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Sampling and analytical methods for phosphine – a review

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An overview of sampling and analysis of phosphine with an emphasis on industrial hygiene is presented. Recent advances in solid sorbents behavior allow these devices to be used followed by gas chromatographic analysis. Sampling with filter paper — AgNO_3 and colorimetric analysis remains a reliable technique. A comparison of the strengths and weaknesses of analytical (gas chromatography, chromogenic, colorimetric and electrochemical) and sampling (impregnated papers, solid sorbents, bubblers and evacuated cylinder) techniques is made.

Sampling and analytical methods for phosphine — a review

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Phosphine, PH_3 , has been determined in the workplace air by reaction, complexation or absorption of the phosphine in a sampler followed by spectrophotometric, color or gas chromatographic detection. The sensitivity and efficiency of these methods and potential new methods of monitoring phosphine will be discussed herein. Phosphine generated from metal phosphide has been used extensively as a fumigant and as a starting material for epitaxial (GaP) conductors. Welding and machining operations produce phosphine; therefore, a danger is posed to a diverse group of workers. Phosphine exposure to workers should not exceed the Federal Standard (OSHA) 8 hour-time weighted average (TWA) of 0.4 mg/m^3 (0.3 ppm).⁽¹⁾ Odor detection of phosphine is limited to 0.1 to 5.0 ppm ,⁽²⁻⁴⁾ in some instances above the TLV-short term exposure limit (STEL) of 1 ppm . Phosphine is odorless in the pure state,⁽⁴⁾ however, impurities in commercial preparations impart a garlic odor attributed to phosphine.⁽³⁾ Concentrations of 50 - 100 ppm may be withstood for short periods without injury; however, above 400 ppm death rapidly occurs. Various symptoms are seen with phosphine poisoning,

masking the identity of the toxic agent. The chemistry and toxicology of phosphine have been reviewed recently and the reader may find details therein.⁽²⁻⁴⁾

sampling

Phosphine is difficult to trap since it is a reactive gas (b.p. -87.8°C) at room temperature. Sampling devices used to collect phosphine are: impregnated filters or papers,⁽⁵⁻⁷⁾ bubblers/impingers,⁽⁷⁻¹⁶⁾ solid sorbents,^(15,16) coated or impregnated solid sorbents,⁽¹⁷⁻²⁰⁾ and evacuated cylinders.⁽²¹⁾ Detector tubes⁽¹⁷⁻¹⁹⁾ and paper strips⁽⁵⁻⁷⁾ can act as both sampling device and the analytical method. Portable detectors^(22,23) (monitors based on a flame photometric detector⁽²²⁾ or a photoionization detector⁽²³⁾) are available for continuous monitoring of phosphine. A portable quadrupole mass spectrometer affords potential as a continuous monitor.⁽²⁴⁾ A summary of present methods of sampling and analysis is presented in Table I.

impregnated paper and filters⁽⁵⁻⁷⁾

Impregnated papers (test strips) are used by workers entering fumigated grain storage areas. Lead acetate, silver nitrate, mercuric chloride and other metal salts have been impregnated on filter paper strips to sample and detect phosphine. Silver nitrate and mercuric chloride

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TABLE I
Methods of Sampling and Analysis

