A FAST, SENSITIVE, INSTRUMENTAL COMBUSTION METHOD FOR THE DETERMINATION OF TOTAL PHOSPHORUS

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ABSTRACT

A FAST, SENSITIVE, INSTRUMENTAL COMBUSTION METHOD FOR THE DETERMINATION OF TOTAL PHOSPHORUS

by Paul R. Handy

An apparatus is described for reduction of phosphorus containing compounds to phosphine in a quartz tube at 900 - 1000°C in a stream of hydrogen. The phosphine is separated from interferences of hydrogen chloride, hydrogen sulfide, and light hydrocarbons by the use of a short alumina column, followed by a 20-inch Porapak® Q column, and measured by a sodium thermionic detector. Both organic and inorganic phosphorus compounds yield phosphine under the specified conditions. The method routinely requires microgram-sized samples with sensitivity capabilities to the nanogram level and requires less than five minutes analysis time per sample.

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By

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I should like to extend a special note of gratitude to Mr. Wendell Brewbaker of the Michigan Department of Agriculture Laboratory for his two major personal introductions. He is responsible for my introduction to the chemistry and problems encountered in residue analysis, including the use of the thermionic detector as used in this work. His second introduction was to his

daughter, now my intended, who has given much moral support and encouragement for the completion of this work.

Table of Contents

List of Tables

List of Figures

List of Appendixes

Introduction

Phosphorus determinations have for many years been based on colorimetric procedures which tend to be slow and cumbersome as well as being difficult to apply to submicrogram quantities. A new look at phosphorus analysis has been taken with the idea of using a high temperature reduction of phosphorus compounds to phosphine in a quartz tube and handling the reduction products in a closed continuous gas-flow system. The final measurement is by means of a gas chromatographic detector sensitized to phosphorus-containing compounds and is sensitive to nanogram quantities.

History

Gas-chromatographic type elemental analysis systems have evolved rapidly within the last eight years from variations of older gas evolution and adsorption techniques to their present sophisticated state. The most popular carbon-hydrogen determination, the Pregl method (1), calls for the oxidation of the sample at temperatures of 700 to 800°C in a stream of oxygen over a catalyst, usually platinum, specific absorption of the combustion gases and final gravimetric determination. An inert carrier gas may be used for the combustion of organic compounds when copper oxide, cobaltic oxide, or silver permanganate is used as

the oxygen donor.

The time consuming aspects of the gravimetric step were attacked simultaneously by Duswalt and Brandt (2) and Sundberg and Maresh (3), who converted the water of combustion to acetylene by reaction with calcium carbide and trapped the resulting carbon dioxide and acetylene at liquid nitrogen temperatures. The combustion products were volatilized, separated via gas-solid chromatography (GSC) on silica gel, and determined with a thermal conductivity detector. This determination was soon extended to include determination of nitrogen as N_2 by both Nightengale and Walker (4) and Huyten and Rijnders (5). Nightengale also eliminated the trapping step by using an induction furnace for rapid sample combustion with collection on a molecular sieve column and subsequent programmed temperature elution. Meloan and co-workers (6,7,8) used the trapping procedure not only to extend the analysis to sulfur, carbon, chloride, and bromide but also to improve the chromatographic separation for simultaneous analysis. Van Hall *et al.* (9) have determined carbon in aqueous solutions of organic substances. The determination is done in an oxygen stream at 950°C with a platinum catalyst and an infrared analyzer as a specific detector for the carbon dioxide produced.

Oxygen determinations have been run by modifications of the Unterzaucher carbon-reduction procedure in which the organic oxygen is converted to carbon monoxide at 1100°C. Harris, Smith, and Mitchel (1) used a stream of helium and pyrolyzed the organic sample over carbon in a closed system. The pyrolysis products, carbon monoxide and hydrogen, were re-circulated through the system to assure complete conversion of all oxygen to carbon monoxide and to remove the hydrogen by diffusion through a heated palladium tube. A thermal conductivity cell in the system monitored the course of the reaction and measured the conductivity of the resulting helium-carbon monoxide mixture versus helium. Götz and Bober (10) developed a flow system to convert oxygen to carbon monoxide at 1120°C but dismissed the necessity of removing the hydrogen formed in the combustion by using hydrogen rather than an inert gas as the carrier. An activated charcoal GSC column separated the carbon monoxide from other combustion products so that no interference from nitrogen, sulfur, or chlorine was observed.

