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Development of Solid State Samplers for Work Atmospheres: Phosphine

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Final Report

Prepared for
National Institute for Occupational Safety and Health
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U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, ***Secretary***
James A. Baker, III, ***Under Secretary***
Dr. Betsy Ancker-Johnson, ***Assistant Secretary for Science and Technology***

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Summary Report, July 1974 - June 1975

ABSTRACT

Investigations to find suitable solid sorber materials for phosphine in work atmospheres at the ppm level are described. The best sorber to date is silver nitrate-impregnated silica gel. Some difficulties remain to be overcome before a procedure for determining the amount of phosphine adsorbed can be recommended.

1. INTRODUCTION

This report describes work on the development of a solid-state sampler for phosphine in industrial atmospheres. It is a continuation of previously reported investigations in which the methodology, contaminant generation system, and gas sampling systems were discussed (1).

The program's objective is to find suitable solid-state sorber materials for phosphine in air at ppm levels, and to quantitatively measure the efficacy of these sorber materials by chemical analysis in the laboratory. Attention has been directed toward sampling phosphine reproducibly and analyzing the sorber materials to determine the quantity of phosphine sorbed. Various procedures for determining phosphine adsorbed on a solid surface have been tested on two candidate sorbers: charcoal, and silver nitrate-impregnated silica gel. Difficulties have been encountered with all the analytical procedures, and these have not yet been completely resolved. The most promising system to date appears to be sorption on silver nitrate-impregnated silica gel, elution of sorbed material with dilute acid, and quantitative determination by a spectrophotometric measurement of the phosphomolybdate according to the ascorbic acid method, ASTM D-515.

1.1 Review of Phosphine Sorption

Liquid and solid sorbers have been described for the direct reaction of phosphine with color-forming reagents. Dechant et al (2) have collected phosphine in air by bubbling the air through a pyridine solution of silver diethyldithiocarbamate and measuring the absorption of the stable complex at 465 nm. The collection efficiency of their bubbler was only 86 percent. Solid sorbers for phosphine have included impregnated papers and impregnated silica gel. Hughes and Jones (3) described silver nitrate impregnated filter paper; they compared the visible spot with standard stains, and dissolved it in hot HNO_3 and reacted it with sodium sulfide and boric acid for spectrophotometric determination at 470 nm. Muthu et al (4) described mercuric chloride papers containing methyl yellow indicator which turned from yellow to red upon liberation of HCl in the presence of phosphine. Nelson and Milun (5) determined phosphine at ppb levels in air by using detector tubes packed with silver nitrate impregnated silica gel, and measuring the length of the black stains as a measure of phosphine concentration.

In recent years, attention has been directed toward phosphine residues remaining after fumigation of cereal grains. Originally thought to leave no residues at all (6,7), recent investigations have indicated that there may be both water-soluble and insoluble phosphorus residues on porous materials exposed to ppm concentrations of phosphine. The studies of Berck (8), Robinson and Bond (9), Robinson (10), Awasthi et al (11), Hilton and Mee (12), Tkachuk (13), Vardell et al (14,15) and Sato and Suwanai (16) point to the existence of non-phosphine residues which cannot be removed by aeration or vacuum, and which are throught to be water-soluble lower oxy-acids of phosphorus. Tkachuk (13) could not remove phosphine residues by aeration for two days in an air flow of 400 linear feet/min, but he was able to extract 64 percent of the phosphorus with water, and so determined that 88 percent of the extract was hypophosphite (H_3PO_2) and 12 percent of it was pyrophosphate ($H_4P_2O_7$). Robinson (9,10) measured phosphine residues on filter paper by neutron activation analysis and found that they consisted mainly of the lower oxyacids hypophosphite (H_3PO_2) and phosphite (H_3PO_3). Robinson found that spectrophotometric analysis of a 24-hr extract into 5 ml dilute H_2SO_4 was unsuccessful because the 0.25 μg phosphorus content (N.A.A. measurement) was below the workable spectrophotometric limit. Robinson (10) postulated that the primary step in the residue deposition mechanism may be the sorption of phosphine as a monomolecular layer on the substrate surface, followed subsequently by fixation through oxidation. Bastick (17-19) and Zorin et al (20) have measured adsorption isotherms for phosphine on charcoal and silica gel.

1.2 Review of Phosphine Determinations

Phosphine has been determined by gas chromatography (21-25), colorimetric methods (2,11,16,26), and radioactive labeling techniques using ^{32}P (8,9,10,27). Other methods for phosphine determination have included titration, fluorescence, potentiometric and conductometric methods, turbidimetry, and gravimetry; these were mentioned in the previous literature review (1). Special mention must be made of the specific ion electrode for phosphate determination (28) which could have been of great value except that its sensitivity was too low to permit measurements to be made at the ppm level.

2. EXPERIMENTAL PROCEDURES

2.1 Gas Regulation and Sampling

To carry out the screening of solid sorbents, Matheson* phosphine gas standard certified to contain 4.5 ppm in nitrogen was used undiluted for rapid screening of candidate materials, and diluted with air to obtain gas concentrations ranging between 1/5 and five times the threshold limit value (TLV) for quantitative measurements. The gas dilution system and contaminant sampling system have been described previously (1). Figure 1 is a diagram of the sampling system. Since the mixing system used air to dilute the compressed gas standard, the composition of the matrix gas was effectively air rather than nitrogen except during the sorber screening tests when a 4.5 ppm mixture of phosphine in nitrogen was used as supplied.

In use, the flow rate was set by adjusting a flow controller needle valve to the desired flow rate as read on a rotameter flowmeter, and the pressure gauge was read to assure that the pressure drop across the sampling tube did not exceed 25.4 mm Hg at a flow rate of one liter/min. The system maintained the preset flow rate to within ±2 percent for sampling periods of minutes to hours. The contaminant gas was sampled by loosely inserting the sampling tube into the sampling manifold. For calibration purposes, to determine the gas concentration supplied to the sampling tube, the gas from the manifold was passed through an empty sampling tube and collected in two liquid bubblers in series for subsequent analysis.

