

Phosphates, Phosphites, and Phosphides in Environmental Samples

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The common assumption that phosphorus occurs exclusively as phosphate in the environment is deserving of increased scrutiny. If a sample contained reduced phosphorus compounds (P in an oxidation state of less than +5), standard methods of phosphorus determination would incorrectly classify the compounds mostly as organic P, although significant fractions were sometimes misclassified as orthophosphates and condensed P. The disappearance of gaseous hydrogen phosphide (PH₃) from samples was a function of solution composition, in that certain acids and metals enhanced removal whereas other constituents increased PH₃ stability. No previously used extraction method could detect a significant portion of reduced phosphorus in representative samples by measuring PH₃ evolution, particularly for highly recalcitrant iron phosphides. Despite analytical limitations, clear evidence was gathered that reduced phosphorus compounds can be leached from cast iron to water and that reduced phosphorus is also present in the scale (rust) that forms on the metal.

Introduction

Phosphorus chemistry controls key aspects of eutrophication, microbial nutrition, corrosion and other environmental processes. Although it has always been presumed that phosphorus occurs in the environment almost exclusively as phosphates [P(V)], some evidence has recently been gathered suggesting that phosphites [hypophosphite P(I) and phosphite P(III)] and phosphides [P(-III)] are present in the environment from manmade and natural sources (1–13). We term any phosphorus species with an oxidation state lower than (+5) “reduced phosphorus”. Some of these molecules are highly toxic, relatively stable in water (14) and exhibit extraordinary catalytic properties (15, 16). Of these forms, phosphides are naturally present in the earth’s crust as schreibersite (Fe,Ni)₃P. The phosphides are also commonly introduced into the environment in steel slag fertilizers, from degradation of corroding metals such as iron, and from routine application of rodenticides and fumigants (13, 14). Phosphorus is also intentionally added to molten iron to enhance abrasion resistance or to lower the casting temperature; however, if the phosphorus content is too high (e.g., >0.5 wt %) a brittle iron phosphide (steadite) network can form (17).

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TABLE 1. Solutions and Approaches Used in the Literature To Extract Phosphine

ref	sample	extraction approach
Glindemann et al. (9)	steel	anoxic 1 N HCl, 100 °C, 5 min
Liu et al. (19)	soil and sediment	anoxic 1 N H ₂ SO ₄ (N ₂ atmosphere), 100 °C, 5 min
Gassmann (5)	sediment	anoxic 10% NaOH, heated
Nowicki (20)	grain fumigated with PH ₃	anoxic 10% H ₂ SO ₄ , vacuum for 1 min until achieving 685 mmHg, and heat to boiling in 20 min

In the limited research to date attempting to detect reduced phosphorus in the environment, samples are often exposed to conditions designed to release reduced phosphorus in the form of phosphine gas (PH₃), which is then detected by highly sensitive gas chromatography. A range of extraction solutions and approaches have been used (Table 1), but their actual efficiencies in converting reduced P to phosphine gas have not been determined. Moreover, to date, no research has been conducted to evaluate how reduced phosphorus compounds would be quantified by the Standard Method protocol if they were present in samples (18). That is, when a typical environmental sample is analyzed for phosphorus, a colorimetric reagent combines with reactive phosphorus to determine the concentration of orthophosphate. Thereafter, aliquots of the sample are treated to selectively convert other types of phosphorus compounds into orthophosphate, allowing their quantification by comparison to the orthophosphate in the original sample. Acid hydrolysis is presumed to convert condensed P (primarily polyphosphates), and a persulfate digestion converts the condensed P and also organic P to orthophosphate. It is typically assumed, but never proven, that all phosphorus in the original sample is present as some form of phosphate.

The goal of this work is to develop an improved understanding of some aspects of reduced phosphorus chemistry related to its analysis and stability in the environment. Specific goals include determining (1) how reduced P species would be quantified in standard methods, (2) loss of phosphine gas from headspaces in contact with various solutions, and (3) quantification of PH₃ recovery from a representative phosphide solid (Fe₃P) after reaction with various solutions. The newly developed insights are then applied to analysis of a few environmental samples.

