70. [CrossRef]
- Xiao, H.; Liu, S. Zirconium Phosphate (ZrP)-Based Functional Materials: Synthesis, Properties and Applications. *Mater. Des.* 2018, 155, 19–35. [CrossRef]
- 7. Pica, M. Zirconium Phosphate Catalysts in the XXI Century: State of the Art from 2010 to Date. Catalysts 2017, 7, 190. [CrossRef]
- 8. Fei, H.; Zhou, X.; Zhou, H.; Shen, Z.; Sun, P.; Yuan, Z.; Chen, T. Facile Template-Free Synthesis of Meso-Macroporous Titanium Phosphate with Hierarchical Pore Structure. *Microporous Mesoporous Mater.* **2007**, *100*, 139–145. [CrossRef]
- Li, X.S.; Courtney, A.R.; Yantasee, W.; Mattigod, S.V.; Fryxell, G.E. Templated Synthesis of Mesoporous Titanium Phosphates for the Sequestration of Radionuclides. *Inorg. Chem. Commun.* 2006, *9*, 293–295. [CrossRef]
- 10. Ma, T.; Yuan, Z. Metal Phosphonate Hybrid Mesostructures: Environmentally Friendly Multifunctional Materials for Clean Energy and Other Applications. *ChemSusChem* **2011**, *4*, 1407–1419. [CrossRef]
- Veliscek-Carolan, J.; Rawal, A.; Luca, V.; Hanley, T.L. Zirconium Phosphonate Sorbents with Tunable Structure and Function. *Microporous Mesoporous Mater.* 2017, 252, 90–104. [CrossRef]
- Ruiz, V.S.; Ribeiro, A.S.; Airoldi, C. A New Elemental Analysis Procedure Based on an ICP OES Technique to Determine Arsenic, Phosphorus and Titanium in Titanium Phenylphosphonate or Titanium Phenylarsonate. *Curr. Anal. Chem.* 2005, 1, 171–175. [CrossRef]
- 13. Chao, T.T.; Sanzolone, R.F. Decomposition Techniques. J. Geochem. Explor. 1992, 44, 65–106. [CrossRef]
- Hu, Z.; Qi, L. 15.5—Sample Digestion Methods. In *Treatise on Geochemistry*, 2nd ed.; Holland, H.D., Turekian, K.K., Eds.; Elsevier: Oxford, UK, 2014; pp. 87–109, ISBN 978-0-08-098300-4.
- 15. Rubatto, D.; Hermann, J. Experimental Zircon/Melt and Zircon/Garnet Trace Element Partitioning and Implications for the Geochronology of Crustal Rocks. *Chem. Geol.* 2007, 241, 38–61. [CrossRef]
- 16. Procop, M.; Röder, A. An Interlaboratory Comparison of Energy Dispersive X-ray Microanalysis (EDX) of Titanium and Zirkonium Nitrides. *Microchim. Acta* **1997**, *125*, 33–39. [CrossRef]
- Mu, W.; Yu, Q.; Zhang, R.; Li, X.; Hu, R.; He, Y.; Wei, H.; Jian, Y.; Yang, Y. Controlled Fabrication of Flower-like α-Zirconium Phosphate for the Efficient Removal of Radioactive Strontium from Acidic Nuclear Wastewater. J. Mater. Chem. A 2017, 5, 24388–24395. [CrossRef]
- Cheng, Y.; Dong (Tony) Wang, X.; Jaenicke, S.; Chuah, G.-K. Mechanochemistry-Based Synthesis of Highly Crystalline γ-Zirconium Phosphate for Selective Ion Exchange. *Inorg. Chem.* 2018, 57, 4370–4378. [CrossRef]

- Gui, D.; Zheng, T.; Xie, J.; Cai, Y.; Wang, Y.; Chen, L.; Diwu, J.; Chai, Z.; Wang, S. Significantly Dense Two-Dimensional Hydrogen-Bond Network in a Layered Zirconium Phosphate Leading to High Proton Conductivities in Both Water-Assisted Low-Temperature and Anhydrous Intermediate-Temperature Regions. *Inorg. Chem.* 2016, 55, 12508–12511. [CrossRef]
- Sheikh, J.A.; Bakhmutov, V.I.; Clearfield, A. Layered Metal (IV) Phosphonate Materials: Solid-state 1H, 13C, 31P NMR Spectra and NMR Relaxation. *Magn. Reson. Chem.* 2018, 56, 276–284. [CrossRef]
