

# **APPENDIX C**

## **Phosphine Analysis Results for Application Air Monitoring Samples**

California Environmental Protection Agency

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 **Air Resources Board**

**Phosphine Analytical Results for Application Air Monitoring Samples**

**DATE: June 2010  
Revision 3**

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This report has been reviewed by staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

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## 1.0 INTRODUCTION

The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) to conduct application air monitoring for phosphine. This report covers the analytical and quality assurance results for phosphine during an application study in Merced County in 2008. DPR requested a method estimated quantitation limit (EQL) of 10.0 microgram per cubic meter ( $\mu\text{g}/\text{m}^3$ ). The EQL achieved during this project was approximately  $8.0 \mu\text{g}/\text{m}^3$ .

## 2.0 METHOD DEVELOPMENT

### 2.1 Overview

Silco™ canisters are used to collect the air samples. Samples are analyzed by cryofocussing 100ml of sample on a gas chromatograph (GC) equipped with a flame photometric detector (FPD) in the phosphorus mode. Sample quantitation uses an external calibration method. Positive results are confirmed using a GC equipped with a mass selective detector (MSD). Appendix A contains the standard operating procedure (SOP) and the method development results for phosphine.

### 2.2 Calibration Curve

Standard volumes of approximately 15, 25, 50, 75, and 100 ml are used to produce a five point calibration curve. All calibrations curves performed have an  $r^2$  (variance) greater than or equal to 0.995. Calibrations are performed at the beginning of the monitoring program, after instrument maintenance, after remaking of external standard, and whenever the continuing calibration verification standard (CCV) did not fall within  $\pm 25$  percent (%) of expected value.

### 2.3 Minimum Detection Limit (MDL)

The MDL calculation follows the United States Environmental Protection Agency (USEPA) procedures for calculating MDL's. Using the analysis of seven low-level matrix analyses (15 ml), the MDL and EQL are calculated as follows:

*s = the standard deviation of the concentration calculated for the seven replicate spikes.*

*For phosphine:  $s = 0.2366$*

$$MDL = (3.14) \times (s) = (3.14) \times (0.2366) = 0.743 \mu\text{g}/\text{m}^3.$$

$$EQL = (5) \times (MDL) = (5) \times (0.743) = 3.715 \mu\text{g}/\text{m}^3$$

Although statistically achievable, based on the daily standard concentration of approximately  $50 \mu\text{g}/\text{m}^3$  and the smallest volume to be sampled, 15 ml, the actual lowest concentration analyzed will be approximately  $8.0 \mu\text{g}/\text{m}^3$ . Thus the EQL for

reporting results will be approximately  $8.0 \mu\text{g}/\text{m}^3$ . The MDL used in this report will then be approximately  $1.6 \mu\text{g}/\text{m}^3$ . Results at or above the EQL will be reported to two significant figures. Results below the EQL but greater than or equal to the MDL are reported to one (1) significant figure. Results less than MDL are reported as the calculated MDL to one (1) significant figure.

### **3.0 PHOSPHINE APPLICATION AIR MONITORING SAMPLE RESULTS**

The laboratory received a total of 62 application samples plus four field spikes, three trip blanks, four trip spikes, and two stability spikes from December 5 through 11, 2008. Five of the 62 canisters did not collect a sample. These sample results are denoted by "na" in the results column. Table 2 presents the results of the analysis of the phosphine application air samples by site.

### **4.0 ANALYTICAL QUALITY CONTROL SAMPLES**

#### *4.1 System Blanks*

Laboratory staff analyzes a system blank with each analytical batch, after each CCV, after every tenth sample, and after samples containing high levels of phosphine or co-extracted contaminants. Staff defines the analytical batch as all the samples analyzed together, but not to exceed 20 samples. The system blank is run to insure the instrument does not contribute interferences to the analysis, and to minimize carryover from high level samples. All system blanks were less than the MDL.