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[*] The use of trade names is for identification only, and does not imply any recommendation or endorsement by the National Bureau of Standards.

2.2 Solid Sorbent

The gas volumes and flow rates required for the prescribed sampling conditions are shown in Tables 1 and 2. The sorber materials had to be capable of capturing between one and 200 μg phosphine, retain it for as long as required for storage and transport to a laboratory, and then permit quantitative desorption of the phosphine or stable phosphorus oxidation products during chemical analysis.

Table 1. Volume of Reactive Gas (Liters)

Time (hr)	Flow Rate (ml/min)		
	50	200	1,000
1/4	---	----	15
4	12	48	----
8	24	96	----

Table 2. Weight of Phosphorus Collected (μg)[1]

Gas Conc.[2] (ppm)	Volume of Gas (Liters) 12	15	24	48	96
0.06	0.91	1.14	1.82	3.65	7.30
1.5	22.8	28.5	45.6	91.3	183.

---

[1] μg = ppm x liters x M/24.45
where M = molecular weight of phosphine = 31

[2] Phosphine conc. range = 1/5 to 5 times the TLV of 0.3 ppm

Additional requirements that the solid state sorber must meet are:

- The resistance to air flow should not exceed 25.4 mm Hg at a flow rate of one liter/min (as specified by NIOSH).
- The device should retain the contaminant of interest in the presence of other substances in the air, and release it for subsequent chemical analysis.
- The device should indicate if breakthrough has occurred.
- The device should be stable to the effects of temperature, humidity, and storage.

2.2.1 Sampling Tube

The sampling tube is a straight 100 mm length of borosilicate glass tubing, 9 mm O.D. x 7 mm I.D. with three identations 20 mm from one end to act as retainers for a wad of quartz wool or polyester fabric which supports the sorber material. The tube is packed with silver nitrate impregnated silica gel or with the sorber material under test, using a 5-10 mm layer of $AgNO_3$/silica gel as a breakthrough indicator. The latter turns yellow at the first traces of phosphine, eventually turning brown and then black upon continued exposure to phosphine. The sorber column is secured with a second wad of quartz wool or polyester fabric, and the tube is capped with plastic end caps (e.g. Caplugs* B-715).

In use, the sampling tube is supported in the manifold by a stainless steel Cajon* high-vacuum tubing coupling (where it is held by an "O" ring), and the coupling is connected to the gas sampling system with 1/4-inch Teflon* tubing.

2.2.2 Breakthrough Experiments

Compressed gas (4.5 ppm phosphine in nitrogen) was flowed through a rotameter flowmeter into a mixing manifold, from which it was sampled into the solid state sampling tube at atmospheric pressure by aspiration through a constant-flow regulator. A subatmospheric reference pressure for flow regulation control was supplied by a rotary vane pump (Figure 1). (Some preliminary screening experiments were carried out by passing 4.5 ppm phosphine through the rotameter directly into the sampling tube.)

The phosphine was flowed into the samping tube until a yellow coloration in the detector section signaled the first traces of breakthrough, or until 80-100 liters of 4.5 ppm gas had been sorbed without breakthrough. For speed and convenience in screening, the 4.5 ppm standard was used without separate analytical confirmation of the concentration. The strongly reducing nature of the phosphine imposed no limitations on materials of construction, which were brass, glass, Teflon* and neoprene.

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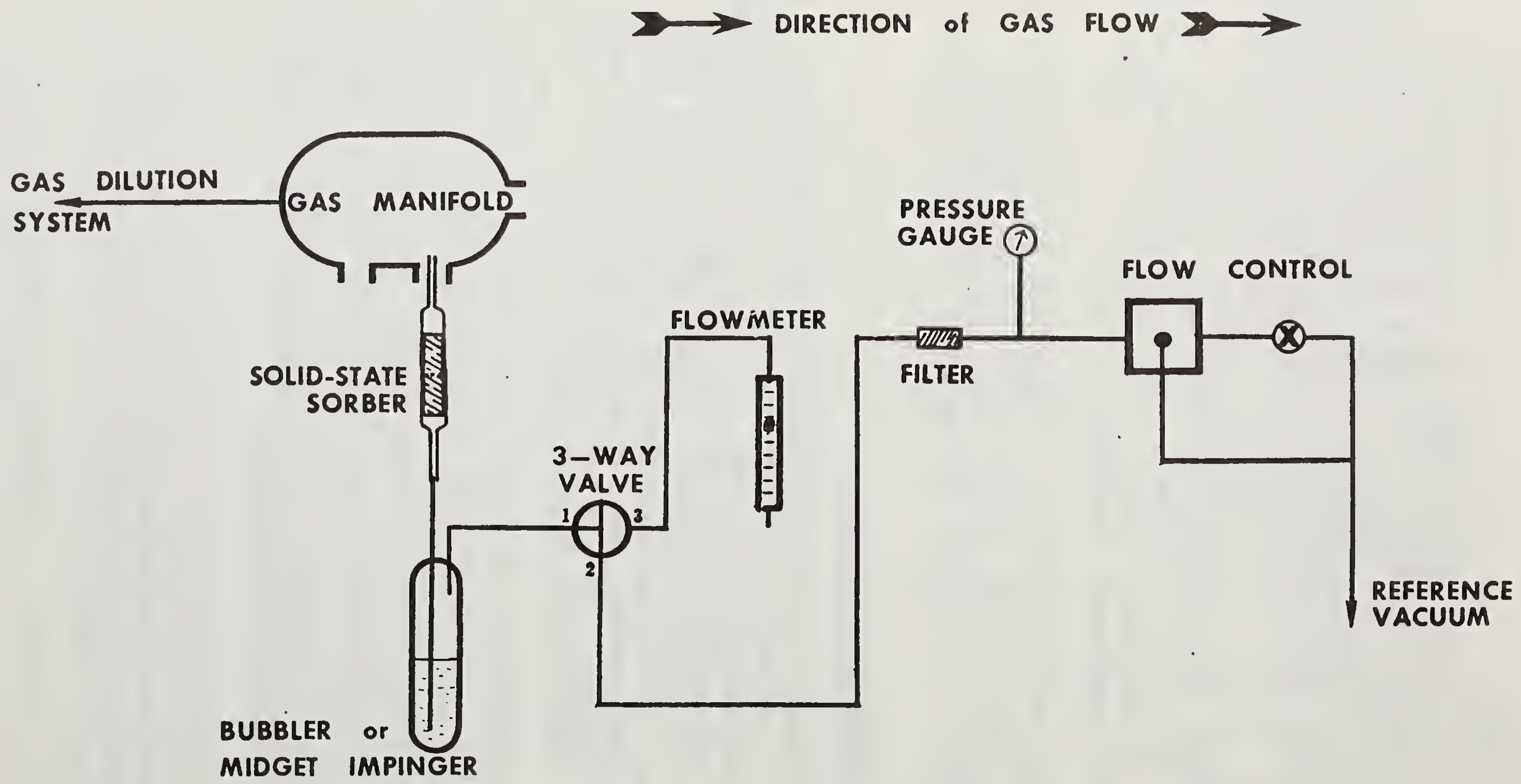

