

Phosphoric Acid

Handling/Processing

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Identification of Petitioned Substance

3 **Chemical Names:**

4 Phosphoric acid
5 Orthophosphoric acid
6 Polyphosphoric acids
7 Metaphosphoric acid

CAS Numbers:

Phosphoric acid/orthophosphoric acid: 7664-38-2
Pyrophosphoric acid: 2466-09-3
Triphosphoric acid: 10380-08-2
Metaphosphoric acid: 37267-86-0
Polyphosphoric acid: 8017-16-1

9 **Other Name:**

10 Phosphoric (V) acid
11 Pyrophosphoric acid
12 Tripolyphosphoric acid
13 Triphosphoric acid

Other Codes:

EC No. (orthophosphoric acid): 231-011-00-6
EC No. (pyrophosphoric acid): 219-574-0
EC No. (triphosphoric acid): 233-840-3
EC No. (metaphosphoric acid): 253-433-4
EC No. (polyphosphoric acid): 232-417-0

15 **Trade Names:**

16 Phosphoric acid solution

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Summary of Petitioned Use

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20 In 2019, Kemin Food Technologies petitioned the United States Department of Agriculture (USDA)
21 National Organic Program (NOP) to amend the existing annotation of phosphoric acid on the National List
22 to include use as a synthetic substance for organic processing and handling (USDA 2019, USDA 2020a,
23 USDA 2020b). This new petition requests the expansion of the use of phosphoric acid “as an acidifier to
24 adjust pH of an extraction solvent to extract antioxidants or other target molecules from *lamiaceae* plants,
25 provided the amount of acid used shall not exceed the minimum needed to lower pH to 2.5” (USDA
26 2020b). In response to the petition by Kemin Food Technologies, the NOSB Materials Subcommittee has
27 requested a technical report focused on the use of phosphoric acid for pH adjustment in the extraction of
28 target compounds from aquatic plants for organic processing and handling.

29

30 In 2002, Aquatic Seaplants Limited petitioned the USDA NOP to expand the approved use of phosphoric
31 acid within the National List to include production of organic aquatic plant extracts (USDA 2002). A
32 technical report on phosphoric acid for organic processing was submitted in 2003 (USDA 2003). In 2004 the
33 NOP contacted the petitioner and stated that phosphoric acid did not need to be petitioned for use in plant
34 extraction “because its use as a pH adjuster in aquatic plant extracts is currently not prohibited through the
35 inclusion of “aquatic plant extracts” in section 205.601(j)(1) of the National Organic Standards” (NOP 2013).
36 In 2013 the NOP sent a memorandum to the National Organic Standards Board (NOSB) requesting a
37 review on the use of phosphoric acid in plant extracts to ensure that this use is consistent with the context
38 to the National List (NOP 2013).

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Characterization of Petitioned Substance

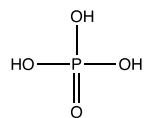
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42 **Composition of the Substance:**

43 Orthophosphoric acid is the most common phosphoric acid used in plant extraction applications and is also
44 generically referred to as phosphoric acid (Silberberg 2003, USDA 2003, Shriver and Atkins 2008, Timberlake
45 2016). Due to the predominance of orthophosphoric acid among the many forms of phosphoric acid, the term
46 phosphoric acid will be used to describe orthophosphoric acid throughout the remainder of this report, unless
47 otherwise stated.

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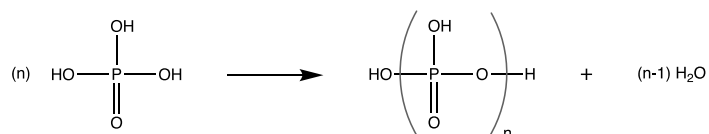
49 Phosphoric acid describes several different substances, all of which feature a tetrahedral phosphorous (V) atom
 50 surrounded by oxygen atoms (Shriver and Atkins 2008, Gilmour 2019). Phosphoric acid and phosphate
 51 compounds are often characterized based on their P₂O₅ content, which is based on the empirical formula of
 52 molecular phosphorus (V) oxide (P₄O₁₀) (Shriver and Atkins 2008, Gilmour 2019). Phosphoric acid may take the
 53 form of a single phosphorous atom as orthophosphoric acid (H₃PO₄), as shown in Figure 1.
 54



orthophosphoric acid

Figure 1

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 59 Phosphoric acid molecules polymerize via dehydration to form a variety of polymeric phosphoric acids, known
 60 generally as polyphosphoric acids, as shown below in Equation 1 (Shriver and Atkins 2008, Gilmour 2019).
 61 Polyphosphoric acids are linked together through phosphoester linkages (P - O - P bond arrangements), as
 62 shown below in Figure 2 (Silberberg 2003, Shriver and Atkins 2008, Timberlake 2016, Gilmour 2019).
 63 Pyrophosphoric acid (H₄P₂O₇), formed through the polymerization of two phosphoric acid monomers, and
 64 triphosphoric acid (H₅P₃O₁₀), formed through the polymerization of three phosphoric acid monomers, are
 65 common polyphosphoric acids and are shown below in Figure 2. In addition to linear polymers, phosphoric acid
 66 monomers may combine to form cyclic structures (Gilmour 2019). Metaphosphoric acid is the tri-cyclic form of
 67 phosphoric acid (H₃P₃O₉, although it is often listed by its empirical formula, H₃PO₄), shown below in Figure 2,
 68 however, the term metaphosphoric acid has also been applied generally to describe cyclic phosphoric acids
 69 (Shriver and Atkins 2008, Gilmour 2019, SA 2020a).
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Equation 1