#### *4.2 Laboratory Control Samples (LCS)*

Laboratory staff analyzed a LCS with each analytical batch. The stock standard used to prepare the LCS should come from a different source or a different lot number than the stock standard used for method calibration. In this case only one source was available so the LCS was made up from a different aliquot and at a different concentration than the calibration standard. The average concentration for the LCS was  $30 \mu\text{g}/\text{m}^3$ . The LCS recoveries averaged 106% with a standard deviation of 19.23%. The acceptable LCS range was 86.3% to 124.8%. All LCS results were within this range.

#### *4.3 Continuing Calibration Verification Standards (CCV)*

Following standard lab procedures, laboratory staff analyzed a CCV after every calibration curve, after every tenth sample and at the end of an analytical batch. The CCV must be within  $\pm 25\%$  of the expected value. If any of the CCVs are outside this limit, the affected samples are re-analyzed. The CCV standard volume is 15 ml. All the CCV's were within the 25% acceptance range.

#### 4.4 *Laboratory Duplicates*

Fifteen pairs of laboratory duplicates were run with this project. The duplicate pairs are made up of two samples run from the same canister in succession. The relative percent difference for each pair is reported in Table 1.

### 5.0 **FIELD, TRIP, AND LABORATORY SPIKES AND TRIP BLANKS**

During the Merced County 2008 project, four field and trip spikes along with five laboratory spikes, and three trip blanks were analyzed. The staff also ran two stability spikes. Laboratory staff prepared the spikes with a target of 30  $\mu\text{g}/\text{m}^3$  of phosphine.

#### 5.1 *Laboratory Spikes*

Table 3 presents the results of the laboratory spikes. The average phosphine recovery was 103% with a standard deviation of 7.51%.

#### 5.2 *Trip Spikes*

Table 3 presents the results of the trip spikes. The average phosphine recovery was 75.7% with a standard deviation of 9.97%.

#### 5.3 *Field Spikes*

Table 3 presents the results of the field spikes. Four field spikes were analyzed during this study. All four were collected during the field background level sampling period. The results for the field spiked samples ranged from 33 to 42  $\mu\text{g}/\text{m}^3$ . Recovery results varied from 83% to 94%. Results for the unspiked collocated samples were all less than the MDL. The average recovery for phosphine was 86.4% with a standard deviation of 5.70%. Values in Table 3 are reported without correction.

#### 5.4 *Stability Spikes*

Table 3 presents the results of the stability spikes. Two trip spikes were prepared at the start of the project and were not returned to the lab until the last samples were returned. These samples are used to evaluate the stability of phosphine during this project. Each stability spike sample was analyzed in duplicate. The two stability spikes had very different recoveries. One had an average recovery of 84.66% while the other spike had an average recovery of 17.17%.

#### 5.5 *Trip Blanks*

Table 3 presents the results of the trip blanks. Three trip blanks were received during this project and all results were less than the MDL.

## 6.0 DISCUSSION

The Laboratory received 62 field samples and 13 field quality control samples. Four each of field spikes and trip spikes along with two stability spikes and three trip blanks were received. Five additional spikes were prepared in the laboratory. Results for phosphine ranged from less than the MDL to 700 mg/m<sup>3</sup>. Forty-four samples were less than the MDL. The MDL varied based on the concentration of the low calibration point. For this project the MDL varied between 1 and 2 ug/m<sup>3</sup>. Seven sample results were between the MDL and EQL. The values ranged from 3 to 7 µg/m<sup>3</sup>. Six samples had results above the EQL. The values ranged from 12 µg/m<sup>3</sup> to 700 mg/m<sup>3</sup>. The three highest results were from the indoor samples taken during the fumigation. The average value for these samples was 607 mg/m<sup>3</sup>. Six samples had values greater than the DPR requested EQL of 10 µg/m<sup>3</sup>.

Three samples required dilution. These samples were the samples taken from inside the fumigating structure. For all three samples a dilution of greater than 40,000 was required. The dilutions were made by taking 2 mls of the original sample which is injected into an evacuated canister. This canister is in turn pressurized to approximately 25 psig. A sample of approximately 19 ml was analyzed.