Materials and Methods

Evaluating Measurement of Reduced P by the Standard Method. This experiment determined how different reduced phosphorus species would be classified and quantified by Standard Method protocol 4500-P (18). The ascorbic acid method was used to detect orthophosphate as recommended by other authors (21, 22), acid hydrolysis was through a combination of sulfuric and nitric acid, and a persulfate digestion was used to convert organic phosphorus to orthophosphate. Reactive P, acid-hydrolyzable P (condensed P), and organic P were determined for stock solutions of phosphorus acid and sodium hypophosphite. For comparison, solutions containing the orthophosphates Na₂HPO₄, glyphosate (C–P bond), and phytic acid (C–O–P bond) were also tested. Preliminary tests with soluble hypophosphite and phosphite confirmed that these constituents were quantified by JY-2000 inductively coupled plasma-emission

TABLE 2. Presence of Reduced P in Synthetic Drinking Water after Iron Corrosion

sample ^{a,b}	speciation by ion chromatography (mg/L)				ICP total P (mg/L)
	PO ₂ P	PO ₃ P	PO ₄ P	total P	
BS	0	0.61	0	0.61	0.59
BS + NaHS (20 mg/L S)	0	0.18	0	0.18	0.17
BS + NaHS (50 mg/L S)	0	0.11	0	0.11	0.17
BS + NaHS (20 mg/L S) + PO ₄ ³⁻ (5 mg/L P)	0	0.14	0	0.14	0.12
BS + NaHS (20 mg/L S) + P ³⁻ (5 mg/L P)	0.48	0.92	0	1.40	1.31
BS + NaHS (20 mg/L S) + P ³⁻ (5 mg/L P) + Fe ²⁺ (50 mg/L Fe)	0	0.17	0	0.17	0.20

^a BS refers to a solution containing 0.001 M NaCl + 0.0005 M NaHCO₃. ^b NaHS dosed at 20 mg/L as S. All phosphorus compounds dosed at 5 mg/L as P. Fe²⁺ dosed at 50 mg/L as Fe.

spectroscopy (ICP-ES) no differently than orthophosphate. Thus, total soluble P in these solutions was determined by ICP-ES according to Standard Method 3120 (18).

Some solid phosphorus compounds including three kinds of phosphides (Ca₃P₂, 12-mm pieces and smaller, 97% pure; Fe₃P, 40 mesh, 99.5% pure; and Cu₃P, <100 mesh, 99.5% pure; All-Chemie Ltd., Mt. Pleasant, SC) were added to water and also tested using the Standard Methods protocol, and phytic acid was also added as a solid. To provide additional insight into transformations occurring in samples, ion chromatography (IC, DX300) was used to separate and quantify phosphate, phosphite, and hypophosphite in a few tests (23). The detection limit of each species via IC was approximately 0.05 mg/L as P.

Absorption of Phosphine Gas by Aquatic Media. To test the stability of gaseous phosphine in contact with various liquids, 30 mL solution samples (distilled–deionized H₂O, 1 N acids, or 10% NaOH) were placed into 250 mL bottles. The bottles were Boston round style clear glass of 6 cm width and 14.4 cm height. Distilled–deionized (DI) water was used to prepare 1 N concentrations of ultrapure hydrochloric acid, nitric acid, and sulfuric acid or 10% NaOH. These solutions and DI water (as a blank) were placed into an anaerobic glovebox. The glovebox and solutions were purged with 99.998% pure N₂ unless stated otherwise in the text. After the solutions had been added, the bottles were sealed inside the glovebox, and 30 mL of 10 ppm PH₃ gas was injected into each bottle. The phosphine concentration in the headspace was measured by GC with a nitrogen phosphorous detector (NPD, HP6890 GC, detection limit of about 0.07 pg of PH₃). A test based on pentane leakage screened out Mininert valves (PTFE, 24 mm cap size, Supelco, Bellefonte, PA) that could leak enough to cause significant loss of PH₃. For the test, 1.5–2 mL of pentane was added to each bottle, and then the bottles were sealed and weighed. Bottles with a weight loss of less than 1.5 mg/day passed the test, and in such cases, the bottles were demonstrated to leak less than 1%/day of PH₃ for conditions present during our experiments. Bottles that failed the pentane test could leak as much as 50% of the PH₃ in 2 days.