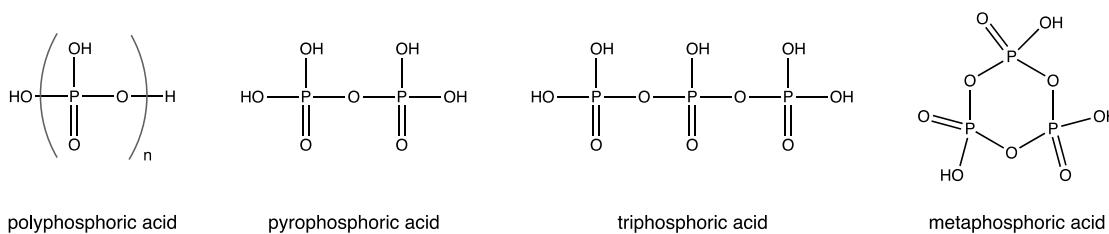


Figure 2

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 79 The composition and form of phosphoric acid is dependent on its concentration in solution, as described in the
 80 plot below in Figure 3 (Gilmour 2019). At relatively low concentrations of H₃PO₄ (~94%, [68% P₂O₅])
 81 orthophosphoric acid is the predominant form. However, as the concentration of H₃PO₄ increases,
 82 polymerization to polyphosphoric acids becomes more prevalent, and the condensed forms of phosphoric acid
 83 become the majority of the species in solution (Gilmour 2019). The P₂O₅ content of phosphoric acid dictates its
 84 physical properties, including appearance, viscosity, and boiling point. Phosphoric acid exists as an oily
 85 substance with P₂O₅ concentration between 72 and 82%. It becomes more viscous with P₂O₅ composition from 82
 86 to 90%. It solidifies when P₂O₅ composition exceeds 90% (Gilmour 2019).
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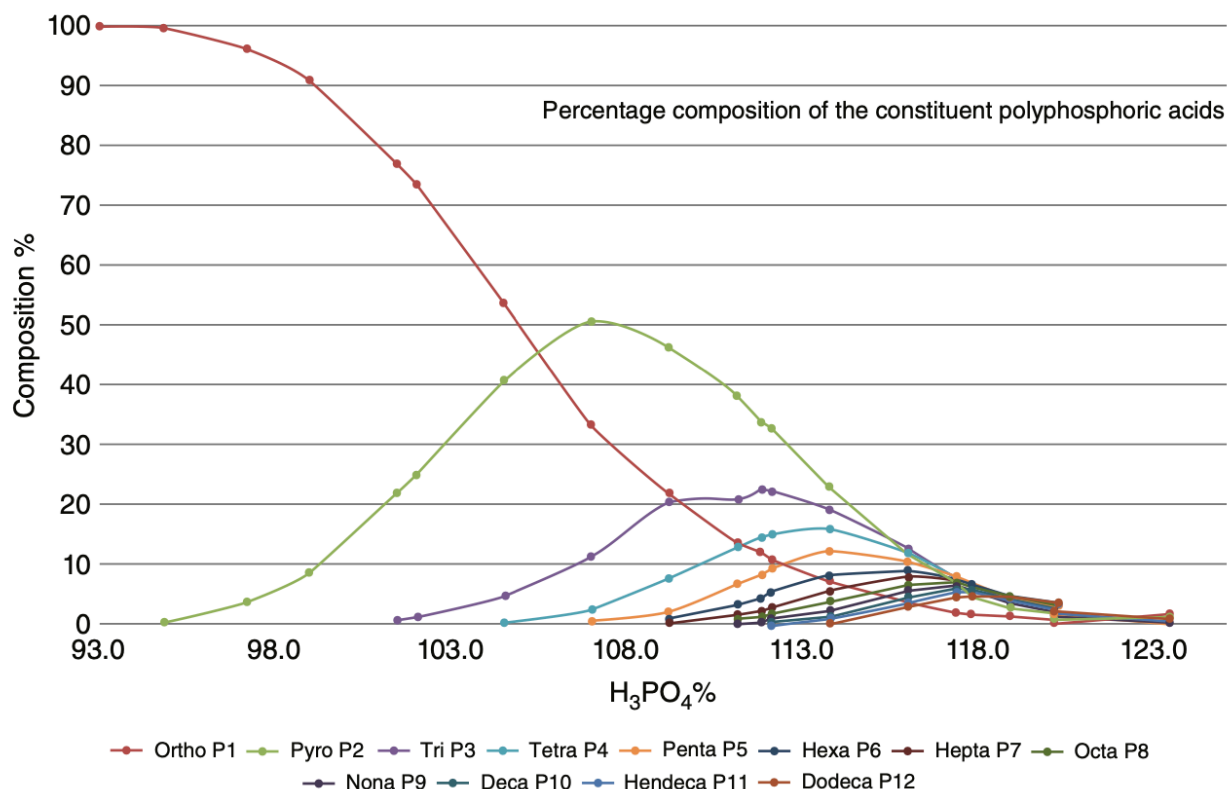
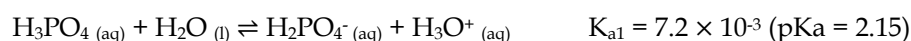
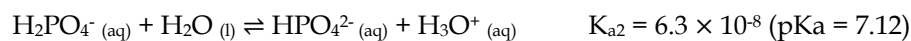


Figure 3

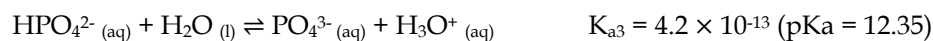
All phosphoric acids are weak inorganic acids that are polyprotic (capable of producing multiple acidic units [H⁺]) (Silberberg 2003, Shriver and Atkins 2008, Timberlake 2016, Kalka 2021). The classification of phosphoric acid as a weak acid is based on its incomplete ionization in water, however, concentrated phosphoric acid is a highly acidic and corrosive substance (Silberberg 2003, Shriver and Atkins 2008). Pure phosphoric acid is a solid, although most phosphoric acid exists as an aqueous solution (PC 983, PC 1004, PC 1023, PC 3084658, Gilmour 2019, SA 2020a, SA 2020b, SA 2020c, SA 2021). The acidic nature of phosphoric acid results in its reaction with water in aqueous solutions to produce phosphate ions (see Equations 2-4) (Silberberg 2003, Shriver and Atkins 2008, Timberlake 2016, Kalka 2021). The multiple equilibria for these acid-base reactions are illustrated with the three ionization reactions possible for phosphoric acid, along with their equilibrium constants (K_a) and their relative strengths (pK_a), shown below in Equations 2 - 4 (Silberberg 2003, Shriver and Atkins 2008, Timberlake 2016, Kalka 2021). As with all polyprotic acids, the initial dissociation is the most favorable, with subsequent compounds being less acidic (i.e., acid strength H₃PO₄ > H₂PO₄⁻ > HPO₄²⁻), as shown with the decreasing equilibrium constants and increasing pK_a values in Equations 2 - 4 (Silberberg 2003, Shriver and Atkins 2008, Timberlake 2016, Kalka 2021).