Sample 19, SF-1, was diluted by a factor of 1.26 by the automated Wasson sampler. This resulted in a value of 12 ug/m<sup>3</sup>. No other samples were diluted based on initial sample concentration being out of calibration range.

All samples received were screened for phosphine within two days of sample receipt using a GC/MSD. All samples were run within six days of sample receipt on the GC/FPD.

The two stability spike samples had very different recoveries. This variation may be due to the condition of the canister lining. Over the course of this study it was noted that some calibrations lasted longer than others. The only difference was the canister they were made up in. During the last 10 years these canisters have been used many times for a variety of analyte studies. During this time the state of the silco lining may have changed and possibly degraded to the point that a very reactive analyte like phosphine would react with the metal surface resulting in lower than expected values. This may be the case with the stability samples. Since the sample canisters were only used once each during this study, a specific canister trend could not be evaluated.

Another factor that may have an effect on the phosphine results is the high level of water present in the samples. During the course of this study the relative humidity ranged from 60% to over 100%. The presence of high levels of water had an effect on the GC system's chromatography. The GC system's Nafion™ dryer was not always able to remove all the water vapor present during sample concentration resulting in peak splitting and a retention time shift. But if the sample was diluted with nitrogen the phosphine peak shape and retention time returned to normal. Since most samples had

no phosphine detected or were at a level far below the MDL, no samples were diluted with nitrogen to improve the peak chromatography.

No other anomalous events occurred.

**Table 1: Duplicate Results  
Merced County 2008**

Log Number	Sample ID	Date Analyzed	Phosphine concentration (ug/m <sup>3</sup> )	Relative Percent Difference
2	S-B-FS	12/6/08	35.71	-0.056
2d	S-B-FS	12/6/08	35.73	
8	E-B	12/6/08	<1	na
8d	E-B	12/6/08	<1	
16	SEC-F-1	12/11/08	<2	na
16d	SEC-F-1	12/11/08	<2	
21	S-F-3	12/11/08	<2	na
21d	S-F-3	12/11/08	<2	
27	W-F-3	12/13/08	58.33	16.017
27d	W-F-3	12/13/08	49.68	
28	NWC-F-1	12/14/08	41.69	6.259
28d	NWC-F-1	12/14/08	39.16	
36	N-F-3CO	12/13/08	<1	na
36d	N-F-3COd	12/13/08	<1	
43	TS(10th)	12/10/08	21.43	-3.033
43d	TS(10th)	12/10/08	22.09	
56	W-A-3	12/14/08	<1	na
56d	W-A-3	12/15/08	<1	
57	NWC-A-1	12/15/08	<2	na
57d	NWC-A-1	12/15/08	<2	
64	N-A-2CO	12/16/08	<1	na
64d	N-A-2CO	12/16/08	<1	
65	N-A-3CO	12/16/08	<1	na
65d	N-A-3CO	12/16/08	<1	
73	TS-A	12/15/08	22.50	0.089
73d	TS-A	12/15/08	22.48	
74	STAB-1	12/16/08	26.29	-5.511
74d	STAB-1	12/16/08	27.78	
75	STAB-2	12/16/08	5.52	1.093
75d	STAB-2	12/16/08	5.46	

Notes:

d            designates the duplicate analysis  
na            not applicable  
ug/m<sup>3</sup>        micrograms per cubic meter