Figure 1. Diagram of Gas Sampling System

Breakthrough experiments reported previously (1) showed that the best sorbers for phosphine at the ppm level were chemisorbers with high surface areas, such as $AgNO_3$ impregnated silica gel, or $KMnO_4$ impregnated silica gel. Physical sorbers such as charcoal were less effective but still satisfactory if used in sufficient quantity to accommodate the expected quantity of phosphine.

Breakthrough experiments were carried out on the following additional candidate sorber materials: ascorbic acid, hydroquinone, chromium chloride hexahydrate, sodium dichromate dihydrate, water-washed charcoal (coal based charcoal with the fines flotated off), acid-washed calcined charcoal (calcined at 400 °C for 1 h), aluminum oxide, silver nitrate impregnated silica gel, and manganese dioxide impregnated silica gel. The solid sorbers included water-soluble material, which would simplify the quantitative determination of sorbed phosphine by eliminating the desorption step in the analytical procedure. An attempt to prepare $KMnO_4$-coated sodium acetate, (taking advantage of the acetone-solubility of $KMnO_4$) was unsuccessful because the $KMnO_4$ was converted to MnO_2 during evaporation of the solvent.

2.2.3 Results of Breakthrough Experiments

The results of the current series of breakthrough experiments on candidate sorber materials are shown in Table 3. For comparison, previous experiments from reference (1) are reproduced in Table 4. The experiments showed that neither strong oxidants nor reducing agents retained PH_3 effectively at a concentration of 4.5 ppm (nominal), nor did highly porous materials alone (e.g. silica gel and acid-washed charcoal). The combination of oxidizing material plus porous substrate gave the most effective sorbers.

Water-washed charcoal, thought to be an effective sorber for phosphine, had a high natural phosphorus content which interfered with subsequent phosphorus determinations. When the charcoal was acid-washed to remove phosphorus impurities, the charcoal was no longer effective as a sorber. Either the activated charcoal was deactivated by the acid treatment, or sorption on charcoal depended on the trace content of oils and metals removed by the acid. Calcining at 400 °C (i.e. heating in a closed container to limit access of air) was attempted to reactivate the charcoal that might have been deactivated by acid treatment but the calcined charcoal was also an unsatisfactory sorber for phosphine.

Table 3. Phosphine Sorption on Solid Materials

Solid Sorber	Column Size		Sorber Weight (mg)	Gas Flow		Time For Breakthrough (min)	Volume Gas Sorbed (l)	Weight PH_3 (g) Sorbed (μg)
	Length (mm)	Tube ID (mm)		Concn. (ppm)	Rate (l/min)			
Ascorbic acid	150	7	--	4.5	0.7	2.5	1.75	11
Hydroquinone	130	7	--	1.4	1.0	3.5	3.5	7
$CrCl_3 \cdot 6H_2O$	90	4	--	4.5	0.5	2.0	1.0	6
$Na_2Cr_2O_7 \cdot 2H_2O$	90	4	--	4.5	0.5	1.0	0.5	3
Al_2O_3	55	7	165	4.5	0.5	3.0	1.5	9
WW Charcoal (a)	15	7	280	4.5	0.5	4.5	2.25	14
WW Charcoal	35	7	630	4.5	0.8	100 (b)	80 (b)	500 (b)
WW Charcoal	45	7	760	4.5	0.5	75 (b)	37.5 (b)	235 (b)
WW Charcoal	130	6	2320	4.5	0.7	180 (b)	126 (b)	788 (b)
AW Charcoal (H_2SO_4) (c)	55	7	1020	4.5	0.8	12.0	9.6	60
AW Charcoal (HCl) (d)	32	7	880	4.5	0.8	1.0	0.8	5
AWC Charcoal (e)	40	7	680	4.5	0.8	4.0	3.2	20
AWC Charcoal	40	7	1030	4.5	0.8	0.5	0.4	2.5
$AgNO_3$ on Silica Gel	50	7	1680	4.5	0.8	127 (f)	102 (f)	638 (f)
MnO_2 on Silica Gel	150	7	4730	4.5	1.7	2.0	3.4	19

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a. WW = water washed charcoal, floated free of fines, dried 3 h at 90 °C.
b. Experiments terminated after 75-180 min, no breakthrough observed.
c. AW = acid washed charcoal; the WW charcoal was washed with 2.2 N H_2SO_4, rinsed, dried 3 h at 146-160 °C.
d. AW = acid washed charcoal; the WW charcoal was washed with 1:1 HCl, rinsed, dried 1 h at 130 °C, cooled in oven.
e. AWC = acid washed calcined charcoal; the AW charcoal (c) was calcined 1 h at 400 °C.
f. Experiment terminated when stain was 2/3 down the tube. Sorber consumed was 2/3 of 1680 mg, or 1120 mg.
g. $\mu g\ PH_3$ = liters X ppm X 34/24.45

Table 4 . Phosphine Sorption on Solid Materials[a] from Reference (1).

