

Alkyl/Aryl Acid Phosphate Technical Information Safety & Handling Bulletin

Manufacturing

Alkyl/Aryl Acid Phosphates are formed by the reaction of phosphoric anhydride (phosphoric pentoxide or P_2O_5) and an alcohol (ROH). The process involves mixing P_2O_5 with the designated ROH until the reaction is complete. The hydrocarbon group (R = alkyl/aryl group) on the alcohol used will determine which alkyl/aryl acid phosphate is formed.

The final product generally contains approximately equimolar quantities of monoalkyl/aryl and dialkyl/aryl acid phosphates for any given alkyl/aryl radical. However, the production process is typically not controlled such that this ratio is predetermined. Other smaller constituents may include: condensed phosphates; mono/dialkyl/aryl orthophosphates; free alcohol; and phosphoric acid.

Applications

The following list represents suggestions from the literature and other sources as actual or potential uses for alkyl/aryl acid phosphates and their alkali metal or amine salts.

- Curing catalysts and accelerators in resins and coatings
- Esterification catalysts and polymerizing agents
- Emulsifying agents and special detergents
- Pigment dispersion agents
- Paint driers and viscosity reducers
- Foam inhibitors and stabilizers
- Degreasing and wetting agents in metal protection
- Lubricating and antistatic agents in synthetic fibers
- Stabilizers for vinyl plastics and peroxide solutions
- Oil additives
- Mineral and ore separations
- Antioxidants in fats
- Components of rust preventative coating for metals
- Anti-foamer in certain detergent applications

AAPS&H 07/08

Product Description

Amyl Acid Phosphate

Chemical Name:Phosphoric Acid, Monopentyl Ester/Dipentyl Ester Mixture

Common Names:Amyl Acid Phosphate

Chemical Formula: $C_5H_{13}O_4P + C_{10}H_{23}O_4P$

n-Butyl Acid Phosphate

Chemical Name:Phosphoric Acid, Monobutyl Ester/Dibutyl Ester Mixture

Common Names:Butyl Acid Phosphate, Dibutyl Acid Phosphate, Dibutyl Phosphate

Chemical Formula: $C_4H_{11}O_4P + C_8H_{19}O_4P$

Methyl Acid Phosphate

Chemical Name:Phosphoric Acid, Monomethyl Ester/Dimethyl Ester Mixture

Common Names:Methyl Acid Phosphate

Chemical Formula: $CH_5O_4P + C_2H_7O_4P$

Phenyl Acid Phosphate (75% in n-Butanol)

Chemical Name:Phenyl Phosphate Solution

Common Names:Phenyl Hydrogen Phosphate

Chemical Formula: $C_6H_7O_4P + C_{12}H_{11}O_4P$

2-Ethylhexyl Acid Phosphate

Chemical Name:Phosphoric Acid, Mono 2-ethylhexyl ester/Di 2-ethylhexyl ester

Common Names:Octyl Acid Phosphate

Chemical Formula: $C_8H_{19}O_4P + C_{16}H_{35}O_4P$

Dimethyl Acid Phosphate

Chemical Name:Dimethyl Acid Pyrophosphate

Common Names:Pyrophosphoric acid, dimethyl ester

Chemical Formula: $C_2H_8O_7P_2$

Dimethyl Acid Phosphate (52% in Isobutanol)

Chemical Name:Dimethyl Acid Pyrophosphate Solution

Common Names:Pyrophosphoric acid, dimethyl ester

Chemical Formula: $C_2H_8O_7P_2$

Chemical and Physical Properties

Methyl, Ethyl, n-Butyl, Amyl Acid Phosphates

	Methyl	Ethyl	n-Butyl	Amyl
Physical State	-----Clear, Colorless Liquid-----			
Acid Number, mg KOH/g	600	530	430	360
Specific Gravity	1.4	1.26	1.12	1.08
Density, lb/gal	11.7	10.7	9.3	9
PH, 10g/L	1.7	1.7	1.7	1.7
Flash Point, C(F), COC	96 (205)	84 (184)	83 (182)	74 (166)
Color, APHA, max	75	100	100	100
Solubility (g/100 ml)				
Water	>10	>10	1 – 5	<1
Ethyl Alcohol	>10	>10	>10	>10
Acetone	>10	>10	>10	>10
Toluene	<1	<1	>10	>10
Petroleum Naphtha	1 – 5	1 – 5	<1	>10

