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A solid sorbent sampling tube packed with Tenax-GC is used with a personal sampling pump to collect samples of white (yellow) phosphorus vapor from air. The phosphorus is leached from the exposed sorbent into xylene and quantitated by gas chromatographic analysis. The capacity of the sorbents is in the range 10 to 20 μg P_4 per 100 mg of sorbent, which allows for up to 4 hrs of sampling at the OSHA Standard, 0.1 mg/m^3. No interferences from red phosphorus, phosphine, water vapor, or other common gases are significant. The effects on the method of variations in temperature, pressure, humidity, sample storage and shipping conditions, and chromatographic parameters were determined.

Solid sorbent sampler for white phosphorus in air

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introduction

Some early methods for the sampling and measurement of white (yellow) phosphorus vapor ($P_4(g)$) in air were based on oxidation to phosphate followed by gravimetric or volumetric analysis.(1-3) However, $P_4(g)$ normally coexists with oxides of phosphorus and phosphine. With no separation prior to oxidation, these compounds interfere in the gravimetric and volumetric analyses.

In 1962 a method was described involving collection of $P_4(g)$ in xylene in Smith-Greenberg impingers.(1) Oxides of phosphorus were removed by washing the xylene with water. The elemental phosphorus was extracted with a silver nitrate solution and the conversion to phosphoric acid completed by addition of nitric acid. The phosphate was determined colorimetrically by the phosphomolybdate procedure after removal of silver.

More recently, the direct determination of elemental phosphorus in xylene was carried out by gas-liquid chromatography.(2) Aliquots of a xylene solution were analyzed by gas chromatography (GC) and by the phosphomolybdate method after oxidation. The large variability in colorimetric results made the GC results appear more reliable.

Although the collection of $P_4(g)$ in xylene in an impinger is efficient and the GC analysis procedure appears to be reliable, the use of an impinger as a device for sampling the breathing zones of individuals in a workroom environment is inconvenient. The handling of liquids often leads to spillage or evaporation of the sample. Sorbent materials packed in small tubes provide compact collection beds for the sampling of vapors with personal sampling pumps. Usually the exposed sorbent material can be shipped to a laboratory for analysis with only minimal handling. This paper describes the development of a solid sorbent sampling method suitable for use at the current OSHA standard of 0.1 mg/m^3 for white phosphorus vapor.(4)

apparatus and reagents

Sorbent Tubes: Glass sorbent tubes, 70-mm long with a 7.4-mm o.d. and a 6-mm i.d., were prepared in the following manner. The sorbent material, Tenax-GC (35/60 mesh), was divided into a 100 mg sorbing section and a 50 mg backup section. The sections were held in place and separated by glass wool plugs. Plastic caps for the tubes were purchased from Niagara Plastic Co., Erie, PA. The usual sampling rate was 0.4 L/min, although 0.2 L/min was used in some experiments. Sampling rates were controlled by calibrated critical orifices. The pressure drop across a sorbent tube at 0.4 L/min was about 5.0 in. H_2O.

Impingers: All-glass, 30-ml capacity. Stem with ground-glass joint, tapered to 1-mm orifice. For sampling $P_4(g)$, two impingers in tandem, each loaded with 10-15 ml xylene, were used, with a flow rate of 0.2 to 0.5 L/min. The usual sampling rate was 0.4 L/min.

Gas Chromatograph: Hewlett-Packard Model No. 5750 Research Chromatograph equipped with a flame photometric detector, Meloy Laboratories, Inc., Model No. FPD 100AT, and a flame ionization detector.

GC Column: A 1-m by 4-mm i.d. glass column packed with 3% OV-1 on 100/120-mesh Gas Chrom Q (Applied Science Laboratories, Inc.).

Yellow Phosphorus: Fisher Chemical Co.

Xylenes: 'Baker Analyzed' Reagent, J.T. Baker Chemical Co.

