Understanding the Different Phosphorus Tests

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Introduction

In wastewater treatment, phosphorus testing can quickly become confusing. For example, there are three different tests. So, which test was performed? Test results can be displayed in two different forms. So, which form was utilized? Tests can measure both particulate and dissolved phosphorus. So, was the sample filtered?

Knowing which test to run, which units of measurement to choose, and how to express the result can be overwhelming for even the most seasoned chemist. This application note is designed to cut through the noise and confusion by applying simple, easy-to-understand information for the non-chemist about the different forms and analytical methods for phosphorus in water—so that you can choose the right test and communicate the results confidently.

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.

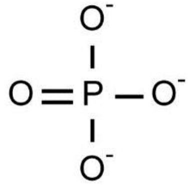


Figure 1: Orthophosphate structure

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
- Molybdovanadate/"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.

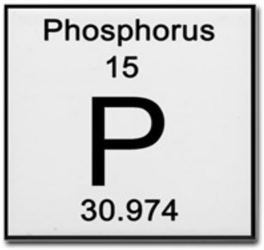
Forms

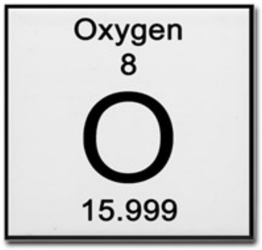
Orthophosphate can be displayed in two different ways:

- PO_4^{3-} spoken as "orthophosphate"
- PO_4-P spoken as "orthophosphate as phosphorus."

The difference between the two is very important. PO_4^{3-} results combine both the phosphorus and the oxygen in the compound, whereas PO_4-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 PO_4-P. If you were





farming some different bacteria and they ate both the phosphorus and the oxygen too, you would display your results as PO_4^{3-}.

The nice part is you can convert from PO_4-P to PO_4^{3-} with simple multiplication. Multiply the PO_4-P result by 3.06 to display the result as PO_4^{3-}. For example, 1.0 mg/L PO_4-P = 3.06 mg/L PO_4^{3-}. Why does this work? The answer is simple, and is due to the relative weights of both compounds: PO_4^{3-} is 3.06 times "heavier" than PO_4-P.

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:

$$16 * 4 = 64$$

$$64 + 31 = 95$$

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:

$$95 / 31 = 3.06$$

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.

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."

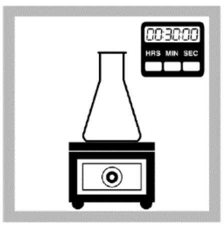
Then you think to yourself, *"I get it—I thought of it as 'wire as wire' while he thinks of it as 'wire as copper'. Just like orthophosphate and orthophosphate as phosphorus!"*

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 PO_4^{3-} or PO_4-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.

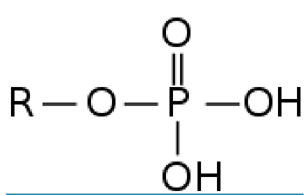


Figure 3: Organic phosphate

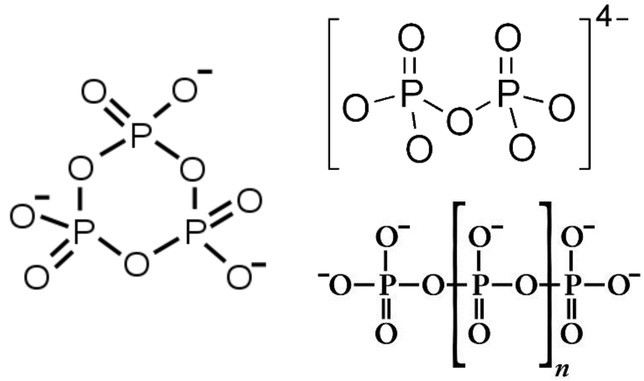


Figure 2: Examples of metaphosphate (left), pyrophosphate (top right), and polyphosphate structure (bottom right)

Methods

Organic phosphates are stubborn compounds that do not like to break down easily. In order to test for them, it is necessary to not only digest the sample first with sulfuric acid and heat, but also add a strong oxidant such as potassium persulfate to break the orthophosphates free from the organic bonds. After digestion, the same ascorbic acid or molybdovanadate methods can be used to measure the concentration. The test just described will convert all of the different forms of phosphate into orthophosphate, which means the results are total phosphorus! If you want to know only the organically bound phosphate concentration, it is necessary to perform the acid hydrolyzable test and subtract those results from the total phosphorus concentration.

Forms

Total phosphorus is typically displayed as a simple "P." For example: 1.0mg/L P means the test that was performed included an acid persulfate digestion at 100°C for 60 minutes followed by the ascorbic acid or molybdovanadate colorimetric test. Since most spectrophotometers and colorimeters have no way of knowing if you digested the sample or not, they will often display the result as PO_4-P or PO_4^{3-}. It is important to make sure that if you want to record your units as "P" that the spectrophotometer is set up to display as PO_4-P. If it is showing as PO_4^{3-} then it is necessary to convert back to PO_4-P by dividing your results by 3.06 as described earlier in the orthophosphate section.

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: Phosphorus tests, digestion requirements and reagents

	Orthophosphate	Acid Hydrolyzable	Total Phosphorus
Digestion?	No	Sulfuric Acid + 150°C for 30 minutes	Sulfuric Acid + Potassium Persulfate + 100°C for 60 minutes
Typical Units	PO_4^{3-} or PO_4-P	PO_4^{3-}- or PO_4-P	P
Reagents	Ascorbic Acid or Molybdovanadate	Ascorbic Acid or Molybdovanadate	Ascorbic Acid or Molybdovanadate

References:

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

Water Analysis Handbook, 8th Edition (2013) Hach, Loveland, CO

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