75% Phenyl in Butanol, 2-Ethylhexyl, Acid Phosphates, 52% and 100% Dimethyl Acid Pyrophosphate

	75% Phenyl	2-Ethylhexyl	100% Dimethyl	52% Dimethyl
Physical State	-----Clear, Colorless Liquid-----			
Acid Number, mg KOH/g	275	280	N/A	360
Specific Gravity	1.13	1.01	1.55	1.04
Density, lb/gal	9.5	8.4	12.9	8.7
PH, 10g/L	1.6	2	1.4	1.4
Flash Point, C(F), COC	56 (132)	81 (177)	>96 (205)	36 (97)
Color, APHA, max	100	250	100	100
Solubility (g/100 ml)				
Water	<1	<1	>10	>10
Ethyl Alcohol	>10	>10	>10	>10
Acetone	>10	>10	1 – 5	1 – 5
Toluene	>10	>10	<1	<1
Petroleum Naphtha	<1	>10	1 – 5	1 – 5

Health Hazards and First Aid

The four areas of concern regarding possible exposure to the Alkyl/Aryl Acid Phosphates are inhalation, eye contact, skin contact and ingestion. The best plan of action involves prevention through safe handling; however, should any type of exposure occur, the discussion below will be most beneficial for the immediate first aid care of the victim. Afterwards, it is still essential to seek prompt professional medical care.

For Inhalation

Exposure to mist, vapor or liquid may cause irritation to the mucous membranes and can produce serious burns of the respiratory tract.

Remove to fresh air. If breathing is difficult, have trained person administer oxygen. If breathing stops, give mouth-to-mouth resuscitation.

For Eyes

Exposure to mist, vapor or liquid may cause irritation to the eyes and can produce severe burns.

Immediately flush eyes with large amounts of running water for at least 15 minutes, forcibly holding lids apart to ensure complete irrigation of all eye and lid tissue. Washing eyes within one minute is essential to achieve maximum effectiveness.

For Skin

Exposure to mist, vapor or liquid may irritate skin and can cause severe burns.

Flush thoroughly with cool water under shower while removing contaminated clothing and shoes. Continue to flush until medical attention arrives. Discard non-rubber shoes. Wash clothing before reuse.

For Ingestion

Ingestion can cause irritation and burning of the mucous membranes of the gastrointestinal tract.

Never give anything by mouth to an unconscious person. If swallowed, do not induce vomiting. With the exception of n-Butyl Acid Phosphate, give large quantities of water (if available, give several glasses of milk). If vomiting occurs spontaneously, keep airway clear and give more water.

For n-Butyl Acid Phosphate, do not give fluids since this material is not water soluble. If spontaneous vomiting is inevitable, prevent aspiration by keeping the victim's head below the knees.

Handling Alkyl/Aryl Acid Phosphates

Safety Equipment

When handling alkyl/aryl acid phosphates, insure good general room ventilation and local exhaust at points of emission. Avoid breathing any vapors which may cause irritation of body tissues. A NIOSH/MSHA approved respirator should be used as a precautionary measure where airborne contaminants may occur. For a more complete discussion of these effects, refer to the health hazards section.

For splash protection wear: impervious clothing; hard hat; rubber boots; chemical splash goggles and face shield; chemical resistant gloves (e.g., neoprene). It is recommended that an eye wash and safety shower be installed less than 100 feet and 10 seconds from the handling area.

Reactivity

Alkyl/Aryl acid phosphates are stable under normal conditions. Avoid exposure to heat or most metals or plastics, especially at elevated temperatures. These phosphates react with alkalis, liberating heat. They also react with aluminum, zinc and other metals, liberating flammable hydrogen gas. Thermal degradation occurs above 124°C (255°F), producing oxides of phosphorus.