Silanizing Reagent: Silyl-8, Pierce Chemical Co.

phosphorus vapor generation and sampling

The most satisfactory technique found for the laboratory generation of $P_4(g)$ was the passage of a stream of nitrogen at 25 to 30°C over a solution of 30 to 50 mg/ml phosphorus in tetralin with subsequent dilution with air. A diagram of the all-glass vapor generation-dilution system is presented in the figure. During the operation of the system, nitrogen (Matheson, 99.9%) was metered at rates of 50 to 100 ml/min into the tube, or well, containing 5 to 10 ml of phosphorus-tetralin solution. The concentration of phosphorus in the solution was maintained below the point of saturation to avoid the precipitation of solid phosphorus. Aluminum foil was placed around the well to prevent photo-induced polymerization of the phosphorus over extended time periods. The well was immersed in a constant temperature bath maintained at 30° C. The phosphorus-laden nitrogen coming from the generator was diluted with charcoal-filtered air, which was metered into the mixing chambers at a rate of 1 to 4 L/min. The relative humidity was increased to greater than 90% when desired by inserting in the air line two wash towers containing distilled water. The effluent from the generator was sampled through a four-port manifold into impingers containing xylene, or sorbent tubes as shown.

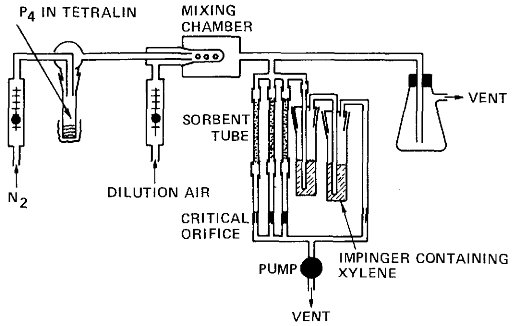

Figure 1 — Phosphorus vapor generator.

To expose the sorbent tubes, one or more tubes were attached to a sampling manifold with short sleeves of rubber tubing. The tubes were mounted vertically during sampling to avoid channeling. Usually, two impingers in tandem, each containing 10 ml of xylene, were attached to one of the ports of the manifold. The amount of $P_4(g)$ collected in the impingers served as a measure of the phosphorus simultaneously sampled through the sorbent tubes. The sampling rate through tubes and impingers was usually 0.4 L/min, with rates of 0.2 or 0.5 L/min used occasionally for comparison.

After the tubes were exposed, each sorbent section was extracted separately with 1 to 10 ml of xylene in a glass vial or sealed with airtight plastic caps or Parafilm and stored. A 5-μl aliquot was removed from each extract or diluted extract with a syringe for GC analysis.

The concentration of $P_4(g)$ in humidified or dry generator effluent was adjusted to the desired value in the range 0.01 to 0.6 mg P/m^3. In a typical run, the average concentration for 9 determinations taken over a 25 hr period was 0.61 mg P/m^3 with coefficient of variation equal to 8%. No difference in phosphorus concentration was found in impingers with or without glass fiber prefilters, indicating that the amount of phosphorus-containing particulate matter was negligible in comparison with the amount of $P_4(g)$.

A possible disadvantage of the generator was that some tetralin vapor was generated along with the $P_4(g)$. By gas chromatographic analysis of pairs of methanol-containing bubblers in series, a tetralin concentration in air of 18 mg/m^3 (3 ppm) was found at a phosphorus concentration of 0.16 mg/m^3. None of the tetralin was present in the backup bubblers. In the absence of organic vapors, it is possible that the sorbent capacity for $P_4(g)$ would be increased.

evaluation of solid sorbents

Two porous polymers, Tenax-GC and Porapak Q, were initially tested as collection media for $P_4(g)$. Tenax-GC was found to collect $P_4(g)$ more efficiently than Porapak Q. Consequently, Porapak Q was not evaluated extensively.

In preliminary experiments, Tenax-GC performed well as a sorbent for phosphorus vapor. Tubes containing Tenax-GC and impingers containing xylene were exposed to $P_4(g)$ simultaneously. The agreement between tubes and bubblers was good. Representative results are presented in Table I.

