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A K-edge P XANES Study of Phosphorus Compounds in Solution

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11 Keywords: Phosphorus K-edge XANES, inorganic and organic phosphates, organophosphorus
12 compounds
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15 16 Abstract

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18 The K-edge X-ray absorption near-edge structure (XANES) spectra of 19 phosphorus-containing
19 compounds have been measured in solution. The energy at maximum intensity of the primary phosphate
20 peak, regardless of chemical species, is 2154.5 ± 0.5 eV. A few of the compounds studied feature XANES
21 spectra which are conceivably characteristic enough to be used as positive identifiers in solution,
22 including *O,O*-diethyldithiophosphate, $(C_2H_5O)_2PS(SH)$, triphenylphosphine oxide, $(C_6H_5)_3PO$, and
23 triphenylphosphite $(C_6H_5O)_3P$. However, most spectra are near-identical or similar enough to another
24 compound to prohibit any useful quantification analysis. The narrow range of absorption edge energy,
25 and all phosphorus compounds studied have an absorption edge at higher energy than elemental
26 phosphorus (red phosphorus). This shows that the electron density of phosphorus in these compounds is
27 lower than in elemental phosphorus, and the conventional use of oxidation numbers cannot be used.
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31 32 Introduction

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34 Sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy has been proven to be
35 very sensitive to the oxidation state with a wide range of absorption edge energies between the oxidation
36 states -II and +VI, spanning ca. 13 eV [1,2]. In general, the energy and intensity of the absorption edge of
37 sulfur compounds increases with increasing oxidation state, and highly symmetric coordination around
38 the sulfur atom, as in the case of the sulfate ion, SO_4^{2-} , further increases the intensity of the absorption
39 edge significantly, a so-called white line; the term white line refers to an intense absorption in the near-
40 edge region, dating back to the use of photographic film when these absorption peaks showed up as a
41 heavily exposed line on the developed film [3]. Furthermore, several kinds of sulfur compounds have
42 unique absorption-edge features making them possible to distinguish from other sulfur compounds. These
43 properties of the X-ray absorption of sulfur compounds made it possible to develop a combined
44 qualitative and quantitative method to accurately determine the relative amounts of sulfur compounds in
45 unknown samples [1].
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50 The objective with the present study was to perform a similar study on phosphorus-containing
51 compounds in solution as only a limited number of such data have been reported, phosphorus oxides and
52 triorganophosphinechalcogenides as pure compounds, primarily in the solid state with data collection in
53 transmission data [4-7]. A vast amount of studies have been performed on solid phosphate minerals to
54 establish the mineral speciation from the phosphorus K-edge XANES spectra using a library of spectra of
55 pure minerals [8,9]. However, this is a challenging task as the absorption edge the position of phosphate
56 compounds hardly varies at all between phosphate minerals, and also due to the fact that the absorption
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intensity is similar between different phosphate minerals. The same difficulty can be said to exist for natural samples studied in soil science and biology, as they also primarily are phosphates [10,11].

Experimental

Chemicals

Adenosine triphosphate (ATP), $C_{10}H_{16}N_5O_3-P_3O_{10}$ (Sigma-Aldrich), di-*n*-butylphosphate, (*n*- C_4H_9O) $_2$ PO(OH) (Sigma-Aldrich), O,O-diethyldithiophosphate (C_2H_5O) $_2$ PS(SH) (Sigma-Aldrich), diphenylphosphate, (C_6H_5O) $_2$ PO(OH) (Sigma-Aldrich), ethylphosphonic acid, $C_2H_5PO(OH)_2$ (Sigma-Aldrich), N-(phosphonomethyl)glycine (a.k.a. glyphosate), $(OH)_2P(O)CH_2NHCH_2COOH$ (Sigma-Aldrich), phosphoric acid, H_3PO_4 (Merck, 97 %), sodium dihydrogenphosphate monohydrate, $NaH_2PO_4 \cdot H_2O$ (Merck), sodium hydrogenphosphate heptahydrate, $Na_2HPO_4 \cdot 7H_2O$ (Merck), sodium phosphate dodecahydrate, $Na_3PO_4 \cdot 12H_2O$ (Merck), tetra-*n*-butylphosphonium bromide, (*n*- C_4H_9) $_4$ PBr (Sigma-Aldrich), tri-*n*-butylphosphine oxide, (*n*- C_4H_9) $_3$ PO (Sigma-Aldrich), triethylphosphate, (C_2H_5O) $_3$ PO (Sigma-Aldrich), triethylphosphite, (C_2H_5O) $_3$ P (Sigma-Aldrich), triphenylphosphate, (C_6H_5O) $_3$ PO (Sigma-Aldrich), triphenylphosphine oxide, (C_6H_5) $_3$ PO (Sigma-Aldrich), triphenylphosphite, (C_6H_5O) $_3$ P (Sigma-Aldrich), tricyclohexylphosphine, (C_6H_{11}) $_3$ P (Sigma-Aldrich), triphenylphosphine, (C_6H_5) $_3$ P (Sigma-Aldrich) were used as purchased. Millipore filtered water was used for the preparation of aqueous solutions, and acetonitrile, CH_3CN (Sigma-Aldrich, analytical grade), for the acetonitrile solutions. For each solution, weighed amounts of the respective phosphorus compound were dissolved in water or acetonitrile to $0.10 \text{ mol} \cdot \text{dm}^{-3}$ concentration.