**Table 2: Application Air Monitoring Results  
Merced County 2008**

Site	Log Number	Sample ID	Date Received	Date Analyzed	Sample Dilution	Phosphine (ug/m3)	
East	8	E-B	12/5/08	12/6/08	1.00	<1	
	8d	E-B	12/5/08	12/6/08	1.00	<1	
	69	E-A-1	12/11/08	12/16/08	1.00	6	
	70	E-A-2	12/11/08	12/16/08	1.00	<1	
	71	E-A-3	12/11/08	12/16/08	1.00	<1	
	40	E-F-1	12/10/08	12/13/08	1.00	<1	
	41	E-F-2	12/10/08	12/13/08	1.00	<1	
	42	E-F-3	12/10/08	12/14/08	1.00	<2	
	Inside	13dl	In-F1	12/11/08	12/16/06	42987	610000
		14dl	In-F2	12/11/08	12/16/06	45405	510000
15dl		In-F3	12/11/08	12/17/06	41222	700000	
North	5	N-B	12/5/08	12/6/08	1.00	<1	
	6	N-B-C	12/5/08	12/6/08	1.00	<1	
	60	N-A-1	12/11/08	12/16/08	1.00	<1	
	63	N-A-1CO	12/11/08	12/16/08	1.00	<1	
	61	N-A-2	12/11/08	12/17/08	1.00	<1	
	64	N-A-2CO	12/11/08	12/16/08	1.00	<1	
	64d	N-A-2CO	12/11/08	12/16/08	1.00	<1	
	62	N-A-3	12/11/08	12/17/08	1.00	<1	
	65	N-A-3CO	12/11/08	12/16/08	1.00	<1	
	65d	N-A-3CO	12/11/08	12/16/08	1.00	<1	
	31	N-F-1	12/10/08	12/13/08	1.00	<1	
	34	N-F-1CO	12/10/08	12/13/08	1.00	<1	
	32	N-F-2	12/10/08	12/13/08	1.00	<1	
	35	N-F-2CO	12/10/08	12/13/08	1.00	3	
	33	N-F-3	12/10/08	12/13/08	1.00	<1	
	36	N-F-3CO	12/10/08	12/13/08	1.00	<1	
	36d	N-F-3COd	12/10/08	12/13/08	1.00	<1	

**Table 2: Application Air Monitoring Results  
Merced County 2008**

Site	Log Number	Sample ID	Date Received	Date Analyzed	Sample Dilution	Phosphine (ug/m3)
Northeast	66	NEC-A-1	12/11/08	12/16/08	1.00	6
	67	NEC-A-2	12/11/08	12/16/08	1.00	<1
	68	NEC-A-3	12/11/08	12/16/08	1.00	<1
	37	NEC-F-1	12/10/08	12/13/08	na	na
	38	NEC-F-2	12/10/08	12/13/08	na	na
	39	NEC-F-3	12/10/08	12/13/08	na	na
Northwest	57	NWC-A-1	12/11/08	12/15/08	1.00	<2
	57d	NWC-A-1	12/11/08	12/15/08	1.00	<2
	58	NWC-A-2	12/11/08	12/15/08	1.00	<2
	59	NWC-A-3	12/11/08	12/15/08	1.00	<2
	28	NWC-F-1	12/10/08	12/14/08	1.00	42
	28d	NWC-F-1	12/10/08	12/14/08	1.00	39
	29	NWC-F-2	12/10/08	12/13/08	1.00	<2
	30	NWC-F-3	12/10/08	12/13/08	1.00	<2
South	1	S-B	12/5/08	12/6/08	1.00	<1
	48	S-A-1	12/11/08	12/14/08	1.00	<1
	49	S-A-2	12/11/08	12/14/08	1.00	<1
	50	S-A-3	12/11/08	12/14/08	1.00	<1
	19	S-F-1	12/10/08	12/11/08	1.26	12
	20	S-F-2	12/10/08	12/11/08	1.00	7
	21	S-F-3	12/10/08	12/11/08	1.00	<2
	21d	S-F-3	12/10/08	12/11/08	1.00	<2
Southeast	45	SEC-A-1	12/11/08	12/14/08	1.00	5
	46	SEC-A-2	12/11/08	12/14/08	1.00	<1
	47	SEC-A-3	12/11/08	12/14/08	1.00	<1
	16	SEC-F-1	12/10/08	12/11/08	1.28	<2
	16d	SEC-F-1	12/10/08	12/11/08	1.28	<2
	17	SEC-F-2	12/10/08	12/11/08	1.00	na

