Introduction

The general procedure for collection and analysis of air samples for phosphine is described in OSHA Method No. ID-180 (11.1.). Phosphine is collected on a solid sorbent composed of beaded activated carbon impregnated with potassium hydroxide (KOH). The sampling and analytical procedure is based on the following proposed chemical reaction:

$$3PH_3 + 6OH^- + 5O_2 \text{ ------> } 6H_2O + HPO_4^{2-} + 2HPO_3^{2-}$$

For every 3 moles of phosphine, 1 mole of phosphate (HPO_4^{2-}) and 2 moles of phosphite (HPO_3^{2-}) are produced. The collected phosphine is extracted from the carbon bead using 30% hydrogen peroxide (H_2O_2) and analyzed as phosphite by ion chromatography (IC). An additional analytical confirmation by IC for phosphate was not performed. The KOH used for impregnating the sorbent contained high background levels of phosphate.

This method has been validated for a 36-L, 240-min sample based on a pump flow rate of approximately 0.15 L/min. All solid sorbent tubes used during the validation contained single sections consisting of approximately 1.5 g of treated carbon. The majority of tubes used were prepared in-house; exceptions are noted where commercially prepared tubes were used. Two different size tubes (9-mm and 5-mm o.d.) were obtained from a commercial source (SKC Inc., Eighty Four, PA). A significant difference in recoveries between the different size tubes was not noted during side-by-side testing.

A cylinder of phosphine (1.02% phosphine in nitrogen, certified, Air Products Co.) was used for generating test atmospheres. An evaluation (11.2.) of the cylinder concentration using the phosphomolybdate method of analysis (11.3.) indicated the manufacturer's stated concentration was accurate. The stated concentration was used for all calculations of theoretical (taken) concentrations. A dynamic generation system (described in Section 2 and Figure 1) was used for all experiments except for the detection limit and field evaluation tests. Detection limit tests were performed using sodium phosphite spikes. Samples for all experiments were analyzed by IC (11.1.).

The method validation consisted of the following experiments and summaries:

1. An analysis of 22 spiked samples to determine desorption efficiency and analytical precision and accuracy.
2. An analysis of 22 samples collected from dynamically generated test atmospheres to determine overall precision and accuracy.
3. A determination of the sampling media collection efficiency.
4. Determinations of breakthrough when sampling time or concentration is increased or when sampling in low humidity environments.
5. An evaluation of the room temperature storage stability of 38 samples taken at the OSHA Permissible Exposure Limit (PEL) of 0.3 ppm. An additional evaluation of the effects of refrigeration on storage stability.
6. A determination of any significant change in recovery when sampling at different humidities.
7. A study of the shelf-life of stored sorbent tubes.
8. A determination of the qualitative and quantitative detection limits.
9. A field evaluation of sampling media at a grain processing mill.
10. An assessment of the method and summary.

An Addendum describing a comparison of different lots of carbon bead, and samples generated at the STEL are included at the end of this backup report. The study of different lots was conducted when it was discovered that some lots of the carbon bead were less efficient at collecting phosphine than previously expected.

Results were calculated using concentration-response curves and were statistically examined for outliers and homogeneity of variance. Possible outliers were determined using the Treatment of Outliers test (11.4.). Homogeneity of variance was determined using the Bartlett's test (11.5.).

1. Analysis

Twenty-two samples were prepared by adding known amounts of phosphine to treated solid sorbent tubes to determine desorption efficiency (DE) and recoveries for the analytical portion of the method. An active method of spiking was used with low flow (0.01 to 0.02 L/min) sampling pumps to determine the amount of gas collected and not necessarily the sampling capability at the low flow rate.

1.1. Procedure: Sampling tubes containing treated carbon bead were spiked by a procedure similar to that described in reference 11.6. The phosphine source mentioned in the Introduction was diluted to approximately 50 ppm using the system shown in Figure 1. Calibrated low flow-rate pumps were connected to the sampling manifold and were used to deliver the spikes for measured time

periods. Air used to dilute the phosphine source was tempered to 50% RH and 25 °C. Pumps used for this experiment were Model No. 222-3-12 (SKC, Eighty Four, PA) and were calibrated to collect samples at 0.010 to 0.020 L/min. Spikes were approximately 6, 12, and 24 µg phosphine. These levels are approximately 0.5, 1, and 2 times the PEL for a 36-L air sample.

1.2. Results: Recoveries are presented in Table 1. For the analytical section of the method, the overall DE was 96.8%, and the analytical precision (CV_1 pooled) was 0.030. One result was omitted as an outlier (1 X PEL group). Results for the three test levels passed the Bartlett's test and were pooled.

2. Sampling and Analysis

To determine the precision and accuracy of the method, known generated samples were prepared and analyzed.

2.1. Procedure:

2.1.1. The phosphine gas source mentioned in the Introduction was used to generate test atmospheres of phosphine. This source was diluted with filtered, humidified air using the system shown in Figure 1.

2.1.2. Dynamic generation system

A Miller-Nelson Research Inc. (Model HCS-301) flow, temperature and humidity control system was used for air flow control and conditioning. All generation system fittings and connections were Teflon. A glass mixing chamber was used to mix the tempered, filtered air with the contaminant gas. The system was set to generate test atmospheres at 50% RH and 25 °C.

2.1.3. The phosphine and diluent air flow rates were adjusted using mass flow controllers. Flow rates were also measured using a dry test meter (diluent air) and a soap bubble flow meter (phosphine gas).

2.1.4. Samples were taken from the sampling manifold using constant flow pumps. Calibrated Du Pont P125 pumps were used. Pump flow rates were approximately 0.12 to 0.15 L/min and sampling times ranged from 240 to 360 min. Sample concentrations were approximately 0.5, 1, and 2 times the

OSHA PEL for 30- to 50-L air samples.

2.2. Results: Results are shown in Table 2. The precision and accuracy data, based on NIOSH statistical protocol (11.5.), is presented in Tables 1 and 2. The generated sample (Sampling and Analysis) results passed the Bartlett's test and were pooled. The pooled coefficients of variation are as follows:

CV_1(pooled) = 0.030 CV_2(pooled) = 0.039 CV_T(pooled) = 0.041

There was insignificant overall bias and the overall error was ±8.3%. Overall error (11.7.) was calculated using the equation:

Overall error % = ±(|mean bias| + $2CV_T$) X 100 (95% confidence)

3. Collection Efficiency

Procedure: Collection efficiency was determined for in-house and commercially prepared tubes.

3.1. In-house Tubes

The collection efficiency at the upper validation limit was determined using double sampling tubes. Two sampling tubes were connected in series. These tubes were prepared at the OSHA laboratory. Eight double tubes were connected to the sampling manifold to collect samples at approximately 2 times the OSHA PEL for 210 min (50% RH and 25 °C). Pump flow rates were 0.12 to 0.15 L/min.

3.2. Commercial Tubes

Six double tubes were also used to collect samples at 0.67 ppm for 240 min. Pump flow rates, humidity and temperature were the same as mentioned in Section 3.1. Tubes prepared by SKC Inc. (Eighty Four, PA.) were used.

3.3. The amount of phosphine vapor collected in the first and second tubes was determined. The collection efficiency was calculated by dividing the amount collected in the first tube by the total amount of phosphine collected in the first and second tube.

Results: Results shown in Table 3 indicate a collection efficiency of 100.0% when sampling at approximately 2 times the OSHA PEL for 210 or 240 min. No breakthrough was evident during the collection efficiency study.