X-ray absorption data collection

The X-ray absorption data were collected at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand, using the bending magnet beamline 8 [12]. SLRI operated at 1.2 GeV and a ring current of 80-150 mA. The radiation was monochromatized by an InSb[111] double crystal monochromator, $d_{111}=3.7405 \text{ \AA}$ [13]. The data were collected in fluorescence mode using a 13-element Ge array detector (Canberra, Ultra LegE Detector (GUL)). For each sample three scans were collected and averaged. The spectrum of red phosphorus, P_n , was collected after each beam fill and thereafter at regular intervals assigning the first inflection point of the K-edge to 2145.5 eV [14] as an external standard. The solutions were contained sample holders made of poly(methyl methacrylate) with one side made of 5 μm polypropylene X-ray film (Nitto Denko Co., Japan).

Results and discussion

The P K-edge XANES spectra of all phosphorus compounds studied except the calibration reference (red phosphorus) and the organophosphines display a strong white line. The XANES spectra of phosphate compounds (inorganic phosphates, and mono-, di- and trialkyl- or triarylphosphates) have very similar XANES spectra with a strong white line at about 2154.5 eV, and a weaker, broader peak at ca. 2170 eV, Figure 1a & 1b and Table 1. One exception is O,O-diethyldithiophosphate with its white line at 2152.2 eV. This is due to that sulfur is less electron-withdrawing than oxygen thus causing a higher electron density on phosphorus and thus a lower excitation energy, Figure 1b. This strong absorption is due to the dipole-allowed transition $1s \rightarrow 3p$, where the 3p orbital is empty for phosphate compounds with phosphorus in the oxidation state +V [6]. The white line intensity of the inorganic phosphates, and mono-, di- and trialkyl- and triarylphosphates in $0.10 \text{ mol} \cdot \text{dm}^{-3}$ solution do not seem to follow any recognizable trend. However, it should be stressed that the intensity of data collected in fluorescence mode are sensitive to total absorption due to self-absorption, which is one of the reasons to collect data in reasonably dilute solutions. These results clearly show that it is *very* difficult, or even impossible, to qualitatively distinguish phosphate compounds in solution from one another with P K-edge XANES spectroscopy.

Table 1. Energy of absorption maxima of phosphorus K-edge XANES spectra of phosphorus compounds in 0.10 mol·dm⁻³ aqueous or acetonitrile solution after normalization of the absorbance to 1.00 at 2200 eV. The spectra are collected in fluorescence mode. Maximum intensity of the peaks are given within parenthesis after the absorption maximum value for identification of the most intense peak; sh = shoulder. Values in italics are those previously reported and the energy shift from our values are given in curly brackets.

	<i>XANES region peaks</i>	<i>XANES region post-edge peaks</i>	<i>Structure-related peaks</i>
Phosphate compounds and ions			
H ₃ PO ₄ (aq), pH = 1.0	2154.7 (4.8)		2170.1 (1.8)
H ₂ PO ₄ ⁻ (aq), pH = 4.7	2154.9 (5.7)		2170.9 (1.7)
HPO ₄ ²⁻ (aq), pH = 9.8	2154.5 (6.8)		2169.8 (1.9)
PO ₄ ³⁻ (aq), pH = 13.0	2154.6 (4.8)		2169.8 (1.7)
ATP (aq)	2154.7 (5.3)		2172.8 (1.7)
(n-C ₂ H ₅ O) ₂ PS(SH) (an)	2152.2 (4.4)		2161.4 (1.7)
(n-C ₄ H ₉ O) ₂ PO(OH) (an)	2154.4 (5.8)		2168.5 (2.0)
(C ₆ H ₅ O) ₂ PO(OH) (an)	2154.8 (5.0)		2170.3 (1.7)
(C ₂ H ₅ O) ₃ PO (an)	2154.2 (6.0)		2168.9 (2.0)
(C ₆ H ₅ O) ₃ PO (an)	2154.4 (6.1)		2169.5 (2.0)
(C ₆ H ₅ O) ₃ PO (s) ^{a,b}	<i>2152.1</i> {-2.3}		