Sorber (mesh size)	Column size	Sorber Weight (g)	Sampling rate (1/min)	Time for breakthrough	Liters Sorbed
Silica gel (30-60)	50 mm in 13 mm tube	3.0	1.0	20 sec	0.3
Silica gel (30-60)	120 mm in 6 mm tube	--	1.0	30 sec	0.5
$AgNO_3$ on Si gel	50 mm in 6 mm tube	--	1.0	~ 43 min[b]	43[b]
MSA charcoal tube	30 mm in 6 mm tube	--	1.0	20 sec	0.3
Charcoal (20-40)	50 mm in 13 mm tube	1.9	1.4	24 min	34
Charcoal (20-40)	75 mm in 13 mm tube	2.5	1.0	34 min	34
$KMnO_4$ crystals	50 mm in 13 mm tube	5.9	1.0	4 min	4
$KMnO_4$ on Si gel	50 mm in 13 mm tube	3.4	1.3	No breakthrough[c] to 31 min	40

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[a] Phosphine 4.5 ppm (nominal) = 15 times TLV.

[b] Estimated breakthrough time from rate of travel of black stain, about 1 mm per minute. Experiment terminated after 17 min (20 mm stain) to save phosphine gas.

[c] Experiment terminated after 31 min to save phosphine gas. Sorption capacity expected to be high, by analogy to $AgNO_3$ on silica gel.

The sorber $KMnO_4$/SiGel could not be prepared in quantity because the $KMnO_4$ reduced to MnO_2. Hence, the only remaining effective sorber for phosphine is $AgNO_3$/SiGel. The preparation of this material is outlined in Appendix A.

2.2.4 Discussion of Sorption Results

Adsorption isotherms for phosphine on charcoal and silica gel have been measured (17-20) but the sorption capacity at flows of about 1 liter/min may have little if any relation to capacity under equilibrium conditions. Zorin et al (20) found that phosphine sorption on silica gel followed the Langmuir isotherm for physical adsorption between +20 °C and 80 °C, with sorption capacities in the range $0.11\text{-}0.33 \times 10^{-3}$ mole/g of silica gel (317-11.2 mg/g). Bastick (17) found charcoal adsorption of phosphine to be 0.3×10^{-3} mole/g of charcoal (10.2 mg/g). However, Table 4 shows that 4.5 ppm phosphine (0.00626 mg/liter) broke through 3 g of silica gel after 0.3 liter at a flow rate of 1 liter/min, so that the apparent sorption was not 3.7-11.2 mg/g but 0.0006 mg/g of silica gel. Even $AgNO_3$/SiGel, the best sorber material, retained 0.64 mg phosphine when the experiment was concluded at the end of 127 min, with about 1 g out of 1.68 g of sorber material darkened (Table 3), which equals about 0.64 mg/g, considerably less than the literature values for silica gel alone.

3. QUANTITATIVE DETERMINATION OF PHOSPHORUS

3.1 General

Two independent analytical determinations are needed: (1) determination of the quantity of phosphine applied to the sampling tube, and (2) determination of the quantity of phosphorus retained on the solid state sorber. A third analysis, useful but not strictly necessary, might be the determination of phosphine concentration in the manifold gas mixture; strictly speaking, this is not the same as analysis #1 because it is independent of sampling time and sampling flow rate.

Gas chromatographic procedures would be suitable for determining phosphine gas concentrations in the manifold, but they would require standardization with phosphine mixtures of known concentration, so that these procedures would be referred back to standard colorimetric analyses anyway. Since analysis #2 requires solvent elution of (probably) nonvolatile species, gas chromatography of the solutions would not be effective. Because the analyzed species is probably nonvolatile, the colorimetric measurement of phosphorus in solution was chosen.

To determine the quantity of phosphine applied to the sampling tube, the gas mixture from the manifold is passed through an empty sampling tube into two bubblers in series, containing either an oxidant to convert PH_3 to phosphate for subsequent analysis, or a color-forming complexant such as silver diethyldithiocarbamate for direct spectrophotometric measurement after calibration with known phosphine mixtures. Analysis #2 involves solvent elution of adsorbed phosphorus and subsequent colorimetric determination of dissolved phosphine or oxyacids of phosphorus as the case may be. The investigations of analytical procedures for phosphorus were directed toward determining (a) whether phosphine could be desorbed from the solid sorber as a gas, or whether the phosphorus was present as a nonvolatile phosphorus oxyacid or soluble phosphate; and (2) whether 100 percent of the sorbed phosphorus could be eluted from the chosen sorber material. The experiments included examination of:

1. Desorption of phosphine as phosphine gas from charcoal
2. Solvent elution of phosphate from $KMnO_4$ impregnated silica gel
3. Solvent elution of phosphine from charcoal
4. Solvent elution of phosphate from charcoal
5. Solvent elution of phosphate from silver nitrate impregnated silica gel

The following paragraphs describe experiments carried out in these areas, and present results which, in each instance, caused the individual analytical procedures to be rejected.

