PURIFIED PHOSPHORIC ACID H₃PO₄

TECHNICAL INFORMATION BULLETIN



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TABLE OF CONTENTS

Introduction	1
General Description	1
Structure	
Specifications	2
Physical Properties	2
Availability	2
Bulk Storage and Handling	3
Storage Considerations	3
Construction Materials	
Health and Safety Information	6
Fire, Explosion and Health Hazard Data	6
Toxicological Information	
Personal Protective Equipment	6
Emergency Information	7
Spill Containment	7
Emergency First Aid Procedures	
Transportation Emergencies	
Applications	8
Chemical Production	8
Food and Beverages	
Metal Treating	
Refractories and Ceramics	
Miscellaneous	11

Basic Properties 1	2
Boiling Points	12
0	12
-	13
Corrosion Data	13
Specific Heat	15
*	15
Density	16
-	17
Electrical Conductivity	17
	17
Heat of Formation,	
Free Energy of Formation, Entropy	18
Latent Heat of Vaporization	18
Refractive Index	18
Relative Sourness	19
Vapor Pressure	19
Vapor Composition	20
Viscosity in Centipoise	21
Kinematic Viscosity of	
Phosphoric Acid Solutions	22
Analytical Methods 2	23
Determination of H_3PO_4 by	
Specific Gravity	23
Determination of H_3PO_4 by	
Molybdovanadate Method	25
Determination of H_3PO_4 by	
Thymolphthalein Titration	26
Endnotes 2	27
PCS Sales and Service 2	28

FIGURES AND TABLES

Figures

Figure 1	
Schematic of Typical Phosphoric	
Acid Storage System	3
Figure 2	
Boiling Point versus Concentration	12
Figure 3	
Freezing Point versus Concentration	12
Figure 4	
Isocorrosion Chart for Type 316L Stainless Steel	
in Phosphoric Acid	13
Figure 5A	
Corrosion Resistance of Non-Metals	
in 80% Phosphoric Acid	14
Figure 5B	
Corrosion Resistance of Metals	
in 80% Phosphoric Acid	14
Figure 6	
Specific Heat at 21.3°C	15
Figure 7	
Titration Curve of Orthophosphoric	
Acid pH versus Increasing Sodium	
Hydroxide Additions	15
Figure 8A	
Orthophosphoric Acid Specific Gravity	
@ 25°C/15.°C versus Concentration	16

	Figure 8B Specific Gravity versus Concentration	16
	Figure 9 Enthalpy versus Concentration	17
	Figure 10 Latent Heat of Vaporization at 25°C	18
	Figure 11 Vapor Pressure versus Concentration	19
	Figure 12 Vapor Composition Over Boiling Solutions	20
	Figure 13A Viscosity in Centipoise of Phosphoric Acid for Various Concentrations and Temperatures	.21
	Figure 13B Viscosity of 75% and 85% Phosphoric Acid versus Temperature	21
	Figure 14 Viscosity in Centistokes of Phosphoric Acid for Various Concentrations and Temperatures	22
Та	bles	
	Table 1 Specific Gravity Temperature Coefficient	23
	Table 2 Phosphoric Acid Solutions Specific Gravity at 25°C/15.5°C	

versus Concentration 24

INTRODUCTION

General Description

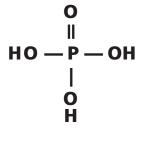
Orthophosphoric acid (H_3PO_4), usually referred to as phosphoric acid, is a clear, water-white liquid which is derived from phosphate rock.

Phosphoric acid is a triprotic acid which means that, in an aqueous solution, it will dissociate to produce three hydrogen ions. Phosphoric acid is a stronger acid than the organic acids, such as acetic, citric and lactic; however it is not as strong as other mineral acids, such as nitric, sulfuric and hydrochloric.

Phosphoric acid is a useful synthesis catalyst since it does not react violently with many organic compounds and exhibits catalytic and dehydrating properties. It will react readily with bases to produce alkali phosphates and will become fairly reactive with metals and metal oxides at elevated temperatures.

These properties give phosphoric acid a wide range of industrial applications from metal finishing to food additives.

Structure



CAS Registry No: 7664-38-2

The molecular structure of orthophosphoric acid represented above in two dimensions, consists of four groups at the corners of a tetrahedron with the phosphorus atom at the center. In aqueous solutions, the phosphate ions are considered to be interconnected by hydrogen bonds. As dilution increases, hydrogen bonding between phosphate ions decreases and is replaced by hydrogen bonding to water.

Specifications

Technical Grades

	75%	80%	85%
Appearance	Water-v	white liquid, colorless, o	dorless.
Specific Gravity (25°C/15.5°C)	1.574	1.629	1.686
Phosphoric Acid (%H ₃ PO ₄)	75.0 – 75.5	80.0 - 80.5	85.0 - 85.5

Food Grade Specifications

		75% Food	80% Food	85% Food
Component		Chemical Codex	Chemical Codex	Chemical Codex
H ₃ PO ₄	%	75.0 – 75.5	80.0 - 80.5	85.0 - 85.5
F	ppm w	10	10	10
As	ppm w	3	3	3
Heavy Metals	ppm w	5	5	5
Cd	ppm w	3	3	3
Pb	ppm w	3	3	3

Physical Properties

	Standard Concentration			
	75%	80%	85%	
P ₂ O ₅ (%)	54.6	58.1	61.7	
Specific Gravity (25°C/15.5°C)	1.574	1.629	1.686	
Pounds per U.S. Gallon	13.1	13.6	14.1	
Melting Point*, Approx.	0°F(-18°C)	41°F(5°C)	70°F(21°C)	
Specific Heat (cal/gm–°C)	0.542	0.518	0.493	
Viscosity (25°C) cp	21.5	29.0	43.5	

* Purified phosphoric acid's melting point is the same as its freezing point.

Availability

PCS phosphoric acid is available in three standard concentrations, 75%, 80%, and 85% meeting the aforementioned specifications. Bulk shipments can be made in tank cars and tank trucks. Phosphoric acid in polyethylene drums is also available from your PCS distributor.

BULK STORAGE AND HANDLING

Storage Considerations

The primary considerations in the design of a bulk storage and handling system for phosphoric acid are its corrosive properties and freezing point. The freezing point of phosphoric acid varies greatly with acid concentration. It is this consideration that determines the tank location and need for an external heating source. Phosphoric acid is subject to supercooling well below the freezing point if there is no seeding or agitation. For this reason 75% acid can be stored outside with little danger of freezing. The 80% and 85% acid grades may require some form of external heat to keep them above their freezing points, depending upon the location of the system. Temperature can be controlled using a recirculation loop with an external heat exchanger. Low temperature steam, electricity or hot water are recommended as heat sources. A schematic of a typical phosphoric acid storage system is shown in Figure 1.