Phosphites and phosphonates			
(C ₆ H ₅ O) ₃ P (an)	2150.5 (4.0)		2166.5 (1.6)
	2153.6 (2.5)		
(C ₆ H ₅ O) ₃ P (s) ^{a,b}	<i>2148.0</i> {-2.5}		
	<i>2149.7</i> {-3.9}		
(C ₂ H ₅ O) ₃ P (an)	2149.4 (1.9)	2160.8 (2.0)	2168.0 (1.6)
	2152.0 (4.5)		
C ₂ H ₅ PO(OH) ₂ (an)	2153.5 (4.4)		2168.2 (1.7)
glyphosate (aq)	2153.7 (3.8)	2159.6 sh (1.28)	2168.9 (1.5)

Phosphine oxides			
(C ₄ H ₉) ₃ PO (an)	2151.1 (4.3)	2164.1 (1.7)	
(C ₂ H ₅) ₃ PO (l) ^a	<i>2148.8</i> {-2.5}		
(C ₆ H ₅) ₃ PO (an)	2149.3 (1.9)	2160.5 (2.0)	2168.3 (1.6)
	2152.0 (4.5)		
(C ₆ H ₅) ₃ PO (an)	<i>2147.3</i> {-2.0}		
	<i>2150.0</i> {-2.0}		

Organophosphines and the phosphonium ion			
(C ₆ H ₁₁) ₃ P (an)	2148.5 (1.3)	2165.5 (1.3)	
	2151.3 (2.4)		
	2155.4 (1.6)		
(C ₂ H ₅) ₃ P (l) ^a	<i>2145.8</i> {-2.3}		
	<i>2148.0</i> {-3.3}		
(C ₆ H ₅) ₃ P (an)	2147.9 sh (1.7)	2157.0 (1.6)	
	2149.6 (2.2)		
	2152.6 (1.7)		
(C ₆ H ₅) ₃ P (s) ^a	<i>2145.4</i> {-2.5}		
	<i>2147.2</i> {-0.8}		
(C ₄ H ₉) ₄ P ⁺ (an)	2150.6 (3.6)	2158.7 (1.5)	2164.1 sh (1.4)

Elemental phosphorus (external reference)			
Pn, red phosphorus (s)	2147.15 (1.0)		
	2153.0 sh (1.0)		
	2155.10 (1.2)		

^a Ref. 6. ^b Ref. 7.