Equation 2

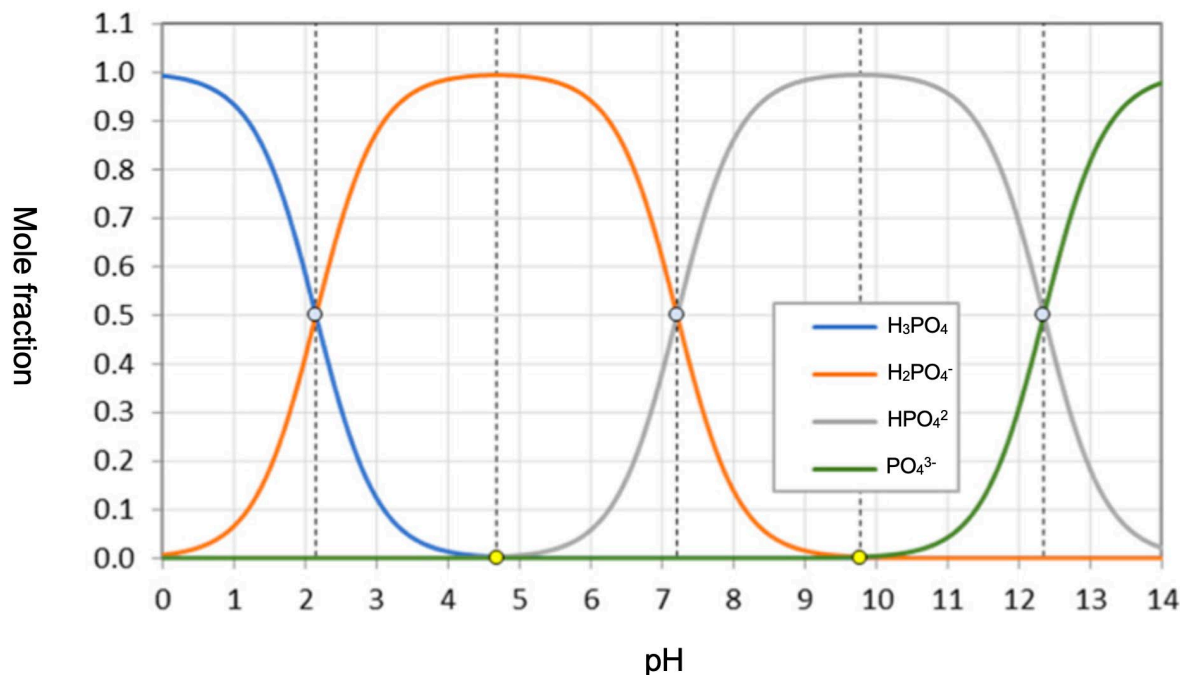


Equation 3



Equation 4

119 The reversible nature of the ionization of phosphoric acid in aqueous solution causes the formation of multiple
 120 buffer systems, based on the equilibrium constants for each reaction. The buffer systems prevent dramatic
 121 changes to the pH of the solution upon addition of either acid or base and are effective when the concentration of
 122 weak acid and conjugate base are within ten times the other (for example, H_3PO_4 and H_2PO_4^- in Equation 1)
 123 (Silberberg 2003, Kalka 2021). The specific composition of phosphoric acid is dependent on the pH of the
 124 solution, as illustrated by the speciation diagram for orthophosphoric acid shown below in Figure 4 (Kalka 2021).
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126
 127 **Figure 4**
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129 The pH of any of the buffer systems can be calculated by applying the Henderson-Hasselbalch equation, shown
 130 below in Equation 5 (Silberberg 2003, Kalka 2021). The intersection of conjugate acid/conjugate base pairs occurs
 131 when the species have equal concentrations, at which point the pH of the solution is equal to the pKa of the acid
 132 (shown in Equations 2 - 4) (Silberberg 2003, Kalka 2021).
 133

$$134 \quad pH = pKa + \log \frac{[conjugate\ base]}{[conjugate\ acid]}$$

135
 136 **Equation 5**
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138 **Source or Origin of the Substance:**

139 Phosphoric acid is a substance that does not exist in nature but rather is produced from mineral sources in
 140 the wet process or elemental phosphorous in the thermal process (EPA 1995, Shriver and Atkins 2008,
 141 Gilmour 2019). The majority of wet process phosphoric acid (~85-90%) is used for the production of
 142 fertilizers for conventional agriculture (Shriver and Atkins 2008).
 143

144 Historically, most high-purity technical and food grade phosphoric acid is produced through the thermal
 145 process to eliminate mineral impurities in the final composition (EPA 1995, Shriver and Atkins 2008).
 146 However, due to the expensive nature of the thermal process, there has been continued development of
 147 purification methods for wet process phosphoric acid (Shlewitt and Alibrahim 2008, Gilmour 2019). The
 148 advances in phosphoric acid purification methods have made wet process the predominant method for the
 149 production of technical and food grade phosphoric acid (Shlewitt and Alibrahim 2008, Jin et al.. 2014,
 150 Gilmour 2019, Haghani and Daneshpazhuh 2020).
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Properties of the Substance:

All forms of phosphoric acid are weak polyprotic inorganic acids (Shriver and Atkins 2008, Gilmour 2019). As discussed above in the “Composition of the Substance” section, phosphoric acids are capable of forming buffered solutions, and may exist as a mixture of phosphoric acid and phosphate species. General properties for common phosphoric acids are described below in Table 1.

Table 1. Properties of phosphoric acids

Property	Orthophosphoric acid	Pyrophosphoric acid	Triphosphoric acid	Metaphosphoric acid	Polyphosphoric acid
Chemical formula	H ₃ PO ₄	H ₄ P ₂ O ₇	H ₅ P ₃ O ₁₀	H ₃ PO ₄	H _{n+2} P _n O _{3n+1}
CAS No.	7664-38-2	2466-09-3	10380-08-2	37267-86-0	8017-16-1
Molecular weight	79.97 g/mol	177.98 g/mol	257.96 g/mol	79.97 g/mol	N/A
Appearance	Clear liquid, solid	Colorless solid	Solid	Solid chips	Liquid
Water solubility	98 g/L at 20 °C	No data listed	No data listed		
Melting point	40 - 42.4 °C	61 - 63 °C			
Boiling point	158 °C	No data listed			
Relative density	1.685 g/cm ³	No data listed			

161 Sources: PC 983, PC 1004, PC 1023, PC 3084658, SA 2020a, SA 2020b, SA 2020c, SA 2021.

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Specific Uses of the Substance:

Phosphoric acid is used in organic handling and processing as a cleaning agent for “food contact surfaces and equipment,” as described in 7 CFR 205.605. Phosphoric acid has been approved for pH adjustment of some soil amendments and as an equipment cleaner in both organic crop and livestock production. (7 CFR 205.601 and §205.603).

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In addition to its appearance in 7 CFR 205.605, phosphoric acid has been used as an ingredient in plant extractions, as described above in “Summary of Petitioned Use” (USDA 2002, USDA 2019, USDA 2020a, USDA 2020b). When used in this manner, phosphoric acid acts as an acidifying agent and stabilizer to facilitate more efficient extraction of target compounds (Yoon et al. 2020).

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In addition to organic applications, phosphoric acid is a widely-used substance in conventional agriculture, with approximately 90% of wet process phosphoric acid used in the production of fertilizers (Shriver and Atkins 2008). Phosphoric acid has uses in food and beverage processing as a pH adjuster, flavor ingredient, and processing agent in dairy products (Wolke 2002, Gilmour 2019). Phosphoric acid is also a precursor to synthetic phosphates, which have a variety of uses including as fertilizers, surfactants, and detergents (Shriver and Atkins 2008).

Approved Legal Uses of the Substance:

181 Phosphoric is listed in the USDA organic regulations, with approved uses for crop and livestock and
182 processing applications in 7 CFR 205. Phosphoric acid is listed as a “nonagricultural (nonorganic)
183 substance allowed as [an] ingredient in or on processed products labeled as “organic” or “made with
184 organic,”” and may be used for the “cleaning of food-contact surfaces and equipment only” in 7 CFR
185 205.605. Phosphoric acid is listed as a “synthetic substance allowed for use in organic livestock production
186 as an equipment cleaner, provided that no direct contact with organically managed livestock or land
187 occurs” in 7 CFR 205.603.
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Phosphoric acid is listed as a “synthetic substance allowed for use in organic crop production” as a pH adjustment for soil amendments in 7 CFR 205.601. Specifically, phosphoric acid can be used to adjust the pH of “liquid fish products,” and “squid byproducts—from food waste processing only,” with the stipulation that “the amount of acid used shall not exceed the minimum needed to lower the pH to 3.5.”

195 The USDA has listed phosphoric acid as an “antioxidant synergist” for the “processing and packaging [of]
196 butter and related products” in 7 CFR 58.305.
197

198 The United States Food and Drug Administration (FDA) has designated phosphoric acid to be generally
199 recognized as safe (GRAS) for several uses. Phosphoric acid is listed as a “multiple purpose GRAS food
200 substance” in 21 CFR 182.1073, and as a GRAS “general purpose food additive” in §582.1073. Additionally,
201 the FDA lists phosphoric acid as a substance used in the production of the GRAS substances monobasic
202 ammonium phosphate in §184.1141, dibasic ammonium phosphate in §184.1141, magnesium phosphate in
203 §184.1366, and hydrogen peroxide in §184.1366.