3.2 Phosphates on $KMnO_4$-Silica Gel Sorber

Preparation of sorber material, described in Appendix A, involved soaking silica gel in a dilute aqueous solution of $KMnO_4$, pouring off the excess liquid, and drying. Since elution of the sorber material would yield a $KMnO_4$ solution of soluble phosphates, the analytical procedure of Muller (29) as described by Dechant et al (2) was used, that is, bleaching of $KMnO_4$ with oxalic acid followed by determination of the phosphate as phosphomolybdate by a standard method. Phosphate standards in acidified 0.01 N $KMnO_4$ solutions were determined by the standard APHA stannous chloride procedure (30) which required that spectrophotometric measurements be made during a very brief time interval, not less than 10 min nor more than 12 min after addition of $SnCl_2$ reagent. The time period proved too short to permit accurate measurements to be made , because samples, blanks, and standards had to be treated one at a time so that the measurements could be made at exactly the same number of minutes after addition of reagent. Identical handling of the standards, blanks, and samples was not assured because they were not prepared all at the same time, in the same series of laboratory manipulations. The hydrazine sulfate procedure of Kingsley and Schaffert (31) was tested and found to be more satisfactory because it permitted a longer working time, up to 24 hr according to these authors; this was the procedure employed by Dechant et al (2). However, the oxalic acid used to decolorize the $KMnO_4$ interfered with the hydrazine reduction procedure, causing a reduction of absorbance of samples, blanks, and standards which could not be compensated for in the calibrations.

Table 5 presents some data on the magnitude of oxalic acid interference with the phosphate determination, and Figure 2 is a plot of these data. To three standard phosphate solutions containing 10, 50, and 100 µg P per 100 ml, were added 20 ml 0.01 N $KMnO_4$ (the composition of the bubbler solution that would be used to determine phosphine concentrations in the gas mixtures, and also the estimated concentration of $KMnO_4$ in the eluted solutions from the solid sorbers) and 10 drops of 10 percent oxalic acid solution. Figure 2 shows the nonlinearity of phosphate standards containing $KMnO_4$ and oxalic acid. The odd point at 50 µg P is the absorbance of a 50 µg P/100 ml solution to which only 10 drops of oxalic acid were added, and no $KMnO_4$. The oxalic acid completely prevented the formation of the molybdenum blue color and the resulting yellow solution had very low absorbance.

The interference of oxalic acid with the determination of phosphate as the phosphomolybdate was studied by Chalmers and Sinclair (32) who found that oxalic acid and tartaric acid decreased the absorbance of phosphomolybdate solution when added in large amounts because of a shift in the equilibrium of the reaction:

$$\text{phosphomolybdate} + \text{oxalic acid} \rightleftharpoons \text{phosphate} + \text{oxalatomolybdate}$$

Since the oxalic acid had such a profound effect on phosphate determination, it was apparent that in effect $KMnO_4$ was interfering with the phosphate analysis.

The subject of quantitative determination of phosphates in the presence of $KMnO_4$ became moot when the initial (40 g)

Table 5. Oxalic Acid Interference in Phosphate Determination as Phosphomolybdate[1]

Solution (μg P/100ml)	Addition[2]	Absorbance
10	---	0.089
100	---	0.891
50	A	0.039
10	B	0.087
50	B	0.387
100	B	0.589

---

[1] Absorbance at 825 nm, 1-cm cell, IR phototube of Beckman DU spectrometer.

[2] A = 10 drops oxalic acid.
B = 10 drops oxalic acid plus 20 ml 0.01 N $KMnO_4$.