Sampling				
Method	Range ppm	Efficiency	Interference	Reference
1. Silver nitrate (0.1N) impregnated paper	0.05-8.0	90%		5
2. Ethanolic mercuric chloride (1%) on paper	0.05-3.0		NH ₃	6
3. Acidic potassium permanganate (0.1N) imp ^a	0.01-0.05 ^h	100%	H ₂ S	7
4. Silver diethyldithiocarbamate (0.5%) bub ^a	0.6 -4.1	86.2%	H ₂ S, AsH ₃ , SbH ₃	8
5. Silver diethyldithiocarbamate (0.5%) bub ^a	0.0 -18.	54%		15
6. Mercuric chloride (0.5%) Aqueous bubbler	10-20	—	AsH ₃	13
7. Toluene - impinger		41.5%		12
8. Mercuric chloride (0.1%) conductance cell	0.05-2.5	88.0%	SO ₂ , H ₂ S, AsH ₃ , SbH ₃	9
10. Metal impregnated solid sorbents				
11. Silver nitrate impregnated silica gel	0.05-4.1	95%	H ₂ S, AsH ₃	16
12. Auric chloride impregnated silica gel	0.01-4.0	100%	AsH ₃ , SbH ₃	17
	50-1000	100%	AsH ₃ , SbH ₃	17
13. Auric chloride impregnated silica gel	0.03-150	95%		18
14. Ethanolic mercuric chloride (0.1%)	0.0006 ^h			19
15. Mercuric cyanide impregnated silica gel	.0144-1.18	80%		20
Analysis				
Method	Sensitivity	R. S. D.	Reference	
1. Bendix phosphorus method/sulfur monitor			22	
2. HNU photoionization detector	0.1 - 100 ppm	5%	23	
3. Gas chromatography - FID, 3% TCP			26	
4. Gas chromatography - Therm, 4.5% QF-1	2 ppt ⁱ	10%	27	
5. Gas chromatography - FPD, 3% Carbowax	0.5 ppt ⁱ	10%	27	
6. Gas chromatography - Coulson	500 ppt ⁱ	10%	27	
7. Gas chromatography - TC, porous beads	10 ppm		28	
8. Gas chromatography - Therm, 30% Apiezon	50 ppb	5%	29	
9. Gas chromatography - FID, FPD, beta-ioniz. Ar Poropak Q	20 ppb		31	
10. Gas chromatography - Helium ionization, Poropak Q	5 ng		34	
11. Mass spectrometry	60 mg		35	
12. Colorimetric - ammonium molybdate 720 nm	0.01 mg/L	5%	40	
13. Colorimetric ammonium molybdate 880 nm	0.01 mg/L	5%	41	
14. Colorimetric-silver DDC ^d 465 nm	0.05 ppm	10%	8,15	
15. Colorimetric-silver sulfide 470 nm	0.02 ppm	10%	5	

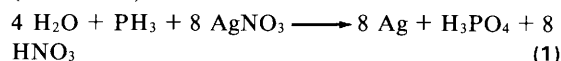
^aimp = impinger; bub = bubbler

^h= milligrams, not ppm

ⁱppt = parts per trillion

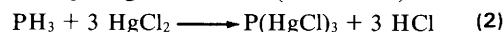
^dDDC = diethyldithiocarbamate

have been most widely used to detect phosphine by the darkening generated on impregnated paper strip. Reduced silver from silver nitrate (reaction 1) is observed as a black stain.



Stain length is the measure of phosphine concentration. Silver nitrate can be used for semi-quantitative analysis of phosphine by determination of the silver as sulfide.⁽⁵⁾ Hydrogen sulfide and light interfere with AgNO₃ reagent by reducing it to elemental silver.

Mercuric chloride reacts with phosphine to generate hydrogen chloride (reaction 2).



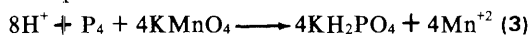
Methyl yellow⁽⁶⁾ or cresol red⁽⁷⁾ acid indicators are used to detect HCl produced as a yellow or red stain. Ammonia interferes with these indicators as a false positive. Other acids in air should also interfere. Impregnated papers detect between 0.05 to 3.00 ppm phosphine. These methods afford a semi-quantitative determination of phosphine in air.

bubblers and midget impingers^(7,16)

Silver diethyldithiocarbamate/pyridine, aqueous or ethanolic mercuric chloride, acidic potassium permanganate, toluene and other reagents have been used to collect phosphine. Potassium permanganate,^(7,8,16) bromine,⁽⁷⁾

iodine⁽⁷⁾ and other redox reagents^(7,16) convert phosphine into phosphate that is determined colorimetrically or by back titration. The silver diethyldithiocarbamate (AgDDC)-phosphine complex (465 nm) forms in five (5) minutes and is stable up to eight hours. Average collection efficiency over a flow rate of 0.5 to 1.0 liters per minute (Lpm) was 86.2%.⁽⁸⁾ National Bureau of Standards (NBS) reports a 54% efficiency for the first impinger,⁽¹⁵⁾ less than the 75% efficiency of Dechant.⁽⁸⁾ Arsine provides an interference to this collection.⁽¹⁵⁾

Permanganate has been a standard collection solution with the phosphine concentration determined colorimetrically. Other phosphorus containing species (i.e., reaction 3) and most redox reactions may lead to a false positive.⁽²⁰⁾



Collection efficiencies of 80-100% have been reported with stabilities ranging from 4 to 12 hours.^(7,15) Arsenates can interfere with analysis of these solutions. Permanganate is non-selective and only provides an adequate sampling system for reference gas streams.