Experiments on Recovery of Phosphine from Phosphide Solids and Cast Iron. Experiments tested the ability of various acids or NaOH to induce release of phosphine from Fe₃P solid. This solid is deemed representative because it is believed to be present in cast iron. In the first set of experiments, 0.1 g of Fe₃P was added to 30 mL of solution, and the bottles were sealed. Each sample was heated to 60 °C (for 3 h), cooled, and then subjected to a repeat heating (overnight) and cooling cycle. Phosphine concentrations in the headspace were analyzed before heating and after heating. In the second set of experiments, the samples were heated to 100 °C for 2 h in a water bath. In some cases, after the phosphine analyses were complete, bottles were opened inside the glovebox. Samples were immediately taken from the water to determine reactive phosphorus (ascorbic acid) and total soluble phosphorus (ICP-ES).

Several other approaches have been described in the literature to extract phosphine from solid environmental samples (9, 24–26), and these were tested in duplicate. In the first test, 30 mL of NaHS solution (200 mg/L as H₂S) was added to a 250 mL bottle, and the pH was adjusted to 7.0 using 0.1 M HCl. Thereafter, 0.1 g of Fe₃P or 7.78 g of cast iron filings was added, and the bottle was sealed. For samples with Fe₃P, phosphine concentrations were analyzed after 2, 5, 8, and 19 days. For samples with cast iron filings, phosphine concentrations were measured after 1 and 13 days. In the second test, pH 4 (hydrogen phthalate) and pH 7 buffers (potassium dihydrogen phosphate and disodium hydrogen phosphate) were prepared using Standard Method 423 (27). Fe₃P (0.1 g) was added to the two buffers, as well as to a solution of 85% phosphoric acid. This set of experiments was repeated once outside the glovebox, with the solution allowed to contact the atmosphere, and the phosphine concentration was analyzed after 1 and 8 days. In the third test, 0.1 g of Fe₃P was added to a 50% NaOH solution. The phosphine concentration was analyzed after 2, 5, 8, and 19 days.

Reaction between Phosphine and Other Elements in Aquatic Media. To examine effects of different elements in aquatic solution on the removal of PH₃ from a headspace, 0.1 mL of standard element stock solution (100 ppm concentration diluted from 1000 ppm ICP standard solutions, Merck or Me, Germany) was placed in a disposable syringe (50 mL, polypropylene, Becton, Dickinson and Co.), along with 1 mL of a background solution. Background solutions were prepared with ultrapure reagents to test extremes in pH: pH 0 was 1 N HNO₃, pH 7 was 1 N sodium acetate adjusted to pH 7 with acetic acid, and pH 14 was 1 N NaOH. Thereafter, 50 mL of 1 ppb PH₃ in air was placed in the syringe. Controls were also tested without any element solutions added. Tests were conducted in duplicate to calculate the average PH₃ concentrations remaining in the syringe after 1 and 5 days using an HP 5890 GC, nitrogen phosphorus detector, and cryotrapping as described elsewhere (9).

Practical Verification of Reduced Phosphorus Release from Iron Metal. Tests were done on samples from two experiment systems to verify that routine measurements would not detect reduced phosphorus in drinking water samples contacting iron pipes. The first sample was created by adding 3 g of cast iron filings (about 0.2% P by weight) to a variety of 150 mL samples (Table 2). After 3.5 months, the solution was collected, and IC and ICP-ES were used to directly measure reduced phosphorus species and total phosphorus. The second sample was generated by exposing small samples of intact cast iron to synthesized drinking water under aerobic, constantly stirred conditions using approaches detailed elsewhere (28). The rust or scale formed on the iron after 3 months was then removed from the metal surface and digested with nitric acid (Standard Method 302 D) (27). A colorimetric method and ICP were used to measure orthophosphate and total P, respectively.