	18	SEC-F-3	12/10/08	12/11/08	1.00	na
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**Table 2: Application Air Monitoring Results  
Merced County 2008**

Site	Log Number	Sample ID	Date Received	Date Analyzed	Sample Dilution	Phosphine (ug/m3)
Southwest	51	SWC-A-1	12/11/08	12/14/08	1.00	<1
	52	SWC-A-2	12/11/08	12/14/08	1.00	<1
	53	SWC-A-3	12/11/08	12/14/08	1.00	<1
	22	SWC-F-1	12/10/08	12/11/08	1.00	3
	23	SWC-F-2	12/10/08	12/11/08	1.00	4
	24	SWC-F-3	12/10/08	12/11/08	1.00	<2
West	3	W-B	12/5/08	12/6/08	1.00	<1
	54	W-A-1	12/11/08	12/14/08	1.00	<1
	55	W-A-2	12/11/08	12/14/08	1.00	<1
	56	W-A-3	12/11/08	12/14/08	1.00	<1
	56d	W-A-3	12/11/08	12/15/08	1.00	<1
	25	W-F-1	12/10/08	12/11/08	1.00	<2
	26	W-F-2	12/10/08	12/11/08	1.00	<2
	27	W-F-3	12/10/08	12/13/08	1.00	58
	27d	W-F-3	12/10/08	12/13/08	1.00	50

Table 2 Notes: Application Monitoring Results, Merced County 2008

If the analytical result is <MDL it is reported as less than the established method detection limit multiplied by the dilution factor. Results are reported to one significant figure. If the analytical result is  $\geq$  MDL and < EQL it is reported in the table as the measured value to one significant figure. Levels at or above the EQL are reported as the actual measured value and are reported to two significant figures.

$\mu\text{g}/\text{m}^3$  = micrograms per cubic meter

Sample ID (Sample identification) numbers followed by the letters CO are collocated samples for the samples with the corresponding number.

Sample ID numbers followed by the letter d are duplicate samples for the samples with the corresponding number.

na = not applicable. Sample was not collected for these log numbers.

Site location identification:

E:	East Side
N:	North Side
NEC:	Northeast Corner
NWC:	Northwest Corner
S:	South Side
SEC:	Southeast Corner
SWC:	Southwest Corner
W:	West Side

**Table 3: Field and Laboratory QC Sample Results  
Merced County 2008**

Quality Control Type	Log Number	Sample ID	Date Analyzed	Phosphine concentration (ug/m <sup>3</sup> )	Spiked Concentration (ug/m <sup>3</sup> )	Percent Recovery
Field Spike	2	S-B-FS	12/6/08	35.71	42.90	83.24
	2d	S-B-FS	12/6/08	35.73	42.90	83.29
	4	W-B-FS2	12/6/08	41.85	44.29	94.49
	7	N-B-FS3	12/6/08	33.08	40.95	80.78
	9	E-B-FS4	12/6/08	37.68	41.85	90.03

Lab Spike	na	na	12/6/08	33.11	31.17	106.22
	na	na	12/10/08	33.40	32.37	103.18
	na	na	12/11/08	32.51	32.53	99.94
	na	na	12/13/08	32.96	29.00	113.66
	na	na	12/15/08	30.29	32.44	93.37

Trip Spike	11	TS1	12/5/08	28.28	30.96	91.34
	12	TS2	12/5/08	26.26	31.05	84.57
	43	TS(10th)	12/10/08	21.43	32.18	66.59
	43d	TS(10th)	12/10/08	22.09	32.49	67.99
	73	TS-A	12/15/08	22.50	31.19	72.14
	73d	TS-A	12/15/08	22.48	31.49	71.39

Stability Spike	74	STAB-1	12/16/08	26.29	32.10	81.90
	74d	STAB-1	12/16/08	27.78	31.78	87.41
	75	STAB-2	12/16/08	5.52	32.14	17.17
	75d	STAB-2	12/16/08	5.46	31.82	17.16