Aqueous and ethanolic mercuric chloride react with PH_3 according to reaction 2. The generated HCl may be stored up to three (3) weeks at -14°C for coulometric quantitation. The reported 88-100% recovery may be biased by HCl generated after six (6) hours of storage.⁽¹⁰⁾ The source of this HCl is unclear. Interferences from arsine, sulfur dioxide, hydrogen cyanide and hydrogen sulfide may be removed by passage of the air through potassium hydroxide before collection in mercuric chloride solution. Mercuric chloride solutions are analyzed by titration or by using a gas chromatographic-microcoulometric detector. Ethanolic silver nitrate may be used to collect phosphine. However, it suffers the same limitations as the silver nitrate impregnated filters. Further development of this sampling tube may lead to a simple sampling system for phosphine. The silver nitrate collected phosphine is quantitated by the silver sulfide suspension method⁽⁵⁾

detector tubes: solid sorbents^(15,16) and coated/impregnated sorbents⁽¹⁷⁻²⁰⁾

Solid sorbents were developed to simplify

collection of samples. The solid sorbents impregnated with metal salts are similar to the impregnated filter papers of section A. Potassium permanganate,⁽¹⁵⁾ silver nitrate,^(15,16) auric chloride,^(17,18) and mercuric chloride⁽¹⁹⁾ coated on silica gel provide detector tubes with a range of 0.03-150 ppm. No detector tube for phosphine has been certified by NIOSH. Phosphine concentration detected by the tube is measured as a stain length. Tubes are subject to the same interferences as paper strips and have designated shelf lives that should be observed to obtain accurate measurements.

Silica gel and acid-washed charcoals have been evaluated for phosphine absorption.⁽¹⁵⁾ Reports of reversible phosphine absorption on charcoal have not yielded a reproducible sampling device.⁽¹⁵⁾ Silver nitrate and potassium permanganate coated silica gels effectively collect phosphine; however, no quantitative release of phosphine was achieved.⁽¹⁵⁾ Many commercially available solid sorbents were evaluated with negative results in an exhaustive methods development program. Mercuric cyanide on silica gel⁽²⁰⁾ quantitatively collects phosphine and permits storage for 24 hours. 80% retention during two weeks storage was observed. The phosphine is released by treatment with alkaline sodium borohydride solution for gas chromatographic analysis. Further development of this system shows promise for simple sampling of phosphine.

evacuated cylinders and air sampling bags⁽²¹⁾

Aluminum or glass evacuated cylinders⁽²¹⁾ and Mylar[®] or Tedlar[®] sampling bags⁽⁸⁾ have been evaluated for industrial hygiene purposes. A search of the literature has not produced any examples of the use of flexible bags or evacuated containers for the collection of phosphine samples. Surface adsorption phenomena may limit quantitative release of phosphine, except for an inert (Teflon[®]) evacuated cylinder. Air sampling bags used for preparing known gas concentrations⁽⁸⁾ are cumbersome and not suitable for personal sampling.

continuous monitors⁽²²⁻²⁵⁾

Two types of continuous monitors using gas chromatographic type detectors^(22,23) are available for detection of phosphine. A sampling

pump (internal) draws metered air into both devices. The flame photometric detector uses a hydrogen rich flame to generate HPO^\bullet detected at 526 nm. The photoionization detector uses a UV lamp to generate PH_3^+ species. The flame photometric detector is phosphorus specific; however, it is cumbersome in this application. The photoionization unit is simpler operationally; however, a complete evaluation of ionization potential interferences is not available.

A portable quadrupole mass spectrometer^(24,25) developed by Varian Instruments for the Army could be used as a portable monitor. This quadrupole has a membrane separator that is inferior to a molecular leak inlet for PH_3 and similar materials. The utility of this system is limited by the substantial cost.

analysis

Methods of analysis are abundant for phosphine and could be fully exploited if a suitable sampling device(s) were available. Gas chromatography (GC), GC-mass spectrometry (MS), electrochemical coulometric, colorimetric/spectrophotometric, column/paper chromatography (chromogenic) methods of analysis have been used for phosphine.