TABLE 3. Fraction of P Recovered after Indicated Treatment and Results for Representative Phosphorus Species Compared to Phosphorus Determined by ICP-ES^a

treatment method ^b	fraction recovered ^b	Na ₂ HPO ₄ (%)	phytic acid (%)	glyphosate (%)	H ₃ PO ₃ (%)	NaH ₂ PO ₂ (%)
no pretreatment	mostly orthophosphate, small fraction of condensed P	98.8 ± 0.9	<DL ^c	1.3 ± 1.3	<DL	<DL
acid hydrolysis	orthophosphate, condensed P, and small part of organic P	105.0 ± 2.5	1.6 ± 0.8	5.4 ± 4.0	5.4 ± 1.9	15.9 ± 5.6
persulfate digestion	orthophosphate, condensed P, and organic P	102.5 ± 5.9	72.5 ± 7.5	97.5 ± 5.3	105.0 ± 2.1	107.5 ± 1.3
filtered and analyzed with ICP-ES	total soluble P	96.3 ± 3.6	88.8 ± 2.4	97.1 ± 3.8	100.0 ± 2.3	98.8 ± 2.6

^a Results of triplicate analysis. ^b According to Standard Methods 4500-P and 3120 (1998) (18). ^c DL = detection limit.

TABLE 4. Recovery of Phosphorus in Solution after Indicated Pretreatment of Solid Phosphides

phosphide	specific steps	persulfate digestion and colorimetric detection ^a (% recovery)	ICP detection (% recovery)
Ca ₃ P ₂	1–2 h in pure water	6.3 ± 1.3	61.3 ± 1.3
Fe ₃ P	3 h in pure water	1.7 ± 0.8	0.5 ± 0.4
Fe ₃ P	acid hydrolysis w/ neutralization	19.0 ± 0.4	58.8 ± 0.4
Fe ₃ P	acid hydrolysis w/o neutralization	23.8 ± 0.6	70.1 ± 0.3
Fe ₃ P	persulfate digestion w/ neutralization	73.3 ± 1.4	4.6 ± 0.1
Fe ₃ P	persulfate digestion w/o neutralization	80.8 ± 0.8	111.6 ± 1.2
Cu ₃ P	1–2 h in pure water	<DL ^b	1.6 ± 0.1
Cu ₃ P	acid hydrolysis w/ neutralization	12.4 ± 1.2	10.8 ± 0.1
Cu ₃ P	acid hydrolysis w/o neutralization	12.0 ± 1.9	19.6 ± 0.2
Cu ₃ P	persulfate digestion w/ indicator, w/ neutralization	66.3 ± 3.3	60.6 ± 2.2
Cu ₃ P	persulfate digestion w/ indicator, w/o neutralization	62.1 ± 3.2	64.3 ± 0.3
Cu ₃ P	persulfate digestion w/o indicator, w/ neutralization	75.0 ± 3.8	87.6 ± 0.5
Cu ₃ P	persulfate digestion w/o indicator, w/o neutralization	87.9 ± 10.2	91.8 ± 1.2

^a Standard Methods specifies neutralization of acid prior to color development. ^b DL = detection limit.

Results and Discussion

Analytical Chemistry of P Species. When various phosphorus standards were subjected to direct ICP detection, most of the phosphorus species were essentially 100% recovered as total P as determined directly by ICP without any hydrolysis or digestion treatments (Table 3). The exception was phytic acid, added as a solid to samples, for which initial recovery was only 88%, which was increased to 100% after persulfate digestion pretreatment. In contrast, when applying the Standard Method protocol with persulfate digestion and colorimetric detection, only 72.5% of the total P in phytic acid was detected (Table 3). Although Hashimoto (29) reported 100% recovery of phytic acid after persulfate digestion, digestion time was not reported, and it is possible that the 30–40 min specified in *Standard Methods* was insufficient to achieve complete recovery. Recovery of orthophosphate and glyphosate was complete after persulfate oxidation and colorimetric detection.

Using the *Standard Methods* definitions, neither hypophosphite nor phosphite would be quantified as reactive P, and only 5–16% was converted to orthophosphate by acid hydrolysis (Table 3). However, virtually all of the phosphorus in phosphite and hypophosphite was detected after digestion with persulfate. Thus, it is clear that, if soluble phosphite and hypophosphite were present in an environmental sample, they would be incorrectly classified partly as polyphosphate but mostly as organic phosphate.

On the basis of recoveries of P from representative phosphide solids (Table 4), substantial portions of the phosphorus in Fe₃P and Cu₃P solid were converted to orthophosphate after persulfate digestion, but relatively little (12–24%) was recovered after acid hydrolysis. Therefore, solid phosphides would also tend to be classified as organic phosphorus. *Standard Methods* also specifies neutralization of the digested acid solution prior to color development.