Trip Blank	10	TB	12/5/08	<1.47
	44	TB(10th)	12/10/08	<1.51
	72	TB-A	12/16/08	<1.43

Notes:

ID Identification  
ug/m<sup>3</sup> micrograms per cubic meter

d      Result reported is from a duplicate analysis  
na     not applicable

**Appendix A:**  
**Standard Operating Procedure for phosphine**

California Environmental Protection Agency

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# Air Resources Board

**Standard Operating Procedure  
Sampling and Analysis of Phosphine**

**Special Analysis Section  
Northern Laboratory Branch  
Monitoring and Laboratory Division**

November 2008

Version 2

Approved by:

Russell Grace, Manager  
Special Analysis Section

## 1. SCOPE

This method is for the sampling and analysis of phosphine in air samples using a six-liter Silco™ canister for sample collection. Collected samples are analyzed by gas chromatography using an automated cryogenic sampler.

## 2. SUMMARY OF METHOD

Air samples are collected in evacuated six-liter Silco™ canisters. The samples are collected automatically using a Tisch Environmental automatic sample collection system. Final pressures after collection are greater than ambient pressures. After collection, samples are analyzed using a Wasson ECE Instrumentation cryogenic sample concentrator and an Agilent 7890A gas chromatograph equipped with a flame photometric detector in the phosphorus mode. Confirmation of positive results is determined using an Agilent 5973 GC/MSD operated in the single ion monitoring mode (SIM). Sample analysis and quantitation uses an external standard method for instrument calibration. The estimated quantitation level (EQL) for this method is approximately 8.0 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) prior to any sample dilution.

## 3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in the Silco™ canisters or the Tisch sampler that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting components may cause significant contamination of the analytical equipment. A system blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

## 4. EQUIPMENT AND CONDITIONS

### A. Instrumentation:

Agilent Instruments 7890A gas chromatograph(GC) with a flame photometric detector (FPD) equipped with a phosphorus filter.

### GC Column:

J&W GS Gaspro 30 meters by 0.32 millimeter ID (or equivalent)

### GC Temperature Program:

Initial temperature 0 degrees centigrade ( $^{\circ}\text{C}$ ) for 5 minutes

0 to 60  $^{\circ}\text{C}$  at 5 $^{\circ}\text{C}/\text{min}$

60 to 100 $^{\circ}\text{C}$  at 50  $^{\circ}\text{C}/\text{min}$

### GC Inlet Parameters:

Pressure at 12.78 pounds per square inch (psi)

Flow at 2.0 ml/min

### GC Detector FPD:

Heater at 225 ° C  
Hydrogen Flow at 75 ml/min  
Air Flow at 100 ml/min  
Makeup Flow at 58 ml/min

Wasson ECE cryogenic sample concentrator with Nafion dryer:  
Cryo Temp #1 at -140° C  
Cryo Temp #2 at -150° C  
Sample Oven at 200 ° C  
Transferline Temp at 150° C  
Mass Flow at 35 ml/min  
Line Purge Time 30 seconds

Agilent 5973 mass selective detector (MSD) with a 6890 GC  
Acquisition Mode: SIM  
Tune File: PFTBA autotune  
Ions monitored: 31.0, 33.0, 34.0  
Quant Ion: 34.0

B. Auxiliary Apparatus

Restek six liter Silco™ canisters with Silco™ valves

C. Reagents

Phosphine gas at 10 ppm +/-2% H.P. Gas Products, Inc.

D. Gases

Helium, grade 5 or better

Liquid Nitrogen at 22 pounds per square inch (psi)

Nitrogen, grade 5

Compressed air, ultra zero

Hydrogen, supplied by a Whatman Hydrogen generator

**5. SAMPLE COLLECTION**

- A. Samples are collected using a Tisch Environmental automated sampler set to deliver ambient air over a fixed amount of time (3 to 12 hours depending on sampler location).
- B. Six liter canisters will be filled so the ending pressure will be above ambient in the range of 10 to 20 psig (psi gauge).
- C. Phosphine is stable for at least five days when kept at ambient temperatures . See section 8F for storage stability summary.