Gas chromatography has been used extensively for analysis, although for industrial hygiene applications colorimetric/spectrophotometric^(6,8,13,15,16) methods have been most widely used. Gas chromatography affords use of a variety of detectors for phosphine analysis: microcoulometric,^(10,27-29) flame photometric,^(22,37-29) flame ionization,^(12,26,31,32) photoionization,⁽²³⁾ and beta ionization.^(31,34) Both mass spectrometry and GC-MS have been used to detect phosphine.^(1,33,35,36) Electrochemical (microcoulometric) methods employ reaction 2 and these potentiometric^(10,11,14) and conductance⁽⁹⁾ methods are the basis of the microcoulometric detector for GC. Column/paper chromatography (chromogenic) combines colorimetric analysis in detector tubes or impregnated papers.^(4-7,15-19)

gas chromatography and gas chromatograph-mass spectrometry

Gas chromatography is the most sensitive analytical method for phosphine analysis. Air

sampling bags could be used with GC, however, this has not been reported. The solid sorbent coated with mercuric cyanide apparently solves this drawback. Continuous monitors such as the photoionization detector are amenable to gas chromatographic use.

Microcoulometric, thermionic and flame photometric detectors can quantitate 5 nanograms, 20 picograms (pg) and 5 pg respectively with a $\pm 10\%$ reproducibility for foodstuffs, air and water contaminated with phosphine.⁽²⁷⁾ The flame photometric detector is used at 526 nm although a 570 nm narrow bandpass filter has been used where CH interferences are present.^(38,39)

Both argon and helium beta ionization detectors have been used to detect phosphine with sensitivity equal to the flame photometric detector.^(31,34) The beta ionization detector suffers from operational stability. It is not comparable to flame photometric or photoionization for routine use. Mass spectrometry allows detection of 10^{-9} grams and possibly lower. Low mass and simple fragmentation of phosphine make it a simple molecule to detect.⁽²⁾

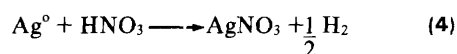
chromogenic and colorimetric/spectrophotometric

The sensitivity and limitations of detector tubes and papers have been discussed in the sampling section. These chromogenic systems offer a semi-quantitative method of analysis.

Classical colorimetric methods are the silver diethyldithiocarbamate (AgDDC) red-orange complex at 465 nm^(8,15) and the phosphomolybdate complexes at 660-690 nm and 820-880 nm.^(6,31,34,40,41) The AgDDC complex is similar to a standard analysis of arsine with AgDDC at 400 nm. Arsine presents an interference. The 0.5% AgDDC in pyridine quantitates between 0.6 and 4.1 ppm phosphine with a sensitivity of 0.05 ppm. The analysis is more specific than phosphomolybdate analysis.

Phosphomolybdate colorimetric analyses are the basis for inorganic phosphate analyses. The conversion of phosphine to phosphate with permanganate is the sampling method for this analysis. Many variations of this analysis are applicable to phosphine. The oxalic acid/permanganate method is most widely used by industrial hygienists affording an analytical

range of 0.01 to 6 mg/l phosphorus with a sensitivity of 0.05 mg P/l. The colorimetric method cannot distinguish between phosphorus species such as elemental phosphorus, phosphine and other phosphorus containing species. Arsenates can be a serious interference as can certain metals at high concentrations. A judicious choice of wavelength can eliminate some interferences. The potassium permanganate collection solution is not as specific as AgDDC and is subject to the analytical interferences. Oxalic acid may interfere with the potassium permanganate present shifting the maxima by shifting the reaction equilibrium.⁽¹⁵⁾



AgS suspension may be determined at 470 nm, forming the basis for a method to quantitate elemental silver generated from silver nitrate detection of phosphine using filter papers or ethanolic solution.⁽⁵⁾ Between 0.05 to 8 ppm can be detected with a sensitivity of 0.02 ppm, however, species such as Ag₃P can complicate this analysis.