4. Breakthrough

Three different breakthrough experiments were conducted to assess potential breakthrough:

Increased sampling time
Increased concentration
Sampling in low humidity environments

4.1. Increased Sampling Time

Procedure: A preliminary study using solid sorbent tubes and phosphine detector tubes (Model No. CH31101, Draeger, Pittsburgh, PA) as colorimetric, qualitative indicators of breakthrough was conducted. The Draeger tubes were chosen because of the very stable, reproducible indication, large size, loose packing, and small pressure drop when attached to a sampling pump. Two lots of Draeger detector tubes had been previously tested at low concentration ranges when using detector tube pumps (11.2.). Additional testing was conducted with continual flow pumps (Du Pont P125) to assess the possibility of using these detector tubes for identification of breakthrough. These tubes were found capable of producing a noticeable colorimetric indication after sampling 0.3 ppm phosphine for 15 min at a flow rate of 0.1 L/min (approximately 0.6 µg phosphine). The detector tubes were attached between the sampling tubes and pumps. Six samples were taken for 360 min at 0.6 ppm and a flow rate of 0.12 to 0.15 L/min (50% RH and 25 °C).

4.2. Increased Concentration

Procedure: Two sampling tubes containing treated carbon bead were attached to each other and five of these double tube samples were taken to determine breakthrough at a concentration level of 1.9 ppm phosphine. Commercially prepared (SKC Inc.) tubes were used for this experiment.

4.2.1. Samples were collected at a flow rate of approximately 0.15 L/min, a concentration of 1.9 ppm phosphine, 25 °C and 50% RH. Samples were taken for 240 min.

4.2.2. Breakthrough was assessed by analyzing both tubes and dividing the amount collected in the second solid-sorbent tube by the total amount collected in both tubes.

4.3. Decreased Humidity

Procedure: An experiment was conducted to determine if breakthrough exists at 30% RH. Sampling at this humidity had given lower recoveries than expected (See Section 6. for further details). This experiment should establish whether these low recoveries are due to breakthrough or an incomplete or unanticipated reaction of phosphine with the treated sorbent. To determine breakthrough, sampling tubes, detector tubes, and pumps were connected together as mentioned in Section 4.1. Samples were taken for 90 min at flow rates of 0.115 to 0.135 L/min. The generation system parameters were 1 ppm phosphine, 25 °C, 30% RH.

Results:

Detector tube color indications were not observed after increasing the sampling time to 360 min at 2 times the PEL. As shown in Table 4, increasing the sampling concentration to 1.9 ppm (240-min sampling time) produced breakthrough; however, the amount was less than 5%. When sampling without a humidifier at 30% RH, breakthrough was evident after a 6 µg sample load (Table 4). Humidifiers are necessary at low RH (<40%) to prevent premature breakthrough.

5. Storage Stability

A study was conducted to assess the stability of phosphine collected on the treated solid sorbent.

5.1. Procedure - storage assessment at room temperatures of 20 to 25 °C.

5.1.1. Thirty-eight samples were collected using the generation system previously described in Section 2. Samples were collected at the PEL, 50% RH, and 25 °C.

5.1.2. Samples were stored at room temperature (20 to 25 °C) on a lab bench.

5.1.3. Six to eight samples were analyzed after various periods of storage (0, 5, 12, 18, and 32 days).

5.2. Procedure - refrigeration assessment

5.2.1. Thirty-five samples were collected in an effort to determine the effect of refrigeration on sample storage stability. Twenty-four samples were collected at the PEL and 11 at 2 times the PEL. The 11 samples were taken using commercially prepared tubes while the other tubes were prepared in-house.

5.2.2. Twelve samples taken at the PEL and four taken at 2 times the PEL were analyzed immediately after generation.

5.2.3. Nine samples were stored at room temperature (20 to 25 °C) and ten were refrigerated (7 °C). Twelve samples were analyzed after a 12- to 13-day storage period. The remaining seven samples were analyzed after 30 days.

5.3. Results: Results of this stability study are shown in Table 5 and Figure 2. The mean of samples (stored at 20 to 25 °C) analyzed was 81% of the known concentration after 12 days, 64% after 18 days, and 48% after a 32-day storage period. Results indicate samples may be stored at typical laboratory temperatures up to 12 days after sampling. Sample refrigeration reduces sample loss. Samples refrigerated for 13 days (7 °C) showed no apparent loss while those refrigerated for 30 days displayed a slight loss in recovery. Samples should be refrigerated whenever possible. Since it is difficult to control the temperature of samples after field collection and during shipment, samples should be analyzed within 12 days of collection regardless of laboratory refrigeration.

6. Humidity Study

A study was conducted to determine any significant effect on recoveries when sampling at different humidities. Test atmospheres were generated at 23, 30, 40, 50, and 80% RH. Samples were taken for 360 min at flow rates of approximately 0.15 L/min. Results are listed in Table 6 and displayed in Figure 3. As shown, samples collected at relative humidities less than 40% result in unacceptably low phosphine recoveries. This loss can be resolved by sampling with an in-line humidifier.

The following techniques were used in an attempt to humidify samples taken in areas having less than 40% RH:

6.1. Deionized water (0.75 mL) was added to the end of a cellulose filter plug (Rainin Instrument Co., Woburn, MA; part no. 23534/B) contained inside a glass tube. This tube was used as a humidifying pre-tube. The 0.75 mL spike should not cause water saturation to the treated sorbent and should provide continuous humidification for up to 6 h of sampling at a flow rate of 0.15 L/min.

6.2. A 25-mL impinger containing approximately 5 mL of deionized water was also used as a humidification device.

6.3. Procedure: Two different experiments were conducted. The first experiment was performed at the PEL while the second was performed at a higher concentration (1.042 ppm). The second experiment was performed to evaluate the potential for humidifier failure or breakthrough at higher concentration levels. Sampling rates for both experiments were 0.11 to 0.15 L/min. Samples were taken for 300 min during the first experiment and 120 min for the high concentration test.

6.4. An additional test was conducted to assess any change in recovery if the humidifier is used at high humidity levels. Three samples with an in-line humidifier and two samples without the humidifier were taken at about 2 times the PEL. Sampling conditions were 25 °C and 80% RH.

Results: Results for either humidifier are shown in Table 6. As shown, acceptable recoveries are noted when the relative humidity is equal to or greater than 40% (25 °C). The results demonstrate the recovery was approximately 55% at 30% RH, and a 46% net recovery was noted at 23% RH. It is, therefore, concluded that the relative humidities below 40% definitely result in low phosphine recoveries. Results using a humidifier (Table 6) show acceptable recoveries when sampling in low humidity environments; therefore, in-line humidifiers are necessary for accurate assessments of phosphine when sampling in low humidities (<40% RH).

The collection of samples with an in-line humidifier at 80% RH was compared to samples taken without a humidifier. Both approaches gave comparable recoveries. Average recoveries were 107.6% and 112.5% for samples collected at 80% RH with a humidifier and for samples collected without one, respectively. For added convenience, humidity levels do not have to be determined if a humidifier is used.

7. **Shelf Life Study**

A shelf life study of the treated sampling tubes was conducted.

Procedure: Sampling tubes were prepared in-house and sealed with plastic caps. After 68 days, the tubes were used to collect samples from the generation system previously mentioned in Section 2.

Commercially prepared tubes were also set aside and used after a period of 6 months. These tubes were then used for the 0 day storage test (Table 5 - Refrigeration vs. Room Temperature - 2 X PEL data).
Results: Commercially prepared tubes stored for 6 months and then used to collect samples gave an average recovery of 113.7%. Sealed tubes can be stored at typical laboratory temperatures (20 to 25 °C) for at least 6 months and then used for sampling.