Fire Fighting

In the case of fire, use dry chemical, halon, foam, carbon dioxide or water spray. A fire containing these acid phosphates will liberate toxic gases and form oxides of phosphorus upon burning.

In fire conditions, wear NIOSH/MSHA approved positive pressure self-contained breathing apparatus (SCBA) and wear full protective clothing.

Unloading and Storage

Since IsleChem, LLC ships these products only in drum quantities, standard drum unloading procedures should be followed.

The alkyl/aryl acid phosphates should be stored in a cool, dry place that is away from heat and separate from alkalis, aluminum, zinc and other metals. Protect from atmospheric moisture.

Storage area for drummed material should have adequate drainage. Do not reuse containers, since corrosive product residues may remain. Storage tanks should be vented and diked.

Materials of Construction

Only limited corrosion data is available. Generally speaking, materials which are known to be resistant to strong acids should be suitable for use with alkyl/aryl acid phosphates.

The liquid products can be handled in glass-lined steel. The recommended material of construction for all of IsleChem's acid phosphates is 316 stainless steel.

Certain plastics such as polyethylene, saran and Tygon[®] compounds are satisfactory at room temperatures. Some plastics may impart color on long exposure. An experienced materials engineer should be consulted to ensure state-of-the-art compatibility.

Release or Spill Response

Contain spills to prevent discharges to water sources or sewer systems. Wear protective equipment and follow all recommended safety precautions.

Soak up small spills with sand, earth or other absorbent material. Scoop up and place in clean, dry, marked and lined steel container for disposal. Neutralize with soda ash. Flush away residue with large quantities of water applied to entire spill area. Pump large spills into marked containers for proper disposal or reclamation.

Waste Disposal

Do not reuse drums since corrosive product residues may remain in containers. Product should be completely removed from any container. Material that cannot be used or chemically reprocessed should be disposed of in a manner meeting government regulations.

Incinerate in equipment designed to handle oxides of phosphorus as combustion products, or submit to an approved chemical disposal service. All Federal, state and local regulations must be observed.

Incinerate in equipment designed to burn this corrosive and flammable material or send to a waste disposal firm.

Spill Reporting

Report any release of IsleChem's Alkyl/Aryl Acid Phosphates if it could cause harm to people or the environment, or if the State requires a more stringent reporting threshold. It is best to report a spill if there is any uncertainty.

Report to each of the following:

National Response Center 800-424-8802 (24 hours)

Appropriate State Agency

Local Agencies

Releases **during transportation** that require **emergency response** should be reported to:
CHEMTREC 800-424-9300 (24 hours)

IsleChem's 24 hour emergency contact number:
800-424-9300 or 716-773-8100 (8:00 a.m. to 5:00 p.m.)

® Tygon is a registered trademark of Norton Performance Plastics Corp.

Method: IC AAP-1**10/04/07****Rev No. 1****IsleChem, LLC****Analytical Sciences Laboratories****Methods of Analysis – Alkyl and Aryl Acid Phosphates****The Determination of APHA Color****Principle:**

The sample color is visually compared to APHA standards using a Color Disc and an APHA color is assigned.

Apparatus:

1. Orbico-Hellige Aqua Tester
2. Color Disc. No. 611-10 (0-70 APHA Platinum-Cobalt Color Units)
3. 200mm Nessler Tubes No. 611-T
4. Plunger (cap) No. 611-PL

Procedure:

1. Fill one tube to the 50ml mark with sample. Fill a second tube to the 50ml mark with de-ionized water. Place a plunger on each making sure the cap is below the level of the liquid.
2. Place the tube containing the de-ionized water on the left side of the Orbico–Hellige Aqua Tester. Place the tube containing the sample on the right side.
3. Turn on the lamp switch.
4. Rotate the color wheel until the color best matches the sample. Record the APHA color. If the sample color is between two standard colors, record the higher APHA color number.

IsleChem, LLC

Analytical Sciences Laboratories

Methods of Analysis – Alkyl and Aryl Acid Phosphates

The Determination of Specific Gravity

Principle:

An aliquot of sample is brought to 25 deg C in a hydrometer cylinder and the specific gravity is determined using standard ASTM hydrometers.