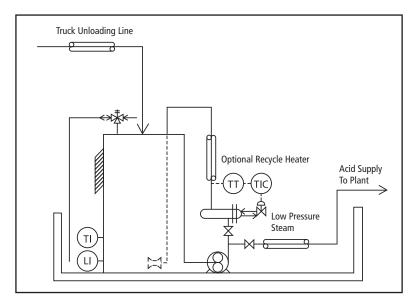


FIGURE 1: Schematic of Typical Phosphoric Acid Storage System

Construction Materials

Storage Tank

Recommended materials for storing phosphoric acid are:

• Stainless Steel

Type 316L Stainless Steel is used successfully for storing all grades of phosphoric acid. It is especially desirable for food grade acids. To avoid welding difficulties, extra low carbon (ELC) stainless steel should be specified. MIG welding should also be specified since the quality of the welds is superior. The corrosion rate for 316L in the temperature range from 77° to 120°F is low. A caution to be observed when considering stainless steel tanks is the detrimental effect of minor amounts of halide impurity (15 – 30 ppm Cl) in the acid. This amount of chloride will increase the aggressiveness of acid to stainless steel enough to increase the Fe, Ni and Cr content in the acid, and impart color to the product.

This is especially true where small amounts of acid remain in contact with a relatively large surface as in pipelines or in the bottom of a tank. PCS phosphoric acid contains less than 5 ppm of chlorides and will cause no difficulty. However, if the acid is diluted with chlorinated water, the chloride concentration can reach a level which results in corrosion of the stainless steel.

• Rubber-Lined Carbon Steel

Rubber-lined steel tanks offer good corrosion resistance and are less expensive than stainless steel. Pure natural gum white rubber and chlorobutyl rubber are recommended, though resistance varies with manufacturers. New rubber linings often impart some color to phosphoric acid but this usually drops to an undetectable level after several storage cycles.

Some rubbers have a tendency to become detached from the steel tank. This is usually due to failure of the bonding cement used. It should be noted that elevated temperatures have a deteriorating effect on the rubber lining, with each lining having its own "critical" temperature.

B.F. Goodrich produces ACID SEAL PW code 2004 which is a soft, white natural rubber and is suitable for installation on site. Goodrich SANIPRENE code 1005 is a hard rubber for smaller tanks which are autoclave cured. ARCO (Schoolcraft, MI) also produces comparable materials: #8310 for field installation and #874 for the smaller applications. Blair Rubber Company produces VE 524WC FDA, which is a white chlorobutyl rubber.

• Fiberglass Reinforced Polyester (FRP)

Filament-wound fiberglass with polyester resins is also used successfully. The performance of the fiberglass tank surpasses that of the rubber-lined tank and is nearly equal to that of stainless steel. The most pronounced advantage of fiberglass is one of initial cost. Fiberglass tanks are less expensive than rubber-lined tanks and can cost one-third as much as stainless steel. Bisphenol-A-Fumarate is recommended as a polyester resin. Do not use steam coils in FRP, rather use hot water or electrical heaters.

The following materials are not recommended:

• Glass-Lined Steel

Glass lined tanks have superior corrosion resistance. However, the cost is excessive for this application.

• 302, 304 and 316 Stainless Steel

Type 302, 304 and 316 stainless steel are less expensive than 316L. However, the corrosion rates with phosphoric acid are greater. They impart a green color to the acid due to the increase in the heavy metals concentration. They are also more sensitive to chloride contamination than type 316L. None are considered suitable materials for storing or handling phosphoric acid.

Carbon Steel

Although carbon steel is much less expensive than stainless steel, it corrodes rapidly when in contact with phosphoric acid. It should never be used in any aspect of the transfer, storage or handling of phosphoric acid.

The foundation around bulk storage tanks should be diked. It is recommended that the dike be designed to hold 110 percent of the volume of the storage tank or of the largest tank in the tank farm. The floor of the dike should drain towards a sump to allow any water accumulating in the diked area to be removed using a pump. The sump and diked areas should be kept drained. The dike walls and floor should be protected with an acid-resistant coating. STONHARD[®] Company, Forté Composites Inc. (Corguard 9000), and AMERON PROTECTIVE COATINGS produce acceptable acid-resistant coatings.

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Pumps

Phosphoric acid pumps should have all wetted parts constructed of 316L stainless steel. Centrifugal pumps capable of meeting the pumping capacity and dynamic head are sufficient. Mechanical seals are recommended over packing due to their longer life span. Centrifugal pumps such as the totally enclosed, sealless Crane Chempump can also be used, but are more expensive and not usually justified.

Piping

In general, any material suitable for storing phosphoric acid will be acceptable as a piping material with 316L being preferred.

When stainless steel piping is used, best results have been obtained using flanged and welded type 316L pipe, fittings and valves. Schedule 40 pipe should be used with type 316L insert-type flanges. These flanges have 316L welding and sealing surfaces with carbon steel back-up flanges. Welding should be done by competent personnel according to methods approved by the stainless steel manufacturer.

All 316L or Alloy 20 flanged valves with outside screw and yoke are recommended. TEFLON gaskets are recommended. Screwed stainless steel pipe, fittings, and valves are used but are not recommended because it is difficult to obtain tight joints, particularly when the piping is to be dismantled and reassembled. The flanged and welded piping system is preferred.

HEALTH AND SAFETY INFORMATION

Phosphoric acid is considered to be a stable chemical not subject to thermal or photochemical decomposition. Hazardous polymerization will not occur. Hazardous decomposition products are the phosphorus oxides which are evolved at approximately 3000° to 3200°F.

Phosphoric acid will react with some metals such as aluminum and zinc liberating hydrogen; however it does not react as rapidly or violently as some of the more active acids. Nevertheless, caution should be exercised since the by-product hydrogen is very flammable.

Material Safety Data Bulletins should be consulted prior to use of the products and are available by contacting PCS Sales Customer Service Department.

North America 1-800-654-4514

Fire, Explosion and Health Hazard Data

Phosphoric acid does not burn and exhibits no unusual fire explosion hazards. The Threshold Limit Value Time Weighted Average (TLV TWA) is 1.00 milligram per cubic meter of air and respiratory irritation from excessive breathing of mists of vapors will occur. There can also be moderate eye irritation and slight skin irritation.

Toxicological Information

Phosphoric acid exhibits slight oral toxicity in rats with an LD50 of 1530 mg/kg of body weight. Dermal toxicity is considered to be slight based on testing of similar products and/or the components. Severe skin irritations or burns may occur. Phosphoric acid will cause eye burns. Detailed toxicological data is available from PCS Environmental Services Department, Northbrook, IL.

Personal Protective Equipment

Properly fitted chemical goggles and protective clothing should be worn. Impervious gloves and aprons are recommended. No special respiratory protection is required under ordinary conditions of use provided that adequate ventilation is maintained. When vapor or mist concentrations exceed applicable standards, approved respiratory protective equipment must be used.

EMERGENCY INFORMATION

Spill Containment

Phosphoric acid is not volatile or flammable. The primary concern in the event of a spill is to contain the material to prevent contamination of sewers or waterways. If the leak or spill is not contained in a diked area, the spilled material should first be contained using dry sand banked around the spill to limit the affected area. Then sprinkle hydrated lime or soda ash on the spill area. Finally, shovel the material into an approved waste disposal container for treatment or disposal in an approved chemical disposal area.

Emergency First Aid Procedures

Eye Contact

Flush eyes thoroughly with water for 15 minutes. Get immediate medical assistance. If medical assistance is not immediately available, flush an additional 15 minutes.