8. **Detection Limits**

Procedure: Detection limits were determined by statistically examining the analytical results of spiked samples and blanks. Low concentration samples were prepared by spiking solutions of deionized water with sodium phosphite. Concentrations of 0.14, 0.28, and 0.57 µg/mL phosphite were used. Analysis of detection limit samples was performed with a full scale detector output setting of 3 microsiemens. A 50-µL sample loop was used for all injections.

8.1. Qualitative Detection Limit - The Rank Sum Test (11.8.) was used for the determination of the qualitative limit.

8.2. Quantitative Detection Limit - A modification or derivation of the International Union of Pure and Applied Chemistry (IUPAC) detection limit equation (11.9.) was used to calculate the quantitative limit. At the sensitivity level tested, blank readings and the standard deviation of the blank were equal to zero. The lack of a blank signal does not satisfy a strict interpretation of the IUPAC detection limit when using the equation shown in Table 8. The quantitative detection limit for this method is calculated using the standard deviation of a standard below the range of the expected detection limit as a substitute for the blank readings.

Results: The results are listed in Table 8 and graphically displayed in Figure 4. The qualitative detection limit is 0.14 µg/mL. The quantitative detection limit is 0.23 µg/mL (both limits are calculated as HPO_3^{2-}). Using a 36-L air volume and a 5 mL sample volume, the qualitative limit is 0.009 ppm and the quantitative limit is 0.015 ppm phosphine (Table 8).

9. Field Evaluation

A field evaluation at a grain processing mill was conducted using a number of different sampling devices.

Procedure: A Teflon sampling manifold was set-up with two exhaust pumps (Du Pont P4000 pumps calibrated at 3 L/min) at one end of the manifold. These pumps continually drew the workplace air-phosphine mixture through the sampling manifold. Side-by-side samples were taken from the manifold during a 3-h sampling period in which Magtoxin(TM) (magnesium phosphide) was used to fumigate an area in which grain is packaged and stored.

Mercuric cyanide-impregnated silica gel tubes manufactured by SKC and Supelco as well as commercially prepared carbon bead tubes were used. Carbon bead samples were taken with two different size tubes. One tube had an outer diameter of 5 mm (thin) while the other was 9 mm (large). Both tubes contained approximately 1.5 g of treated sorbent. The thin tube was tested since it could be used at higher humidity levels (without the humidifier) and provide more convenience during use. The thin tube is easier to break open and connect to a pump than the larger tube. The 9-mm o.d. tube is used with the humidified filter tube since the dimensions of both tubes are similar and are easily connected together with flexible tubing.

Results: Results are listed in Table 9. The field validation indicated good agreement between the mercuric cyanide-treated silica gel tubes and the KOH-impregnated carbon bead samples with in-line humidifiers. The results of the non-humidified carbon bead samples are similar to the laboratory recoveries for low humidity sampling (Table 6). A significant amount of breakthrough was noted for the treated silica gel tubes at the apparent concentration of 1.4 to 1.5 ppm phosphine. The SKC tubes had less breakthrough than the Supelco tubes at this concentration.

10. Summary

The results indicate the method meets the NIOSH criteria for accuracy and precision (11.5.).

A side-by-side method comparison was not performed; however, detector tube and mercuric cyanide-treated silica gel samples were taken during the same period and under the same generation conditions as the carbon

bead tube. Recoveries for the silica gel samples were within accepted limits (see reference 11.2. for further details).

Method No. ID-180 has the disadvantage of low recoveries at low humidities if a humidifier is not used. Unacceptable recoveries are also noted if samples are stored at ambient temperatures longer than 12 days before analysis. However, the overall method offers a simple, accurate and precise assessment of phosphine concentrations if the appropriate steps are taken:

1) When sampling in low humidity environments, a humidifier is necessary. Humidifiers can be used regardless of the humidity at the sampling site.
2) Analyses should be performed within 12 days and samples should be refrigerated during this time period.

Experiments have been conducted after this backup report was written. Please consult the Addendum at the end of this report for further information.

11. References

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Table 1

Analysis

Level*	0.5 X PEL			1 X PEL			2 X PEL		
	µg taken	µg found	DE	µg taken	µg found	DE	µg taken	µg found	DE
	5.19	5.62	1.083	11.99	11.11	0.927	24.04	(LIA)	-
	5.17	5.00	0.967	12.98	12.21	0.941	25.83	25.39	0.983
	5.17	4.99	0.965	13.46	12.44	0.924	26.55	25.42	0.957
	5.14	5.11	0.994	12.70	12.55	0.988	25.06	24.69	0.985
	5.10	5.10	1.000	11.82	11.20	0.948	23.84	22.35	0.938
	5.02	4.97	0.990	12.75	12.18	0.955	25.78	24.75	0.960
				13.20	12.38	0.938	26.57	24.83	0.935
				12.39	10.18	0.822**	25.09	23.89	0.952
	n	6			7			7	
	Mean	1.000			0.946			0.959	
	Std Dev	0.043			0.022			0.020	
	CV_1	0.043			0.023			0.021	

CV_1 (pooled) = 0.030

Ave. DE = 0.968

* Levels are approximate

** Excluded from statistical analysis as an outlier

LIA = Lost In Analysis

DE = Desorption Efficiency

Table 2

Sampling and Analysis

Test Level	Found µg	Air Vol (L)	ppm	Taken ppm	Recovery percent
0.5 X PEL	8.85	41.0	0.155	0.152	102.0
	9.39	42.3	0.160	0.152	105.3
	10.76	47.7	0.162	0.152	106.6
	8.40	37.1	0.163	0.152	107.2
	11.68	51.1	0.164	0.152	107.9
	9.40	41.9	0.161	0.152	105.9
	10.12	44.1	0.165	0.152	108.6
	8.56	38.6	0.160	0.152	105.3
		n	8		
		Mean	0.161		106.1
		Std Dev	0.003		
		CV_2	0.019		
1 X PEL	18.47	45.1	0.295	0.284	103.9
	16.95	44.1	0.276	0.284	97.2
	13.95	39.0	0.257	0.284	90.5
	15.80	37.7	0.301	0.284	106.0
	19.52	51.1	0.275	0.284	96.8
	17.59	41.2	0.307	0.284	108.1
	17.37	42.9	0.291	0.284	102.5
	16.72	41.7	0.288	0.284	101.4
		n	8		
		Mean	0.286		100.8
		Std Dev	0.016		
		CV_2	0.057		
2 X PEL	28.35	35.1	0.581	0.666	87.2
	23.55	28.6	0.592	0.666	88.9
	27.22	31.8	0.616	0.666	92.5
	26.21	30.2	0.624	0.666	93.7
	27.80	32.9	0.608	0.666	91.3
	26.57	30.6	0.624	0.666	93.7
		n	6		
		Mean	0.608		91.2
		Std Dev	0.018		
		CV_2	0.029		

* Excluded from statistical analysis as an outlier

CV_2 (pooled)	= 0.039	CV_T (pooled)	= 0.041
Bias	= 0.1%	Overall Error	= ±8.3%

Table 3

Collection Efficiency

50% RH, 25 °C

Sample No.	ppm Phosphine		% Collection Efficiency
	First Tube	Second Tube	
1	0.49	ND	100
2	0.55	ND	100
3	0.58	ND	100
4	0.58	ND	100
5	0.51	ND	100
6	0.54	ND	100
7	0.52	ND	100
8	0.57	ND	100
9	0.58	ND	100
10	0.59	ND	100
11	0.62	ND	100
12	0.62	ND	100
13	0.61	ND	100
14	0.62	ND	100

Note: (1) Samples 1 to 8 were taken at 0.12 to 0.15 L/min flow rate for 210 min. These tubes were prepared at the OSHA lab. Samples 9 to 14 are commercially prepared tubes used to take samples for 240 min and at the same flow rates as the in-house tubes.