The storage of phosphorus on Tenax-GC was also investigated by aging studies on tubes used to sample various amounts of generated $P_4(g)$. For tubes containing 12 to 25 µg P, about 10% was lost after 1 week's storage at 25° C. Others, each containing about 1 µg P, were stored at 0° C; after 12 days of storage, more than 90% of the collected phosphorus was recovered.

evaluation of the sampling and analytical method with Tenax-GC

Sensitivity and range. It was found that 16 ng $P_4(g)$ could be sorbed from about 5.5 liters of air, extracted into 2 ml of xylene, and determined with fair precision. In five concentration measurements, the coefficient of variation was 11%. The detection limit would be lower for air samples larger than 5.5 liters. The determination of 16 mg $P_4(g)$ in a 20-liter air sample would correspond to a concentration of about 0.001 mg/m^3, which is 1% of the OSHA Standard.(4)

TABLE I
Comparison of Tenax-GC Tubes and Impingers Containing Xylene

Collection Device	Section	P_4 Recovered, µg	Calculated P_4 Conc, mg/m^3
Impinger	--	11.2	0.62
Impinger	--	10.7	0.59
Tube	1	10.7	
	2	0.0	0.59
Tube	1	14.9	
	2	0.2	0.62

TABLE II
Capacity of Tenax-GC for P_4

P_4 Conc, mg/m^3	Relative Humidity, %	Temperature, °C	Capacity, µg/100 mg
0.15	<10	27	20
0.16	>90	27	8
0.11	<10	50	2
1.52[a]	<10	27	90

[a]Generated by sublimation.

The upper limit of the range was fixed by the load capacity of a Tenax-GC sorbent tube. The load capacity was determined under various sampling conditions of $P_4(g)$ concentration, relative humidity, and temperature. A summary of the results is presented in Table II. In general, the load capacity appeared to increase as the $P_4(g)$ concentration increased. The effect of increasing the relative humidity was to lower the load capacity. The temperature of the sample air appeared to have a more deleterious effect than any other variable upon the load capacity. Increasing the temperature of the dilution air of the generator from 27 to 50° C decreased the load capacity by a factor of 10. A temperature of 50° C is probably an extreme that will not be encountered for any appreciable time period in an industrial situation.

The possibility of migration of sorbed phosphorus was investigated by first exposing Tenax-GC tubes with three 100-mg sorbing sections to 10 to 17 µg of $P_4(g)$ from the generator and then drawing phosphorus-free room air through the tubes over long periods of time. No room air was drawn through some of the loaded tubes which served as controls. Typical results of the analyses are shown in Table III. They show that 10 to 15 µg $P_4(g)$ can be collected over long sampling periods without significant loss from the tube and with no more migration than 10 to 20% of the sample into the second section. The sampling of large volumes of air at 50% relative humidity appeared to have little, if any, effect on the stability of the sorbed phosphorus.

TABLE III
Migration of Phosphorus on Tenax-GC

Gas Volumes Sampled, liters					
P_4 in Air	P_4 - Free Air[a]	Section	P_4 Recovered μg	Fraction, %	P_4 Conc, mg/m^3
27.5	0.0	1	15.70	97	
		2	0.41	3	
		3	0.02	0	
		Total	16.13	100	0.59
20.4	72.0	1	10.00	86	
		2	1.16	10	
		3	0.47	4	
		Total	11.63	100	0.57

[a] The relative humidity was 50%.

Interferences. Potential interferents that are gases at room temperature were introduced with a syringe pump or through a glass tee into the dilution air line of the vapor-saturation generator. Hydrogen sulfide and sulfur dioxide were premixed and injected simultaneously in the 50-ml syringe as were carbon dioxide and carbon monoxide. The flow of a mixture of phosphine in nitrogen into the dilution air through the glass tee was measured with a flowmeter. The three gas mixtures were added to the dilution air in three individual tests concurrent with collection of phosphorus samples. The average recoveries of phosphorus appear in Table IV. Approximately 2 to 3 μg of phosphorus was sampled. No significant amounts of phosphorus were found in the backup sections of the tubes. There were no interfering flame photometric responses in the GC analysis of Tenax-GC exposed to the sulfur gases or to phosphine. Apparently, these gases were not sorbed during sampling or were not extracted into xylene. The results indicated some loss of sample in one set of tubes exposed to hydrogen sulfide and sulfur dioxide and in one set exposed to carbon dioxide and carbon monoxide at phosphorus concentrations above the OSHA Standard.(4) The recovery of phosphorus when sampling at concentrations near 0.1 mg/m^3 was good.