This neutralization step tended to decrease recovery of phosphorus in samples as determined after filtration and ICP detection, most likely through the formation of a precipitate such as Fe₃(PO₄)₂. This loss was most noteworthy for Fe₃P, recovery of which decreased from 112 to 5%. Colorimetric detection after neutralization (but without filtration) also tended to be lower compared to that without neutralization as per *Standard Methods* but not as strongly as for ICP detection after filtration, suggesting that any precipitate was at least partly redissolved upon reaction with the colorimetric reagent.

Another interesting nuance is that *Standard Methods* specifies addition of a pH indicator (about 1.6 × 10⁻⁵ mol/L phenolphthalein) before the persulfate digestion. This indicator was determined to interfere with recovery of P from Cu₃P solid, because 4–15% more P was recovered and more solid was observed to dissolve when this indicator was not used (Table 4). Therefore, use of a pH meter is recommended instead of the phenolphthalein indicator if higher recovery of phosphorus from phosphide is desired. It was expected that natural organic matter might produce an effect as the indicator, but a direct test of this hypothesis using a final concentration of 2.2 mg of C/L of fulvic acid solution indicated that this did not occur. It remains possible that different natural organic materials in environmental samples could interfere with the recovery of phosphorus from phosphides during acid digestion.

Absorption of Phosphine Gas and Extraction of Phosphine from Phosphide Solid. Significant analytical effort was devoted to the determination of phosphides in environmental samples by evolution of phosphine and gas chromatography detection. The first set of experiments examined the stability of the evolved PH₃. It is generally understood that PH₃ is relatively stable in gaseous samples stored in N₂ and pressurized gas cylinders and that the

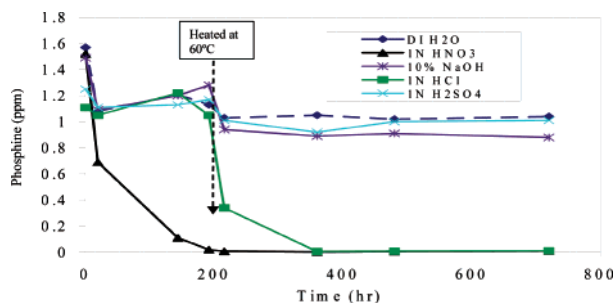


FIGURE 1. Phosphine (ppm) remaining in headspace in contact with indicated solutions.

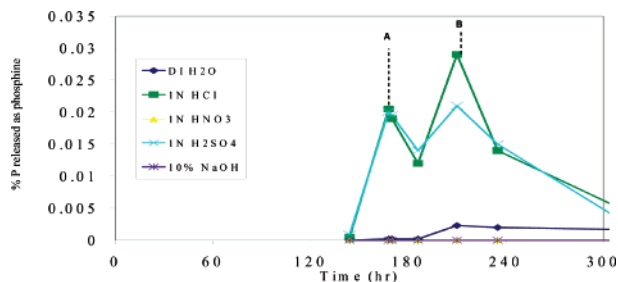


FIGURE 2. Percentage of total P in Fe_3P released as phosphine over time and as the temperature of solution changed. (A) Heat at 60°C for 3 h. (B) Heat at 60°C overnight.

reaction of PH_3 with oxygen is kinetically slow in the absence of certain catalysts such as UV light or ozone (8, 30). Because this was confirmed in the quality control conducted for this work, the disappearance of gaseous PH_3 is attributed to reactions with constituents of the liquid solution present. In the presence of DI water, about 30% of the PH_3 disappeared within 20 h, and the PH_3 content was relatively stable thereafter. This same trend was observed in the presence of HCl, H_2SO_4 , and 10% NaOH. In contrast, contact with a 1 N HNO_3 solution led to a 95% decrease in the PH_3 concentration after 1 week even without heating (Figure 1), a trend consistent with earlier reports that PH_3 could be oxidized violently by concentrated nitric acid (24). PH_3 rapidly decreased to undetectable levels after heating in the presence of HCl. Gmelin reported the formation of a PH_4Cl complex at about $51\text{--}54^\circ\text{C}$ and high pressure ($64.5\text{--}70.5$ atm) in a mixture of PH_3 and HCl (24). It is possible that a similar complex formed during tests in this work.