(2) ND = None detectable < 0.015 ppm phosphine

(3) Samples 1 to 8: Generation concentration = 0.6 ppm phosphine
Samples 9 to 14: Generation concentration = 0.67 ppm phosphine

Table 4

High Concentration Breakthrough

50% RH, 25 °C

Sample No.	-------μg PH_3 Found-------- 1st	2nd	% Breakthrough
1	83.07	3.34	3.9
2	82.60	1.22	1.5
3	71.92	2.22	3.0
4	81.84	2.37	2.8
5	77.80	3.00	3.7
		Ave:	3.0

Note: (1) 1st and 2nd = Commercially prepared (SKC) sampling tubes
(2) Sample rate = approximately 0.15 L/min flow rate for 240 min
(3) Generation concentration = 1.90 ppm phosphine

Low Humidity Breakthrough

30% RH, 25 °C

Sample No.	------μg PH_3 Found-------- 1st	2nd*	% Breakthrough
1	5.69	3.90	40.6
2	5.45	2.50	31.5
3	5.62	3.20	36.3
4	5.66	1.88	24.9
5	5.61	3.13	35.8
n	5	5	
Mean	5.61	2.92	33.8
Std Dev	0.093	0.76	
CV	0.017	0.26	

Note: (1) 1st = Sampling Tube; 2nd = Draeger phosphine detector tube
(2) Sampled at 0.115 to 0.135 L/min flow rate for 90 min
(3) Generation concentration = 1 ppm phosphine
* Results obtained using calibrated detector tubes. These results are approximate.

Table 5

Storage Stability Test

Ambient (20 - 25 °C) Storage

(1 X PEL) Storage	Found µg	Air Vol (L)	ppm	Taken ppm	% Recovery
Day 0	18.47	45.1	0.295	0.284	103.9
	16.95	44.1	0.276	0.284	97.2
	13.95	39.0	0.257	0.284	90.5
	15.80	37.7	0.301	0.284	106.0
	19.52	51.1	0.275	0.284	96.8
	17.59	41.2	0.307	0.284	108.1
	17.37	42.9	0.291	0.284	102.5
	16.72	41.7	0.288	0.284	101.4
		n	8		
		Mean	0.286		100.8
		Std Dev	0.016		
		CV	0.057		
Day 5	16.70	44.0	0.273	0.284	96.1
	16.85	45.2	0.268	0.284	94.4
	16.15	42.8	0.271	0.284	95.4
	12.08	39.4	0.220	0.284	*
	19.33	52.0	0.267	0.284	94.0
	15.86	42.1	0.271	0.284	95.4
		n	5		
		Mean	0.270		95.1
		Std Dev	0.002		
		CV	0.009		
Day 12	12.90	41.4	0.224	0.300	74.7
	14.19	42.4	0.241	0.300	80.3
	16.63	47.8	0.250	0.300	83.3
	13.27	37.4	0.255	0.300	85.0
	16.99	50.3	0.243	0.300	81.0
	13.54	41.0	0.237	0.300	79.0
	15.28	43.2	0.254	0.300	84.1
	16.60	37.9	0.315	0.300	*
		n	7		
		Mean	0.243		81.0
		Std Dev	0.011		
		CV	0.045		

* Excluded from statistical analysis as outliers

Table 5 (Continued)

Storage Stability Test

Ambient (20 - 25 °C) Storage

(1 X PEL) Storage	Found µg	Air Vol (L)	ppm	Taken ppm	% Recovery
Day 18	12.55	44.2	0.204	0.280	72.9
	11.88	43.7	0.195	0.280	69.6
	10.96	41.7	0.189	0.280	67.5
	9.58	38.6	0.178	0.280	63.6
	11.53	51.1	0.162	0.280	57.9
	9.87	41.5	0.171	0.280	61.1
	9.08	43.4	0.150	0.280	53.6
	11.55	42.8	0.194	0.280	69.3
		n	8		
		Mean	0.180		64.4
		Std Dev	0.018		
		CV	0.102		
Day 32	7.92	44.1	0.129	0.284	45.4
	7.97	44.8	0.128	0.284	45.1
	7.70	42.8	0.129	0.284	45.4
	7.19	38.9	0.133	0.284	46.8
	10.87	53.1	0.147	0.284	51.8
	8.61	41.6	0.149	0.284	52.5
	7.61	43.0	0.127	0.284	44.7
	9.08	43.3	0.151	0.284	53.2
		n	8		
		Mean	0.137		48.1
		Std Dev	0.010		
		CV	0.077		

Samples listed above were collected at 1 X PEL, 25 °C and 50% RH.

Table 5 (Cont.)

Storage Stability Test

Refrigeration (7 °C) vs. Room Temperature (20 to 21 °C)

	Found			Taken	
	µg	Air Vol (L)	ppm	ppm	% Recovery
Day 0	15.37	38.65	0.286	0.309	92.6
	11.96	39.09	0.220	0.309	*
(1 X PEL)	16.13	38.80	0.299	0.309	96.8
	15.80	38.78	0.293	0.309	94.8
	14.14	36.72	0.277	0.309	89.6
	15.58	38.11	0.294	0.309	95.1
	16.11	38.62	0.300	0.309	97.1
	16.75	40.84	0.295	0.309	95.5
	16.65	38.88	0.308	0.309	99.7
	16.44	38.27	0.309	0.309	100.0
	15.42	34.98	0.317	0.309	102.6
	15.99	37.58	0.306	0.309	99.0
		n	11		
		Mean	0.299		96.6
		Std Dev	0.011		
		CV	0.038		
	25.75	31.82	0.582	0.525	110.9
(2 X PEL)	26.53	31.62	0.603	0.525	114.9
	25.58	30.88	0.596	0.525	113.5
	26.54	31.37	0.608	0.525	115.8
		n	4		
		Mean	0.597		113.7
		Std Dev	0.011		
		CV	0.019		

* Tubing connecting the pump and sampling tube disconnected during sampling. This result was not used in statistical calculations.

Day 0 samples were desorbed and analyzed immediately after collection.
In-house prepared tubes were used for 1 X PEL samples; commercial tubes were used for 2 X PEL samples.

Table 5 (Cont.)