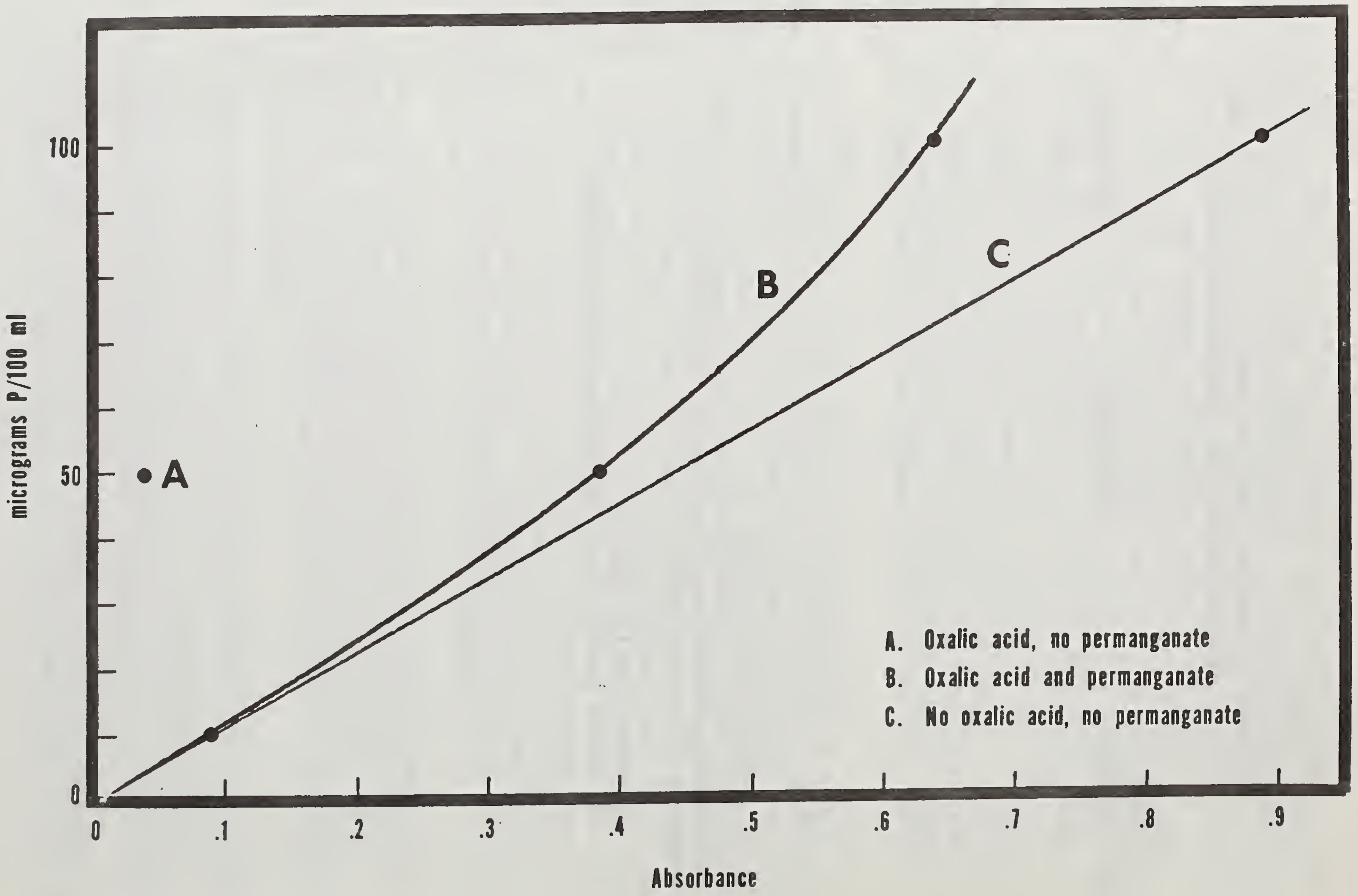

Figure 2. Oxalic acid interference with phosphate determination

quantity of sorber material was exhausted, and attempts to prepare it in quantity were unsuccessful. Impregnation of 200 g of silica gel with $KMnO_4$ gave MnO_2 instead of $KMnO_4$ due to the extended drying time required by the larger quantity of material. The MnO_2 impregnated silica gel was not a satisfactory sorber for phosphine.

3.3 Phosphine Desorption from Charcoal

If phosphine is adsorbed physically onto charcoal as maintained by Bastick (17, 18) and Zorin et al (20), then it should be removed by aeration or by heating in a furnace if it is unchanged as phosphine.

3.3.1 Aeration Experiment

Phosphine-containing charcoal was aerated to see whether phosphine could be removed from the charcoal column onto a silver nitrate impregnated silica gel indicator section. A 6 mm I.D. glass sampling tube containing a 10 mm indicator section $AgNO_3$ on SiGel was filled with 130 mm of water-washed charcoal (2.44 g), and exposed to 4.5 ppm phosphine in nitrogen at a flow of 0.7 liter/min for 25 min corresponding to 17.5 liters of gas containing 110 µg of phosphorus. No breakthrough was expected, nor was any observed. Room air was substituted for phosphine, flowing in the same direction at a rate of 1.4 liters/min. After 24 hrs the $AgNO_3$/SiGel indicator section was still white, demonstrating that the phosphine was converted to a nonvolatile species; for if it was still present as a physically adsorbed gas it would surely have been flushed into the indicator section in 24 hrs.

3.3.2 Furnace Experiment

Phosphine at a concentration of 1.2 ppm (about 4 times TLV) was sampled into a 7 mm I.D. x 130 mm long charcoal tube at a flow rate of 1 liter/min for 15 min. The sampling tube was transferred to a tube furnace where it was heated at 300 °C for 22 min under a helium flow of 25 ml/min. The helium was led into two bubblers in series, each containing 15 ml silver diethyldithiocarbamate (AgDDC) in pyridine. The resulting solutions were measured spectrophotometrically in 2 cm cells at 465 nm against fresh AgDDC in pyridine. For calibration, 1.2 ppm phosphine was flowed directly into 2 bubblers in series, at 1 liter/ min for 15 min. (An $AgNO_3$/SiGel indicating tube downstream of the second bubbler signaled phosphine breakthrough as soon as the calibration flow started, showing that the bubblers were not 100 percent efficient). Table 6 presents the results of the spectrophotometric measurements.

Table 6. Furnace Elution of Phosphine

Sample	Absorbance*
Bubbler #1, 15 ml reagent containing 15 liters of 1.2 ppm phosphine	0.127
Bubbler #2, 15 ml reagent containing overflow from Bubbler #1	0.110
Bubbler #1, 15ml reagent containing evolved gas from 300 °C heating of charcoal	0.009

---

*Measured at 465 nm in a 2 cm cell

In the absence of a complete calibration curve of AgDDC absorbance vs phosphine standards, for these initial experiments, one can still draw several rough (and unfavorable) conclusions about the efficiency of furnace elution of phosphine from charcoal, and the efficiency of midget bubblers containing 15 ml AgDDC in pyridine for measuring phosphine concentrations in the gases applied to the sampling tubes. Assuming a linear response and taking the total absorbance of bubblers #1 and #2 as representing the total phosphine (even though the $AgNO_3$/SiGel indicator showed that collection was not 100 percent complete), then the furnace eluted only about 3.8 percent of the sorbed phosphine [i.e. 0.009/0.237]. The collection efficiency of the first bubbler of the calibration experiment was 54 percent [i.e. 0.127/0.237], much less than the 75.1 percent efficiency claimed by Dechant et al (2) with their tall form bubblers. It was concluded from these tests that (1) midget bubblers containing only 15 ml of AgDDC in pyridine were not efficient enough for use in measuring phosphine gas concentrations, and (2) that phosphine sorbed on charcoal was either changed to a nonvolatile species as previously suspected, or else was decomposed at 300 °C into P and H_2 which would not have reacted with AgDDC. Support for the latter view is given by Mellow (33) who writes the equilibrium constant for the reaction

$$4\ PH_3\ (g) \rightleftharpoons P_4\ (g) + 6\ H_2(2)$$

as $K_p = 1 \times 10^{11}\ atm^3$ at a temperature of 627 °K (354 °C), where K_p is defined as

$$K_p = \frac{[P_4] x [H_2]^6}{[PH_3]^4}$$

3.4 Effect of Charcoal on AgDDC Color Reaction

Charcoal tended to decolorize solutions of AgDDC in pyridine by variable amounts depending on contact time. The magnitude of this effect was demonstrated by adding charcoal (from the furnace-treated sample tube) to 15 ml of phosphine-containing AgDDC/pyridine from Bubbler #1 (absorbance = 0.127 at 465 nm). After 5 min contact and filtration through Whatman 42 paper, an absorbance of 0.105 was measured, down about 21 percent. This effect, plus the consideration that phosphine might no longer be present as phosphine in the sampling tubes, led to the decision not to pursue the AgDDC method any further.

