Testing for Phosphorus

The three ways to test for phosphorus in water are:

• The orthophosphate test
• The acid hydrolyzable phosphate test
• The total phosphorus test.

Elemental phosphorus never occurs by itself in water, but always as some type of compound. These tests use different techniques to measure the three main types of phosphorus in water:

• Orthophosphate
• Condensed phosphate
• Organic phosphate.

It’s important to note that only orthophosphate can be measured directly. The other forms must be digested in either an acid or an acid plus an oxidant in order to convert them to orthophosphate so they can be measured. These types of phosphorus can be either dissolved or particulate forms so it is critical when discussing results to make sure you know if the sample was filtered first (dissolved) or not (dissolved + particulate), and what type of filter was used.

For example, a paper filter with a pore size of 0.45µm will remove all the particles, but a glass fiber filter with a pore size of 1.5µm will allow some particles through which could show up as phosphorus. Just remember: More documentation is always better than less when it comes to describing the testing procedure you use!

Orthophosphate

Structure

Orthophosphate is one phosphorus atom bonded to four oxygen atoms as shown in Figure 1.

Orthophosphate is also called “phosphate” and “reactive phosphorus” because it is very easy to make it bond with other positive elements and compounds since it has three “extra” electrons that strongly want to bond with protons.

Methods

The two common colorimetric methods of measuring orthophosphate are:

• Ascorbic Acid/“Blue” Method
• Molybdatovanadate/“Yellow” Method.

Both methods combine orthophosphate with molybdate in an acidic environment but differ in how they form the final compound, which creates the blue or yellow color. Be aware that no analytical test is perfect, and some condensed phosphate may be measured with these tests too. Due to the acidic chemistry, some particulate orthophosphate may be detected if the sample was not first filtered to 0.45 micron. To measure all of the particulate orthophosphate it is necessary to use a total phosphorus test which incorporates a rigorous digestion to convert most of the particulate phosphate to dissolved phosphate.

Forms

Orthophosphate can be displayed in two different ways:

• \( \text{PO}_4^{3-} \) spoken as “orthophosphate”
• \( \text{PO}_4^- \text{P} \) spoken as “orthophosphate as phosphorus.”

The difference between the two is very important. \( \text{PO}_4^{3-} \) results combine both the phosphorus and the oxygen in the compound, whereas \( \text{PO}_4^- \text{P} \) only considers the phosphorus in the compound. Think of it this way: if you were “farming” bacteria, and they only ate phosphorus, you would want to know exactly how much edible phosphorus is in your feed. You wouldn’t care how much oxygen is bound with the phosphorus because the bacteria don’t care either. You would display your results as \( \text{PO}_4^- \text{P} \). If you were...
farming some different bacteria and they ate both the phosphorus and the oxygen too, you would display your results as \( \text{PO}_4^{3-} \).

The nice part is you can convert from \( \text{PO}_4^{3-} \) to \( \text{PO}_4 \) with simple multiplication. Multiply the \( \text{PO}_4^{3-} \) result by 3.06 to display the result as \( \text{PO}_4^{3-} \). For example, 1.0 mg/L \( \text{PO}_4^{3-} \) = 3.06 mg/L \( \text{PO}_4^{3-} \). Why does this work? The answer is simple, and is due to the relative weights of both compounds: \( \text{PO}_4^{3-} \) is 3.06 times “heavier” than \( \text{PO}_4^{3-} \).

If you want to figure out the ratio for yourself, you first need to determine how "heavy" a molecule of orthophosphate is, so off you go to the periodic chart and find the molecular weights of phosphorus and oxygen. Phosphorus weighs 31 atomic units, and oxygen weighs 16. Since there is one phosphorus and four oxygen in the orthophosphate compound, you add the weight of four oxygen to one phosphorus to determine the total weight:

\[
16 \times 4 = 64
\]
\[
64 + 31 = 95
\]

One molecule of orthophosphate weighs 95 atomic units. To determine the multiplication factor required to convert between the two species, you then divide the total weight by the weight of just the phosphorus:

\[
\frac{95}{31} \approx 3.06
\]

In other words, the entire orthophosphate compound is 3.06 times heavier than just the phosphorus by itself.

It’s important to realize that the test itself only measured orthophosphate, so this 3.06 ratio only converts the orthophosphate results between the two species. It does not change the results to total phosphorus—that is an entirely different test requiring a digestion with sulfuric acid and potassium persulfate. It’s easy to be confused by this, but the simple way to know what the results represent is to ask the analyst if he/she performed a digestion first. If the answer is “No,” then you know the results are just orthophosphate and not total phosphorus.