Skin Contact

Wash contaminated skin with mild soap and water. If clothing is contaminated, remove clothing immediately and wash exposed area with large quantities of water. Launder contaminated clothing separately before reuse. If contact is widespread, remove clothes and wash skin under a safety shower.

Inhalation

Remove from further exposure. If breathing has stopped, use mouth-to-mouth resuscitation. Keep affected person warm and get immediate medical attention.

Ingestion

Do not induce vomiting. Give one to two glasses of water or milk immediately. Get medical assistance immediately. Do not give anything by mouth to an unconscious person.

Transportation Emergencies

For help with emergencies involving spill, leak, fire or exposure involving transportation equipment, immediately notify the closest Emergency Center:

U.S. CHEMTREC 1-800-424-9300 or 202-483-7616 Canada CANUTEC 613-996-6666

The information specialist on duty will ask for a brief description of the emergency, the name and location of the caller, the name of the shipper, the product, the shipping point and destination, what happened, the nature of any injuries, weather conditions, proximity of populated area, etc. He will then give the recommendation for controlling the emergency situation until the shipper's specialist can relay help. CHEMTREC will advise PCS of the emergency and one of our specialists will contact the caller.

APPLICATIONS

Chemical Production

Alkali Phosphates

Phosphorus-based builders for the detergent industry is a major application for phosphoric acid. A base such as potassium hydroxide, sodium hydroxide or soda ash (sodium carbonate) is reacted with phosphoric acid and the resulting "wet mix" is dried to form alkali phosphates in the ortho or condensed form. The properties of the resulting alkali phosphate are dependent on the method of drying, the temperature and process time, and the alkali-to-phosphorus molar ratio. Some common phosphate builders are sodium tripolyphosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, potassium tripolyphosphate, and trisodium phosphate.

Phosphoric acid can also be combined with an ammonia base to produce monoammonium phosphate, diammonium phosphate, or ammonium polyphosphate. These compounds are used in fertilizer manufacture and flame proofing.

Catalysts

Purified Phosphoric acid is used in the production of several catalysts. Vanadium/phosphorus oxide catalysts have been produced⁽¹⁵⁾ for use in hydrocarbon oxidation reactions. It is claimed to deliver higher yields with better selectivity in the production of maleic anhydride from C₄ hydrocarbons. Phosphoric acid is also used in the manufacturing of aluminum phosphate catalysts and can be used to extend the life of catalysts by reducing coking.⁽¹⁶⁾

Specialty Fertilizers

Purified Phosphoric acid is used as the phosphorus source in the production of specialty and foliar fertilizers. Because of its higher purity and lack of solids, purified phosphoric acid is used for spray and house plant fertilizers.

Fire Retardants

Wood and cellulose materials can be treated to obtain flame, glow and decay resistance. The current formulation⁽¹⁷⁾ uses urea, dicyandiamide, formaldehyde and phosphoric acid to form coatings, impregnated substrates, adhesives and resins. The fire retardant formulation is stable and leach resistant, and exhibits a useful shelf life.

Food and Beverages

Beverages

Food grade phosphoric acid is used in the beverage industry as an acidulant and flavoring agent. The presence of 0.05% phosphoric acid contributes to the unique taste of cola drinks. Phosphoric acid is also a less expensive additive for beverages than citric, tartaric, acetic and lactic acids.

Cheese

Phosphoric acid is used in the dairy industry as an acidulant to cause curdling in the production of cottage cheese.

Egg Products

Phosphoric acid can be used to minimize the viscosity and browning in the spray drying of egg albumen.

Fats and Oils

Phosphoric acid can be added to fats and oils as an emulsifier and to aid in the control of fatty peroxides. It is also used as a degumming agent during vegetable oil refining.

Gelatin

Phosphoric acid can improve the setting rates and clarity of gelatins.

Jams and Jellies

Small amounts of phosphoric acid can be added to jams and jellies for acidifying, buffering and preservation.

Salad Dressings

Phosphoric acid is used as an acidulant in some salad dressings.

Sugar Refining

In the refining of raw sugar, phosphoric acid is reacted with lime to form a calcium phosphate precipitate which aids in the filtration of particulates.

Pet Foods

Phosphoric acid is used in the production of semi-moist pet food.

Metal Treating

In the metal finishing industry phosphoric acid is utilized to chemically polish, clean and coat a wide range of metals, including aluminum, brass, copper, steel and stainless steel.

Aluminum Brightening

Most of the solutions employed in the metal finishing industry for the chemical polishing of aluminum are based on a mixture of phosphoric acid, nitric acid, and sometimes sulfuric acid. These solutions, commonly referred to as bright dip solutions, chemically remove the microscopic peaks of the aluminum surface to produce a highly specular or mirror-like finish. Chemically polished aluminum can be utilized in a variety of applications including automotive trims, architectural structures, home appliances, aircraft construction, electronic components, window frames, shower doors, cosmetic containers, athletic equipment, office equipment, and many more. PCS's *Phosbrite* and *DAB* solutions set the standard for bright dipping of aluminum and they can be custom formulated to include any combination of the following additives: copper metallic brightener, fume suppressant, or etch inhibitor.

Consistent production of a high quality finish requires a thorough understanding of the bright dip bath and its function, as well as careful control of the entire finishing process. PCS maintains a technical staff with laboratory and pilot facilities to assist metal finishing customers with implementing process improvement modifications on existing bright dip/anodizing lines or with designing new lines, and with troubleshooting to determine the cause of various finishing problems. PCS provides analytical services at no charge to customers for determining the different operating parameters of the customer's bright dip baths. PCS also provides, at no charge, sample kits for sending bright dip samples to PCS's lab and reagents to assist in bright dip bath control.

Aluminum Cleaning

In the aluminum industry, it is of vital importance to have a clean surface on the aluminum part prior to implementing any finishing process. The cleaning of aluminum can be accomplished by either an alkaline cleaner alone or an alkaline cleaner followed by an acid cleaner. PCS offers a phosphoric acid-based cleaner referred to as *342 Acid Cleaner*. This cleaner is designed to remove ground-in, caked-on buffing compounds and drawing oils from drawn, stamped, or extruded aluminum parts and leaves the aluminum surface "activated" for subsequent bright dipping or etching processes. It will also remove some heat and watermarks, which are normally carried through conventional alkaline or neutral cleaners. *342 Acid Cleaner* is designed as a second-stage cleaner that follows an alkaline cleaner, but it may be used as a single-stage cleaner where the soil load is light.

Boiler Cleaning

Many boiler cleaning formulations utilize phosphoric acid to remove carbonate scale, oil or grease. The advantage of phosphoric acid is that the boiler surfaces will develop a light phosphate coating which will resist further oxidation. Phosphoric acid is also less corrosive and volatile than other mineral acids.

Dairy Equipment Cleaning

Phosphoric acid is used in the dairy industry as a cleaner and sanitizer. It has the advantage of being non-toxic and very effective at removing "milk stone" from the processing equipment.

Electropolishing⁽¹⁸⁾

Carbon steel, stainless steel, copper, brass and aluminum can be electropolished using a bath of phosphoric-sulfuric-chromic acid in varying concentrations. The metal is made the anode and the bath selectively removes the microscopic metal peaks resulting in increased specularity.