204
205 The FDA has approved phosphoric acid as a component for the production of the food polymer
206 polydextrose in 21 CFR 172.841.

207
208 The FDA has approved the use of phosphoric acid as an acidifying agent in dairy products, including:

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- 210 • acidified milk in §131.111
- 211 • cold pack-cheese and club cheese “in such quantity that the pH of the finished cold-pack cheese is
212 not below 4.5” in §133.123 and §133.124
- 213 • dry curd cottage cheese to facilitate curd formation in cottage cheese and “reach a pH of between
214 4.5 and 4.7” in §133.129
- 215 • pasteurized process cheese “in such quantity that the pH of the pasteurized process cheese is not
216 below 5.3” in §133.169
- 217 • pasteurized process cheese food “in such quantity that the pH of the pasteurized process cheese is
218 not below 5.0” in §133.173
- 219 • pasteurized Neufchatel cheese spread with other foods in §133.178
- 220 • pasteurized process cheese spread “in such quantity that the pH of the pasteurized process cheese
221 is not below 4.0” in §133.179
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223 The FDA has approved the use of phosphoric acid as a neutralizing agent in cacao products, including:

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- 225 • cacao nibs, with the stipulation that “for each 100 parts by weight of cacao nibs, used as such, or
226 before shelling from the cacao beans, the total quantity of phosphoric acid used is not greater than
227 0.5 part by weight, expressed as P₂O₅” in §163.110
- 228 • chocolate liquor in §163.111
- 229 • breakfast cacao in §163.112
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231 The FDA has approved the use of phosphoric acid in the formulation of “color additives exempt from
232 certification,” including:

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- 234 • caramel “to assist caramelization, in amounts consistent with good manufacturing practice” in
235 §73.85
- 236 • silver “prepared by the reaction of silver nitrate with ferrous sulfate in the presence of phosphoric
237 acid” in §73.2500
- 238 • manganese violet “obtained by reacting phosphoric acid, ammonium dihydrogen orthophosphate,
239 and manganese dioxide at temperatures above 450 °F” in §73.2775
- 240

241 The FDA has approved phosphoric acid as a component of sanitizing solutions in 21 CFR 178.1010.
242 Phosphoric acid triesters with ethylene glycol have been approved as an “antioxidant and/or stabilizer for
243 polymers” in §178.2010. Phosphoric acid has been approved as a reactant in the production of industrial
244 starch-modified articles “for use in producing, manufacturing, packing, processing, preparing, treating,
245 packaging, transporting, or holding food” in 21 CFR 178.3520. Phosphoric acid has been approved as a
246 “miscellaneous material” of resinous and polymeric coatings in 21 CFR 175.300. Phosphoric acid is
247 approved for use as an adjuvant in resin-bonded filters in 21 CFR 177.2260.

248
249 The FDA has approved phosphoric acid as a component of treatment rinses in anticaries active ingredients
250 and anticaries drug products in 21 CFR 355.10 and §310.545.

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252 The FDA has approved the use of phosphoric acid for the production of food additives for animal feeds,
253 including:

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- 255 • for the hydrolysis of meat byproduct in the production of “condensed animal protein hydrolysate,”
256 in §573.200
- 257 • for the production of diammonium phosphate when neutralized with ammonia in §573.320
- 258 • as a “free-choice feed” ingredient in fenbendazole when included as “phosphoric acid 75% (feed
259 grade)” up to 2.00 percent in §558.258.
- 260 • as a “ruminant free-choice liquid Type C feed” ingredient in lasalocid when included as
261 “phosphoric acid (54%)” up to 3.0 percent in §558.311.
- 262

263 The United States Environmental Protection Agency (EPA) has identified phosphoric acid as an “inert
264 ingredient used pre- and post-harvest [with an] exemption from the requirement of a tolerance” when used
265 as a buffer in 21 CFR 180.910. The EPA has identified phosphoric acid as an ingredient “in an antimicrobial
266 pesticide formulation that may be applied to dairy processing equipment and food-processing equipment
267 and utensils” without limitation in 40 CFR 180.940.

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269 The EPA has designated phosphoric acid and orthophosphoric acid as a hazardous substance in 40 CFR
270 116.4 and §302.4, with a final reportable quantity of 5000 pounds or 2270 kg. The EPA has listed wastes
271 generated from process wastewater and phosphogypsum from phosphoric acid production as “solid
272 waste” in 40 CFR 261.4

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274 The EPA limits the pollutant content of process and non-process wastewater from phosphoric acid
275 production to the levels shown in Table 2 below, as stipulated in 40 CFR 418.12, §418.13, §418.15, §422.52,
276 §422.53, and §422.55

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278 **Table 2. Effluent limitations for wastewater from phosphoric acid production**

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Effluent characteristic	Maximum for any 1 day	Average of daily values for 30 consecutive days shall not exceed –
Total phosphorus (as P)	105	35
Fluoride	75	25
TSS [total suspended solids]	150 (process wastewater only)	50 (process wastewater only)
pH	6.0 to 9.5	6.0 to 9.5

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281 The United States Occupational Safety and Health Administration (OSHA) has listed phosphoric acid as an
282 air contaminant with a maximum concentration of 1 mg/m³ in 29 CFR 1910.1000.

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284 **Action of the Substance:**

285 When used for plant extractions, phosphoric acid facilitates the extraction of target molecules by lowering
286 the pH of solution and stabilizing target molecules against decomposition. The acidic nature of phosphoric
287 acid results in its ability to lower the pH of solutions used for extractions. By changing the pH of the
288 extraction solution, the solubility of acidic and basic compounds can be manipulated to improve their
289 solubility in the extraction solvent (Pavia et al. 1995). The acidic pH produced by the addition of
290 phosphoric acid to extraction mixtures will result in the protonation of basic functional groups (e.g.,
291 amines), increasing the net charge of target molecules and increasing their solubility in polar solvents
292 (Pavia et al. 1995, Silberberg 2003, Albuquerque et al. 2005, Nicoué et al. 2007, Dai and Mumper 2010,
293 Timberlake 2016).

294

295 The ability to protonate functional groups is dependent on the strength of the specific acid, described by
296 the acid pKa value (lower pKa = stronger acid) (Silberberg 2003, Shriver and Atkins 2008, Kalka 2021). The
297 relatively high strength of phosphoric acid (pKa₁ = 2.15) allows for an environment that is sufficiently
298 acidic to ensure that carboxylic acid groups (pKa ≈ 5) remain protonated and neutrally charged (Silberberg
299 2003, Timberlake 2016). The manipulation of the molecular charge of target compounds enhances their
300 extraction from solid or liquified plant material (Porter and Lodge 2021). Acidic solutions also improve the

301 extraction of some molecules as the acid is able to degrade cell walls, lignin, cellulose and other structural
302 components, improving the accessibility of target molecules. (Revilla et al. 1998, Albuquerque et al. 2005,
303 Dai and Mumper 2010, Zeng et al. 2014, Yao et al. 2017).