3.5 Phosphorus Oxyacids on Charcoal

Evidence in the literature that phosphine residues on cereal grains consisted of the lower oxyacids of phosphorus, e.g. hypophosphite H_3PO_2, phosphite H_3PO_3, and ortho-phosphate H_3PO_4 (9,10) introduced the possibility that these compounds might be present in the solid state sorbers, and be acid extractable. Contact with air would oxidize these substances to phosphate, so that a standard method could be used for analysis. The Ascorbic Acid method, ASTM D-515 was chosen; the modifications from the standard analytical procedure are summarized in Appendix B.

It was discovered that water washed charcoal had a high phosphate blank. This was to be expected because the charcoal was of plant origin. Acid washing (Appendix C) reduced the blanks to near zero, however the absorptivity of the acid-washed charcoal was reduced drastically (Table 2). Since the choice was between prohibitively high phosphate blanks and poor absorptivity, the use of charcoal as a solid sorber was discontinued.

3.6 Silver Nitrate Silica Gel Sorber

Although this was the best sorber for phosphine, difficulties were anticipated due to the possible interfence of silica with the phosphate measurements, since the silicomolybdate and the phosphomolybdate complexes absorb at the same wavelength. Considerable investigation into silica interference with phosphate analysis has been documented (27-32), and some investigators have concluded that only automated stopped-flow kinetic methods which take advantage of the different rates of formation of silicomolybdate and phosphomolybdate can remove silica interference completely. However, rapid elution of sorber tubes with dilue acid (2 N H_2SO_4) gave satisfactorily low blanks because the silica did not elute from the silica gel in the expected quantity. Thus, silver nitrate impregnated silica gel could be analyzed for phosphate content despite the expected silica interference.

3.7 Ascorbic Acid Procedure

Phosphates were eluted from $AgNO_3$/SiGel tubes with 2 N H_2SO_4, the solutions neutralized with NaOH, acidified slightly with one drop of acid, and determined by the Ascorbic Acid Procedure, ASTM D 515 as summarized in Appendix B. The silver interfered in two ways: (a) precipitating as the solution became momentarily alkaline during neutralization, and (b) precipitating slowly after addition of the ascorbic acid molybdate combined reagent. The precipitation during neutralization could be avoided by changing from a phenolphthalein end point to instrumental pH measurement, where the solution would not have to become alkaline to determine neutral pH. The precipitation during molybdate color development has not yet been satisfactorily solved. Work on the reduction of silver interference ought to be continued, for this approach appears to offer the most promising chance of success. When the procedure for determining sorbed phosphorus on $AgNO_3$ impregnated silica gel is brought under control, the phosphine in the gas entering the sampling tubes may be measured by the method of Bruce et al (6), using saturated bromine water to oxidize phosphine to phosphate, destroying the oxidant by boiling it out of solution, then determining the phosphate in solution by a standard method, viz. ASTM D515, the Ascorbic Acid Method. The Bruce et al method has the advantage that the bromine water is destroyed thermally, an advantage over the use of oxalic acid to destroy $KMnO_4$, qv.

4. RECOMMENDATIONS FOR FUTURE WORK

The proposed analytical procedure for determining phosphorus after sorption on $AgNO_3$/SiGel, is as follows: Two measurements are required for its evaluation, (1) determination of phosphine applied to the solid state sorbers by passing the gas through bubblers containing saturated bromine water to oxidize phosphine to phosphate, then boiling to drive off bromine, and determining phosphorus as the phosphomolybdate; and (2) introducing phosphine gas mixtures into the $AgNO_3$/SiGel solid state sorbers at the same flow rates and sampling times as the calibration runs above, and determining sorbed acid-soluble materials by eluting with 2.2 N H_2SO_4 neutralizing, and determining phosphomolybdate spectrophotometrically by the Ascorbic Acid Method, D-515.

The interference of silver with phosphate determination as the phosphomolybdate may be controllable by a suitable choice of neutralizing the dilute acid extract. If the interfering silver can be complexed, and the $AgNO_3$/SiGel sorber can be analyzed for phosphorus content, then a sampling and analysis procedure will be available.

The solubility of phosphorus oxyacids in organic solvents for possible gas chromatographic determination has not been investigated. Although pyridine extraction of phosphine collected on charcoal was not successful for determining phosphorus as the colored AgDDC complex, it is possible that silated compounds may form volatile adducts with phosphites, hypophosphites, phosphates, etc. to permit gas chromatographic methods of analysis to be used. Such an instrumental approach would have considerable advantage over the difficult colorimetric procedures now employed to determine phosphorus in aqueous solutions.

5. SUMMARY

The sorption of phosphine at ppm levels by physical sorbers such as silica gel and charcoal, under non-equilibrium conditions of active gas flow and in the presence of air and moisture was considerably less than the air- and moisture-free equilibrium values reported in the literature. Physical adsorbers depending on porosity alone (e.g. silica gel, acid-washed charcoal) were not effective sorbers for 4.5 ppm phosphine at flow rates up to 1 liter/min. Sorbers depending on reactivity alone (e.g. $KMnO_4$, $Na_2Cr_2O_7$, $AgNO_3$) also were ineffective; only those providing both porosity and reactive sites $AgNO_3$ impregnated silica gel, $KMnO_4$ impregnated silica gel, water-washed charcoal) retained phosphine in sufficient quantity to be considered useful for solid sampling tubes for work atmospheres.