Phosphate Coatings

Metal phosphate coatings are applied to various metal surfaces to reduce corrosion, to improve paint bonding and to aid in forming or break-in processes.

Many phosphatizing solutions have been developed but the most common ones contain free phosphoric acid, a dissolved metal phosphate, an accelerator and a surfactant. The coating is formed when the free phosphoric acid reacts with the metal to produce a metal phosphate which is insoluble and precipitates. The accelerator can be nitrate, chlorate or a nitrite and serves to increase the reaction rate. The surfactant acts as a wetting agent to improve the contact between the metal surface and the solution.

The phosphate coating is bonded tightly to the metal surface and is normally formulated to be porous, which provides an excellent substrate for paint adhesion. In addition, the pores can hold lubricant to improve the forming operations and reduce friction during equipment break-in periods.

Refractories and Ceramics

Phosphoric acid is useful as a bonding agent in many refractories and ceramics. It is also used as a raw material in the production of the improved bonding agents such as monoaluminum phosphate and monomagnesium phosphate solutions. The high purity of PCS acid allows for an extended shelf life of the mixes plus consistently high strength bonds in the final refractory.

Much research has been done on the bonding of high alumina refractories and these compositions display high temperature resistance and high strength. Various additives have been patented to improve specific properties of the refractory compositions.

A refractory with a large amount of chromic oxide has been proposed⁽¹⁹⁾ which is claimed to have improved thermal shock resistance and reheat expansion. The addition of tetrasodium pyrophosphate and bentonite⁽²⁰⁾ has been shown to improve workability and storage life of ramming or hand mixes. A refractory containing silicon metal and graphite has been claimed to be resistant to slag and hot metal erosion.⁽²¹⁾

Miscellaneous

Fuel Cells

Phosphoric acid is used as an electrolyte in fuel cells which produce electricity from the conversion of hydrogen to water.

Activated Carbon Production

The production of activated carbon involves mixing wood fibers or sawdust with phosphoric acid followed by calcination in a rotary kiln.

Waste Treatment

Phosphoric acid is used as a nutrient for bacteria in activated-sludge waste treatment systems.

Lead Fixation

Phosphoric acid can be used to form non-leachable lead phosphate in land areas where potential lead runoff is a problem.

BASIC PROPERTIES

Boiling Points

The boiling point for orthophosphoric acid is shown in Figure 2 which graphs the boiling point at one atmosphere pressure versus the concentration expressed as weight percent phosphoric acid (% H₃PO₄). Through the concentration range of 0% to 100%, boiling acid will give off very nearly pure water.

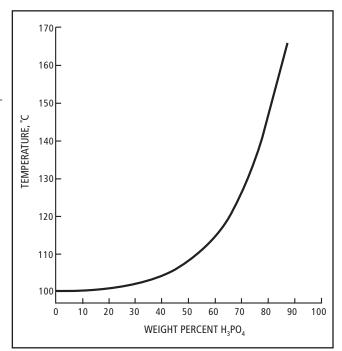


FIGURE 2: Boiling Point versus Concentration

Freezing Points

Figure $3^{(1)}$ is the phase diagram of the $H_3PO_4 - H_2O$ system showing the freezing point curve for phosphoric acid through the range of 0 to 100 weight percent H_3PO_4 . Concentrated phosphoric acid tends to supercool before crystallization occurs. The freezing points of standard concentrations are as follows:

Acid Strength

(% H ₃ PO ₄)	75%	80%	85%
Freezing Point	0.5°F	40.2°F	70.0°F
	–17.5°C	4.6°C	21.1°C

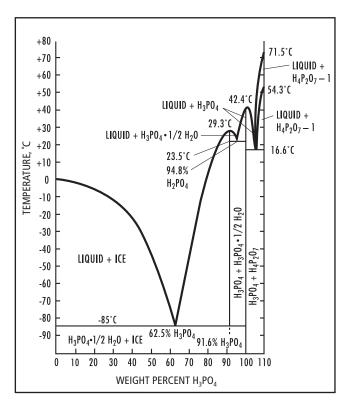


FIGURE 3: Freezing Point versus Concentration

Conversion Factors

Phosphoric acid concentrations can be expressed in several ways: percent phosphoric acid (%H₃PO₄), percent phosphorous pentoxide (%P₂O₅), or percent phosphorus (%P). The following chart gives the factors to convert from one of the above concentration units to another.

To Convert			To:	
From:		H ₃ PO ₄	P ₂ O ₅	Р
H ₃ PO ₄	Х	_	0.724	0.316
P ₂ O ₅	х	1.381	_	0.436
Р	х	3.164	2.291	_

For example, to convert from 75% H_3PO_4 to % P_2O_5 : 75% $H_3PO_4 \times 0.724 = 54.3\% P_2O_5$

Corrosion Data

One of the most widely used alloys for phosphoric acid is stainless steel type 316L. Figure 4 (right) is an isocorrosion chart⁽²⁾ for type 316L stainless steel showing the corrosion rate for various concentrations at various temperatures. Fiberglass reinforced polyester is also a corrosion resistant and cost effective material for phosphoric acid (HF free) but only at ambient temperatures.

In addition, numerous other metallic and non-metallic materials have been tested in phosphoric acid and are listed in Figures 5A and $B^{(3)}$ (pg. 14). The corrosion values are only applicable to high purity phosphoric acid. The values will be higher for PCS phosphoric acids depending on acid purity.

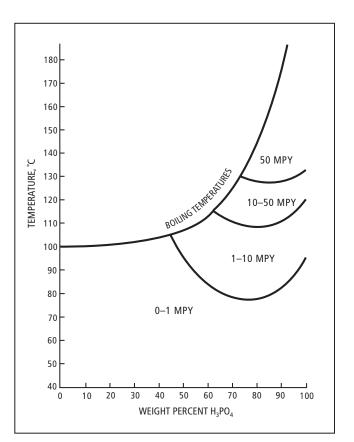


FIGURE 4: Isocorrosion Chart for Type 316L Stainless Steel in Phosphoric Acid

Material	Recommended Temperature Limit (°C)	Effect on Material
Carbon	100	None
Chlorinated Polyvinyl Chloride (CPVC)	20	None
Fiberglass Reinforced Vinylester (Hetror	n 942) 100	None
Fluorocarbons (TFE & FEP)	100	Slightly permeable at high temperatures
Polypropylene	20	None
Polyvinyl Chloride (PVC)	40	Some weight loss
Chlorobutyl Rubber	80	Some weight gain
Fluoroelastomer	80	Some weight gain

FIGURE 5A: Corrosion Resistance of Non-Metals in 80% Phosphoric Acid

		С	orrosion I	Rate (mils	per year)
Metal		Tempera	ture °C	_	
	25	50	75	100	Other
Mild Steel	>50	11,000			
Stainless Steel					
Туре 304	_	—	—	50	Discolors
Туре 316	_	—	_	2	
Туре 347	—	—	—	0	
Туре 430		_	_	3	Rate increases without aeration
Hastelloy B	<1	<1	1	5	
Hastelloy C	<1	<1	1	5	
Carpenter 20	_	_	_	2	
Nickel	0.3	4.2	_	150	
Monel	_	10	_	20	