The colorimetric methods are most widely used; however, their accuracy is questionable. The colorimetric methods do not speciate. Any permanganate oxidizable phosphorus species will yield a positive quantity in colorimetric analysis.

conductimetric and potentiometric

Phosphine has been analyzed at the ppm level with these methods. A conductance cell with mercuric chloride (reaction 2) generates HCl that is directly proportional to the amount of phosphine present.⁽⁹⁾ Suggestions for using this method as a continuous air monitor never lead to a marketed product.

Potentiometric titration of HCl with NaOH coupled with an impinger sampling device quantitates as little as 10 µg phosphine.⁽¹⁰⁾ Sample storage, unless frozen, limits the analytical method to immediate phosphine determinations. An automated potentiometric system has been developed; however, a ten-fold loss in sensitivity is observed, limiting the usefulness in industrial hygiene applications.

discussion

Impregnated papers and filters afford a simple, semi-quantitative determination of phosphine in air. This simplicity is offset by the semi-quantitative determination based on comparison of color tone (density) change. Chromogenic tubes, solid sorbents coated with the same salts as impregnated filters and papers, are the best semi-quantitative measure of phosphine concentration. Color tubes are more difficult to use than papers; however, the graduated stain length is easier to quantitate. Only the mercuric cyanide chromogenic tube can be used for accurate quantitation by instrumental analysis. This tube like the AgNO₃ filter paper allows immediate semi-quantitative detection and later quantitative laboratory analysis by gas chromatography. The accuracy of chromogenic tubes is limited by their specified shelf life. Both filters and chromogenic tubes are subject to interferences from Group V hydrides and some gases (See Table I).

Bubblers and midjet impingers suffer from similar interferences as filters and chromogenic tubes. Silver diethyldithiocarbamate (AgDDC) is most widely accepted because it offers less interferences than permanganate or mercuric chloride. AgDDC forms a distinctly orange complex that gives an immediate semi-quantitative measure of phosphine concentration. The drawback of AgDDC is the accurate measure of collection efficiency. Permanganate is useful primarily as a reference for a phosphine generator. Multiple interferences from other phosphorus species limit the use of permanganate for field sampling. Mercuric chloride midjet impingers are best used for immediate colorimetric (potentiometric) detection. Limited storage stability seriously curtails wide use of mercuric chloride impingers for field sampling. All midjet impinger sampling methods are limited by bulkiness and spillage. Although these methods can be quantitative these are not as easily used as chromogenic tubes.

Little can be said about evacuated cylinders or air bags. Both are bulky and subject to leakage. Neither offers semi-quantitative (immediate) detection of phosphine. The continuous monitors give immediate quantitative detection of phosphorus species. The photoionization

(PID) appears to afford greater speciation potential than the flame photometric (FPD) unit. The portability of the PID makes it more desirable to use in the field than FPD. The energy of the PID lamp must be at least 9.9 eV to determine phosphine.

Instrumental methods are tied to the sampling technique. Gas chromatography is the best method of analysis for phosphine because it affords specificity using FPD with good sensitivity (Table I). Use of GC is limited to sampling with mercuric cyanide/silica gel or evacuated cylinders/air bags. GC has been used as a continuous monitor by using automated repetitive sampling. Sample collection using mercuric cyanide has been combined with coulometric GC detection; however, it should be continuous considering sample storage. As a continuous monitor coulometry is not as simple or sensitive as PID or FPD. Non-phosphorous interferences such as AsH_3 and H_2S are more severe in the coulometric method. The deficiencies of the GC coulometric technique are less severe than a simple potentiometric/coulometric method. The GC column permits some speciation not present with simple potentiometry.

Chromogenic and spectrophotometry have been the mainstay of phosphine analysis. Some interferences from sampling can be minimized in the analysis. With AgDDC a judicious choice of the 470 nm λ max minimizes the arsine interference at 405 nm. This analysis has less interferences and greater specificity than molybdate analysis. Gas chromatography is preferable to spectrophotometry where equally accurate sampling methods are available.