Apparatus:

1. 250 ml hydrometer cylinders (Fisher cat. # 08-530K)
2. ASTM hydrometers, ranges specified in the procedure section table
3. ASTM thermometer (ASTM# 90C or equivalent)

Procedure:

1. Pour approximately 200ml sample into a 250ml hydrometer cylinder. Adjust the sample temperature to 25deg C \pm 1 deg C.
2. Place a hydrometer of the appropriate range (see table below) in the hydrometer cylinder. Be sure the hydrometer floats freely in the sample and does not rest on the sides of the hydrometer cylinder. Read and record the specific gravity from the graduations on the hydrometer. If the sample meniscus is above or below the calibrated range of the hydrometer, try a different hydrometer until a proper range is found.

AAP Specific Gravity Ranges

AAP	Specific Gravity Range	ASTM Hydrometer #
MAP	1.400-1.430	133H
BAP	1.120-1.125	127H
Amyl	1.050-1.100	126H
DOAP	0.985-1.025	108H, 111H
DMAP	1.520-1.580	135H
DMAP in i-BuOH	1.020-1.070	125H, 126H
MIBCAP	1.000-1.150	125H, 126H, 127H
EAP	1.280-1.300	130H
EHAP	0.990-1.010	108H, 111H
PAP in n-BuOH	1.130-1.160	127H, 128H

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Methods of Analysis – Alkyl and Aryl Acid PhosphatesThe Determination of Acid Number**Principle:**

A solution of the sample in a mixture of methyl ethyl ketone (MEK), isopropanol (IPA) and water is titrated with standard sodium hydroxide to the cresol red endpoint. The Acid Number is calculated from the total alkali consumed.

Apparatus:

1. Balance, capable of weighing to 0.0001 g
2. Burette, Class A, 50 ml, with Teflon Stopcock
3. Flasks, Erlenmeyer, wide mouth, 250 ml
6. Assorted routine laboratory glassware.

Reagents:

1. NaOH, 0.1 N, Freshly standardized
2. Cresol Red Indicator, 0.04%. Available already prepared from Fisher Scientific as Cat No LC13520-7. Or dissolve 0.1 g of o-cresolsulphonephthalein in 26.2 ml of 0.01 N NaOH and dilute to 250 ml with DI water.
3. Methyl ethyl ketone (MEK), acid and base free, Fisher Certified ACS, Cat. No. M209-4 or equivalent.
4. Isopropanol, acid and base free, Fisher Certified ACS, Cat. No. A416-4 or equivalent.
5. DI water, CO₂ Free-2-

Procedure: Determination of Sample

Weigh an appropriate amount of sample to be analyzed (see Table 1) into a 250 ml wide mouth Erlenmeyer flask which contains a magnetic stirring bar. Dissolve the sample in 50 ml of MEK (warming may be necessary in the case of stearyl acid phosphate.) Add 50 ml IPA and 30 ml deionized water and immediately titrate with standard 0.1 N NaOH from yellow to a bright purple endpoint. (The solution will go from yellow through a faded purple cast as the endpoint is approached.) (See Note 1)

Call the volume of NaOH consumed Vol_{smp}

Procedure: Determination of Blank**1. Solvent Blank:**

Prepare a blank comprised of 50 ml MEK, 50 ml of IPA and 30 ml deionized water. Titrate to the same color as was used for the sample

Call the volume of NaOH consumed Vol_{blk}

Calculations:

$$\text{Acid Number (mg KOH/g)} = \{(\text{Vol}_{\text{smpl}} - \text{Vol}_{\text{blk}})(\text{N NaOH})(56.109 \text{ mg KOH/meq})\} / \text{g sample}$$

Notes:

1. In a totally aqueous matrix, Congo Red indicator would be expected to turn from yellow to red. However, in the solvent mixture employed for this test, the indicator turns purple rather than red.