Another test with 1 N H_2SO_4 was conducted with 10 ppm PH_3 , and after 20 days, there was no obvious loss of PH_3 in H_2SO_4 samples compared to controls. According to our literature review, only very concentrated H_2SO_4 (concentration in excess of 90 wt %) is expected to remove PH_3 from gas (31).

Having established the reactivity of PH_3 in various acids and NaOH, experiments were conducted to determine the abilities of such solutions to extract PH_3 from samples containing iron phosphides at various temperatures. For all conditions tested, no more than 0.1% P in Fe_3P was recovered as PH_3 in the headspace even after heating to 100°C (Figures 2 and 3). In the samples held at 25°C , the vast majority of the solid did not even dissolve after 6 days. After being heated at 60°C overnight, most solid dissolved in the solutions of HCl, HNO_3 , and H_2SO_4 but did not dissolve in H_2O or 10% NaOH. After being heated at 100°C for 1 h, most solid in HNO_3 had dissolved, and dissolution was mostly complete by 2 h in HCl and H_2SO_4 . However, in all cases, very little P was released to the headspace as PH_3 under any circumstance (Figure 2).

Several other researchers have reported conversion of a high-percent phosphorus in solid phosphides to PH_3 , and

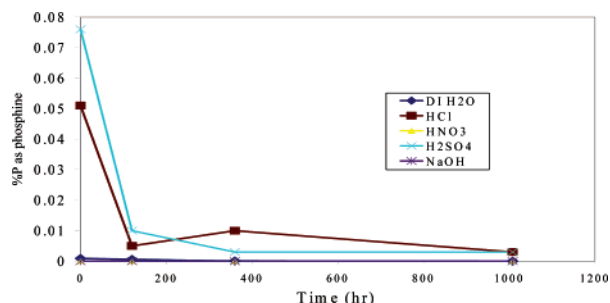


FIGURE 3. Percentage of total P in Fe_3P released to headspace as phosphine with time and after heating at 100°C for 2 h (in different aquatic media).

TABLE 5. Recovery of Phosphide P (Fe_3P) in Acids/NaOH Solutions Heated to 60°C as Phosphate P and Total P^a

sample	colorimetric detection		ICP detection	
	concentration (mg/L P)	recovery (%)	concentration (mg/L P)	recovery (%)
DI H_2O + Fe_3P	0.02	0.45 ± 0.23	0.01	0.27 ± 0.03
NaOH + Fe_3P	0.33	6.41 ± 0.39	0.54	10.37 ± 0.38
HCl + Fe_3P	0.19	36.54 ± 1.92	5.06	97.39 ± 0.58
H_2SO_4 + Fe_3P	0.19	35.58 ± 3.75	6.25	100.88 ± 0.32
HNO_3 + Fe_3P	0.30	57.69 ± 5.77	4.92	94.62 ± 0.58

^a 1:100 dilution.

these tests were also examined including exposure to NaHS, 50% NaOH, pH 4 buffer, pH 7 buffer, and concentrated phosphoric acid. None of these tests resulted in recovery of more than 0.001% of Fe_3P as PH_3 . Thus, it is clear that the Fe_3P used in this work was much less reactive than the zinc, calcium, magnesium, aluminum, or even iron phosphides tested in earlier studies (9, 24–26). The results also clearly indicate that, if Fe_3P were present in environmental samples, no existing extraction method detecting PH_3 evolution could have quantified a significant amount of the reduced phosphorus actually present. It follows that recovery of other metal phosphides might also be incomplete, although other research indicates that the percent recovery can be as high as 100% for Zn_3P_2 (25).

It was interesting to note that there was an initial peak release of PH_3 in the samples with HCl and H_2SO_4 after heating but the PH_3 concentration dropped rapidly thereafter. This demonstrates that PH_3 evolution and absorption co-occur when Fe_3P is in HCl or H_2SO_4 and that the change in headspace PH_3 concentration depends on which process is dominant. The previously noted PH_3 stability in the 1 N pure H_2SO_4 solution, where no PH_3 removal occurred, suggests that iron species from Fe_3P somehow promote the removal of PH_3 from the gas phase in the presence of sulfuric acid. This further reinforces the idea that previous research probably measured only a small portion of the P present as phosphides, given that iron is commonly present in sediment.