conclusions

The most reliable method for sampling is the silver nitrate impregnated filter paper followed by colorimetric analysis of the silver sulfide suspension. The methods both offer an immediate indication (chromogenic) of phosphine present. The most promising method of sampling for phosphine is the recently developed mercuric cyanide on silica gel that allows quantitation of 0.02 mg/m^3 to 1.64 mg/m^3 . This method of sampling is coupled with flame photometric GC analysis that is sensitive to 50 pg. Unfortunately, this solid sorbent

material is not commercially available thus requiring preparation by the industrial hygienist or his laboratory support. Further developments in the solid sorbent will increase sampling versatility and reliability.

references

1. **American Conference of Governmental Industrial Hygienists:** Threshold Limit Values 1976, p.25.
2. **Fluck, E.:** *The Chemistry of Phosphine, Topics in Current Chemistry*, Vol. 35, Springer-Verlag, New York, 1973, p. 1-64.
3. **Bond, E.J. and T. Dumas:** Loss of Warning Odor from Phosphine, *J. Stored Prod. Res.* 3:389-392 (1967).
4. **Fluck, E.:** The Odor of Phosphine. *J. Air Pollut. Control Assoc.* 28:795 (1976).
5. **Hughes, J.H. and A.J. Jones:** The Estimation of Phosphine in Air. *Am. Ind. Hyg. Assoc. J.* 24:164-167 (1963).
6. **Murthu, M., S.K. Majumder and H. Parpia:** Detector for Phosphine at Permissible Levels in Air. *J. Agr. Food Chem.* 21:184-186 (1973).
7. **Borrowdale, J. and C.E.A. Shanahan:** The Determination of Phosphine in Air. *Ann. Occup. Hyg.* 4:36-48 (1961).
8. **Dechant, R., G. Sanders and R. Graul:** Determination of Phosphine in Air, *Am. Ind. Hyg. Assoc. J.* 27:75-79 (1966).
9. **Greenfield, S., H.A. Moule and R. Perry:** The Conductimetric Determination of Microgram Amounts of Phosphine in Air. *Analyst* 91:10-14 (1966).
10. **Berck, B:** Potentiometric Determination of Phosphine, *J. Agr. Food Chem.* 16:415-418 (1968).
11. **Hild, K. and W. Heidemann:** *Detection of Phosphine Traces with Automatic Titrator, Model K.* Beckman Rep. 3/4, 12(1965). (CA 70, 74030b (1969).
12. **Robinson, W.H. and H.W. Hilton:** Gas Chromatography of Phosphine Derived from Zinc Phosphite in Sugarcane, *J. Agr. Food Chem.* 19:875-878 (1971).
13. **Gertner, A., V. Grdinic and D. Pavisic:** New Possible Determination of Impurities in Medical Gases, *Acta Pharm. Jugoslav.* 18:167-179 (1968) [CA, 73, 48572x(1970)].
14. **Zugravescu, P.G. and M.A. Zugravescu:** (CA, 66, 101326d(1967) Determination of Trace Impurities in Gases (Acetylene, Phosphine, Arsine, Hydrogen Sulfide, Carbon Dioxide). *Rev. Chim.* 17:704-5 (1966).
15. **Greifer, B. and J.K. Taylor:** Development of Solid State Samplers for Work Atmospheres: Phosphine. *National Bureau of Standards* IR 75-977 (Jan. 1976) 1-27.
16. **Nelson, J.P. and A.J. Milun:** Rapid Determination of Phosphine in Air, *Anal. Chem.* 29:1665-6 (1957).