TABLE 1**Sample Weights (g)**

Sample Type	Approx. Sample Size
methyl	0.13
Ethyl	0.15
n-butyl	0.15
DMAP	0.15
Amyl	0.20
2-EHAP	0.25
DOAP	0.25
Phenyl	0.23
MIBCAP	0.25

Method: IC AAP-4

10/04/07

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Methods of Analysis – Alkyl and Aryl Acid Phosphates

The Determination of Mono and Dialkyl (or Aryl) Phosphate, Free Phosphoric Acid and Acid Number

Principle:

A solution of the sample in a mixture of methyl ethyl ketone (MEK), isopropanol (IPA) and water is titrated potentiometrically with standard carbonate free sodium hydroxide through two well defined endpoints. The titration to the first inflection is equivalent to all of the diester, one half of the mono ester and one third of the free phosphoric acid. The titration to the second endpoint represents the neutralization of the remaining half of the mono ester plus an additional third of the free phosphoric acid. At the second endpoint, addition of an excess of calcium chloride precipitates calcium salts of all the phosphates and liberates an equivalent of strong acid per mole of free phosphoric acid. The Acid Number is calculated from the total acid consumed to the second endpoint.

Apparatus:

1. Balance, capable of weighing to 0.0001 g
2. Automatic Titrator, with 20 ml burette. Metrohm E536 or equivalent.
3. pH electrode half cell, glass. Beckmann 39322 or equivalent
4. Calomel reference electrode half cell, reverse sleeve type. Fisher 13-62-

61 or equivalent. The inner filling solution of this electrode is replaced with methanol saturated with KCl.

5. Beakers, 300 ml tall form.
6. Assorted routine laboratory glassware.

Reagents:

1. NaOH, 0.1 N, Freshly standardized and carbonate free
2. HCl, about 0.1 N (for pH adjustment)
3. Methyl ethyl ketone (MEK), acid and base free, Fisher Certified ACS, Cat. No. M209-4 or equivalent.
4. Isopropanol, acid and base free, Fisher Certified ACS, Cat. No. A416-4 or equivalent.
5. Calcium chloride, 10% (w/v), aqueous

Procedure: Determination of Sample

Weigh an appropriate amount of sample to be analyzed (see Table 1) into a 300 ml tall form beaker which contains a magnetic stirring bar. Dissolve the sample in 50 ml of MEK (warming may be necessary in the case of stearyl acid phosphate.) Add 50 ml IPA and 30 ml deionized water and immediately titrate with standard 0.1 N NaOH through the second inflection. Adjust the pH of the titrated solution back to the pH of the endpoint of the second inflection by adding 0.1 N HCl dropwise. Add 15 ml of 10% aqueous CaCl₂ solution and allow the solution to stir about 2 minutes. Continue the titration at a slow rate through the final inflection.

Procedure: Determination of Blanks

1. Solvent Blank:

Prepare a blank comprised of 50 ml MEK, 50 ml of IPA and 30 ml deionized water. Titrate at a very slow rate through one inflection.

Call the volume of NaOH consumed Blk_{sol}

2. CaCl₂ Blank:

Prepare a blank as per above and add 15 ml of 10% CaCl₂ solution. Titrate very slowly through one inflection.

Call the volume of NaOH consumed $\text{Blk}_{\text{CaCl}_2}$

Calculations:

Let V_1 = ml of NaOH consumed to the first endpoint

Let V_2 = ml of NaOH consumed **between** the first and second endpoint.

Correct the volume V_2 for the solvent blank by subtracting Blk_{sol} from the sample titration

$$V_{2C} = V_2 - \text{Blk}_{\text{sol}}$$

Let V_3 = ml of NaOH consumed in reaching the third endpoint after the addition of the calcium chloride.