## 6. ANALYSIS OF SAMPLES

- a) Connect each canister to a port on the Wasson ECE cryoconcentrator using a short length of polypropylene tubing. Reserve ports one and two for the blank and calibration standard.
- b) For this method the standard volume will be 100 milliliters.
- c) Perform an initial calibration curve using the following volumes of known concentrations of Phosphine: 15, 25, 50, 75, 100 milliliters. At least five (5) points must be analyzed to establish a calibration curve. Appendix 1 lists the standard concentrations used when the EQL is approximately 8.0  $\mu\text{g}/\text{m}^3$ .
- d) Prepare a sample sequence for the GC. The sequence should include a system blank and a continuing calibration verification standard (CCV) for every ten (10) samples analyzed. If this batch of samples includes a method blank and /or LCS, they should be run prior to field samples to verify that QC criteria have been met.
- e) To minimize excessive carry over of contaminants from one analysis to the next, a system blank should be run after every twenty (20) samples or more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.
- f) Review and edit the quantitation reports as needed.
- g) Rerun samples with results greater than the EQL by GC/MSD to confirm the presence of phosphine.
- h) Samples with concentration greater than the upper point of the calibration curve must be run at a smaller volume. Every attempt should be made to have the results fall within the upper half of the calibration curve. If running a volume of 15 mls results in a value greater than the upper calibration point, then the sample will need to be diluted with compressed nitrogen. Either add nitrogen to the original canister being sure to record the beginning and ending pressures, or transfer a known amount of sample from the original canister into a clean fully evacuated canister. Pressurize with nitrogen again recording the final pressure.
- i) The final results will be adjusted by an appropriate dilution factor and reported in  $\mu\text{g}/\text{m}^3$ .
- j) The atmospheric concentration is calculated as follows:

$$\text{Ambient Sample Conc. } (\mu\text{g}/\text{m}^3) = \frac{\text{Sample Vol (ml)}}{100 \text{ ml}} \times \text{Instrument result } (\mu\text{g}/\text{m}^3) \times \text{Dilution Factor}$$

- k) Given instrument sensitivity and a minimum sample volume of 15 ml the EQL for this method will be approximately 8.0  $\mu\text{g}/\text{m}^3$ .

## 7. QUALITY ASSURANCE

### A. Instrument Reproducibility

Establish the reproducibility of the instrument and analytical method as follows: Analyze three different volumes of standard (low, medium, and high levels) by injecting each five times. Table 1 lists the results for the Phosphine instrument reproducibility.

TABLE 1  
INSTRUMENT REPRODUCIBILITY  
Phosphine (ug/m<sup>3</sup>)

Low Level (15ml)	Medium Level (50ml)	High Level (100ml)	
7.74	25.9	51.1	
7.69	25.9	58.3	
7.75	25.4	54.2	
8.26	27.2	52.6	
7.79	26.9	52.6	
7.846	26.26	53.76	Average
0.234	0.757	2.765	Std Dev
2.984	2.883	5.142	RSD

### B. Linearity

A five point calibration is performed. Calibration standards ranging from at or near the EQL to approximately 7 times higher are used for phosphine. The results are used to calculate calibration curves using linear or quadratic regression. An  $r^2$  of 0.995 or higher is required for an initial calibration to be acceptable. See Appendix 1 for an example calibration curve. A CCV will be run at the start of each analytical batch, and after every tenth sample to verify the system linearity. The CCV quantitated value must be within 25% of the actual value.