Reduction techniques using hydrogen gas as a carrier have been shown to be a successful route for the determination of sulfur. Schulter, Parry, and Matsuyama (11) converted sulfur-containing compounds to hydrogen sulfide at 1200°C using a nickel catalyst. The hydrogen sulfide was determined amperometrically with mercuric chloride or

colorimetrically after absorption in dilute sodium hydroxide. A gas-chromatographic sulfur determination was developed by Okuno, Morris, and Haines (12), who used a hydrogen carrier gas for reduction of the sample at 1000°C in a quartz tube with a platinum gauze catalyst. The combustion products (hydrogen sulfide and hydrocarbons other than methane) were trapped at liquid nitrogen temperatures and the methane was retained on a molecular sieve at carbon dioxide temperatures. The separation of the trapped combustion products was done sequentially on a tandem gas-liquid-chromatographic (GLC) column consisting of 12-foot silicone plus a 6-foot tricresyl phosphate column. It was observed that conversion of the organic matter to methane was not complete but that an estimation of a carbon to sulfur ratio could be made. A major source of error in the chromatographic determination of hydrogen sulfide or other reactive gases produced by hydrogenation (e.g. hydrogen chloride or hydrogen bromide) is adsorption losses in the separation column. Huyten and Rijnders (5) improved the determination of hydrogen sulfide by splitting the combustion stream, selectively removing the hydrogen sulfide from one, and comparing the thermal conductivity response of the two. This procedure reduced the errors to about 2% relative to sulfur.

Hydrogenation gas chromatography techniques have been used more extensively for structure determination than for

elemental analysis. Thompson *et al.* (13 - 16) used a catalyst of 0.5% palladium on alumina in a stream of hydrogen to effect a low temperature (below 400°C) replacement of sulfur, nitrogen, oxygen, or halogen in organic molecules. The hydrogenation products, after gas-chromatographic separation and identification, were used to reconstruct the sample's structure. Beroza (17,18) extended this work to include a rather comprehensive list of compounds and their hydrogenation skeletons for use as an analytical tool for identification of unknown gas-chromatographic peaks. Mausha and Nishimiua (19) used a similar combustion technique but eliminated the trapping procedure used by Thompson and Beroza by direct coupling of two chromatographs through a hydrogenation unit. The first chromatograph was used for determination of the sample volume delivered to the combustion unit. A heated calcium carbide column converted the inorganic gases formed in the combustion to acetylene, which was then separated from the basic hydrocarbon skeleton on the second chromatographic column. The elemental analysis had little utility at the reduction temperatures used (230 - 250°C) due to excessive broadening and tailing of the chromatographic peaks.

Combustion techniques have become quite sophisticated in the development of specific detectors for gas chromatography. Coulson and Cavanaugh (20) developed a microcoulometric

titration system for chloride analysis of combustible samples. The samples were ignited in a stream of oxygen at 800°C, and the effluent fed into a titration cell where the chloride was precipitated by silver ion. The silver ion was generated coulometrically and the current used related to the halide concentration. Coulson et al. (21) adapted the microcoulometric titration system for use with sulfur by changing the titration medium to iodide-triiodide for the oxidation of sulfur dioxide to sulfate.

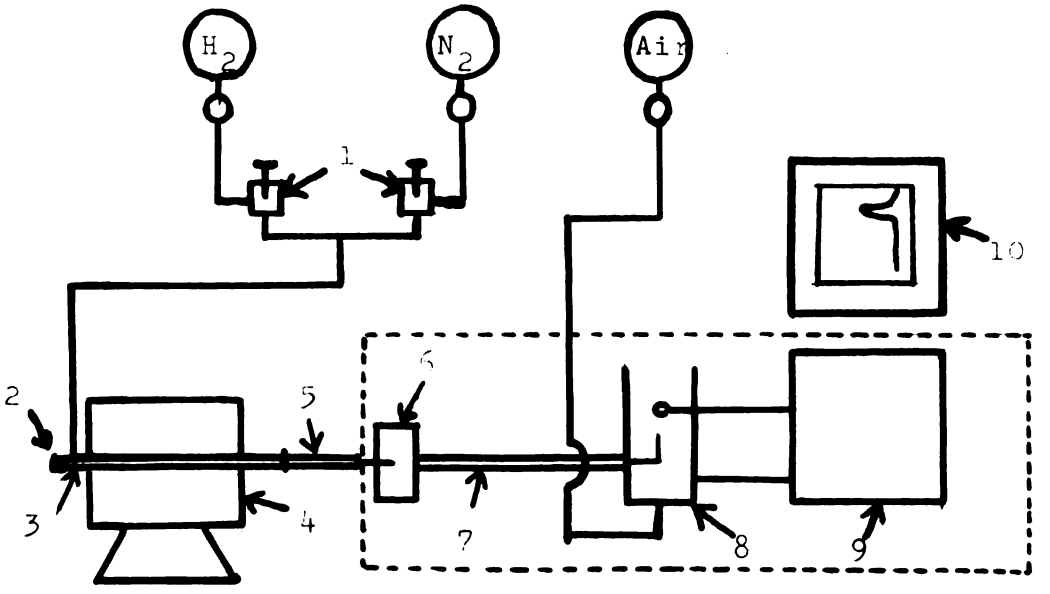
Burchfield et al. (22 - 24) used the hydrogenation technique on chromatographic effluents to determine combined chlorine and sulfur and extended the procedure to include phosphorus. This was accomplished by the reduction of the chromatographic effluent by the hydrogen carrier in an empty quartz tube at temperatures of 925 - 1000°C. The silver ion microcoulometric titration cell used gave response only to hydrogen chloride, hydrogen sulfide, and phosphine of the reduction products. It was found that the addition of a silica gel GSC column would irreversibly adsorb hydrogen chloride and separate hydrogen sulfide from phosphine for the simultaneous determination of relative phosphorus and sulfur composition of a single chromatographic peak. The system could be made absolutely specific for phosphorus by replacing the silica gel with an alumina GSC column which would retain both hydrogen chloride and hydrogen sulfide, yet allow passage of phosphine.