Correct the volume V_3 for the contribution of any CaCl₂ Blank

$$V_{3C} = V_3 - (\text{Blk}_{\text{CaCl}_2} - \text{Blk}_{\text{sol}})$$

$$\% \text{ Monoalkyl (or aryl) phosphate (RH}_2\text{PO}_4) * = \frac{(V_{2C} - V_{3C})(N \text{ NaOH})(\text{MW RH}_2\text{PO}_4)(10^{-3} \text{ g/mg})(10^2 \%)}{\text{g sample}}$$

$$\% \text{ Dialkyl (or aryl) phosphate (R}_2\text{HPO}_4) * = \frac{(V_1 - V_{2C})(N \text{ NaOH})(\text{MW R}_2\text{HPO}_4)(10^{-3} \text{ g/mg})(10^2 \%)}{\text{g sample}}$$

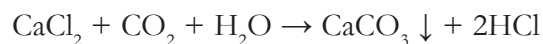
$$\% \text{ Free Phosphoric Acid} = \frac{(V_{3C})(N \text{ NaOH})(97.997 \text{ mg/meq})(10^{-3} \text{ g/mg})(10^2 \%)}{\text{g sample}}$$

* See Table 2 for molecular weights.

$$\text{Acid Number (mg KOH/g)} = \frac{(V_1 + V_{2C})(N \text{ NaOH})(56.111 \text{ mg KOH/meq})}{\text{g sample}}$$

Notes:

Any carbonate present in the NaOH titrant will dramatically interfere with the titration of the free phosphoric acid. Since the latter is used in the calculations of the mono- and di- amounts, they too are affected. It is hypothesized that the interference occurs when the CaCl₂ is added in the free acid step of the titration via the following:



The HCl thus produced will be titrated along with the third proton of the free phosphoric acid.

It is highly recommended that the titrant supply be protected from CO₂ adsorption by a nitrogen purge or an Ascarite® Scrubber. Suspect titrant supplies should be discarded.

TABLE 1
Sample Weights (g)

Sample Type	Approx. Sample Size
methyl	0.13
Ethyl	0.15
n-Butyl	0.15
DMAP	0.15
Amyl	0.20
2-EHAP	0.25
DOAP	0.25
Phenyl	0.23
MIBCAP	0.25

Table 2
Molecular Weights

Sample Type	MW RH_2PO_4	MW R_2HPO_4
methyl	112	126
Ethyl	126	154
n-Butyl	154	210
DMAP	---	190
Amyl	168	238
2-EHAP	211	322
DOAP	222	348
Phenyl	174	250
MIBCAP	182	266