Storage Stability Test

Refrigeration (7 °C) vs. Room Temperature (20 to 21 °C)

	Found			Taken		
	µg	Air Vol (L)	ppm	ppm	% Recovery	
Day 13	16.37	39.11	0.301	0.309	97.4	Refrigerated
	15.77	36.95	0.307	0.309	99.4	
(1 X PEL)	16.94	39.16	0.311	0.309	100.6	
	16.59	37.75	0.316	0.309	102.3	
	15.59	34.82	0.322	0.309	**	
	15.93	37.31	0.307	0.309	99.4	
		n	5			
		Mean	0.308		99.8	
		Std Dev	0.006			
		CV	0.018			
Day 12	14.00	39.16	0.257	0.309	83.2	Room Temperature
	13.47	36.56	0.265	0.309	85.8	
(1 X PEL)	14.61	39.79	0.264	0.309	85.4	
	13.55	37.20	0.262	0.309	84.8	
	11.97	34.17	0.252	0.309	81.6	
	13.78	37.25	0.266	0.309	86.1	
		n	6			
		Mean	0.261		84.5	
		Std Dev	0.005			
		CV	0.021			
Day 30	19.81	30.99	0.460	0.523	88.0	Refrigerated
	22.48	31.35	0.516	0.523	98.7	
(2 X PEL)	20.47	29.01	0.508	0.523	97.1	
	21.29	29.80	0.514	0.523	98.3	
		n	4			
		Mean	0.500		95.5	
		Std Dev	0.027			
		CV	0.053			
Day 30	17.28	31.63	0.393	0.523	75.1	Room Temperature
(2 X PEL)	13.47	30.84	0.314	0.523	60.0	
	15.94	29.65	0.387	0.523	74.0	
		n	3			
		Mean	0.365		69.7	
		Std Dev	0.044			
		CV	0.121			

** Pump flow rate change was greater than 10%. This result was not used.

Table 6

Humidity Experiments (25 °C)

% RH	23	30	40	50	80
ppm PH_3 Taken	0.309	0.298	0.307	0.284	0.294
ppm PH_3 Found	0.148	0.169	0.302	0.295	0.257
	0.134	0.181	0.306	0.276	0.262
	0.133	0.175	0.315	0.257	0.272
	0.151	0.192	0.308	0.301	0.271
	0.159	0.105	0.301	0.275	0.267
	0.135	0.195		0.307	0.274
		0.198		0.291	0.158*
		0.105		0.288	0.268
n	6	8	5	8	7
Mean, ppm	0.143	0.165	0.306	0.286	0.267
Std Dev, ppm	0.011	0.038	0.006	0.016	0.006
CV	0.076	0.232	0.018	0.057	0.022
Ave Recovery	46.4%	55.3%	99.8%	100.8%	90.9%

* Excluded from statistical analysis as an outlier
Samples were taken for 360 min at a flow rate of approximately 0.15 L/min.

Table 6 (Continued)

Humidifier vs. No Humidifier

25 °C & 30% RH

Low Concentration

Sample Type	ppm Phosphine Found: Humidifier	No Humidifier
FP	0.33	0.26
FP	0.44	0.22
IMP	0.34	0.28
IMP	0.34	0.28
n	4	4
Mean	0.36	0.26
Std Dev	0.052	0.028
CV	0.143	0.109
% Recovery	90	65

Generation concentration = 0.4 ppm phosphine
Sampling rate = 0.11 to 0.15 L/min,
Sampling time = 300 min

High Concentration

Sample No.	ppm Phosphine Found: Humidifier FP	Humidifier IMP	No Humidifier
1	0.9196	0.9608	0.3524
2	1.0271	0.9675	0.3413
3	1.0194	1.0221	0.2509
4	1.0314	0.9980	0.3460
5	1.0239	1.1107	0.3827
6	0.9186	1.0417	0.3191
n	6	6	6
Mean	0.990	1.017	0.332
Std Dev	0.055	0.055	0.045
CV	0.056	0.055	0.135
% Recovery	95.0	97.6	31.9

Generation concentration = 1.042 ppm phosphine
Sampling rate = 0.11 to 0.15 L/min, Sampling time = 120 min

FP = cellulose plug was wetted with DI water prior to sampling and used as pre-tube (Section 6.1.).

IMP = an impinger containing 5 mL DI water was placed in front of sampling tube (Section 6.2.).

Table 7

Shelf Life

Storage	Found µg	Air Vol (L)	ppm	Taken ppm	% Recovery
Day 0	18.63	42.9	0.312	0.297	105.1
	16.38	37.4	0.315	0.297	106.1
	18.76	41.4	0.326	0.297	110.0
	15.09	37.6	0.289	0.297	97.3
		n	4		
		Mean	0.310		104.5
		Std Dev	0.016		
		CV	0.051		
Day 68	17.33	42.0	0.297	0.297	100.0
	20.88	48.0	0.313	0.297	105.4
	22.09	50.3	0.316	0.297	106.4
	19.15	43.2	0.319	0.297	107.4
		n	4		
		Mean	0.311		104.7
		Std Dev	0.010		
		CV	0.032		

Eight blank sampling tubes were prepared in the laboratory. Four tubes were used to take samples from the generation system (1 X PEL, 25 °C, 50% RH) and then immediately analyzed (Day 0). The other 4 blank sampling tubes were stored at 20 to 25 °C for 68 days. Samples were then collected using the same conditions as the Day 0 samples.

Commercial tubes were stored for 6 months on a lab bench and then used for sampling. These tubes were used to collect samples for the 0 Day Storage Stability experiment (See Table 5 - Refrigerated vs. Room temperature, 0 Day Storage, 2 X PEL for data). Four samples were collected at 2 times the PEL, 25 °C and 50% RH. Recoveries were 113.7% and the CV was 0.019.

Table 8

Qualitative Detection Limit

Rank Sum Test

For n(s) = n(b) = 6

Rank	--------STD Concentration (as HPO_3^{2-})------- 0.14 µg/mL PA	SAM	0.28 µg/mL PA	SAM	0.57 µg/mL PA	SAM
1	0.00	RBL	0.00	RBL	0.00	RBL
2	0.00	RBL	0.00	RBL	0.00	RBL
3	0.00	RBL	0.00	RBL	0.00	RBL
4	0.00	RBL	0.00	RBL	0.00	RBL
5	0.00	RBL	0.00	RBL	0.00	RBL
6	0.00	RBL	0.00	RBL	0.00	RBL
7	1.42	STD	3.87	STD	8.54	STD
8	2.09	STD	4.00	STD	8.60	STD
9	2.17	STD	4.06	STD	8.63	STD
10	2.22	STD	4.06	STD	8.64	STD
11	2.22	STD	4.23	STD	8.73	STD
12	2.30	STD	4.47	STD	8.73	STD
Blank rank sum =	21		21		21	
Confidence level =	99.9%		99.9%		99.9%	

Qualitative detection limit for phosphine = 0.14 µg/mL or 0.70 µg (5 mL sample volume). This corresponds to a 0.009 ppm phosphine concentration for a 36-L air volume at 0.15 L/min sampling rate.

Note: SAM denotes sample type:

(1) RBL = Reagent Blank

(2) STD = Standard

PA = Integrated Peak area ($HPO3^{2-}$)/100,000

Table 8 (Continued)

Quantitative Detection Limit (IUPAC Method)

	-------STD Concentration (as HPO_3^{2-})--------		
	0.14 µg/mL	0.28 µg/mL	0.57 µg/mL
Sample No.	PA	PA	PA
1	1.42	4.47	8.63
2	2.09	4.06	8.73
3	2.17	4.06	8.64
4	2.30	4.23	8.54
5	2.22	4.00	8.73
6	2.22	3.87	8.60
n	6	6	6
Mean	2.07	4.12	8.65
Std Dev	0.33	0.21	0.07
CV	0.16	0.05	0.01

PA = Integrated Peak Area (HPO_3^{2-})/100,000

The mean blank reading and standard deviation (Std dev) were equal to zero.

Using the equation: $C_{ld} = k(sd)/m$

Where:

C_{ld} = the smallest reliable detectable concentration an analytical instrument can determine at a given confidence level.

k = 10, thus giving greater than 99.9% confidence that any detectable signal will be greater than or equal to an average blank (or low standard) reading plus ten times the standard deviation (area reading $\geq Bl_{ave} + 10sd$).

sd = standard deviation of low standard readings.

m = analytical sensitivity or slope as calculated by linear regression.