Karman and Guiffrida (25 - 27) reported that the inherently sensitive hydrogen flame detector could be sensitized specifically for halogen and phosphorus containing compounds. The conventional hydrogen flame detector is composed of a burner at which the column effluent is mixed with hydrogen and combusted in a stream of air. A conventional electrometer is used to measure the ion current between the burner jet and a collector ring above the flame held at several hundred volts potential relative to the jet. This detector is characteristically sensitive to the carbon content of organic molecules, relatively flow insensitive, and has a good dynamic range. The hydrogen flame detector was modified by the addition of a sodium salt to the tip of the jet and produced a six-hundred-fold increase in the response for a ten-carbon phosphorus compound and a twenty-fold increase for a hexachloro hydrocarbon relative to that observed with the normal hydrogen flame detector (27). The large response to phosphorus containing compounds indicates that the "sodium thermionic" detector is essentially specific for such compounds. The mechanism is not completely understood but experiments by Karman (25) indicate that the presence of a hot alkali metal salt is necessary. Apparently, the ion current increase is due to the increased rate of volatilization of this metal salt rather than a lowering of the ionization potential of some flame species.

The experimental apparatus was designed to incorporate the hydrogen reduction of organophosphates with the sensitive and more readily available thermionic detector into a single, continuous flow instrument. The apparatus is presented in outline form in Figure I and has three general components: the carrier gas supply and control, reduction tube with its associated tube furnace, and a basic laboratory hydrogen flame chromatograph.

The carrier gas used is dictated by the reaction to be performed and the detector used for the determination. This system requires hydrogen to be present in both the reduction zone and the detector to support combustion of the sample. The detector flame stability requires that a diluent gas be present in approximately a 1:1 ratio with the hydrogen; therefore, a hydrogen-nitrogen mixture was used as carrier gas. The nitrogen (Matheson, prepurified), hydrogen (M.S.U. stores), and compressed air (M.S.U. stores) cylinders were fitted with two-stage regulators, shutoff valves, and sensitive micrometer barrel needle valves (Ideal V 52-3-14). The hydrogen flow was further regulated by inserting a resistance composed of a one-foot length of one-quarter inch copper tubing filled with 80- - 200-mesh alumina between the regulator and needle valve. The nitrogen flow was split so as to feed the

FIGURE I Apparatus for
Elemental Analysis of Phosphorus

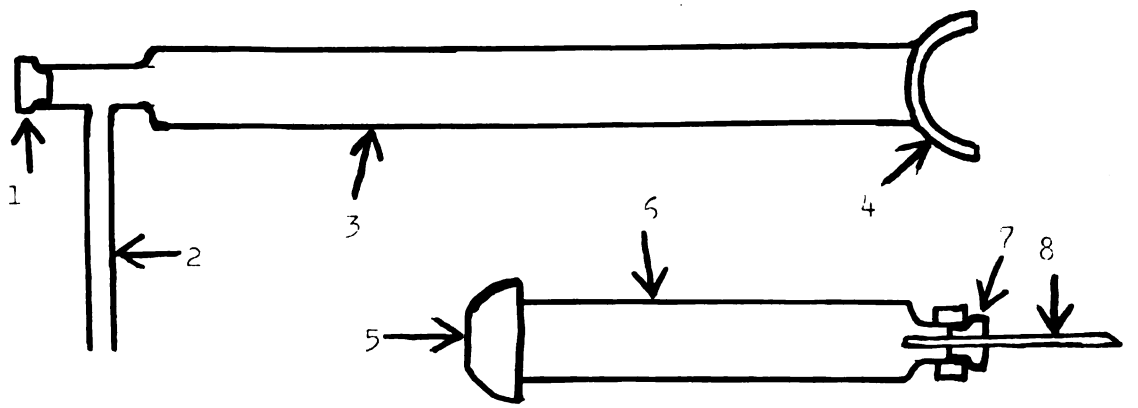


1. H_2 and carrier flow control
2. sample injection
3. quartz reduction tube
4. tube furnace
5. subtraction column
6. chromatograph injection port
7. separation column
8. thermionic detector
9. electrometer
10. data display

chromatograph carrier system as well as join the hydrogen flow through the reduction tube, the needle valve controlling the flow through the reduction zone. The compressed air is fed directly to the chromatograph which due to the high flow rate requires no further control. A Hoke toggle valve allowed air to be supplied to the reduction tube, with the hydrogen turned off, for the purpose of burning out the hydrocarbon residue which accumulates in the reduction tube. All tubing connections were made with Swagelok fittings using either one-quarter inch copper tubing or one-quarter o.d. by one-eighth inch i.d. Tygon® tubing and each connection carefully checked for leaks.