- Silbernagel, R.; Martin, C.H.; Clearfield, A. Zirconium(IV) Phosphonate–Phosphates as Efficient Ion-Exchange Materials. *Inorg. Chem.* 2016, 55, 1651–1656. [CrossRef]
- 22. Xiong, L.; Lv, K.; Gu, M.; Yang, C.; Wu, F.; Han, J.; Hu, S. Efficient Capture of Actinides from Strong Acidic Solution by Hafnium Phosphonate Frameworks with Excellent Acid Resistance and Radiolytic Stability. *Chem. Eng. J.* **2019**, 355, 159–169. [CrossRef]
- 23. Greenberg, R.R.; Bode, P.; Fernandes, E.A.D.N. Neutron Activation Analysis: A Primary Method of Measurement. *Spectrochim. Acta Part B At. Spectrosc.* 2011, 66, 193–241. [CrossRef]
- 24. Contreras-Ramirez, A.; Tao, S.; Day, G.S.; Bakhmutov, V.I.; Billinge, S.J.L.; Zhou, H.-C. Zirconium Phosphate: The Pathway from Turbostratic Disorder to Crystallinity. *Inorg. Chem.* **2019**, *58*, 14260–14274. [CrossRef]
- Wildhagen, D.; Krivan, V. Multielement Characterization of High-Purity Titanium for Microelectronics by Neutron Activation Analysis. Anal. Chem. 1995, 67, 2842–2848. [CrossRef]
- 26. Rebagay, T.V.; Ehmann, W.D. Simultaneous Determination of Zirconium and Hafnium in Standard Rocks by Neutron Activation Analysis. J. Radioanal. Chem. 1970, 5, 51–60. [CrossRef]
- 27. Szekely, G. Determination of Traces of Copper in Germanium by Activation Analysis. Anal. Chem. 1954, 26, 1500–1502. [CrossRef]
- Byrne, A. Neutron Activation Analysis of Tin in Biological Materials and Their Ash Using 123 Sn and 125 Sn. J. Radioanal. Nucl. Chem. 1974, 20, 627–637. [CrossRef]
- Fajgelj, A.; Byrne, A. Determination of Lead, Cadmium and Thallium by Neutron Activation Analysis in Environmental Samples. J. Radioanal. Nucl. Chem. 1995, 189, 333–343. [CrossRef]
- Alberti, G.; Marmottini, F.; Vivani, R.; Zappelli, P. Preparation and Characterization of Pillared Zirconium Phosphite-Diphosphonates with Tuneable Inter-Crystal Mesoporosity. J. Porous Mater. 1998, 5, 221–226. [CrossRef]
- 31. Suarez, M.; Garcia, J.R.; Rodriguez, J. The Preparation, Characterisation and Ion Exchange Properties of an Amorphous Titanium Phosphate. *Mater. Chem. Phys.* **1983**, *8*, 451–458. [CrossRef]
- Warwick, C.; Guerreiro, A.; Soares, A. Sensing and Analysis of Soluble Phosphates in Environmental Samples: A Review. *Biosens. Bioelectron.* 2013, 41, 1–11. [CrossRef]
- Zhang, W.; Hietala, S.; Khriachtchev, L.; Hatanpää, T.; Doshi, B.; Koivula, R. Intralanthanide Separation on Layered Titanium (IV) Organophosphate Materials via a Selective Transmetalation Process. ACS Appl. Mater. Interfaces 2018, 10, 22083–22093. [CrossRef]
- Veliscek-Carolan, J.; Rawal, A.; Oldfield, D.T.; Thorogood, G.J.; Bedford, N.M. Nanoporous Zirconium Phosphonate Materials with Enhanced Chemical and Thermal Stability for Sorbent Applications. ACS Appl. Nano Mater. 2020, 3, 3717–3729. [CrossRef]
- Oromí-Farrús, M.; Minguell, J.M.; Oromi, N.; Canela-Garayoa, R. A Reliable Method for Quantification of Phosphonates and Their Impurities by 31P NMR. Anal. Lett. 2013, 46, 1910–1921. [CrossRef]
- Pica, M.; Donnadio, A.; Mariangeloni, G.; Zuccaccia, C.; Casciola, M. A Combined Strategy for the Synthesis of Double Functionalized α-Zirconium Phosphate Organic Derivatives. *New J. Chem.* 2016, 40, 8390–8396. [CrossRef]