17. **Leichnitz, K.:** *Detector Tube Handbook*: Draeger, 2nd Ed. 1973, p. 103-104.
18. **Kobayaski, Y. and T. Meguro:** A Rapid Method for Microdetermination of Phosphine in Air by Means of Detector Tubes. *Bunseki Kagaku* 16: 1359-64 (1967) [CA, 68, 10769j (1968)].
19. **Murthu and S.K. Majunder:** Chromogenic Column for Determining Phosphorus and Phosphine in Air. *Pestic. Sci.* 4: 707-11 (1973).
20. **Dillon, J.K. and W.J. Barrett:** *Determination of Elemental Phosphorus and Phosphine in Air*. NIOSH Contract No. 210-75-0047, Final Report. (SORI-EAS-77-060).
21. **Eaton, H.K., J.P. Stone and F.W. Williams:** *Personal Atmospheric Gas Sampler with Critical Orifice*. NRL Rep. 7963, 13 Feb. 1976.
22. **Bendix P/S Monitor:** Engineering Report #1050, NIOSH, MRB, Charles McCammon, Jr. (Private Comm.).
23. **Driscoll, J. and F.F. Spaeion:** Photoionization Detector, Development Gives New Performance Levels. *Res. Dev.* 77:50-54 (1976).
24. **Arnold, J.T. and J.E. Evans:** Monitoring Organic Vapors, *Envir. Sci. Technol.* 9:1134-1138 (Dec. 1975).
25. **Arnold, J. and P. Robbiano:** *Portable Vapor Surveillance System*. NTIS AD-782 844, June, 1974.
26. **Chelmu, L.:** Gas-phase Chromatography Analysis of the Impurities in acetylene Produced from Carbide. *Chim. Anal.* 2:212-3 (1972) [CA, 78:92278h (1973)].
27. **Berck, B., W.E. Westlake and F.A. Gunther:** Microdetermination of Phosphine by Gas-Liquid Chromatography with Microcoulometric, Thermionic and Flame Photometric Detection, *J. Agr. Food Chem.* 18:143-147 (1970).
28. **Gnauck, G. and H. Schoen:** Analysis of Traces of Impurities in Gases with Gas Chromatography, *Proc. Conf. Appl. Phys.-Chem. Methods Chem. Anal.* Budapest, 2:182-8 (1966) [CA, 79:8178j (1968)].
29. **Dumas, T.:** Determination of Phosphine in Air by Gas Chromatography, *J. Agr. Food Chem.* 12:257-258 (1964).
30. **Baudler, M., H. Staendeke and M. Kemper:** Chemistry of Phosphorus. 43. Gas Chromatographic Separation of Phosphine. *Z. Anorg. Allg. Chem.* 388:125-136 (1972).
31. **Chakrabarti, B. and H.E. Wainman:** Determination by Gas Chromatography of Phosphine Used in Fumigation, *Chem. Ind. (London)* 7:300-302 (1972).
32. **Blades, A.T.:** Response of the Flame Ionization Detector to Nitrogenous Compounds. *J. Chrom. Sci.* 10:693-695 (1972).
33. **Dudorov, V.Y., N.K. Agliulov and V.I. Faerman:** Mass Spectrometric and Gas Chromatographic Analysis of Hydrogen Iodide. *ZH. Anal. Khim.* 29:361-4 (1974) [CA, 81:9361y (1974)].
34. **Burford, J.R. and J.M. Bremmer:** Is Phosphate Reduced to Phosphine in Waterlogged Soil? *Soil Biol. Biochem.* 4:489-495 (1972).
35. **Devatykh, G.G., N.V. Larin and I.L. Agafonov:** Mass Spectrometric Determination of Trace Impurities in Monosilane and Monogermane. *Tr. Kom. Anal. Khim. Akad. Nauk S.S.S.R. Insti. Geokhim. Anal. Khim.* 16:206-209 (1968) [CA, 69, 73740a (1968)].
36. **Halmann, M. and Y. Klein:** Positive and Negative Ion Mass Spectra of Phosphorus, *Adv. Mass Spec.* 3:267-272 (1966).
37. **Brody, S.S. and J.E. Chaney:** *J. Gas Chromatog.* 4:42-44 (1966).
38. **Sevcik, J. and N.P. Thao:** Selectivity of the Flame Photometric Detector. *Chromatographic* 8:559-562 (1975).
39. **Pighucci, R., W. Averill, J.E. Purcell and L.S. Ettre:** Routine Use of Selective G.C. Detectors. *Ibid.* 8:165-174 (1975).
40. **Rushing, D.E.:** Tentative Method for the Determination of Elemental Phosphorus in Air, *Am. Ind. Hyg. Assoc. J.* 23:383-387 (1962).
41. **Phosphate by Stannous Chloride Method 223.E:** *Standard Methods for the Examination of Water and Wastewater*, 13th ed. p. 530-532, N.Y. (1971).

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Tennessee Valley Local Section Annual Meeting

AIHA's Tennessee Valley Local Section's annual meeting is slated for September 7 and 8, 1978. It will be held in Chattanooga, Tennessee at the Choo Choo Read House. For more information, contact James A. Bruce, Cities Service Company, Copperhill, TN 37317.