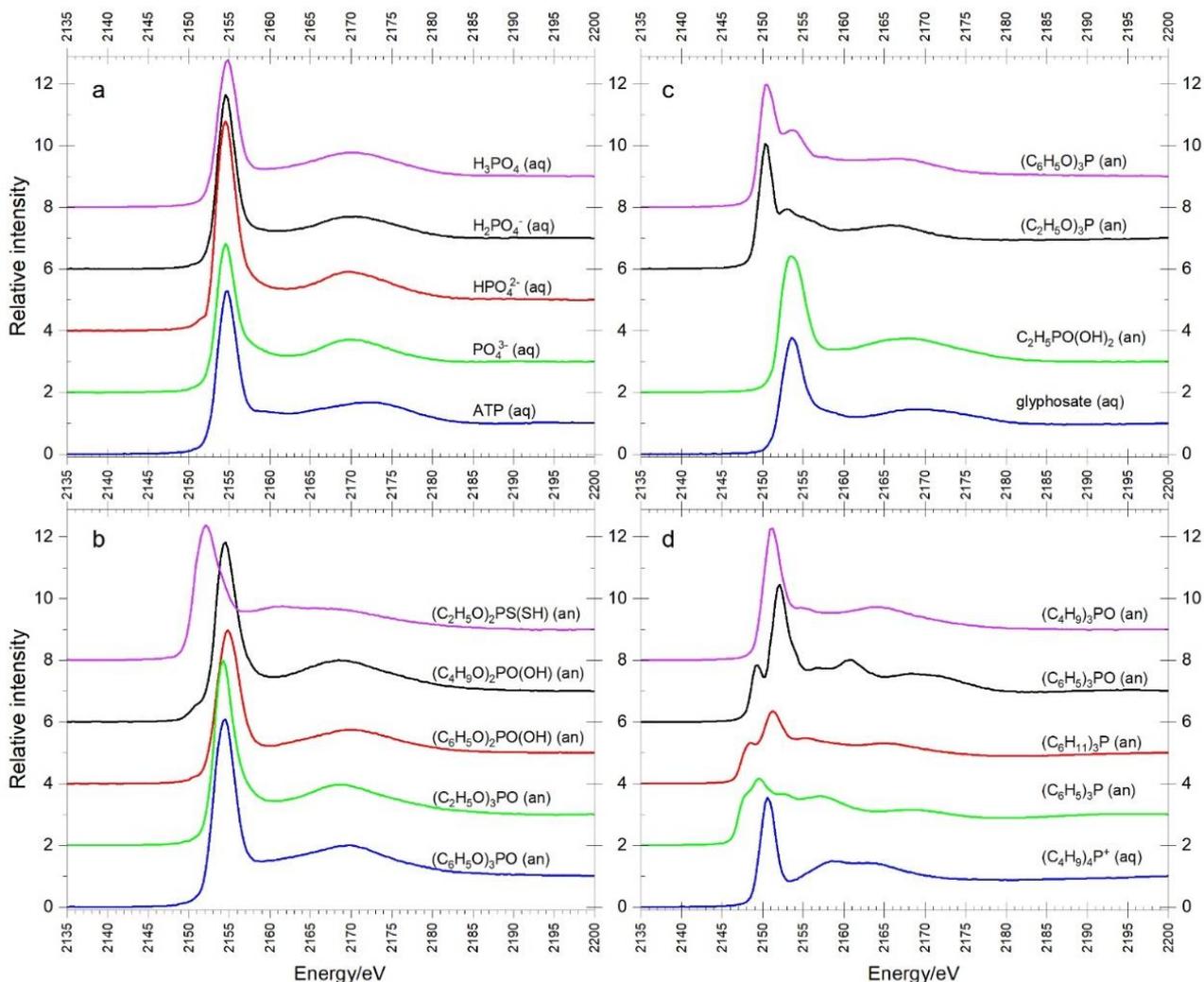


Figure 1. P K-edge XANES spectra of $0.1 \text{ mol} \cdot \text{dm}^{-3}$ aqueous (aq) or acetonitrile (an) solutions of a) adenosine triphosphate (ATP (aq); blue, no offset), sodium phosphate (PO_4^{3-} (aq); green, offset = 2), sodium hydrogenphosphate (HPO_4^{2-} (aq); red, offset = 4), sodium dihydrogenphosphate (H_2PO_4^- (aq); black, offset = 6), phosphoric acid (H_3PO_4 (aq); purple, offset = 8); b) *N*-(phosphonomethyl)glycine, (glyposate (aq), blue, no offset), ethylphosphonic acid ($\text{C}_2\text{H}_5\text{PO}(\text{OH})_2$ (an); green, offset = 2), triethylphosphite ($(\text{C}_2\text{H}_5\text{O})_3\text{P}$ (an), black, offset = 6), triphenylphosphite ($(\text{C}_6\text{H}_5\text{O})_3\text{P}$ (an), purple, offset = 8); c) triphenylphosphate ($(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ (an), blue, no offset), triethylphosphate ($(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ (an), green, offset = 2), diphenylphosphate ($(\text{C}_6\text{H}_5\text{O})_2\text{PO}(\text{OH})$ (an), red, offset = 4), di-*n*-butylphosphate ($(n\text{-C}_4\text{H}_9\text{O})_2\text{PO}(\text{OH})$ (an), black, offset = 6), *O,O*-diethyldithiophosphate ($(\text{C}_2\text{H}_5\text{O})_2\text{PS}(\text{SH})$ (an), purple, offset = 8); d) tetra-*n*-butylphosphonium bromide, $(\text{C}_4\text{H}_9)_4\text{P}^+$ (an), blue, no offset), triphenylphosphine ($(\text{C}_6\text{H}_5)_3\text{P}$ (an), green, offset = 2), tricyclohexylphosphine ($(\text{C}_6\text{H}_{11})_3\text{P}$ (an), red, offset = 4), triphenylphosphine oxide ($(\text{C}_6\text{H}_5)_3\text{PO}$ (an), black, offset = 6), tri-*n*-butylphosphine oxide ($(n\text{-C}_4\text{H}_9)_3\text{PO}$ (an), purple, offset = 8).