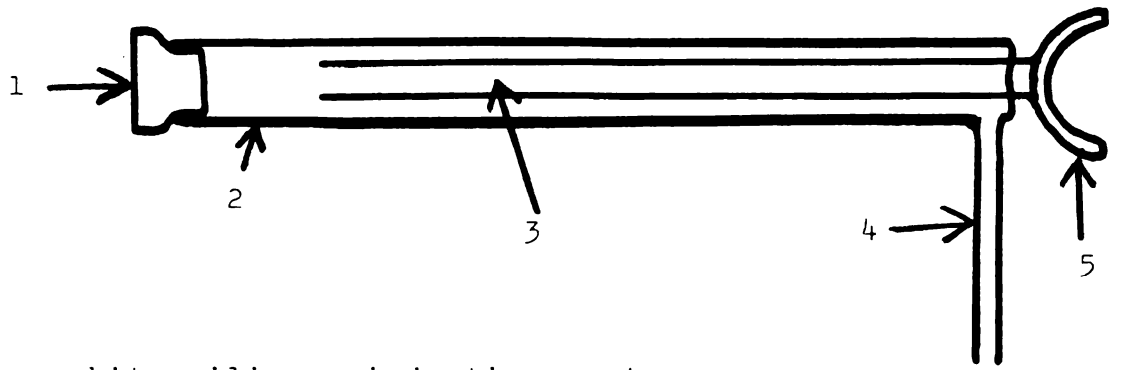
The basic reduction tube design is shown in Figure II. This design has the hydrogen-nitrogen carrier entering through a 3-mm i.d. side arm into a 5-mm joint connecting the reduction zone on one side and the injection septum on the other. The early reduction tubes were constructed using a Pyrex®- to quartz-graded seal for connection of the Pyrex inlet tube and septum socket to the quartz-reduction zone. Because no special provisions were made for heating the injection port to volatilize the injected liquid sample, the furnace was moved as close as possible to the injection area. This construction was found to be undesirable since the graded seal was subjected to a higher temperature than it was designed for. Furthermore, it was observed when repairing one broken seal that the

FIGURE II 11 mm Reduction Tube Design



1. white silicone injection septum
2. 2 mm i.d. quartz inlet tube
3. 11 mm i.d. quartz tube
4. female spherical joint, quartz
5. male spherical joint, Pyrex
6. 11 mm i.d. Pyrex tube
7. brown silicone septum
8. 0.092 inch needle stock

FIGURE III Concentric Reduction Tube Design



1. white silicone injection septum
2. 5 mm i.d. quartz tube
3. 2 mm i.d. quartz tube
4. 2 mm i.d. quartz inlet tube
5. female quartz spherical joint, quartz

walls were much thinner after use, indicating that the tube in the injection area is involved in the reaction. Therefore, all quartz construction was used in subsequent tubes to eliminate the weakness of the graded seal and allow injection of the sample directly into the reduction zone. Burchfield (24) reported that the optimum size and length of the reduction tube was 2 mm i.d. by 45 cm in length, which seemed to indicate that we should favor smaller reduction tubes. A second reduction tube was constructed of 5-mm i.d. quartz tube compared to the original 11-mm i.d. tube. The response was not appreciably increased; and furthermore, it was observed that when samples in excess of one microliter were injected, the expansion of the solution caused a back flash of the vapor down the inlet tube thus losing a portion of a slightly volatile sample. A laboratory fabricated check valve placed in the inlet stream just before the inlet tube failed to remedy the problem. A new reduction tube was designed to eliminate the problem of sample back flash by using two concentric tubes as in Figure III. The inner tube of this new reduction apparatus was of 2-mm i.d. quartz tube; and it was observed that although the back flow problem was apparently corrected, the inner tube quickly became coated with combustion residue causing an increased noise level and decreased reduction efficiency.

According to Burchfield, the temperature requirement for

reduction of phosphates to phosphine in a quartz tube is in the temperature range of 900 to 1000°C. The most frustrating portion of the experimental work has been concerned with achieving a constant temperature within this range. Initially, a Sargent S-36400 microcombustion furnace was used but was found to be totally incapable of operating consistently above a temperature of 850°C. An older Sargent tube furnace, Model No. 49090, incorporating ceramic-backed elements, was obtained along with a supply of spare elements which produced temperatures within the desired range if steady maintenance was supplied.

Once the reduction products are formed, the problem becomes one of detector response to the various products and the necessary separation of interferences. The sodium thermionic detector, basically still a hydrogen flame detector, gives a definite response to hydrocarbons; this constitutes the major interference. The other two major interferences would be hydrogen halides and hydrogen sulfide. Separation of the phosphine from hydrogen chloride and hydrogen sulfide was achieved using a short GSC column of either silica gel or activated alumina. Burchfield (24) found that silica gel will irreversibly adsorb hydrogen chloride and separate hydrogen sulfide from phosphine, while activated alumina will adsorb both hydrogen chloride and sulfide. The adsorbent (2 to 4 centimeters of alumina) was held in a 4.5-inch Pyrex subtraction tube joined to the

quartz reduction tube via a spherical joint connection. This spherical joint was responsible for much of the early irreproducibility observed between one series of reductions and another. The joint became quite warm due to its proximity to the tube furnace as well as the linear heat conducting properties of quartz. It was observed that channeling of the silicone vacuum grease used to seal the joint acted as a variable relief valve so that the flow through the system would change from series to series as well as within a particular series itself. The problem was rectified by shielding the joint from the furnace with a transite-aluminum foil heat reflector and using Apiezon W wax instead of silicone grease.