At the end of the tests, the bottles that had been heated to 60°C were opened and analyzed using the Standard Method protocol. In the HCl, HNO_3 , and H_2SO_4 samples, greater than 85% Fe in Fe_3P was detected, whereas 90–100% P was recovered in solutions as total soluble P measured by ICP-ES. Only one-third to one-half of the total P was recovered by the colorimetric method as orthophosphate (Table 5), and it was assumed that the remainder was reduced P. Ion chromatography (IC) analysis on the sample with H_2SO_4 , which is the only sample that could be analyzed by IC because high levels of Cl^- and NO_3^- interfere with phosphite and hypophosphite peaks, indicated that virtually all of the

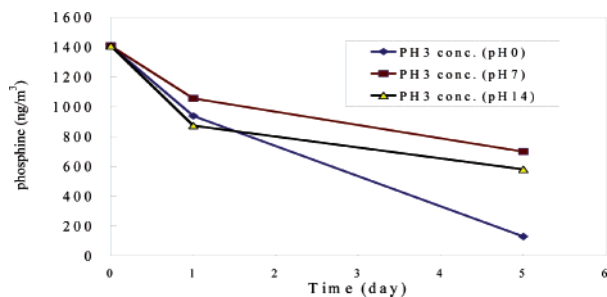
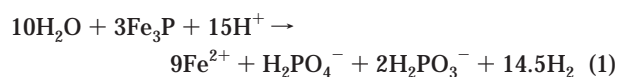


FIGURE 4. Phosphine concentration in control samples with time for an original PH₃ concentration of 1408 ng/m³.

reduced phosphorus in the H₂SO₄ sample was phosphite. Because the test was conducted in the glovebox, the question arises as to what species was reduced to oxidize phosphide to phosphite and phosphate. The following decomposition reaction was proposed on the basis of the measured yields of phosphate and phosphite



The H₂ concentrations in the headspaces of a few samples where Fe₃P was exposed to HCl were measured using a GC (RGA5 Process Gas Analyzer). The measured H₂ concentration was within 10% of that predicted by the above reaction. In other words, iron phosphide reduced water to produce H₂ with concurrent production of soluble phosphate and phosphite. The above reaction has a standard redox potential (*E*₀) of -0.6 V, which indicates that the overall reaction is thermodynamically favorable (32, 33).

Stability of Phosphine in Contact with Solutions Containing Other Elements. The presence of iron enhanced the removal of PH₃ in the presence of H₂SO₄. That finding prompted further examination of the reactions between phosphine and a wide variety of other elements in solution at pH 0, 7, and 14. In the pH 0 control with 1 N HNO₃, more than 90% of the phosphine was lost after 5 days, consistent with the earlier trends. Significant loss also occurred in the pH 7 and pH 14 controls, which is contrary to the observation noted earlier using bottles that had been pretested versus the syringe reactor used in this test (Figure 4). When PH₃ was added to the above solutions but other elements were also present, the relative PH₃ concentration difference (over 5 days) between the solutions and the controls at the same elapsed time was calculated as

$$\frac{(\text{PH}_3 \text{ concentration})}{(\text{PH}_3 \text{ concentration in appropriate control sample})} \times 100\%$$

Thus, if an element reduced the rate of PH₃ loss in a given solution compared to the control, the relative amount of PH₃ left would be above 100%. If it enhanced the rate of loss, the relative PH₃ left would be less than 100%. In solutions with HNO₃ and addition of Fe, Cu, As, Se, Te, Hg and Ag, there were dramatic increases in PH₃ loss relative to control (Table 6). Among these elements, a light brown precipitate was observed if Fe was present after 1 day, whereas in Cu solution, black particles formed. It also seems possible that some of the PH₃ was precipitated as a phosphorus solid in the samples. For instance, Dorfman (31) mentioned that silver(I) and mercury(II) in water could remove PH₃ by forming phosphide solids.