Ethylphosphonic acid and *N*-(phosphonomethyl)glycine (glyposate) have their white line-peak ca. 1.0 eV lower than the phosphates, Figure 1c and Table 1. On other hand, the XANES spectra of triphenyl- and triethylphosphite have two well-defined absorption bands at 2150.5 and 2153.6 eV, and 2149.4 and 2152.0 eV, respectively, Figure 1c. The reason for the presence of two strong bands is the lower symmetry around the phosphorus atom with three

1 P-O bonds and a lone electron-pair. Tri-*n*-butyl- and triphenylphosphine oxide have
2 significantly different P K-edge XANES spectra with white lines at 2152.0 and 2151.1 eV,
3 respectively, Figure 1d and Table 1. Triphenylphosphine oxide has also a relative intense pre-
4 peak at 2149.3 eV. Tricyclohexyl- and triphenyl- phosphine are three-coordinate with three P-
5 C bonds and a lone electron-pair and two significant transitions are observed on the
6 absorption edge. Conversely, as the tetra-*n*-butylphosphonium ion is four-coordinate with a
7 symmetric tetrahedral configuration around phosphorus, it has only one strong white line, at
8 2150.6 eV, Figure 1d.
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10 Solid red phosphorus, used as energy calibration compound, display several transitions in
11 the edge region with the strongest ones at 2147.15, 2153.0 and 2155.1 eV in the absorption
12 edge region. The previously reported data on pure triorganophosphinechalcogenides [4-7] are
13 in good agreement with data reported in this study, Table 1, even though those data were
14 collected as pure compounds. The approximately shift of -2.5 eV in peak position between the
15 data in this study and those previously reported are attributed to the different fixed reference
16 energies for the two calibration substances used, tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) and
17 red phosphorus (P_n), respectively [6].
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22 The energy range for absorption of sulfur compounds is wide, ca. 13 eV between sulfur
23 compounds in oxidation states -II to +VI, and the XANES characteristics for different kind of
24 sulfur compounds are easy to distinguish from each other [1,2]. Furthermore, the absorption
25 energy of the sulfur compounds increases in the order of the oxidation state. This makes it
26 possible to both qualitatively and quantitatively analyze sulfur compound mixtures with S K-
27 edge XANES spectroscopy. Conversely, the studied phosphorus compounds display a very
28 different pattern with an absorption energy range of only ca. 8 eV including elemental red
29 phosphorus, Figure 1 and Table 1. In order to understand the different behavior of sulfur and
30 phosphorus compounds, and especially the more narrow absorption energy range observed for
31 phosphorus compounds, it is necessary to look at these elements from a different perspective
32 than their formal oxidation number. The Allen electronegativity scale, where phosphorus is
33 assigned a value of 2.253, hydrogen 2.300 (fixed reference value), carbon 2.544, sulfur 2.589,
34 and oxygen 3.610 Pauling units, respectively [15-17], shows that carbon attracts electrons
35 more efficiently than phosphorus, while the opposite is found for sulfur albeit ever so slightly.
36 This means that in a P-C bond, phosphorus will get electron deficit and carbon electron
37 excess, and it is not correct to apply a negative oxidation number on phosphorus in e.g. most
38 organophosphine and phosphonium compounds. Of the compounds used in the present study,
39 elemental red phosphorus feature the lowest oxidation number, zero, and the phosphates the
40 highest, +V, as the difference in Allen electronegativity is large between phosphorus and
41 oxygen. For compounds where phosphorus bind both carbon and oxygen it is much more
42 difficult to apply a correct oxidation number, but it is certainly positive. It shall be pointed out
43 that electronegativity is a property of an atom alone, but it is most likely affected by its
44 surroundings and bonding situation. The position of the absorption edge of such a compound
45 can be a guide to a proper estimation of both the electron density and oxidation number of the
46 absorbing atom, here phosphorus. It can be noted that all phosphorus compounds in this study
47 have absorbance energies higher than that of red phosphorus, P_n .
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55 All phosphate compounds display very similar XANES spectra with a strong white line at
56 2154.5 ± 0.5 eV, but there is no systematic trends in the white-line intensity, Figure 1a & 1b
57 and Table 1. This makes it impossible to use P K-edge XANES spectroscopy as a tool to
58 distinguish and analyze unknown phosphate compounds in a solution sample. In solid
59 samples, back-scattering to surrounding metal ions may introduce additional specific features
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1 in the P K-edge XANES spectra. Other phosphorus compounds are easier to distinguish from
2 each other, but the systematic pattern with increasing absorption energy with increasing
3 oxidation state observed for the sulfur compounds is not applicable for phosphorus
4 compounds with P-C bond and/or a lone electron-pair as carbon has a higher Allen
5 electronegativity than phosphorus, *vide supra*.

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8
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16 **Note**

17 The authors declare no competing financial or personal interests.

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Figure(s)

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