The exit end of the subtraction tube was a septum socket holding a silicone septum pierced by a 1.5-inch length of 0.092-inch o.d. stainless steel needle stock. The needle stock is used to connect the reduction apparatus to the injection port of the F and M 700 chromatograph through two septums to insure against development of leaks at the injection port.

The F and M 700 is a dual-column hydrogen flame instrument incorporating its own flow control for both carrier and detector gases, an oven capable of being used for temperature programming, and a battery-powered electrometer for measurement of the detector output. The instrument was

initially operated with only an empty glass capillary crossover column for connecting the injection port to the detector. An additional separation procedure was sought since no separation of phosphine from the light hydrocarbons was evident. The low pressure limit, using the adsorbents in the subtraction tube, was dictated by the spherical joint connection eliminating the use of the long GLC columns normally used. A new column packing, a porous polymer bead (Porapak®, Waters Associates), introduced by O. L. Hollis (28) has been used for room temperature separation of light hydrocarbons and inorganic gases. A twenty-inch column of Porapak® Q performed complete separation of phosphine from small amounts of light hydrocarbons with minimum peak tailing. The greatest problem encountered using glass columns occurred when fitting them into the instrument using Swagelok fittings to seal the system. Manufacturer's instructions indicated that three silicone rubber O-rings should be used between the nut and back ferrule to form the gas-tight seal. Several broken columns later, it was apparent that this system puts a little too much strain on the glass. Another method (29), using only a back ferrule in reverse with only one O-ring replacing the front ferrule, has provided a tight seal with minimal strain on the glass.

The separated gases pass from the column to the detector where the hydrogen used for the combustion of the column effluent is usually added; however, with hydrogen composing

the greater part of the carrier, this is unnecessary and the chromatograph hydrogen supply is turned off since the carrier alone will support combustion. The air necessary to support combustion of the effluent is introduced in the normal manner around the base of the detector jet. The conversion of the detector from hydrogen flame to sodium thermionic is accomplished by crowning the jet with a platinum spiral that has sodium sulfate fused to it. The platinum spiral is made by taking 22-gauge platinum wire and winding four turns around the threads of a 4/40 screw then bringing the excess down and wrapping it around a one-eighth inch copper tube so that the spiral winding sets flat over the end of the tube. The wire is then trimmed, cleaned, dipped into a saturated sodium sulfate solution, and fused in a Bunsen flame. After several applications of the salt solution and subsequent fusion, the inside of the spiral portion is uniformly coated with the salt and the spiral is then placed over the jet (30). The flame obtained has the yellow-orange color characteristic of the sodium flame test rather than the almost invisible hydrogen flame.

The ion current across the flame was measured by the chromatograph electrometer and displayed on a Sargent MR recorder. The recorder was equipped with a disc integrator but most of the peak areas were determined by a polar compensating planimeter, K and E No. 620000.

The samples used were 0.01 molar solutions in water for sodiumdihydrogen phosphate and in benzene for the organophosphorus compounds. These solutions were injected using a 10-microliter Hamilton No. 701 N syringe with sample sizes varying from 0.4 to 2 microliters. The injection technique employed was to flush the syringe several times with solvent. A 0.3- to 0.5-microliter slug of solvent is drawn in, followed by a 1- to 2-microliter air space before the sample is drawn completely into the barrel for reading. Benzene was the organic solvent of choice as it combusted to minimal amounts of methane and ethane. The use of hexane as a solvent with organophosphate at concentrations less than 0.01 molar produced an ethane peak which began to swamp the phosphine peak. The samples were obtained from the following sources: sodiumdihydrogen phosphate, Baker reagent; tributyl phosphate, Eastman white label; triphenyl phosphine, Carlisle Chemical Works, Inc., (recrystallized from 95% ethanol, m.p. 81°C); malathion and ronnel, American Cyanamid and Dow Chemical Companies respectively.

Results and Discussion

The experimental device just described has been used successfully to effect the reduction of phosphorus containing compounds to phosphine for measurement of total phosphorus content. The system rudimentarily resembles that of

Burchfield (25) but differs in several basic ways. First, his samples were all volatile therefore would be easily swept into and through the heated reduction zone for reaction. Our extension of this method to solutions of compounds with low vapor pressures is sure to extend the utility of the method.

Secondly, his use of a chromatographic column for the separation of sample components and solvent caused problems in column losses for the solutes. These column losses obviously differ between compounds and thus contributed to the qualitative response he obtained for phosphorus compounds. However, the GLC column provided separation of the organophosphate from the solvent which was vented around the reduction zone while using direct injection we are forced to contend with a large volume of solvent vapor in the reduction zone. Indeed this has caused difficulty with the smaller reduction tubes as the expansion of the solvent did cause some observable losses. However this seemed to be of minor importance in the larger sized reduction tubes.