**The Determination of Mono and Dialkyl (or Aryl)
Phosphate and Phosphoric Acid by Titration**

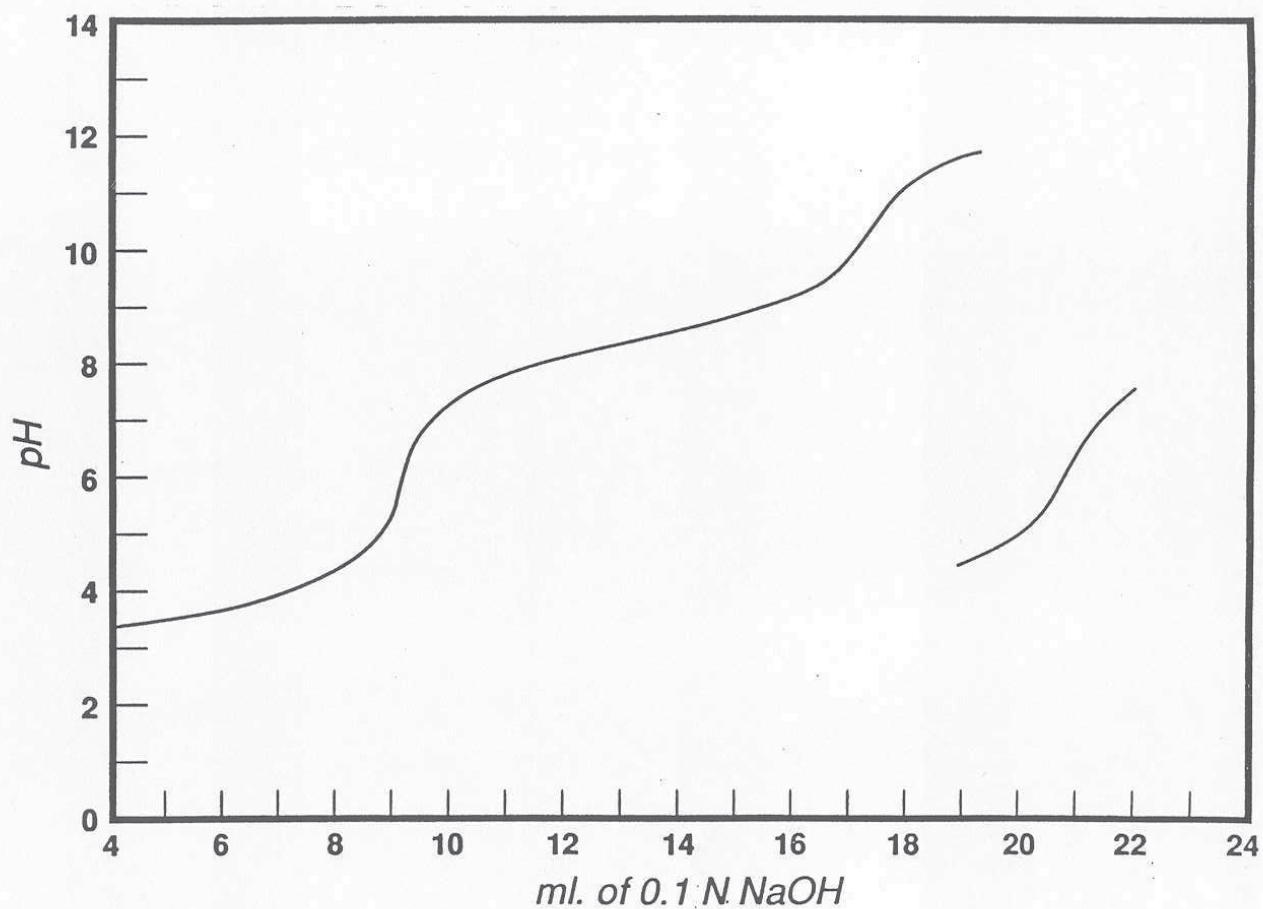


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Table 2**Molecular Weights**

Sample Type	MW RH_2PO_4	MW R_2HPO_4
methyl	112	126
Ethyl	126	154
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DMAP	---	190
Amyl	168	238
2-EHAP	211	322
DOAP	222	348
Phenyl	174	250
MIBCAP	182	266

Method: IC AAP-5
11/08/07
Rev No. 1

IsleChem, LLC

Analytical Sciences Laboratories

Methods of Analysis – Alkyl and Aryl Acid Phosphates

The Determination of Turbidity

Principle:

The turbidity of AAP samples is determined using a Hach DR/3000 Spectrophotometer. The method is based on nephelometry, which is a photometric analytical technique for measuring the light scattered by finely divided particles of a substance in suspension in a liquid. The turbidity is expressed in nephelometric turbidity units (NTU). The Hach DR/3000 Spectrophotometer is preprogrammed with a calibrated turbidity method. The calibration is checked with a 10.0 NTU standard

Apparatus:

1. Hach DR/3000 Spectrophotometer; Hach Cat # 19600-00
2. Hach Sample Cells, matched pair, 25ml volume; Hach Cat # 19935-00
3. 10.0 NTU Turbidity Standard; Fisher Cat # 15-426-5 or equivalent; used as a calibration check standard.

Procedure:

1. Turn on and set up the DR/3000 according to the instrument manual. Warm up for 15 minutes.
2. Press “59” and the Stored Program button. “450” will be displayed as a reminder to set the wavelength dial to 450nm. Press the “clear” button.
3. Fill a sample cell to the mark with filtered deionized water. Open the sample compartment door and place the cell into the holder with the mark facing forward. Close the compartment door. Press “zero” and “conc.” buttons to zero the instrument.
4. Fill a sample cell to the mark with the 10.0 NTU standard. Open the sample compartment door and place the cell into the holder with the mark facing forward. Close the compartment door. Read the turbidity in NTUs. The value of the check standard should be between 9.0-11.0 NTUs.
5. Fill a sample cell to the mark with the sample to be analyzed. Open the sample compartment door and place the cell into the holder with the mark facing forward. Close the compartment door. Read the turbidity in NTUs.