### C. Method Detection Limit

Method detection limits (MDL) are based on the US EPA MDL calculation. Using the analysis of seven replicates of a low-level standard, the MDL and EQL for Phosphine are calculated as follows:

$$\text{MDL} = 3.143 \cdot \text{STD}$$

$$\text{EQL} = 5 * \text{MDL}$$

STD equals the standard deviation of the calculated results for the seven replicate spikes. The calculated MDL for phosphine is 0.743 µg/m<sup>3</sup> based on a 100 ml sample analysis volume. The EQL for phosphine based on the MDL would be approximately 4.0 µg/m<sup>3</sup>. Although statistically achievable, based on the daily standard concentration of approximately 50 µg/m<sup>3</sup> and the smallest volume to be sampled, 15 ml, the actual lowest concentration analyzed will be approximately 8.0 µg/m<sup>3</sup>. Thus the EQL for reporting results will be approximately 8.0 µg/m<sup>3</sup>. Since the EQL used is based on the calibration curves high point, the MDL will also be effected by the same factor which in most case is approximately two. Thus the MDL used for this analyte will be around 1.5 µg/m<sup>3</sup>.

D. Laboratory Control Sample

A laboratory control sample (LCS) is included with each analytical batch. The LCS stock standard should come from a different source or lot than the daily calibration standards. The analytical value of the LCS must be within three standard deviations of its historical mean. If the LCS is outside these limits then the samples in the analytical batch must be reanalyzed. The LCS is prepared like the calibration standards using a volume of standard that will result in a final concentration that is in the middle of the calibration curve, in this case approximately 30 µg/m<sup>3</sup>.

E. Storage Stability

Storage stability was determined for phosphine by spiking an evacuated canister and collecting ambient air using the Tisch Environmental sampler. This sample was then analyzed on the following days: 0, 1, 5, 13, and 25 days. Table 2 lists the results for the storage stability study.

Table 2  
Storage Stability Study  
Phosphine 2008

Day	Sample 1 %recovery	Sample 2 %recovery	Sample 3 %recovery	Average %recovery	Standard Dev
0	87.17	89.52	100.31	92.34	7.008
1	89.40	97.85	94.12	93.79	4.235
5	92.94	93.29	94.52	93.58	0.828
13	60.30	62.30	61.02	61.21	1.013
25	48.43	49.12	47.82	48.46	0.650

Because there is a significant loss between day 5 and 13 all samples should be analyzed within 5 to 6 days of sampling.

## H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure. Phosphine gas is highly toxic at levels greater than 11.5 mg/kg of body weight. All prep of standards and expected high samples should be performed in a shielded fume hood.

## Appendix 1

### Calibration Standard Preparation for Phosphine

The certified gas standard used for calibration was purchased from H.P. Gas Products, Inc., Baytown, Texas and has the following specification:

Cylinder No: CC177430  
Expiration date: December 10, 2008  
Phosphine:  $10 \pm 2$  ppm

The calibration standard is made by taking an aliquot of the stock standard (10ppm) and diluting in a six liter Silco™ canister with nitrogen. A typical dilution is as follows:

75ml of Phosphine (10ppm) at  $13,906 \mu\text{g}/\text{m}^3$   
[  $\mu\text{g}/\text{m}^3 = \text{ppm} \times \text{molecular weight} \times 40.90$  ]

Pressurize canister to approximately 30 psig  
[ Volume in ml = (Final Pressure (psig)/14.7 psig x 6000ml) + 6000ml ]

Resulting concentration in can is approximately  $57 \mu\text{g}/\text{m}^3$   
Final concentration  $\mu\text{g}/\text{m}^3 = \text{vol of std}/\text{vol in canister} \times \text{std conc} (\mu\text{g}/\text{m}^3)$

A minimum of five sample volumes are used to generate the calibration curve, with the standard at 15 ml being the low point. The sample volumes for the calibration curve are 15, 25, 50, 75, 100 ml. The 100ml represents a concentration of  $57 \mu\text{g}/\text{m}^3$ . The low point (15ml) equates to approximately  $8.5 \mu\text{g}/\text{m}^3$ .

All continuing calibration verification standards (CCV) are run at 15 ml, while all samples are run at 100 ml.

Initial calibration curve acceptance requires an  $r^2$  of at least 0.995.