304
305 In addition to changing the charge and solubility profile for target compounds, phosphoric acid also acts as
306 a stabilizer in extraction processes. The stabilizing nature of phosphoric acid is possible through two main
307 mechanisms. One mechanism is connected to the manipulation of charge and solubility as discussed in the
308 paragraph above. Some compounds are less susceptible to decomposition in charged states (Revilla et al.
309 1998, Nicoué et al. 2007, Dai and Mumper 2010, Porter and Lodge 2021). The improved stability of some
310 salts in comparison to their related neutral compounds is commonly used to protect amines and other
311 sensitive compounds from undesired reactions (Albuquerque et al. 2005, Nicoué et al. 2007). Additionally,
312 the acidic pH established by phosphoric acid may denature plant proteins and oxidizing enzymes,
313 preventing the oxidation of antioxidants and other sensitive target compounds (Nicoué et al. 2007, Dai and
314 Mumper 2010, Timberlake 2016, Porter and Lodge 2021).

315
316 **Combinations of the Substance:**
317 When used as an ingredient for plant extractions, phosphoric acid is combined with the extraction solvent.
318 The solvent varies dependent on the plant and target molecule, but common extraction solvents include
319 water, alcohols (e.g., methanol, ethanol, isopropanol, etc.), and ketones (e.g., acetone) (Nicoué et al. 2007,
320 Dai and Mumper 2010, Yoon et al. 2020).

321

Status

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323
324 **Historic Use:**

325 Phosphoric acid has been historically used in organic agriculture production as a cleaner and pH adjuster.
326 Phosphoric acid has been historically used in fertilizer and animal feed production within conventional
327 agriculture. Fertilizer production continues to be the most prominent application of phosphoric acid
328 (Shriver and Atkins 2008, Gilmour 2019). Additionally, phosphoric acid has been used as a pH adjuster and
329 flavoring ingredient in food and beverage production, and as an industrial cleaner and source of phosphate
330 detergents in many industries, including textiles, laundry, and dishwasher applications (Flomenbaum et al.
331 2002, Wolke 2002, Shriver and Atkins 2008).

332

333 **Organic Foods Production Act, USDA Final Rule:**

334 Phosphoric acid is not listed in the Organic Foods Production Act of 1990 (OFPA). However, phosphoric
335 acid is listed in the USDA organic regulations, with approved uses for crop and livestock and processing
336 applications in 7 CFR Part 205. Phosphoric acid may be used for the “cleaning of food-contact surfaces and
337 equipment only” in 7 CFR 205.605. Phosphoric acid can be used to adjust the pH of “liquid fish products,”
338 and “squid byproducts—from food waste processing only,” with the stipulation that “the amount of acid
339 used shall not exceed the minimum needed to lower the pH to 3.5” in 7 CFR 205.601. Phosphoric acid is
340 listed as a “synthetic substance allowed for use in organic livestock production as an equipment cleaner,
341 provided that no direct contact with organically managed livestock or land occurs” in 7 CFR 205.603.

342

343 **International**

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345 **Canada, Canadian General Standards Board – CAN/CGSB-32.311-2015, Organic Production Systems**
346 **Permitted Substances List**

347 Phosphoric acid is listed in the Organic Production Systems Permitted Substances List as an approved
348 substance for pH adjustment of “fish meal, fish powder, fish wastes, hydrolysate, emulsions and solubles”
349 that are used for “soil amendments and crop nutrition.” Phosphoric acid is also listed as a “cleaner,
350 disinfectant and sanitizer permitted on organic product contact surfaces for which a removal event is
351 mandatory [for use] on dairy equipment.”

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353 **CODEX Alimentarius Commission – Guidelines for the Production, Processing, Labelling and**
354 **Marketing of Organically Produced Foods (GL 32-1999)**

355 Phosphoric acid is not listed in the CODEX.

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European Economic Community (EEC) Council Regulation – EC No. 834/2007 and 889/2008

Phosphoric acid is not listed in EC No. 834/2007 or EC No. 889/2008.

Japan Agricultural Standard (JAS) for Organic Production

Phosphoric acid is not listed in the JAS.

International Federation of Organic Agriculture Movements (IFOAM)

Phosphoric acid is listed in the IFOAM NORMS for organic production and processing as an “equipment cleanser and equipment disinfectant only for dairy equipment,” and as a “substance for pest and disease control and disinfection in livestock housing and equipment [for] dairy equipment.”

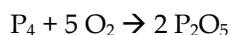
Evaluation Questions for Substances to be used in Organic Handling

Evaluation Question #1: Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).

Phosphoric acid is produced through two methods, the wet process and the thermal process (EPA 1995, Gilmour 2019, Haghani and Daneshpazhuh 2020). Historically, the end-point use for the phosphoric acid was determined by its production method. High purity, technical and food grade phosphoric acid was produced by the thermal process (EPA 1995, Gilmour 2019). Lower purity phosphoric acid, primarily used in animal feed and fertilizer applications, was produced by the wet process (EPA 1995, Shriver and Atkins 2008, Gilmour 2019). Due to the expensive nature of the thermal process, there has been continued development of purification methods for wet process phosphoric acid, which now serve as the predominant method for the production of technical and food grade phosphoric acid (Gilmour 2019).

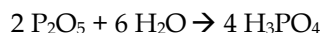
Thermal process

The thermal process is broken down into three major steps: combustion, hydration, and demisting (collection) (EPA 1995, Gilmour 2019). In the combustion step, elemental yellow phosphorus (P_4) is reacted with oxygen gas, which oxidizes the phosphorous from its 0 to V oxidation state, as shown below in Equation 6 (EPA 1995, Gilmour 2019). The heat of combustion for phosphorus is highly endothermic and the reaction must be carried out at high temperatures (1650 – 2760 °C) (EPA 1995, Gilmour 2019).



Equation 6

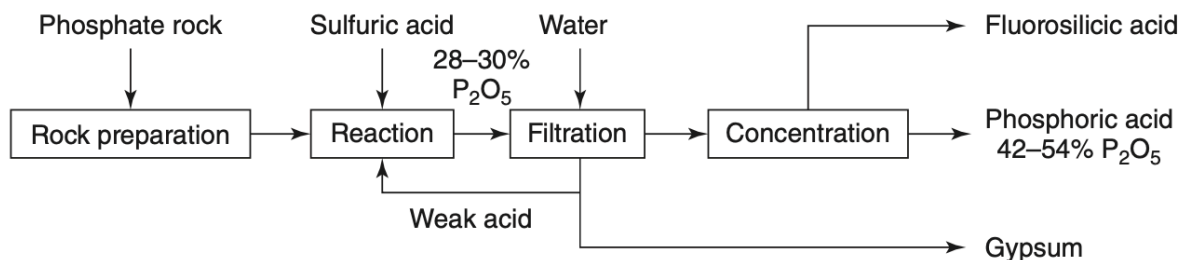
Once the elemental phosphorus is oxidized to P_2O_5 , it undergoes the hydration process to form orthophosphoric acid, as shown below in Equation 7 (EPA 1995, Gilmour 2019). In this process P_2O_5 is generally reacted with water, although in some cases dilute solutions of phosphoric acid are used instead of water alone (EPA 1995). Once phosphoric acid has been produced, it is isolated in the demisting process. In this step, phosphoric acid is collected as a mist with high-pressure drop demisters. The thermal process produces phosphoric acid with P_2O_5 concentrations between 54 and 62%, which are sufficiently pure for use in technical and food grade applications (EPA 1995, Gilmour 2019).