The possibility of the interference of red phosphorus in the determination of white phosphorus in xylene was investigated. Each of three different amounts of red phosphorus (51, 100, and 150 mg) was added to one of three vials containing 5 ml of xylene. The vials were capped and the mixtures were agitated on a mechanical shaker for 20 min. If the responses observed had been a direct result of the saturation of the xylene with red phosphorus, then a constant GC response should have been seen for the different weights of red phosphorus mixed with xylene. The responses, however, were proportional to the amounts of red phosphorus taken and therefore suggest that any interference would be due only to the presence of trace amounts of white phosphorus in red phosphorus.

Accuracy and precision. The combined effect of air sampling, sample preparation, and GC analysis was determined by sampling generator effluent into Tenax-GC tubes, extracting the sorbent material with xylene within about 1 hr of the exposure, and analyzing the extracts within several hours of the exposure. Several sets of tubes were exposed to different phosphorus concentrations. The sampling rate for all of the tubes and impingers was about 0.2 L/min. Twenty liters of generator effluent was sampled at each level except at 0.01 mg/m^3 where 1 to 5 liters was sampled. The results summarized in Table V indicate that less than 10% error was experienced in the measurement of phosphorus

TABLE IV
Interference Tests for Gases

Interferent	P_4 Conc, mg/m^3	Average Recovery from Tubes, %
H_2S and SO_2 (each at 15 ppm)	0.150	88
	0.085	103
CO_2 (9000 ppm) and CO (50 ppm)	0.203	82
	0.091	100
PH_3 (0.4 ppm)	0.229	94
	0.102	94

TABLE V
Accuracy and Precision of Sampling and Analytical Method

Conc. of Phosphorus, mg/m^3	No. of Samples	Percent Recovery[a]	Coefficient of Variation, %
0.010	8	108	11
0.048	6	98	7
0.102	12	94	6
0.160	3	99	4
0.164	9	97	5
0.186	3	100	3
0.370	6	94	4

[a] Reference method was concurrent collection in xylene in impingers.

concentrations ranging from 0.05 to 0.37 mg/m^3, with a lower limit for acceptable precision at about 0.01 mg/m^3.

Sample handling. A test was undertaken to establish the error introduced by storing exposed sorbent tubes containing about 0.7 µg P. The tubes were sealed with plastic caps, stored for 1 week at room temperature, and for an additional 6 days at 0°C. The recovery of phosphorus after 13 days was very near the recovery from tubes analyzed soon after exposure. These results are given in Table VI, along with results discussed below.

If the shipment of capped, exposed tubes will require more than a week's storage at ambient temperature, a possible alternative approach is to mix the sorbent with xylene immediately after exposure and to ship the mixture in an appropriate container. Success with this approach requires that the phosphorus be stable in the presence of xylene, Tenax-GC, and other substances that may be present in the sample, such as water. In another experiment, 5 ml of a 0.4 µg/ml solution of phosphorus in xylene was added to each of 48 glass vials with aluminum-lined plastic caps. To 32 of the vials was added 50 mg of Tenax-GC. To 16 of the vials containing Tenax-GC was added 0.5 ml of water. Water was also added to 8 vials containing the phosphorus solution only. Eight vials contained xylene solutions only. The capped vials were stored at room temperature (27°C) in the dark. The average results of the analysis of samples and standards after the indicated time periods are presented in Table VI. The results indicated that phosphorus is stable for at least 14 days in xylene with Tenax-GC and water present at 27°C.

Since white phosphorus gradually polymerizes to red phosphorus in the presence of light, the consequence of storing exposed tubes in a laboratory lighted with incandescent bulbs was determined. Six exposed tubes were stored in the dark for 1 week to serve as controls and six were stored in the light for 1 week. Slightly more variation in response was introduced by storage in the light, but the average recovery (about 0.7 µg) was identical to that found from tubes stored in the dark.