FIGURE 5B: Corrosion Resistance of Metals in 80% Phosphoric Acid

Specific Heat

Figure 6 shows the weight percent of phosphoric acid in an aqueous solution versus the specific heat expressed as calories per gram — °C or (BTU/lb. — °F) at 21.3°C.¹²

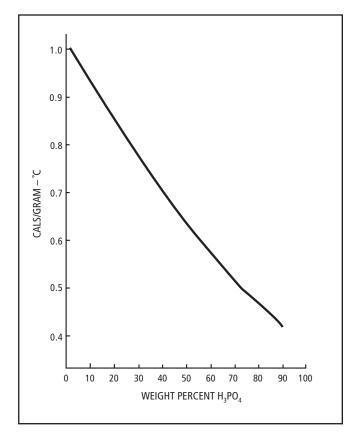


FIGURE 6: Specific Heat at 21.3°C

Titration Curve

Figure 7 shows the curve for the titration of a 0.1 molar solution of phosphoric acid with sodium hydroxide. There are two distinct breaks in the titration curve which represent titration of the first hydrogen at about 4.2 pH and the second hydrogen at about 9.0 pH. Titration of the third hydrogen does not display a pH break but it is calculated to occur at about 11.5 pH.

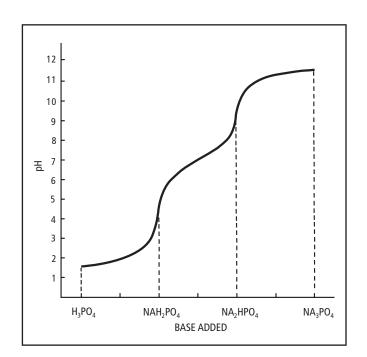


FIGURE 7: Titration Curve of Orthophosphoric Acid pH versus Increasing Sodium Hydroxide Additions

Density

The density (expressed as specific gravity) versus concentration of orthophosphoric acid is given in the following chart⁽⁴⁾ (Figure 8A) and graph (Figure 8B). Specific gravity is an accurate measure of the concentration of phosphoric acid for laboratory analysis. Linear interpolation between the values given in Figure 8A will yield acid concentrations with an accuracy of $\pm 0.05\%$ H₃PO₄ (see page 23 — Analytical Methods).

H ₃ PO ₄										
Wt. %	0	1	2	3	4	5	6	7	8	9
0	.9981	1.0036	1.0091	1.0145	1.0200	1.0255	1.0311	1.0367	1.0423	1.0480
10	1.0538	1.0595	1.0654	1.0713	1.0773	1.0833	1.0894	1.0955	1.1016	1.1080
20	1.1143	1.1207	1.1271	1.1336	1.1400	1.1467	1.1534	1.1601	1.1669	1.1738
30	1.1807	1.1877	1.1948	1.2019	1.2092	1.2164	1.2238	1.2312	1.2387	1.2462
40	1.2539	1.2616	1.2694	1.2772	1.2852	1.2932	1.3014	1.3096	1.3178	1.3263
50	1.3347	1.3432	1.3518	1.3605	1.3692	1.3781	1.3870	1.3960	1.4051	1.4143
60	1.4236	1.4330	1.4425	1.4520	1.4617	1.4714	1.4813	1.4912	1.5013	1.5114
70	1.5216	1.5320	1.5424	1.5529	1.5635	1.5742	1.5849	1.5958	1.6067	1.6178
80	1.6290	1.6403	1.6516	1.6630	1.6745	1.6861	1.6977	1.7095	1.7214	1.7334
90	1.7455	1.7578	1.7688	1.7813	1.7937	1.8062	1.8186	1.8311	1.8436	1.8560
100	1.8686	1.8810	1.8935	1.9060	1.9184	1.9309	1.9433	1.9558	1.9684	1.9808
110	1.9933									

FIGURE 8A: Orthophosphoric Acid Specific Gravity @ 25°C/15.5°C versus Concentration

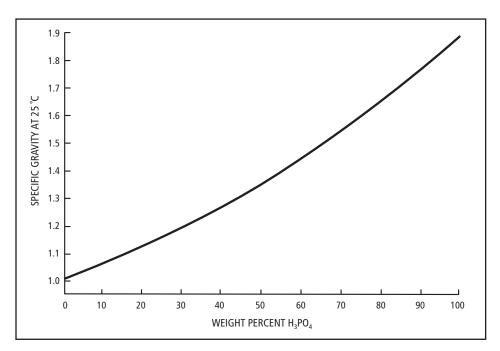


FIGURE 8B: Specific Gravity versus Concentration

Dissociation

Orthophosphoric acid is a triprotic acid which means that it can contribute or dissociate three hydrogen ions. Dissociation of the first hydrogen is very strong and is exothermic. Dissociation of the second and third is weak and very weak, respectively, and both dissociations are endothermic. There is abundant research on the dissociation constants for the three hydrogens. R.G. Bates B⁽⁵⁾ developed the following:

Hydrogen	Equation	Constant at 25°C
First H ₊	– log K ₂ = 799.31/T* – 4.5535 + 0.013486T	0.7107 x 10 ^{−2}
Second H+	– log K ₂ = 2073.0/T – 5.9884 + 0.020912T	7.99 x 10 ^{−8}
Third H+	_	4.8 x 10 ⁻¹³

* T is absolute temperature in degrees Kelvin

Electrical Conductivity

The specific electrical conductivity of phosphoric acid increases with increasing concentrations reaching a maximum value at about 50% H_3PO_4 . As the concentration continues to increase, the conductivity decreases. The electrical conductivity of any concentration increases with increasing temperature.

Enthalpy — Concentration

Figure $9^{(8)}$ (right), is a graph of the enthalpy versus concentration for phosphoric acid. This graph shows the heat evolved in calories per mole H_3PO_4 when a certain concentration of acid is diluted to an infinitely low concentration. The heat evolved when acid of one concentration (C₁) is diluted to a second concentration (C₂) is found by subtracting the enthalpy of the second from the enthalpy of the initial solution (Ec₁ – Ec₂).

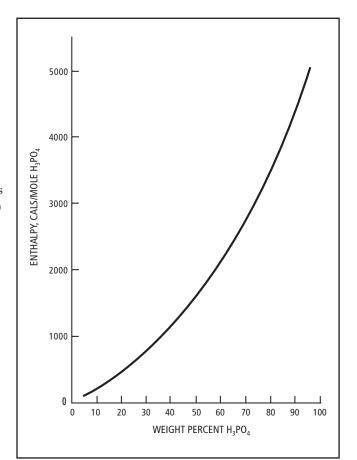


FIGURE 9: Enthalpy versus Concentration

Heat of Formation, Free Energy of Formation, Entropy

The following is the heat of formation, free energy of formation and entropy of orthophosphoric acid as a solid and as an aqueous solution of 400 moles of water to 1 mole of H_3PO_4 .⁽⁹⁾

	Heat (kcal/mole) H ₁₈ °C	Free Energy (kcal/mole) F ₂₅ °F	Entropy (cal/°C) S
100 wt. % H ₃ PO ₄ (solid)	303.37	_	_
100 wt. % H ₃ PO ₄ (liquid)	300.74		
Aqueous Dilutions			
84.5 wt. % H ₃ PO ₄	302.49		
64.5 wt. % H ₃ PO ₄	304.04		
37.7 wt. % H ₃ PO ₄	305.26		
21.4 wt. % H ₃ PO ₄	305.69		
9.8 wt. % H ₃ PO ₄	305.93		
1.3 wt. % H ₃ PO ₄	306.17	-270.0	42.1

Latent Heat of Vaporization⁽⁸⁾

The latent heat of vaporization for phosphoric acid at 25°C is given in Figure 10.