Equation 7

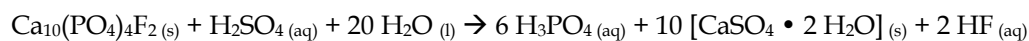
Wet Process

411 The wet process produces phosphoric acid from naturally occurring phosphate mineral sources
 412 (fluorapatite [Ca₁₀(PO₄)₆F₂] and hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂]) (EPA 1995, Shriver and Atkins 2008,
 413 Gilmour 2019, Haghani and Daneshpazhuh 2020). Once mined, these minerals are converted to phosphoric
 414 acid in four main steps, as outlined in Figure 5 below (Gilmour 2019). The phosphate rock is prepped in the
 415 initial step by being milled and ground to increase its surface area (EPA 1995, Haghani and Daneshpazhuh
 416 2020).
 417



418
 419
 420 **Figure 5**
 421

422 Once milled, the mineral phosphates are reacted with a strong mineral acid and converted to phosphoric
 423 acid, as shown in Equation 8 below (EPA 1995, Shriver and Atkins 2008, Gilmour 2019, Haghani and
 424 Daneshpazhuh 2020). While sulfuric acid is shown in both Figure 5 and Equation 8, other strong mineral
 425 acids (e.g., nitric acid [HNO₃] and hydrochloric acid [HCl]) may also be used (Jin et al. 2014, Haghani and
 426 Daneshpazhuh 2020). However, most commercial processes use sulfuric acid because it provides higher
 427 phosphoric acid yields, lower costs, and a solid form of calcium (Al-Fariss et al. 1992, EPA 1995, Shriver
 428 and Atkins 2008, Gilmour 2019). The specific reaction conditions dictate the type of calcium sulfate hydrate
 429 (CaSO₄ • n H₂O) formed, with lower temperatures favoring the formation of gypsum (CaSO₄ • 2 H₂O), as
 430 shown in Equation 8 (EPA 1995). The prevalence of fluorapatite among mineral phosphates also produces
 431 hydrofluoric acid (HF), as shown below in Equation 8.
 432



434
 435 **Equation 8**
 436

437 The gypsum formed during the reaction with the mineral acid is removed via filtration. Once removed, the
 438 gypsum solids undergo several aqueous wash cycles to remove residual phosphoric acid from the solid
 439 surface, producing phosphoric acids yields of 99.9% (EPA 1995, Gilmour 2019). As shown previously in
 440 Figure 5, the aqueous gypsum washes are sent back to the reaction vessel to aid in the conversion of
 441 mineral phosphates (EPA 1995, Gilmour 2019). The presence of mineral silicon in the initial composition
 442 reacts with hydrofluoric acid to produce less reactive forms of silicon tetrafluoride (SiF₄) and SiF₆²⁻ ions,
 443 some of which are removed as solids with the gypsum (Gilmour 2019).
 444

445 The phosphoric acid isolated following the filtration process is dilute, with P₂O₅ concentrations between 26
 446 – 30% (EPA 1995, Gilmour 2019). Vacuum evaporation is used to remove water and concentrate the
 447 phosphoric acid to 42 – 54% P₂O₅ (Gilmour 2019). Activated silica or clay is added during the concentration
 448 process to react with residual hydrofluoric acid. Silicon tetrafluoride isolated from the concentration step is
 449 hydrolyzed to fluorosilicic acid (H₂SiF₆), as shown in Figure 5 (Gilmour 2019).
 450

451 Mineral impurities, including heavy metal contaminants, remain in phosphoric acid produced via the wet
 452 process, which have historically limited its use to agricultural fertilizer applications (EPA 1995, Shriver and
 453 Atkins 2008, Gilmour 2019, Haghani and Daneshpazhuh 2020). Wet process phosphoric acid results in
 454 concentrations of between 42 and 54% P₂O₅, which is largely unsuitable for technical applications (Gilmour
 455 2019). The elemental phosphorous used in the thermal process can be purified via sublimation, resulting in
 456 no carry-over of heavy metal contaminants so that thermal phosphoric acid can be used in technical and

457 food applications (Shriver and Atkins 2008). However, the thermal process is much more expensive and
458 energy intensive than the wet process (~2000 °C vs ~80 °C) (EPA 1995, Gilmour 2019).

459
460 *Wet process purification methods*

461
462 Wet process phosphoric acid is commonly purified by crystallization or solvent extraction (Gilmour 2019).
463 Crystallization is a common purification technique, which is based on the differing solubilities of pure and
464 impure mixtures, with pure substances selectively crystallizing at reduced temperatures (Pavia et al. 1995).
465 When phosphoric acid is concentrated to 61% P₂O₅ or higher, it selectively forms hemihydrate crystals
466 (H₃PO₄ • ½ H₂O) when cooled to 8 – 12 °C (Gilmour 2019). The crystals are removed from the mixture and
467 can be melted to undergo additional recrystallization cycles to improve purity, with each cycle yielding a
468 10 to 100 times increase in purity (Gilmour 2019).

469
470 Solvent extraction is another traditional purification method based on solubility. In solvent extraction, the
471 target compound migrates between immiscible phases (usually aqueous [polar] and organic [nonpolar])
472 based on solubility (Pavia et al. 1995). The selectivity of phosphoric acid does not differ greatly compared
473 to its impurities, requiring additional purification steps. Prior to solvent extraction, concentrated
474 phosphoric acid undergoes precipitation with calcium or barium salts to remove sulfate (SO₄²⁻), sodium
475 salts to remove fluorosilicates, and sulfides to remove arsenic (Shlewitt and Alibrahim 2008, Gilmour 2019,
476 Haghani and Daneshpazhuh 2020). Phosphoric acid extractions are performed in one or more extraction
477 columns with many possible organic solvents, including alcohols, ethers, ketones, amines, and kerosene
478 blends (Shlewitt and Alibrahim 2008, Jin et al. 2014, Gilmour 2019). Following extraction with an organic
479 solvent, phosphoric acid is recovered with water. Residual organic solvents are removed via evaporation
480 during the concentration of the recovered phosphoric acid from the aqueous solution (Shlewitt and
481 Alibrahim 2008, Gilmour 2019). Solvent extraction of wet process phosphoric acid improves the purity of
482 the substance from 42-54% P₂O₅ in the raw form to up to 97% P₂O₅ (Gilmour 2019).

483
484 **Evaluation Question #2: Discuss whether the petitioned substance is formulated or manufactured by a**
485 **chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)). Discuss**
486 **whether the petitioned substance is derived from an agricultural source.**

487
488 Phosphoric acid is not a naturally occurring substance. As described in Evaluation Question 1, phosphoric
489 acid can be derived from natural phosphate minerals in the wet process or elemental phosphorus in the
490 thermal process. In both methods, phosphoric acid is produced through chemical processes.

491
492 According to the NOP decision trees, phosphoric acid is classified as a nonagricultural, synthetic substance
493 due to its chemical change from a natural mineral phosphate to an acid during processing (NOP 2016a,
494 NOP 2016b). Furthermore, the mineral source of phosphoric acid is classified as a nonagricultural source
495 (NOP 2016a, NOP 2016b).