For some of the elements, after 5 days and at pH 0, the PH₃ concentration remaining in these solutions was much higher than that in the control sample (e.g., Mn, Co, Ni, Bi,

TABLE 6. Concentration of PH₃ in Headspace after 5 Days of Contact with Solutions and Added Element Compared to Controls^a

element	acid in stock solution (conc after dilution)	PH ₃ relative to control (%)		
		pH 0 control	pH 7 control	pH 14 control
Fe (+3)	HNO ₃ (0.05 M)	1	9	146
Cu (+2)	HNO ₃ (0.05 M)	1	0	4
Sn (+4)	HCl (0.7 M)	52	98	192
Sb (+3)	HCl (0.2 M)	87	59	132
Ti (+4)	(NH ₄) ₂ TiF ₆ in H ₂ O	12	67	125
As (+5)	HNO ₃ (0.05 M)	0	6	131
Se (+4)	HNO ₃ (0.05 M)	0	92	124
Te (+6)	HNO ₃ (0.05 M)	26	43	132
Hg (+2)	HNO ₃ (0.2 M)	1	0	0
Ag (+1)	HNO ₃ (0.05 M)	0	0	0
Mn (+2)	HNO ₃ (0.05 M)	305	89	220
Co (+2)	HNO ₃ (0.05 M)	195	110	94
Ni (+2)	HNO ₃ (0.05 M)	238	130	90
Bi (+3)	HNO ₃ (0.05 M)	338	114	30
Cr (+3)	HNO ₃ (0.05 M)	341	169	130
V (+5)	HNO ₃ (0.05 M)	169	127	151
Mo (+6)	(NH ₄) ₂ MoO ₄ in H ₂ O	188	111	157
P (+5)	KH ₂ PO ₄ in H ₂ O	270	122	142
Pb (+2)	HNO ₃ (0.05 M)	282	108	115

^a For controls, see Figure 4.

Cr, V, Mo, P, Pb). In other words, these elements in solution somehow reduced the loss of PH₃ compared to the control. Mn and Co formed brown precipitates, and Cr formed a light blue precipitate. The oxidation states of chromium and manganese in the stock solution (with HNO₃) were +3 and +2, respectively, and it is anticipated that chromium(VI) and manganese(VII) would behave differently because they are widely used in sulfuric acid solution to remove PH₃ from gases (31).

Clearly, some elements promote the oxidation of PH₃ (31), whereas others might inhibit the oxidation of PH₃. The latter result has not been reported previously, and this complex chemistry is deserving of future research.

Practical Verification of Reduced Phosphorus Release from Iron Metal. In all samples of water in contact with cast iron filings, reduced phosphorus in the form of phosphite (PO₃³⁻) was present at levels up to 0.6 mg/L (Table 2). The phosphite concentration was at least 70% of the total P as determined by ICP. This phosphite would not be detected by routine monitoring of a conventional distribution system using colorimetric tests as described in Table 3, because only reactive and acid-hydrolyzable phosphorus are typically quantified and it is assumed that only phosphate and polyphosphate could be present. In samples generated by acid digestion of scale removed from iron metal surfaces, on average, the difference between these two measurements was greater than 40% (Table 7). As before, such differences strongly imply that at least 40% of the total P is present as reduced phosphorus. To further confirm the existence of reduced P in the extract from the scale, the digested samples were further oxidized with K₂S₂O₈ (Standard Method 424 C) (27) and measured again for orthophosphate. The recovery of total P (as orthophosphate) after this oxidation increased, a trend that is again consistent with the presence of reduced P (Table 7). In addition to the results from the above two systems, a trace amount of phosphine gas was evolved when 10% sulfuric acid was added directly to a scale sample from iron pipe surfaces that had been exposed to Boulder, CO, tap water for 4 years (34). This is a direct verification that reduced P species are present in the scale; however, the amount actually present cannot be ascertained because of the poor recoveries of reduced PH₃ from iron solids as discussed earlier

TABLE 7. Difference in Orthophosphate Recovery with and without Persulfate Digestion in Iron Coupons

temperature (°C) of iron exposure ^a	ICP detection of total P (mg/L P)	% recovery ^b	
		w/o persulfate	w/ persulfate
5	0.74	49	85
20	0.95	32	87
25	1.07	35	83
5–20	0.81	46	95
20–25	1.07	40	79

^a Reference. ^b % recovery = (mg/L measured by colorimetric method)/(total dissolvable P) × 100%.

in this paper. Further work should examine the possible leaching of reduced phosphorus compounds into drinking water and their possible role in corrosion phenomena.

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