$C_{ld} = 10(0.33)/14.397 = 0.23$ µg/mL

Quantitative detection limit = 0.23 µg/mL (as HPO_3^{2-}) or 1.15 µg (5-mL sample volume). This corresponds to 0.015 ppm phosphine for a 36-L air volume at 0.15 L/min sampling rate.

Table 9

Field Evaluation - Grain Processing Mill

Sampling conditions: 26 to 30 % RH, 29 °C
Sampling system: Samples were taken side-by-side using a Teflon sampling manifold and two exhaust pumps.
Sampling time: 3 h
Pumps: Du Pont P4000
Sampling rates: 0.11 to 0.14 L/min

Tube Type	n	Average Results	CV
Supelco MC tube	3	1.41 ppm	0.098
SKC MC tube	3	1.51 ppm	0.044
IBC large tube and humidifier	3	1.43 ppm	0.13
IBC large tube (no humidifier)	3	0.63 ppm	0.048
IBC thin tube (no humidifier)	3	0.56 ppm	0.11

Supelco MC and SKC MC tubes contain silica gel impregnated with mercuric cyanide. Sampling and analysis for the silica gel tubes were performed using the NIOSH phosphine method S332 (11.3.) with some modifications.

IBC = Impregnated Beaded Carbon. The thin tube is approximately 170-mm long and 5-mm o.d. The large tube is approximately 110-cm long and 9-mm o.d. Both tubes contain 1.5 g of treated sorbent. All IBC tubes were sampled and analyzed according to reference 11.1.

The humidifier is a cellulose filter plug saturated with 0.75 mL deionized water.

The Supelco MC and SKC MC tubes exhibited some breakthrough; results listed above represent both A (front) and B (backup) sections. The amount found in each section is shown:

Sample #	ppm A	ppm B
SKC MC 1	1.34	0.10
SKC MC 2	1.38	0.15
SKC MC 3	1.30	0.27
Supelco MC 1	0.94	0.37
Supelco MC 2	1.19	0.38
Supelco MC 3	1.06	0.30

The block diagram of the major components of the generation system is shown below. This system provided a means of generating dynamic test atmospheres. The system consists of four essential elements:

1) Flow, temperature, and humidity control system
2) Phosphine vapor generating system
3) Mixing chamber
4) Active sampling manifold