- Dines, M.B.; Griffith, P.C. The Mixed-Component Layered Tetravalent Metal Phosphonate System Th (O3PPh) x (O3PC6H4Ph) 2-x. *Inorg. Chem.* 1983, 22, 567–569. [CrossRef]
- Chakraborty, D.; Chandrasekhar, V.; Bhattacharjee, M.; Krätzner, R.; Roesky, H.W.; Noltemeyer, M.; Schmidt, H.-G. Metal Alkoxides as Versatile Precursors for Group 4 Phosphonates: Synthesis and X-Ray Structure of a Novel Organosoluble Zirconium Phosphonate. *Inorg. Chem.* 2000, *39*, 23–26. [CrossRef]
- Chen, T.; Ma, X.; Wang, X.; Wang, Q.; Zhou, J.; Tang, Q. Organosoluble Zirconium Phosphonate Nanocomposites and Their Supported Chiral Ruthenium Catalysts: The First Example of Homogenization of Inorganic-Supported Catalyst in Asymmetric Hydrogenation. *Dalton Trans.* 2011, 40, 3325–3335. [CrossRef]
- 40. Mosby, B.M.; Díaz, A.; Bakhmutov, V.; Clearfield, A. Surface Functionalization of Zirconium Phosphate Nanoplatelets for the Design of Polymer Fillers. *ACS Appl. Mater. Interfaces* **2014**, *6*, 585–592. [CrossRef]
- 41. Nakayama, H.; Eguchi, T.; Nakamura, N.; Yamaguchi, S.; Danjyo, M.; Tsuhako, M. Structural Study of Phosphate Groups in Layered Metal Phosphates Byhigh-Resolution Solid-State31P NMR Spectroscopy. J. Mater. Chem. 1997, 7, 1063–1066. [CrossRef]
- 42. Zhang, X.; Shen, J.; Pan, S.; Qian, J.; Pan, B. Metastable Zirconium Phosphate under Nanoconfinement with Superior Adsorption Capability for Water Treatment. *Adv. Funct. Mater.* **2020**, *30*, 1909014. [CrossRef]
- 43. Cheng, Y.; Wang, X.; Jaenicke, S.; Chuah, G.-K. Minimalistic Liquid-Assisted Route to Highly Crystalline A-Zirconium Phosphate. *ChemSusChem* 2017, *10*, 3235–3242. [CrossRef]
- Bakhmutov, V.I.; Clearfield, A. 31P, 1H NMR Relaxation and Molecular Mobility in Layered α-Zirconium Phosphate: Variable-Temperature NMR Experiments. J. Phys. Chem. C 2017, 121, 550–555. [CrossRef]
- 45. Trublet, M.; Rusanova, D.; Antzutkin, O.N. Revisiting Syntheses of Ti (Iv)/H₂PO₄–HPO₄ Functional Ion-Exchangers, Properties and Features. *New J. Chem.* **2018**, *42*, 838–845. [CrossRef]
- Zhang, W.; Koivula, R.; Wiikinkoski, E.; Xu, J.; Hietala, S.; Lehto, J.; Harjula, R. Efficient and Selective Recovery of Trace Scandium by Inorganic Titanium Phosphate Ion-Exchangers from Leachates of Waste Bauxite Residue. ACS Sustain. Chem. Eng. 2017, 5, 3103–3114. [CrossRef]

- 47. Bortun, A.I.; Bortun, L.N.; Clearfield, A.; Khainakov, S.A.; Strelko, V.V.; Khryashevskii, V.N.; Kvashenko, A.P.; Voitko, I.I. Synthesis and Characterization of Ion Exchange Properties of Spherically Granulated Titanium Phosphate. *Solvent Extr. Ion Exch.* **1997**, *15*, 515–532. [CrossRef]
- 48. Ironside, M.S.; Duer, M.J.; Reid, D.G.; Byard, S. Bisphosphonate Protonation States, Conformations, and Dynamics on Bone Mineral Probed by Solid-State NMR without Isotope Enrichment. *Eur. J. Pharm. Biopharm.* **2010**, *76*, 120–126. [CrossRef]
- Fadeeva, V.P.; Tikhova, V.D.; Nikulicheva, O.N. Elemental Analysis of Organic Compounds with the Use of Automated CHNS Analyzers. J. Anal. Chem. 2008, 63, 1094–1106. [CrossRef]
- 50. Clearfield, A.; Blessing, R.H.; Stynes, J.A. New Crystalline Phases of Zirconium Phosphate Possessing Ion-Exchange Properties. J. Inorg. Nucl. Chem. 1968, 30, 2249–2258. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.