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**The Copper Wire Analogy**

Here is a handy way to think about orthophosphate vs orthophosphate as phosphorus...

Pretend that your electrician friend gives you a large box full of insulated copper wire. You don’t need the wire, but you know you might be able to make some money by bringing it to a scrap yard and selling the copper.

You bring the box of wire down to the scrap yard, and the owner says he’ll pay you $5.00 for each pound of copper. Off to the scales you go, and after dumping the entire box of insulated wire on the scale you see the display showing 10 lbs.

Not a bad way to make $50. But, the owner pushes the wire off the scale; cuts off a five foot long piece, and puts it back on the scale weighing in at 3.06 pounds. He then pulls out a knife and strips the insulation off the five foot long piece of wire, and weighs just the copper core—which weighs exactly 1 lb.

“I’ll give you $16.34 for the whole box,” he says.

"Wait!" you say. "The total weight was 10 lbs! That’s worth $50!"

"I only pay for the copper, not the insulation. For each 3.06 pounds of insulated wire there was only a pound of copper. Ten pounds divided by 3.06 equals 3.27 times $5 a pound is $16.34."

Then you think to yourself, "I get it—I thought of it as ‘wire as wire’ while he thinks of it as ‘wire as copper’. Just like orthophosphate and orthophosphate as phosphorus!"
**Acid Hydrolyzable Phosphate/Condensed Phosphate**

**Structure**
Condensed phosphates are multiple orthophosphate molecules “condensed” together and sharing a covalent bond between adjoining phosphorus (P) and oxygen (O) atoms. This group includes metaphosphate, pyrophosphate, and polyphosphate—which are often used for corrosion control in drinking water distribution systems. Examples of their respective structures are shown in Figure 2.

**Methods**
In order to measure condensed phosphates, it is first necessary to transform them into orthophosphate using a sulfuric acid and heat, digesting the sample at 150°C for 30 minutes. This is also called ‘Acid Hydrolyzable Phosphate’ since the condensed phosphates are hydrolyzed into orthophosphate. After the digestion, either the ascorbic acid or molybdovanadate methods are used to measure the orthophosphate. Some organic phosphate will also be hydrolyzed into orthophosphate so the results are not “pure” condensed phosphate.

Of course, just performing the digestion and colorimetric test will tell you the concentration of both the original orthophosphate and condensed phosphates. If you want just the condensed phosphate concentration then simply run the orthophosphate test on the same sample without a digestion and subtract those results from the first concentration.

**Forms**
Condensed phosphates are displayed just as orthophosphate, since the analytical method changes them into orthophosphate molecules. Therefore, either PO₄³⁻ or PO₄-P may be used to describe the results, as long as the same rules are followed as described for orthophosphate.

**Total Phosphorus/Organic Phosphate**

**Structure**
Organic phosphates are any phosphates contained inside or bonded to an organic compound. In the same sample, total phosphorus concentrations will always be larger than the orthophosphate concentration. A popular form that most people are familiar with is adenosine triphosphate (ATP), which is considered the “molecular unit of currency” of energy transfer between cells inside our body. The structure of organic phosphates is shown in Figure 3. Note that the letter “R” is a typical proxy for any organic, carbon-based molecule.
Summary

Measuring phosphorus in water and discussing the results is easy to do if you accurately communicate how the sample was prepared and which test was performed. Often, we make this much harder than it needs to be by swapping forms or changing units without considering the consequences. The table below summarizes the different phosphorus tests, digestion requirements and reagents so that in a pinch you can ask clarifying questions to make sure everyone is communicating on the same page.

<table>
<thead>
<tr>
<th>Digestion?</th>
<th>Orthophosphate</th>
<th>Acid Hydrolyzable</th>
<th>Total Phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No</td>
<td>Sulfuric Acid + 150°C for 30 minutes</td>
<td>Sulfuric Acid + Potassium Persulfate + 100°C for 60 minutes</td>
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<tr>
<td>Typical Units</td>
<td>PO₄³⁻ or PO₄-P</td>
<td>PO₄³⁻ or PO₄-P</td>
<td>P</td>
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<tr>
<td>Reagents</td>
<td>Ascorbic Acid or Molybdovanadate</td>
<td>Ascorbic Acid or Molybdovanadate</td>
<td>Ascorbic Acid or Molybdovanadate</td>
</tr>
</tbody>
</table>

References:
Methods for Wastewater Characterization in Activated Sludge Modelling (2003), Water Environment Research Foundation, Alexandria, VA