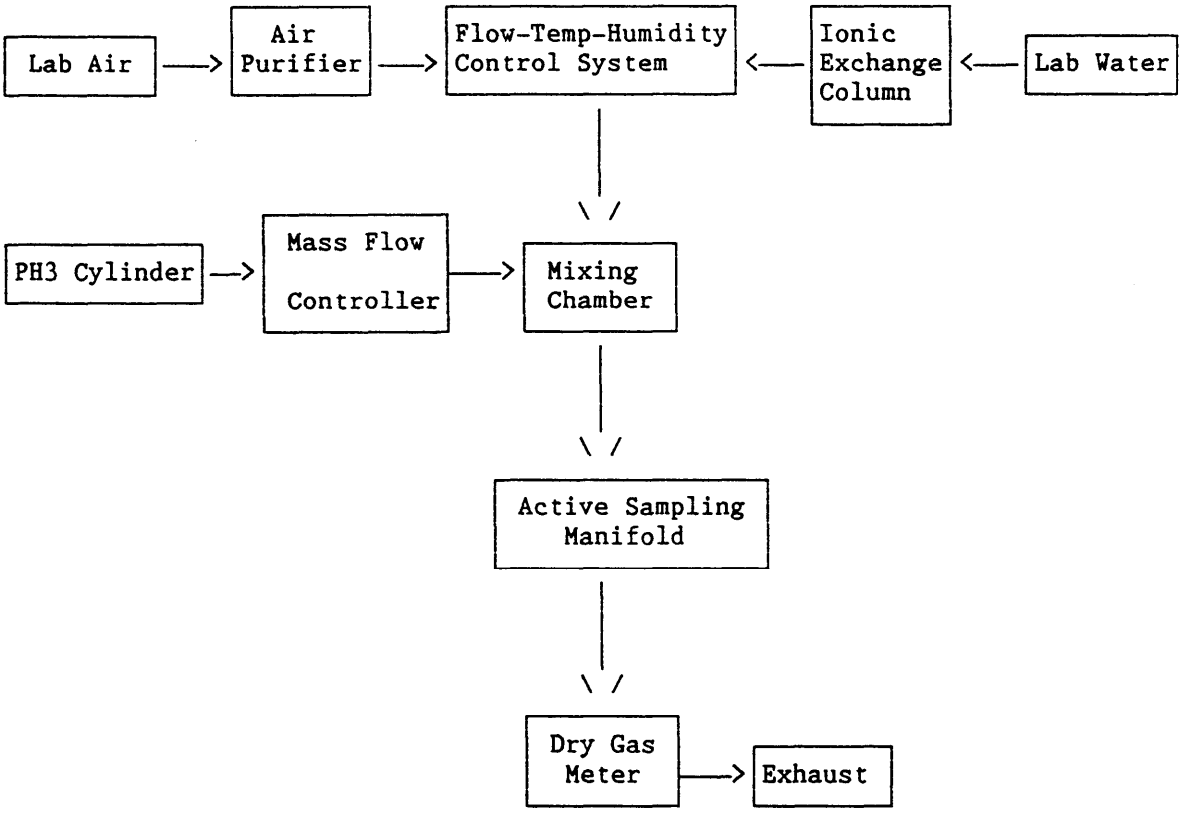

Figure 1

Storage Stability - Collected Samples

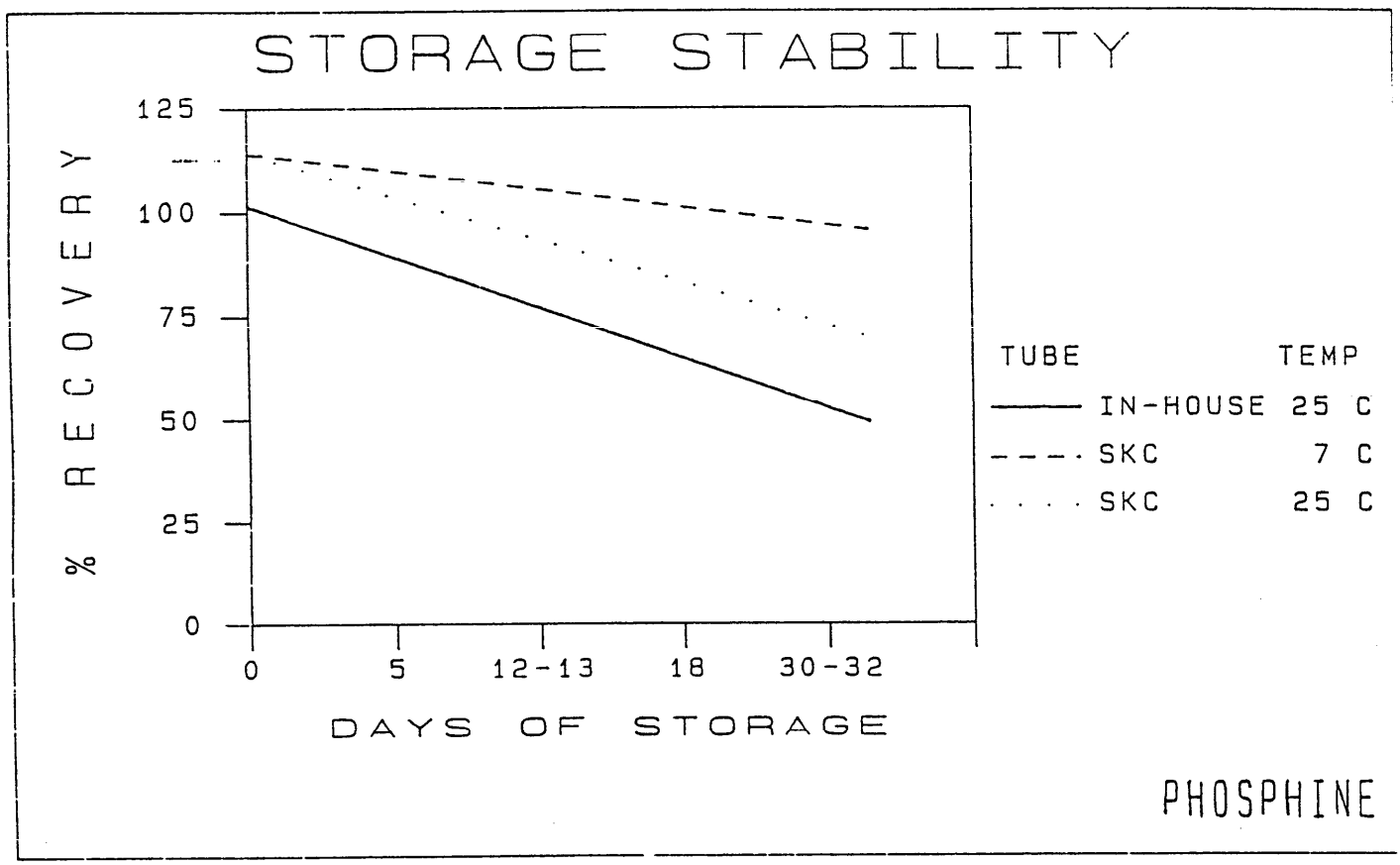

Figure 2

Effects of Humidity on Phosphine Sample Collection

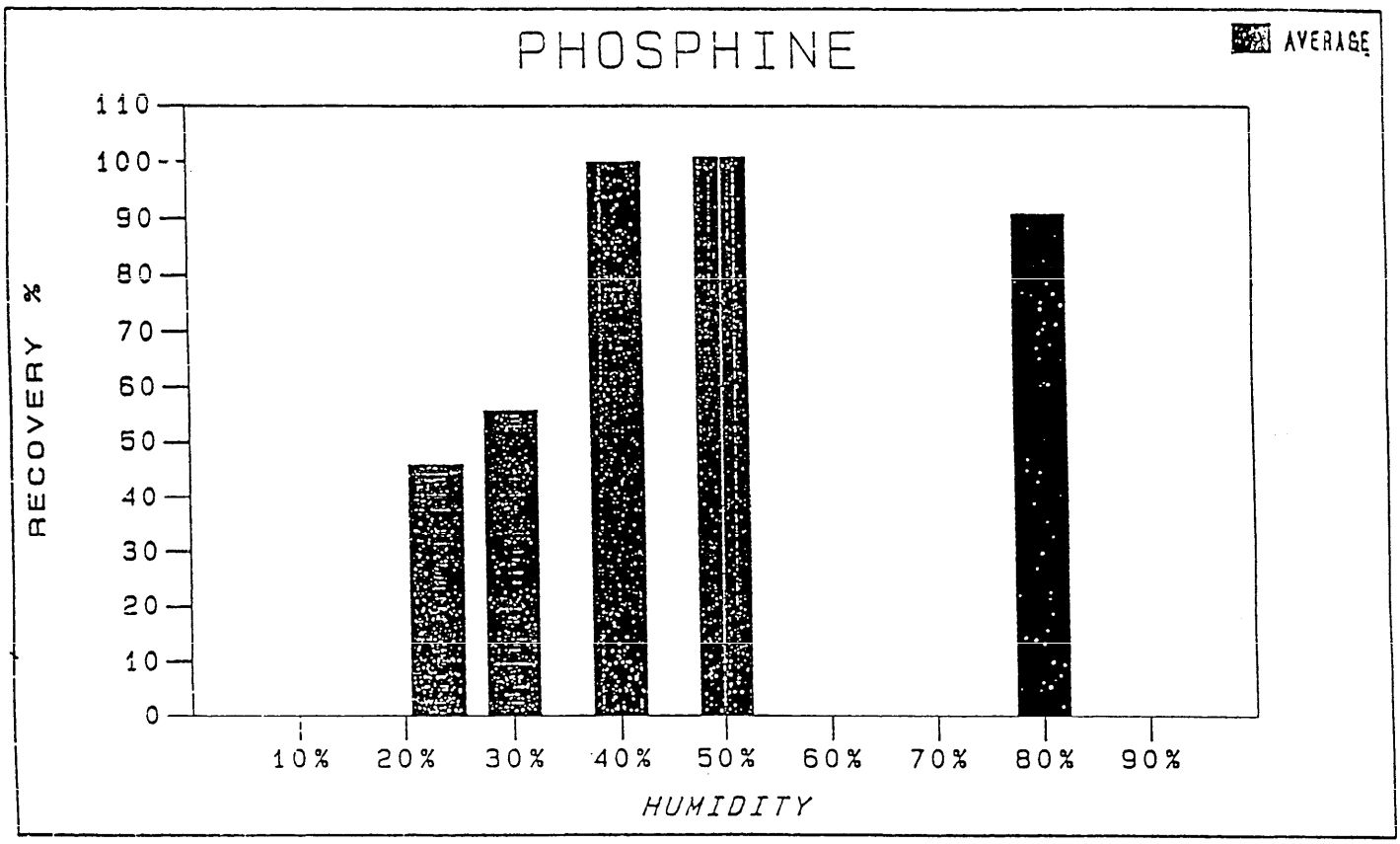

Figure 3

Detection Limit Curve

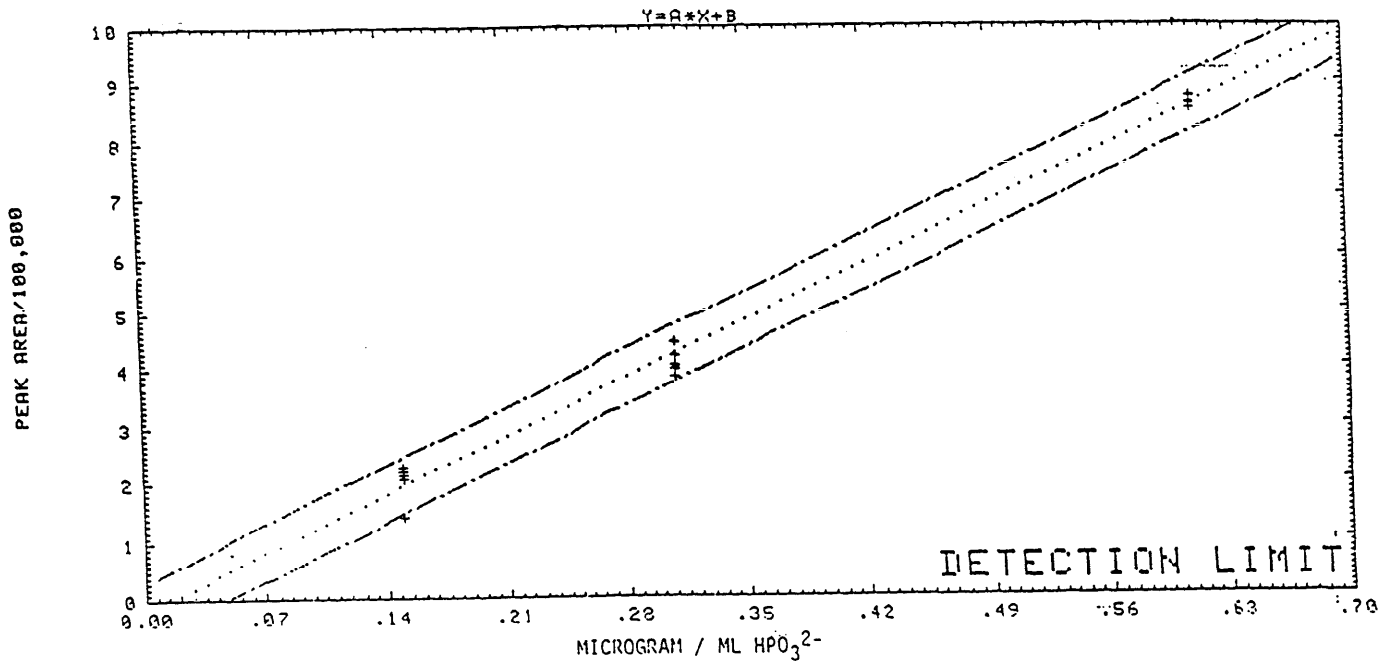

Figure 4

Addendum 1

Comparison of Different Lots of Carbon Bead

The original evaluation of the treated carbon bead was conducted with bead obtained from Union Carbide [(Tonawanda, NY) Note: The carbon bead was called "Purasieve" by Union Carbide]. More recent lots have been obtained from Kureha Chemical, NY. Recent lots of carbon bead have been less efficient in collecting phosphine when using the sampling and analytical parameters described in the method (11.1.). A series of experiments were conducted to determine phosphine recoveries for different lots and to find a lot that gave adequate recoveries.

Procedure: A generation system as mentioned in Section 2 was used to generate dynamic atmospheres of phosphine. Sampling tubes were prepared at the laboratory or were obtained commercially from SKC Inc. (Eighty Four, PA) or Supelco (Bellefonte, PA). All samples were collected using the following conditions:

80% RH, 25 °C, sample flow rate of approximately 0.15 L/min

Results: As shown below, the Union Carbide bead and the Kureha Chemical Co. lot no. 820601 and 15161 carbon bead gave acceptable recoveries for the collection of phosphine. The Supelco bead recovery was slightly low at approximately 75%.

Experiment #		Results		
1				
	ppm, PH_3	OSHA-New	OSHA-Old	
		0.74	2.68	
		Sampling time = 60 min		
		Theoretical PH_3 concentration = 2.70 ppm		
2a				
	ppm, PH_3	SKC-567	SKC-646	SKC-537
		0.23	0.26	0.66
2b				
	ppm, PH_3	SKC-567	SKC-646	SKC-537
		0.17	0.18	0.41
		Sampling time = 120 min		
		Theoretical PH_3 concentration:		
		2a = 0.70 ppm		
		2b = 0.40 ppm		

Addendum (Continued)

Comparison of Different Lots of Carbon Bead

Experiment #		Results	
3		Supelco	OSHA-Old
	ppm, PH_3	0.52	0.70
		Sampling time = 240 min	
		Theoretical PH_3 concentration = 0.70 ppm	
4		JKC	SKC-537
	ppm, PH_3	0.56*	0.61
*Average value, n = 4		Sampling time = 240 min	
		Theoretical PH_3 concentration = 0.60 ppm	
5		JKC2	SKC-537
	ppm, PH_3	1.25**	1.41
		1.40***	
** Sampling rate 0.3 L/min			
*** Sampling rate 0.15 L/min, n=2			
		Sampling time = 120 min	
		Theoretical PH_3 concentration = 1.40 ppm	

Identities	Source
OSHA-New:	Kureha Chemical Co. lot no. G270R 77137
OSHA-Old:	Union Carbide, lot no. unknown; used to validate method ID-180
SKC-537:	Same as OSHA-Old
SKC-567:	Same as OSHA-New
SKC-646:	From SKC Inc., lot no. unknown
Supelco:	From Supelco, lot no. 765-93, 20/40 mesh.
JKC:	Kureha Chemical Co. (Japan) Grade MU-AZ, lot no. 820601
JKC2:	Kureha Chemical Co. (Japan) Grade MU-AZ, lot no. 15161