The third and most obvious difference is the use of the sodium thermionic detector instead of the microcoulometric detection system. The microcoulometric detection system approaches the sensitivity of the flame ionization detector and is somewhat more selective as it is insensitive to

hydrocarbons. However it does lack in availability and operating convenience. A more generally useful method of phosphorus determination would result using the more commonly available hydrogen flame detector which is easily adapted to phosphorus detection as described previously.

The temperatures required for reduction of phosphorus compounds seems to fall into the region of 600 to 1000°C as shown in Figure IV. Although reduction does apparently occur at lower temperatures, it is indicated that the reproducibility tends to suffer below 900°C. At the highest temperatures attained, the production of light hydrocarbons is increased as shown in Figure V. An attempt was made to correlate the methane peak height with sample volume injected, but it was found that the methane peak was extremely temperature dependent. The light hydrocarbon production diminishes with temperature until only the sample injection spike, due to sample expansion, and phosphine peak remain. Phosphine formation was noted for aqueous inorganic compounds such as sodiumdihydrogen phosphate, diammoniumhydrogen phosphate, sodium pyrophosphate, and phosphine gas, as well as, organophosphates including triphenyl phosphine ($\emptyset_3P$), tributyl phosphate ($TBPO_4$), ronnel, and malathion.

The reaction products were separated as stated earlier by the use of two columns. Of the GSC adsorbents used to