496
497 **Evaluation Question #3: If the substance is a synthetic substance, provide a list of nonsynthetic or**
498 **natural source(s) of the petitioned substance (7 CFR 205.600(b)(1)).**

499
500 As described in Evaluation Questions 1 – 2, phosphoric acid is a synthetic substance that does not exist in
501 nature. Therefore, there are no natural sources of phosphoric acid.

502
503 **Evaluation Question #4: Specify whether the petitioned substance is categorized as generally**
504 **recognized as safe (GRAS) when used according to FDA's good manufacturing practices (7 CFR**
505 **205.600(b)(5)). If not categorized as GRAS, describe the regulatory status.**

506
507 As described in the "Approved Legal Uses of the Substance" section, the FDA has designated phosphoric
508 acid generally recognized as safe (GRAS) for several uses. Phosphoric acid is listed as a "multiple purpose
509 GRAS food substance" in 21 CFR 182.1073, and as a GRAS "general purpose food additive" in §582.1073.
510 Additionally, the FDA lists phosphoric acid as a substance used in the production of the GRAS substances

511 monobasic ammonium phosphate in §184.1141, dibasic ammonium phosphate in §184.1141, magnesium
512 phosphate in §184.1366, and hydrogen peroxide in §184.1366.

513
514 **Evaluation Question #5: Describe whether the primary technical function or purpose of the petitioned**
515 **substance is a preservative. If so, provide a detailed description of its mechanism as a preservative**
516 **(7 CFR 205.600(b)(4)).**

517
518 When used as petitioned, the primary function of phosphoric acid is to improve the extraction of target
519 molecules, not to act as a preservative. However, in some cases, the addition of phosphoric acid stabilizes
520 target molecules from decomposition, as described above in the “Action of the Substance” section.

521
522 Phosphoric acid is also used as an equipment sanitizer in organic agriculture in 7 CFR 205.605 and
523 §205.603. The low pH of phosphoric acid solutions makes it an antimicrobial substance, as high acid
524 content is not tolerated by microorganisms (Winniczuk and Parish 1997, Prado et al. 2015). The
525 antimicrobial nature of phosphoric acid may result in some preservative characteristics if incorporated into
526 food and beverage products (Winniczuk and Parish 1997).

527
528 **Evaluation Question #6: Describe whether the petitioned substance will be used primarily to recreate**
529 **or improve flavors, colors, textures, or nutritive values lost in processing (except when required by law)**
530 **and how the substance recreates or improves any of these food/feed characteristics (7 CFR 205.600(b)(4)).**

531
532 When used as petitioned, the primary function of phosphoric acid is to improve the extraction of target
533 molecules, not to improve or recreate flavors in processed food products. However, phosphoric acid has
534 been used as a flavoring agent in conventional food and beverage production, as described above in the
535 “Specific Uses of the Substance” and “Historical Use” sections.

536
537 **Evaluation Question #7: Describe any effect or potential effect on the nutritional quality of the food or**
538 **feed when the petitioned substance is used (7 CFR 205.600(b)(3)).**

539
540 When used as petitioned, phosphoric acid will be used in the extraction of target molecules from plant
541 material. The extraction of antioxidants and other compounds from the initial plant material will reduce
542 the nutritional quality of the material from which they are extracted. However, the purpose of plant
543 extracts is to improve the quality of other products to which they are added. (Nicoué et al. 2007, Proestos
544 2020). Phosphoric acid is a source of phosphates, which are important nutrients in human health, and can
545 be found in many biomolecules, including ATP and DNA (Shriver and Atkins 2008, Timberlake 2016,
546 Gilmour 2019). However, phosphoric acid is typically used in low concentrations (1 – 3%) in extraction
547 processes and is unlikely to contribute directly to improved nutritional quality.

548
549 **Evaluation Question #8: List any reported residues of heavy metals or other contaminants in excess of**
550 **FDA tolerances that are present or have been reported in the petitioned substance (7 CFR 205.600(b)(5)).**

551
552 As described in Evaluation Questions 1 – 2, wet process phosphoric acid is produced from mineral
553 phosphates. The presence of heavy metals in the initial mineral source may result in carry over to the
554 phosphoric acid product (Haghani and Daneshpazhuh 2020). The prevalence of contaminants in
555 phosphoric acids based on their source and application are listed below in Table 3 (Gilmour 2019).

556

557
558

Table 3. Impurities in phosphoric acid

	Morocco	North Carolina	Idaho	Kola	Raffinate	Technical	Food	Thermal	LCD	Semi
% H ₃ PO ₄	82	78	73	73	62	76	85	85	85	85
% P ₂ O ₅	59.3	56.6	53	53	45	54.8	61.6	61.6	61.6	61.6
<i>ppm</i>										
SO ₄	9600	7100	20,300	19,260	13,300	2100	78.0	1.0	1.9	0.9
F	1300	4060	8100	1010	25	310	5.1	4.0		
Cl	60	44		507	0					
Al	221	3050	7700	2400	560	1.0	1.0	1.3	0.49	0.05
As	5	0	17	12	13	2.5	0.4	0.2	0.05	0.03
B	19		40	0	48	18.1	17.1	0.0	0.46	0.04
Ba									0.46	0.04
Ca	500	1029	68		215		3.5	3.0	1.44	0.15
Cd	47	29	125	29	119	0.5	0.2	0.3	0.04	0.04
Co									0.04	0.03
Cr	374	230	634	19	946	1.1	0.5	0.4	0.20	0.04
Cu	19	2	58	96	48	0.5	0.1	0.0	0.05	0.03
Fe	1421	8729	5760	0	3594	6.7	1.0	6.7	1.80	0.09
K	480	1344	422	1152	1214	73.8	49.2	4.9	1.20	0.12
Mg	5160	6950	2880	7010	13,100	2.9	0.5	0.4	0.20	0.05
Mn	10	58	86	365	25	0.5	0.5	0.4	0.10	0.05
Mo	21	14		8	53	30.8	4.8	1.0	0.10	0.05
Na	1740	650	140	890	1670	25800	100	11.3	2.00	0.24
Ni	75	33	163	36	190	0.5	0.5	0.4	0.20	0.04
Pb	1	0	1	1	3	0.3	0.1	0.1	0.10	0.04
Sb						1	0.8	5.2	0.40	0.26
Si	58	59	557		147					
Ti	120	864	125	720	304	4.9	0.5	0.1	0.20	0.05
U	72	91	192	0	182	0.01	0.01	0.09	0.05	0.02
V	264	48	1248	67	668	0.5	0.5	0.1	0.04	0.02
Zn	797	518	2208	19	2016	64.3	1.0	1.3	2.00	0.05
TOC	48	144	384	144	121					

Source: Gilmour 2019.

559
560
561

Evaluation Question #9: Discuss and summarize findings on whether the manufacture and use of the petitioned substance may be harmful to the environment or biodiversity (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).

562
563
564
565

As described in Evaluation Question 7, when used as petitioned phosphoric acid is used in low concentrations (1 – 3%), and is a source of phosphates for incorporation to biomolecules. The low concentration in extraction applications and the prevalence of phosphates throughout biology make phosphoric acid from plant extractions unlikely to be harmful to the environment or biodiversity.