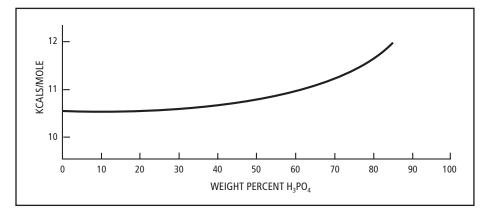


FIGURE 10: Latent Heat of Vaporization at 25°C

Refractive Index

The refractive index of aqueous phosphoric acid solution is linear with concentration. The formula $(17.5^{\circ} \text{C})^{(10)}$ is:

Refractive Index = 0.000792 x (weight % H₃PO₄) + 1.3346

or wt. % $H_3PO_4 = \frac{RI \ 17.5^{\circ}C - 1.3346}{0.000792}$

Relative Sourness

Phosphoric acid is frequently used as a flavoring agent. It imparts a sour taste similar to citric, tartaric and acetic acid, however, the same level of sourness can be obtained using less phosphoric acid. The following table lists several acids, the relative sourness of a 0.01 N solution of each and the pounds of the listed acid equivalent to one pound of 75% phosphoric acid:⁽¹¹⁾

	Relative Sourness (0.01 N)	Equivalent Pounds of Acid
Tartaric acid crystals (99.5%)	100	1.39
Citric acid crystals (91%)	100	1.29
Citric acid solution (50%)	100	2.35
Acetic acid (56%)	70	2.81
Lactic acid (44%)	100	3.76
Lactic acid (40%)	100	4.13
Phosphoric acid (75%)	120	1.00

Bottled soda of the acid type has a sourness approximately the same as 0.01 N solutions of citric, tartaric, or lactic acids.

Vapor Pressure

Figure 11 below gives the vapor pressure of water over aqueous solutions of phosphoric acid at various temperatures.⁽¹³⁾

Concentration	Vap	or pressure (I	mm Hg) at te	mperature (°	C)
(wt. % H ₃ PO ₄)	25°	40 °	60°	80 °	100°
0	23.76	55.32	149.4	355.1	760.0
5	23.47	54.6	148.0	349.0	745.0
10	23.16	54.0	145.0	345.0	736.0
20	22.40	52.2	141.0	335.0	713.0
30	21.27	49.6	135.0	320.0	683.0
50	16.68	39.4	108.0	262.0	567.0
65	10.66	25.4	71.5	176.0	388.0
85	2.24	5.7	15.5	46.5	108.0
100	0.044	0.12	0.43	1.33	3.65

FIGURE 11: Vapor Pressure versus Concentration

Vapor Composition

The composition of the vapor which exists over a boiling solution of phosphoric acid is depicted in Figure 12.⁽¹³⁾ An aqueous solution of H_3PO_4 will give off almost pure water for temperatures up to about 300°C at which point the acid strength is about 103%. As the temperature of the solution increases, the vapor evolved will contain increasing amounts of P_2O_5 . For example, the approximate composition of the vapor at 760 mm pressure over a boiling solution at 600°C is 25% P_2O_5 .

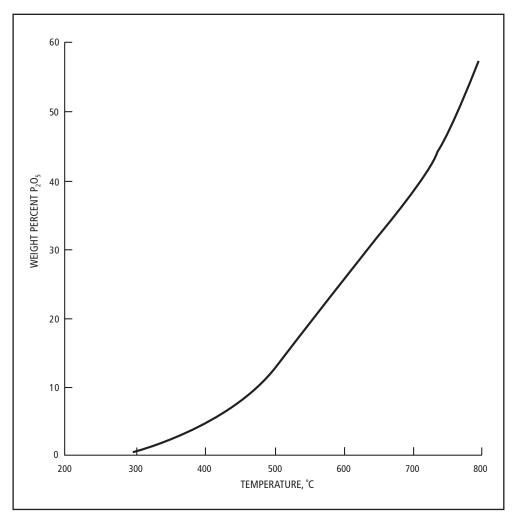


FIGURE 12: Vapor Composition Over Boiling Solutions

Viscosity in Centipoise

Figure 13A below gives approximate viscosity in centipoises of aqueous phosphoric acid solutions for various concentrations and temperatures.⁽¹⁴⁾ Figure 13B is a graph of the viscosity versus temperature for 75% and 85% phosphoric acid.

oncentration			٦	Temperature	(°C)			
(%H₃PO₄)	20 °	30 °	40 °	60°	80°	100°	140°	180°
0	1.0	0.80	0.66	0.47	0.36	0.28	0.19	0.14
5	1.1	0.91	0.75	0.55	0.42	0.33	0.22	0.15
10	1.3	1.0	0.87	0.63	0.48	0.38	0.26	0.18
20	1.8	1.4	1.2	0.86	0.65	0.52	0.34	0.24
30	2.6	2.0	1.6	1.2	0.91	0.72	0.49	0.37
50	5.7	4.4	3.4	2.4	1.8	1.4	1.0	0.82
75	24.	16.	12.	7.4	5.1	3.8	2.4	1.8
85	47.	32.	23.	13.	8.4	5.8	3.5	2.4
105		644.	365.	145.	67.	35.	18.	
110		4510.	2240.	600.	250.	110.	40.	
115		16900.	10800.	2900.	975.	490.	155.	

FIGURE 13A: Viscosity in Centipoise of Phosphoric Acid for Various Concentrations and Temperatures

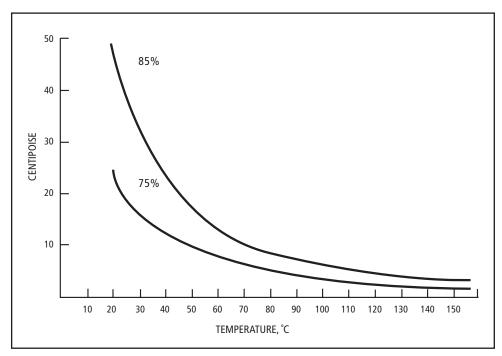


FIGURE 13B: Viscosity of 75% and 85% Phosphoric Acid versus Temperature

Kinematic Viscosity of Phosphoric Acid Solutions

Figure 14 gives approximate viscosity in centistokes of aqueous phosphoric acid solutions for a full range of concentrations and temperatures.