The shipment of sample tubes by mail or commercial freight lines may subject the samples to rough physical handling by storage at elevated temperatures in a poorly ventilated vehicle or storage at reduced pressures in the hold of an airplane. These stresses were simulated in several tests. Sample tubes, sealed with plastic caps, were wrapped with packing material, placed in an envelope, and mailed from a local post office. Similar samples were stored at 0.7 atm and room

TABLE VI
Storage of Phosphorus Samples

	P_4 Conc, µg/ml[a] Elapsed Time, days				
Type of Sample	0	3	7	13	14
Tenax-GC tubes	0.075	–	0.069	0.074[b]	–
Glass vials containing:					
P_4 + Xylene	0.40	0.40	0.40	–	0.39
P_4 + Xylene + H_2O	0.44	0.40	0.39	–	0.39
P_4 + Xylene + Tenax-GC	0.40	0.40	0.38	–	0.40
P_4 + Xylene + Tenax-GC + H_2O	0.39	0.40	0.38	–	0.39

[a] Averages for 3 to 6 samples.
[b] Six samples stored for 1 week at 27°C and an additional 6 days at 0°C.

temperature for 8 hrs, and other samples were stored at 60° C and atmospheric pressure for 24 hrs. The tubes stored at 60° C lost about 30% of the phosphorus, about 1.3 μg of the 4.3 μg collected. Although 60° C is an extremely high temperature for ambient conditions, such temperatures may be encountered inside closed vehicles. Reduced pressure and shipment through the mail had no significant adverse effect upon the stability of comparable amounts of phosphorus.

One other aspect of sample handling, the preparation of the sample for GC analysis by extraction with xylene, was investigated. Amounts of phosphorus ranging from 0.5 to 2.7 μg were collected on sorbent tubes and then extracted with 10 ml of xylene for 5, 10, or 30 min. No improvement in desorption resulted for extraction times greater than 5 min, and desorption was quantitative.

Variations in the sampling and analytical procedure. The effects of variations in the steps of the total sampling and analytical method were determined by the "ruggedization" method of Youden.(5) The GC analysis procedure and the sampling procedure were tested separately. In the test of the GC procedure, the factors varied and their chosen values were as follows:

- Phosphorus concentration in the stock standard solution, 10 and 25 mg/ml.
- Injection volume, 3 and 5 μl.
- Injection mode, regular and solvent flush.
- Column temperature, 70 and 90° C.
- Flowrate of carrier gas, 50 and 75 ml/min.
- Injection port temperature, 160 and 200° C.
- Detector temperature, 200 and 225° C.

A calibration curve was determined for each of eight combinations of the seven factors. The effect of each factor upon the precision of peak height and peak area measurements was determined. The estimated coefficients of variation for measurements near the center of the resulting calibration curves varied from 2 to 4% for peak height measurements and 1 to 6% for peak area measurements. Column temperature had the largest effect on peak height; the concentration of the stock standard solution demonstrated the largest effect on peak area.

Three factors that had not been examined systematically previously were evaluated in the test of the sampling procedure. These were the sample volume (10 and 50 liters), the sampling rate (0.2 and 0.4 L/min), and the volume of the xylene extract (5 and 10 ml). The sampling rate and the volume of xylene extract had a less significant effect upon precision than the sample volume. The coefficient of variation for all results was 4% at an average concentration of 0.164 mg/m^3.

discussion

The collection of trace amounts of $P_4(g)$ on a porous polymer such as Tenax-GC appears to provide a suitable substitute for the xylene impinger method. Used with a personal sampling pump, the solid sorbent tube provides a convenient device for taking personal samples in an industrial atmosphere. It is recommended that sampling be done at 50 to 400 ml/min, for a total sample volume of 10-50 liters. The tubes, when exposed and capped, are stable within 10% at 25° C for 1 week, but refrigeration at 0° C or storage of a xylene extract of the sorbent is recommended if longer storage times are needed. The only major disadvantage of the method that was found was the deleterious effect of elevated temperatures upon the collection and storage of samples. This method appears as P&CAM 257 in the new NIOSH Manual.(6)

A recent comparison of the solid sorbent method with the xylene bubbler method for the determination of white phosphorus in a phosphorus manufacturing plant indicated that the two methods agree well.(7)

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