566
567
568
569
570

However, the production of phosphoric acid does have the potential to be harmful to the environment. As described in Evaluation Question 1, the thermal process for producing phosphoric acid is energy intensive and requires high temperatures. The high energy requirements of the thermal process may contribute to atmospheric CO₂ levels if the energy is produced from fossil fuels. The thermal process also requires the treatment of combustion gases by scrubbers, cyclonic separators, mist eliminators, and electrostatic precipitators to prevent the release of phosphoric acid to the environment (EPA 1995, Gilmour 2019). The small size (< 3 μm diameter) makes these phosphoric acid and phosphorus oxide (P₂O₅) particles difficult to capture, and contributes their release to the atmosphere at levels of “< 25 mg P₂O₅ per dry standard cubic meter of stack gas” (Gilmour 2019).

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580

Wet process phosphoric acid is produced from chemical changes to mined mineral phosphates. There may be initial harm to the environment and biodiversity in the mining process. Once the minerals are isolated,

581
582

583 hydrofluoric acid presents the most likely source of environmental harm (Shriver and Atkins 2008). As
584 described in Evaluation Question 1, hydrofluoric acid is removed as a solid or as fluorosilicic acid by
585 reaction with silica sources. These include natural silicates present within the initial mineral, as well as
586 activated silica and clay added during the manufacturing process (Shriver and Atkins 2008, Gilmour 2019).
587 Additionally, scrubbers are used to remove gaseous fluorine compounds from concentration steps to
588 prevent their release to the environment (EPA 1995).

589
590 In addition to the hazards from fluorine compounds, the gypsum produced may pose a hazard to the
591 environment. Isolated gypsum may be used for other commercial applications if it is sufficiently pure
592 (Gilmour 2019). In other cases, gypsum is left in gypsum stacks, or pumped out to sea (Gilmour 2019).
593 However, the gypsum may also contain silicon fluorides, acids, and other impurities from the initial
594 mineral source, which has resulted in its designation as a hazardous substance by the EPA in 40 CFR 261.4.

595
596 **Evaluation Question #10: Describe and summarize any reported effects upon human health from use of**
597 **the petitioned substance (7 U.S.C. § 6517(c)(1)(A)(i), 7 U.S.C. § 6517(c)(2)(A)(i) and 7 U.S.C. § 6518(m)(4)).**

598
599 Concentrated phosphoric acid is corrosive, and can result in burning and irritation of the eyes and skin on
600 contact (Flomenbaum et al. 2002, NJDHSS 2004, Gilmour 2019). Phosphoric acid can desiccate epithelial
601 cells, resulting in the drying and cracking of skin where long-term exposure occurs (Flomenbaum et al.
602 2002, NJDHSS 2004). Inhalation of phosphoric acid may result in irritation to the nose, lungs, and throat
603 and may induce coughing and wheezing (NJDHSS 2004, Gilmour 2019). Ingestion of phosphoric acid may
604 damage gastric and esophageal mucus linings (Flomenbaum et al. 2002).

605
606 Phosphoric acid is frequently used in food processing and production and is a common component of food
607 and beverages (Wolke 2002). As described in Equations 2 – 4 in the “Composition of the Substance” section,
608 phosphoric acid is the source of several phosphates, which are important components of biomolecules (e.g.,
609 ATP, DNA, etc.) (Shriver and Atkins 2008, Timberlake 2016, Gilmour 2019). When used as petitioned,
610 phosphoric acid is used in low concentrations (1 – 3%), making it unlikely to be harmful to human health
611 (Gilmour 2019).

612
613 **Evaluation Question #11: Describe any alternative practices that would make the use of the petitioned**
614 **substance unnecessary (7 U.S.C. § 6518(m)(6)).**

615
616 There are alternative methods to extract target molecules from plant material. One of the simplest ways to
617 improve solvent extraction processes is to increase the solvent temperature (Pavia et al. 1995, Silberberg
618 2003). Increased temperature improves the solvation of most solids and liquids by disrupting the
619 intermolecular forces that prevent the target molecule from entering the solution (Silberberg 2003).

620
621 Supercritical carbon dioxide extraction offers an alternative to acidic extractions. This extraction method
622 uses temperatures and pressures that push the solvent beyond its critical point, so that it no longer exists as
623 a liquid or gas (Silberberg 2003, Babovic et al. 2010). Carbon dioxide is the most common supercritical fluid
624 used in extraction applications due to its low cost and the low temperatures and pressures required to
625 reach supercritical conditions (31.1 °C and 7.38 MPa) (Babovic et al. 2010). The selectivity of supercritical
626 fluids can be modulated by changing its temperature and pressure to target different classes of molecules.

627
628 Subcritical extractions offer another alternative to acidic extractions. In such applications, the solvent
629 remains in liquid form, although conditions may approach the critical point of the solvent (Ibañez et al.
630 2003). As with supercritical fluid extractions, the selectivity of the subcritical extractions can be
631 manipulated by modifying temperature and pressure. Subcritical water extractions have been successful in
632 the extraction of essential oils and antioxidants (Ibañez et al. 2003). However, some antioxidants and other
633 compounds are sensitive to decomposition, and may not survive increased solvent temperatures or the
634 high pressure conditions needed in supercritical and subcritical extractions (Ibañez et al. 2003).

635

636 **Evaluation Question #12: Describe all natural (non-synthetic) substances or products which may be**
637 **used in place of a petitioned substance (7 U.S.C. § 6517(c)(1)(A)(ii)). Provide a list of allowed substances**
638 **that may be used in place of the petitioned substance (7 U.S.C. § 6518(m)(6)).**
639

640 Many natural and currently allowed synthetic acids offer an alternative to phosphoric acid for plant
641 extractions, such as acetic acid, citric acid, gibberellic acid, lactic acid, and tartaric acid (NOP 2016c).
642 Polyprotic carboxylic acids (for example, ascorbic acid, citric acid, etc.) are also able to chelate positively
643 charged species, facilitating improved extraction (Albuquerque et al. 2005).
644

645 However, the strength of the acid is important in determining the effectiveness in the extraction of the
646 target molecules. Carboxylic acids are weaker acids than phosphoric acid (pKa ~5 vs 2.15) meaning that
647 they may be less effective in extracting some molecules, including anthocyanin antioxidants (Silberberg
648 2003, Nicoué et al. 2007, Timberlake 2016). The target molecule and plant structure determine the optimal
649 solvent conditions, although phosphoric acid solutions have been reported to be among the most effective
650 for antioxidant extractions (Nicoué et al. 2007).
651

652 **Evaluation Information #13: Provide a list of organic agricultural products that could be alternatives for**
653 **the petitioned substance (7 CFR 205.600(b)(1)).**
654

655 Alternatives to phosphoric acid are naturally acidic agricultural substances, including wine and vinegar.
656 Both mixtures include natural acids that can provide an acidic extraction solution. However, as described
657 in Evaluation Question 12, carboxylic acids are weaker than phosphoric acid and may be less effective in
658 the extraction of some target molecules. Additionally, the complex mixture of compounds in wine and
659 vinegar would make purification of the plant extracts more difficult.
660

Report Authorship

661
662
663 The following individuals were involved in research, data collection, writing, editing, and/or final
664 approval of this report:

- 665 • Philip Shivokevich, Chemistry Lecturer, California State University Bakersfield
 - 666 • Laura M. Weinberg, Technical Editor, Savan Group
- 667
668

669 All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11 – Preventing
670 Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.
671

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