The "OSHA, Supelco, and JKC" designated sampling tubes were impregnated with potassium hydroxide and prepared in-house. The "SKC" sampling tubes were prepared by SKC Inc. The "SKC 646" series is assumed to be carbon bead recently obtained from Kureha and is similar to OSHA-New.

Summary: The Kureha Chemical Co. lot no. 820601 carbon bead appears acceptable to use for phosphine sampling after it is impregnated with potassium hydroxide. The lot obtained from Union Carbide is no longer available. Presumably, this lot had also originated from Kureha Chemical.

Further testing using electron microscopy and X-ray fluorescence to determine if any significant physical differences existed among the lots of carbon bead have been inconclusive. Subtle differences in physical structure and sulfur content were noted between the lots. Greater collection efficiency was noted for those lots showing the presence of small amounts of sulfur. Examination of the physical character of the beads with a scanning electron microscope revealed less surface fissures and cracks, and more smooth surface indentations for the more efficient beads; however, at this point in time it is unknown as to why lot differences exist for the collection retention of phosphine. Personnel at Kureha Chemical Co. indicated the pitch used in the bead production sometimes varies widely.

Addendum 2

An additional study was conducted to assess the ability of the Kureha Chemical Co. lot no. 820601 carbon bead to collect samples near the STEL concentration of 1 ppm PH_3. The bead was impregnated with KOH and prepared as mentioned in the method. The generation system as described in Section 2 was used to produce a dynamic atmosphere of approximately 1.3 ppm PH_3 at 25 °C and 80% RH. Samples were taken from the system first at different flow rates to determine the potential for breakthrough. Two sampling tubes were connected in series and samples were taken for 15-min at each of the flow rates. Results are shown below.

Sample	Flow Rate, L/min	--ppm PH_3 Found--- 1st Tube	2nd Tube	% Breakthrough
1	0.15	1.22	ND	0
2	0.30	1.22	ND	0
3	0.50	1.03	ND	0
4	1.00	1.07	0.07	6.1

ND = None detectable < 0.012 ppm PH_3

The amount of breakthrough and sensitivity of the analytical instrument for the amount of PH_3 collected for 15-min was assessed. The sampling flow rate of 0.3 L/min and a sampling time of 15-min was considered acceptable for STEL determinations of PH_3.

Seven samples were then taken from the generation system using the conditions mentioned above. A sampling flow rate of approximately 0.3 L/min was used for 15-min.

Sample	PH_3 ppm Found	PH_3 ppm Taken	% Recovery
1	1.18	1.30	90.8
2	1.21	1.30	93.1
3	1.21	1.30	93.1
4	1.27	1.30	97.7
5	1.17	1.30	90.0
6	1.21	1.30	93.1
7	1.30	1.30	100.0
n	= 7		
Mean	= 1.22		94.0
Std Dev	= 0.047		
CV_2	= 0.039		

Overall Error (STEL) = 13.8%