Difficulties were encountered with various analytical methods for determining phosphorus collected on solid sorbers. At this writing, only $AgNO_3$/SiGel appears to be capable of being analyzed for sorbed phosphorus, but all the problems have not been solved for this material, either.

Phosphine appears to be oxidized to a non-volatile, pyridine-insoluble form on the solid sorber, so that it is not removable by aeration, furnace heating, or elution with pyridine; hence an instrumental method of gas analysis (such as gas chromatography) does not appear to be usable for sorbed phosphorus.

In summary, the following approaches toward developing a solid sorber system for samping and determining phosphine in work atmospheres were shown to be unsatisfactory:

1. Charcoal as a sorber, because of its high natural phosphorus content.

2. AgDDC colorimetric analysis for phosphine, because the sampled gas did not remain as phosphine.

3. $KMnO_4$ impregnated silica gel as a sorber, because it was difficult to prepare in quantity, and because the oxalic acid destruction of $KMnO_4$ interfered with the colorimetric determination of phosphate.

4. Instrumental methods (e.g. gas chromatography) for phosphine because phosphates eluted from the solid sorbers in aqueous acids were not volatile.

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7. APPENDICES

7.1 Appendix A. Preparation of $AgNO_3$-Impregnated Silica Gel

1. Calculation of Required $AgNO_3$ Concentration

$$PH_3 + 6AgNO_3 = Ag_3P.3AgNO_3 + 3HNO_3$$

$$Ag_3P.3AgNO_3 + 3H_2O = 6Ag^\circ + 3HNO_3 + 3H_3PO_3$$

Require 6 moles $AgNO_3$ for each mole P. To contain 200 μg P, use at least

$$x = (1020)(200\ \mu g)/(31)$$

$$= 6.6\ mg\ AgNO_3$$

Sampling tube filled to 5 cm contains about 1.5 g silica gel. Thus, 6.6 mg $AgNO_3$/g silica gel would occupy 2/3 of the sampling tube.

To prepare 200 g impregnated silica gel containing 6.6 mg/g $AgNO_3$, takes about 1.3 g $AgNO_3$. Use 1.4 g to compensate for losses.

2. Dissolve 1.4 g $AgNO_3$ in 300 ml H_2O and pour 200 g silica gel (a) into it slowly, with constant stirring.

3. Stir vigorously for 10 min while air is being displaced from the silica gel, then once every 5 min for about 40 min.

4. Pour off excess solution (b) and dry for 4 h at 90 °C, with occasional stirring of the mass of crystals.

5. Cool in a vacuum desiccator away from light (to protect it from ambient air and moisture).

6. Sieve through a 16-mesh screen to remove fines caused by decrepitation of the silica gel during drying, and store in a foil-wrapped polyethylene bottle. (c)

(a) W. R. Grace silica gel, grade 05, 6-16 mesh, non-indicating, available from laboratory suppliers under various trade names.

(b) Although some $AgNO_3$ is undoubtedly lost when excess solution is poured off, this is preferable to attempting to evaporate off the excess solution, with risk of obtaining a non-uniform product.

(c) $KMnO_4$-impregnated silica gel was prepared in the same manner, using 0.8 g $KMnO_4$ in 50 ml H_2O, adding silica gel until the total volume was 100 ml (about 40 g silica gel).

7.2 Appendix B. Modification of ASTM D515-72, Standard Methods of Test for Phosphorus in Water, Method A (Colorimetric Ascorbic Acid Reduction Method)

Extraction Procedure

Suspend the solid sorption tube vertically over a 50 ml Erlenmeyer flask. Add 20 ml of 2.2 N H_2SO_4 dropwise (D515 reagent 11.6 diluted 1:4) to the top of the tube, allowing the acid to drain into the flask. Neutralize to phenolphthalein with sat. NaOH (but NH_4OH may be better if silver is present) and immediately acidify with 1 drop of 2.2 N H_2SO_4.

Add 10 ml combined ascorbic acid reagent (D515 reagent 11.2), dilute to 50 ml, wait 10-30 min, and read the absorbance at 880 nm using a 20 mm cell.

Calibrate against phosphate standards and blanks prepared in the same manner (i.e. percolated through an unused solid state sorber tube and eluting with acid as described).

These modifications to ASTM D515 are designed to extract phosphate from the solid sorber material, and include the effects of the sorber material in the calibration curves.

7.3 Appendix C. Charcoal Treatments

A. WATER WASHING TO REMOVE FINES

1. Soak activated charcoal* in water for 10 min. with stirring. Pour off fines. Repeat 3-4 times, pouring off fines after each soaking.

2. Pour off excess water, dry at 150 °C for 3 h.

3. Cool in vacuum desiccator.

B. ACID WASHING TO REMOVE PHOSPHORUS IMPURITY

1. About 80 g of charcoal* which had been dried at 150 °C for 3 h was rinsed twice in 2.2 N H_2SO_4, six times with H_2O, and left overnight in 2.2 N H_2SO_4.

2. Next day the charcoal was heated at 90 °C for 1 h in 200 ml 2.2 N H_2SO_4.

3. The acid was poured off, and the heating repeated twice more, 1 h each time.

4. The charcoal was rinsed three times in 200 ml portions of water.

5. The charcoal was boiled 1 h in water.

6. The charcoal was rinsed three times in room temp. water, until the water from the charcoal was neutral to phenolphthalein.

7. The charcoal was dried for 3 h at 146-160 °C and cooled in a vacuum desiccator.

8. Acid elution of this treated charcoal gave no detectable phosphorus blank.

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*Pittsburgh Activated Carbon Div., Calgon Corp., Pittsburgh, Pa., Type BPL, 20-50 mesh (coal-based vapor adsorption grade) was used.