FIGURE IV Response vs. Reduction Temperature

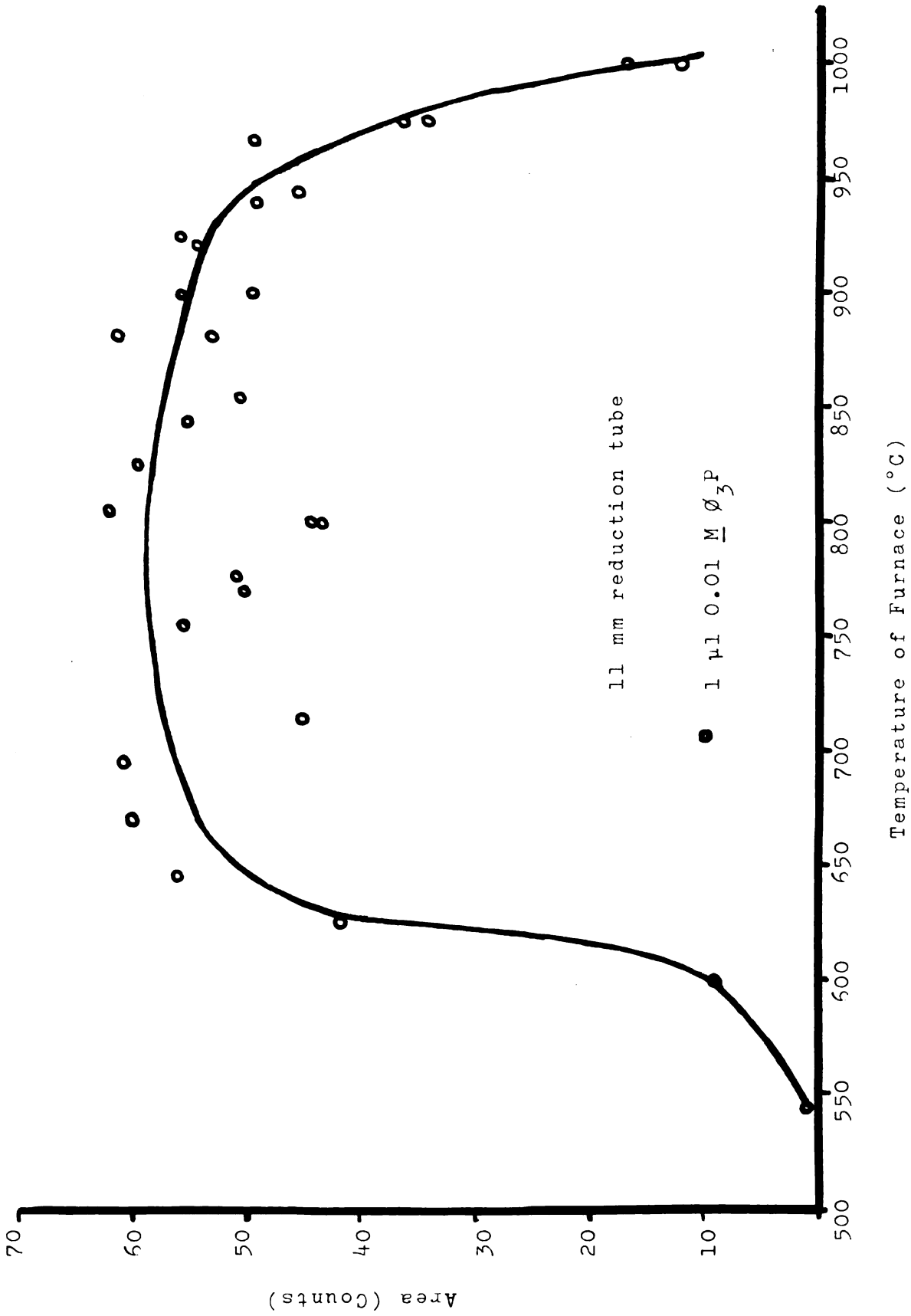
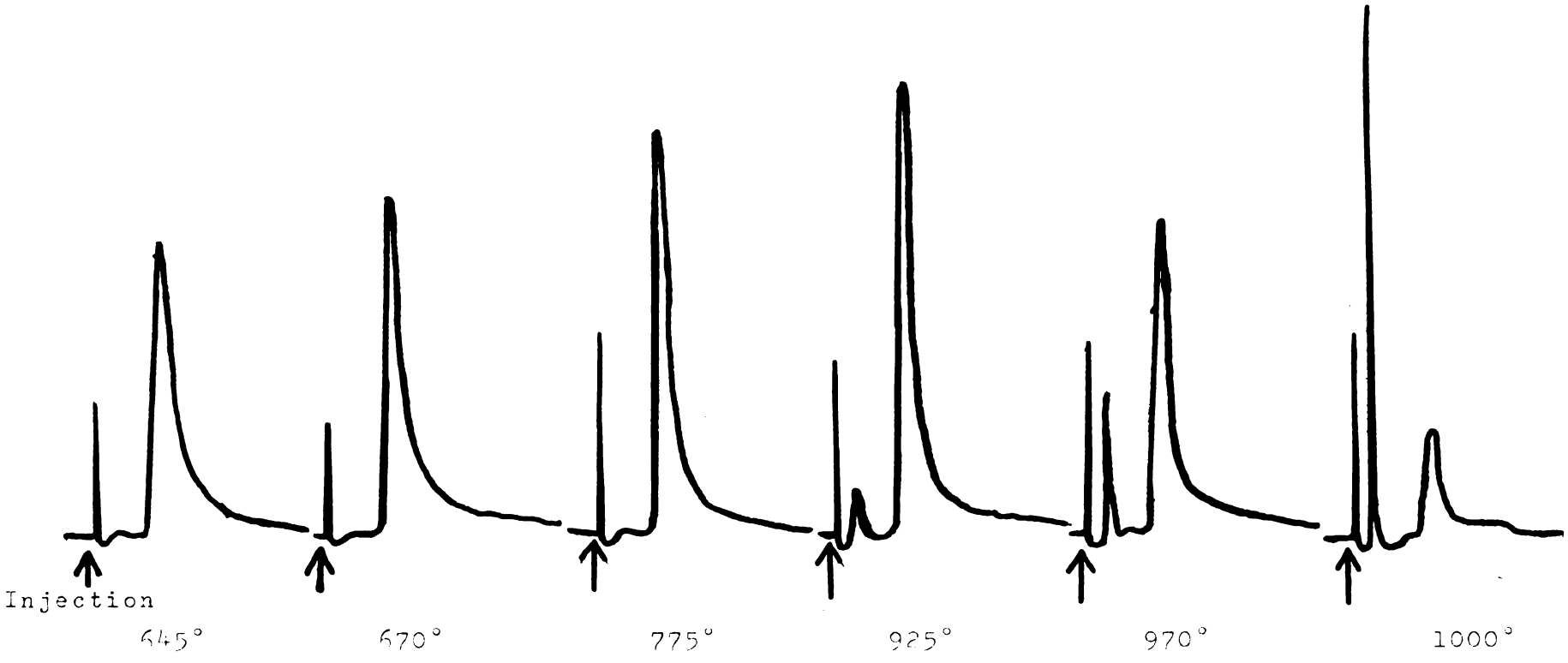