%								Temp	peratu	ıre, (°0	C.)							
H ₃ PO ₄	20 °	25°	30°	40 °	50 °	60°	70 °	80 °	90°	100°	110°	120°	130°	140°	150°	160°	170°	180
0	1.0	0.90	0.80	0.66	0.56	0.48	0.42	0.37	0.33	0.30								
5	1.1	0.99	0.89	0.74	0.63	0.54	0.47	0.42	0.37	0.33								
10	1.2	1.1	0.99	0.83	0.71	0.61	0.54	0.47	0.42	0.38								
15	1.4	1.2	1.1	0.94	0.81	0.69	0.61	0.53	0.47	0.43								
20	1.6	1.4	1.3	1.1	0.92	0.78	0.69	0.60	0.54	0.48								
25	1.8	1.6	1.5	1.2	1.0	0.89	0.79	0.69	0.61	0.55								
30	2.2	1.9	1.7	1.4	1.2	1.0	0.90	0.79	0.70	0.62								
35	2.6	2.2	2.0	1.6	1.3	1.1	1.0	0.90	0.79	0.71								
40	3.0	2.6	2.3	1.9	1.5	1.3	1.2	1.0	0.90	0.81								
45	3.6	3.1	2.7	2.2	1.8	1.5	1.3	1.2	1.0	0.92								
50	4.3	3.7	3.3	2.6	2.1	1.8	1.6	1.4	1.2	1.1								
55	5.3	4.5	4.0	3.2	2.5	2.1	1.9	1.6	1.4	1.2	1.1							
60	6.6	5.6	5.0	3.9	3.1	2.5	2.2	1.9	1.7	1.4	1.3							
65	8.4	6.8	6.2	4.9	3.8	3.1	2.6	2.3	2.0	1.7	1.5	1.4						
70	11	9.2	7.8	6.1	4.7	3.9	3.2	2.7	2.4	2.0	1.8	1.6						
75	15	12	10	7.8	5.9	4.8	3.9	3.3	2.8	2.4	2.1	1.9	1.7					
80	20	17	14	10	7.6	6.2	4.9	4.1	3.4	3.0	2.6	2.3	2.0	1.8				
85	28	23	19	14	10	8.1	6.3	5.1	4.2	3.8	3.2	2.8	2.4	2.2	1.9			
90	41	34	27	19	14	11	8.3	6.5	5.4	4.8	4.0	3.5	3.0	2.8	2.4	2.1		
95	68	55	42	30	20	15	12	8.7	7.3	6.2	5.2	4.4	3.8	3.3	3.0	2.6	2.3	2.1
100	140	100	81	53	36	25	19	14	11	9.2	7.7	6.2	5.2	4.5	4.1	3.5	3.2	2.9
105	600	440	330	173	110	70	50	33	25	19	15	12	9.6	8.0	7.1	6.0	5.2	4.5
110		2200	1600	810	410	270	170	100	67	50	38	29	22	18	15	13	10	8.8
115						1500	1000	600	380	250	190	120	99	68	54	41	34	28
118								2000	1200	830	550	400	320	210	170	130	107	87

Bichowsky & Rossini: "The Thermochemistry of the Chemical Substances." Reinhold Publishing Corp.

FIGURE 14: Viscosity in Centistokes of Phosphoric Acid for Various Concentrations and Temperatures

ANALYTICAL METHODS

Determination of H₃PO₄ by Specific Gravity

Method: ASTM E358

Principle

The specific gravity can be accurately related to the strength of orthophosphoric acid.

Apparatus

- 1. Hydrometer, streamline or torpedo design, precision grade for liquids heavier than water in ranges suitable to the acid strength of thermal orthophosphoric acid.
- 2. Thermometer.
- 3. Hydrometer cylinder, glass, with or without lip, diameter 30 to 40 mm, height 325 to 375 mm.

Procedures

- 1. Adjust the temperature of the sample to be tested to 20° to 30° C, thoroughly mix the sample and rinse a clean hydrometer cylinder with the sample.
- 2. Add the sample, and place the cylinder in a vertical position in a location free of air currents.
- 3. Grasp the top of the stem of a clean dry hydrometer between thumb and forefinger and slowly lower it into the center of the cylinder containing the sample. By sense of feel, gently release it just before it comes to rest. The free fall should be no more than 6 mm. No portion of the hydrometer should touch the cylinder.
- 4. The reading should not be taken until the liquid is free of any air bubbles and the hydrometer is at rest. In taking the reading, the eye should be placed slightly below the plane of the surface of the liquid and then raised slowly until this surface, seen as an ellipse, becomes a straight line. The point at which this line cuts the hydrometer scale should be taken as the reading.

Calculation

1. Determine acid strength opposite the appropriate specific gravity at 25° C/15.5° C in Table 2 (page 24) using the appropriate temperature coefficient factor in Table 1. (sp gr at T) + (T – 25) (temperature coefficient factor) = sp gr at 25° C/15.5° C

If the temperature of the determination is higher than 25° C, plus correction will result. If lower than 25° C, a minus correction will result.

H ₃ PO ₄	Solution, Temperature, °C							
Percent	15	25	40					
75	0.00074	0.00075	0.00076					
80	0.00076	0.00077	0.00078					
85	0.00078	0.00078	0.00080					

TABLE	1:	Specific	Gravity	Temperatur	e Coefficient

TABLE 2: Phosphoric Acid Solutions Specific Gravity Table based on ASTM Method E 358

Percent Percent Percent Percent /15.SC 74,00 53.95 1.564 80.71 58.46 1.637 74,50 53.96 1.569 80.80 58.52 1.638 74,60 54.03 1.570 80.89 58.59 1.639 74,80 54.11 1.571 81.00 58.66 1.640 74,80 54.25 1.573 81.21 58.82 1.643 75.01 54.33 1.576 81.52 59.04 1.646 75.31 54.46 1.576 81.52 59.04 1.646 75.31 54.66 1.580 81.79 59.33 1.687 75.60 54.76 1.581 82.19 59.42 1.653 75.60 55.05 1.585 82.31 59.62 1.654 76.60 55.48 1.592 82.49 59.44 1.657 76.13 55.42 1.591 82.79 59.90 1.666	H ₃ PO ₄	P ₂ O ₅	Sp. Gr. 25C	H ₃ PO ₄	P ₂ O ₅	Sp. Gr. 25C
74.50 52.96 1.569 80.80 98.52 1.639 74.50 54.03 1.570 80.89 98.59 1.639 74.80 54.11 1.571 81.00 58.66 1.640 74.80 54.25 1.573 81.21 58.82 1.643 75.01 54.33 1.575 81.39 58.95 1.645 75.20 54.46 1.576 81.52 59.04 1.646 75.31 54.54 1.578 81.61 59.11 1.647 75.40 54.61 1.579 81.70 59.17 1.643 75.50 54.76 1.581 81.92 59.33 1.651 75.70 54.83 1.582 82.00 59.39 1.652 75.90 54.97 1.584 82.18 59.52 1.655 76.00 55.05 1.585 82.31 59.62 1.656 76.42 55.35 1.590 82.79 59.99 1.661 76.60 55.48 1.592 82.88 59.81 1.662	Percent				Percent	
74.71 54.01 1.570 80.89 58.59 1.639 74.71 54.11 1.571 81.02 58.75 1.642 74.80 54.18 1.572 81.12 58.75 1.643 75.01 54.33 1.574 81.30 58.88 1.644 75.01 54.33 1.575 81.52 59.04 1.646 75.20 54.46 1.576 81.52 59.04 1.646 75.31 54.54 1.578 81.70 59.17 1.648 75.60 54.76 1.581 81.92 59.33 1.651 75.60 54.76 1.581 82.40 59.62 1.654 76.00 55.05 1.585 82.31 59.62 1.654 76.10 55.11 1.586 82.40 59.81 1.658 76.42 55.35 1.590 82.71 59.90 1.661 76.60 55.48 1.592 82.88 60.03 1.662 76.70 55.52 1.593 83.01 60.12 1.663		53.59		80.71		
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74.80 54.18 1.572 81.21 58.75 1.642 75.01 54.33 1.574 81.30 58.88 1.643 75.10 54.33 1.575 81.39 58.85 1.645 75.20 54.46 1.576 81.52 59.04 1.647 75.31 54.54 1.578 81.61 59.11 1.647 75.40 54.61 1.579 81.70 59.17 1.648 75.50 54.76 1.581 81.22 59.33 1.652 75.81 54.91 1.583 82.09 59.46 1.653 75.90 54.97 1.584 82.18 59.52 1.654 76.00 55.05 1.585 82.31 59.68 1.655 76.19 55.18 1.587 82.49 59.74 1.657 76.42 55.35 1.590 82.71 59.99 1.661 76.60 55.42 1.594 83.10 60.12 1.663 76.79 55.62 1.594 83.10 60.12 1.663		54.03	1.570		58.59	
74.90 54.25 1.573 81.21 58.82 1.643 75.01 54.33 1.575 81.39 58.95 1.646 75.20 54.46 1.576 81.52 59.04 1.646 75.31 54.54 1.576 81.52 59.04 1.646 75.31 54.54 1.578 81.61 59.11 1.648 75.50 54.76 1.580 81.78 59.23 1.651 75.70 54.83 1.582 82.00 59.39 1.652 75.80 54.97 1.584 82.18 59.52 1.655 76.10 55.05 1.585 82.31 59.62 1.655 76.10 55.11 1.587 82.44 59.68 1.656 76.10 55.18 1.587 82.44 59.68 1.656 76.10 55.18 1.587 82.44 59.68 1.656 76.10 55.18 1.587 82.44 59.68 1.656 76.63 55.28 1.589 82.29 59.97 1.661 76.65 55.42 1.591 82.79 59.97 1.661 76.63 55.78 1.595 83.19 60.25 1.662 76.79 55.62 1.593 83.40 60.41 1.664 77.29 55.99 1.599 83.40 60.47 1.667 77.11 55.85 1.597 83.40 60.45 1.677 77.79 56.64 1		54.11	1.571	81.00	58.66	1.640
75.01 54.33 1.575 81.39 58.88 1.644 75.10 54.39 1.575 81.52 59.04 1.645 75.31 54.54 1.576 81.52 59.04 1.647 75.40 54.64 1.579 81.70 59.17 1.648 75.51 54.69 1.580 81.78 59.23 1.649 75.60 54.76 1.581 81.92 59.33 1.651 75.60 54.97 1.584 82.18 59.52 1.654 75.60 54.97 1.584 82.18 59.52 1.654 76.00 55.05 1.586 82.40 39.62 1.655 76.10 55.11 1.586 82.40 39.74 1.657 76.33 55.28 1.589 82.48 59.31 1.660 76.70 55.55 1.593 83.01 60.12 1.666 76.70 55.55 1.593 83.40 60.41 1.666 77.20 55.91 1.595 83.19 60.25 1.666						
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Determination of H₃PO₄ by Molybdovanadate Method

Principle

In a dilute orthophosphate solution, ammonium molybdate reacts under acid conditions to form a heteropoly acid, molybdophosphoric acid. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow color is proportional to the phosphate concentration.

Reagents

Molybdovanadate Reagent:

- 1. Solution A dissolve 40 g ammonium molybdate tetrahydrate in 400 ml hot water and cool to room temperature.
- 2. Solution B dissolve 2 g ammonium metavanadate in 250 ml hot deionized water. Cool to room temperature and add 330 ml of concentrated (36%) hydrochloric acid. Cool to room temperature.
- 3. Stirring constantly, slowly add Solution A to Solution B. Dilute to 2 liters with deionized water.

Standard Phosphate Solution — Dissolve 0.3835 g reagent grade KH_2PO_4 (dried at 105° C for 2 hours) in deionized water and dilute to 500 ml. This solution contains 0.4 mg P_2O_5/ml . Make up weekly.

Special Apparatus

Visible Spectrophotometer.

Analytical Procedure

- 1. Turn spectrophotometer on, set the wavelength to 420 nm, and allow to warm up for the recommended period.
- 2. Weigh approximately 0.1 g of sample into a 100 ml volumetric flask. Record the weight (W) to the nearest 0.1 mg. Dilute to the mark with deionized water.
- 3. Pipet a 5 ml aliquot of above solution into a 100 ml flask. Add 40 ml of deionized water and, from a pipet, 20.0 ml of molybdovanadate reagent. Dilute to the mark with deionized water, mix well.
- 4. With each set of samples, a reagent blank and a phosphate standard must be run. They are prepared as follows:
 - a. Blank: Pipet 20 ml of molybdovanadate reagent into a 100 ml volumetric flask and dilute to the mark with deionized water. Mix well.
 - b. Standard: Pipet 5 ml of $0.4 \text{ mg P}_2O_5/\text{ml}$ standard phosphate solution into a 100 ml volumetric flask. Add 40 ml of deionized water, pipet 20 ml of molybdovanadate reagent and dilute to the mark with deionized water. Mix well.
- 5. Allow all samples, including the reagent blank and phosphate standard, to stand for 10 minutes.
- 6. When the spectrophotometer has warmed up, adjust the zero to read infinite absorbance. Place the blank in the spectrophotometer and adjust the light control to read 0 on the absorbance scale or display.
- 7. Place standard in the spectrophotometer and read the absorbance (A_{STD}) .
- 8. Place the sample in the spectrophotometer and read the absorbance (A_{SPL}). Calculate the % P_2O_5 or the % H_3PO_4 as shown in the calculation section.

Calculation

Weight % $P_2O_5 = 4 \bullet A_{SPL}$ A_{STD} (Sample Wt.)

Weight % $H_3PO_4 = \% P_2O_5 \times 1.3807$

- NOTE 1. HCIO₄, or HNO₃ can be substituted for HCl. A final acid concentration of about 0.5 N is recommended. See Note 2 for HCIO₄ precautions.
- NOTE 2. Concentrated perchloric acid is an extremely strong acid and an extremely strong oxidizer. Contact with natural rubber or any other organic materials may cause a violent explosion. It must be stored away from heat and other materials. Never let any sample containing perchloric acid evaporate to dryness.

Determination of H₃PO₄ by Thymolphthalein Titration

Reagents

- 1. Thymolphthalein Indicator: Dissolve 0.10 g of thymolphthalein in 100 ml of methyl alcohol.
- 2. Sodium Hydroxide, 1.0 N: Standardized Titration Reagent.

Procedure

- 1. Accurately weigh 1 ml (1.6 to 1.8 g) of the sample into a beaker. Add 120 ml of distilled or deionized water. Stir.
- 2. Add 0.5 ml of thymolphthalein indicator solution.
- 3. Titrate with 1 N sodium hydroxide (NaOH) to the first appearance of a blue color.

Calculation

$$\% H_3PO_4 = \frac{\text{ml NaOH x 4.900}}{\text{Sample Wt.}}$$

ENDNOTES

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