FIGURE 5 Reduction Profile at Various Temperatures

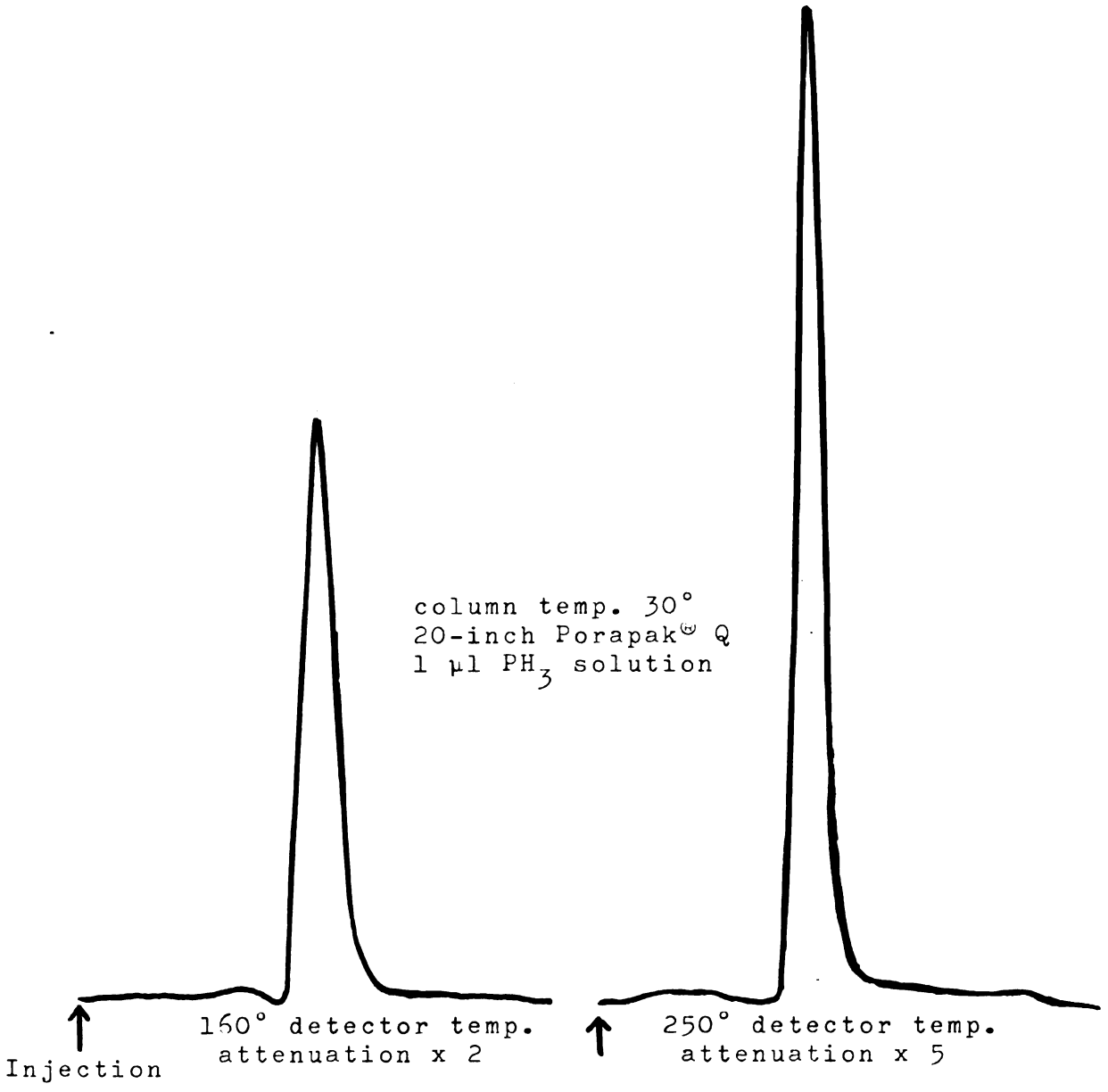


1 µl 0.01 M $\emptyset_3P$

remove the hydrogen halides, silica gel especially tended to broaden the phosphine peak and increase tailing. The Porapak® section is effective in separating the phosphine from the lower hydrocarbons as well as completely retaining the solvent at near room temperatures. Benzene was found to have a retention time of about two minutes at a column temperature of 160°C in the twenty-inch column used. When water is used as the solvent, it does tend to bleed off the adsorbent and although the hydrogen-type flame is not responsive to water, it does cause a decrease in the flame temperature and thus change the sensitivity of the detector. The characteristics of the Porapak® column are such that peaks are almost perfectly symmmetrical as in Figure VI while the reduction peaks are characteristic as in Figure V. An authentic sample of PH_3 was injected and gave the typical reduction peak shape with its characteristic retention time.

Response seems to be a greater function of the detector rather than reduction efficiency once a sufficient hydrogen flow rate is established in the reduction zone. Flow rates were measured from the cold detector with a soap film flow meter and stopwatch. The flows were determined individually and were found to vary from trial to trial. However the hydrogen flow was in the range of 130 to 150 ml per minute and total nitrogen flow a composite of 70 to 100 ml per minute through the reduction tube plus 30 to 50 ml

FIGURE VI Chromatographic Separation of PH_3



per minute added at the injection port. The air flow rate was set at 40 psi gauge pressure and was not directly measurable. The flow through the reduction zone depends upon the pressure drop created by adsorbents in the subtraction tube and column packing. Leaky joints between the subtraction and reduction tubes also caused changes in flow rates before the heat shielding and wax sealing of the joint. The procurement of the phosphine solution allowed the study of the characteristics of the detector apart from the reduction system. The chromatographic mode was used and the effects of detector temperature and hydrogen flow rate were determined. Figure VII shows the response to phosphine with detector temperature which increases until something greater than 300°C beyond which the response drops to zero. This is most likely due to decomposition within the detector block. The detector was routinely operated near 270°C but was set at 255°C as a temperature rise of about 15 degrees was observed within forty-five minutes after ignition of the flames. The presence of an optimum hydrogen flow is obvious from Figure VIII which shows response versus gauge pressure of hydrogen. Detector response to variations in nitrogen pressure seemed to be more important as far as flame stability and noise level are concerned rather than direct changes in response. The detector itself was found to lose sensitivity with time; and if used daily, the platinum wire adapter would have to be removed, cleaned, and

FIGURE VII Detector Response vs. Detector Temperature

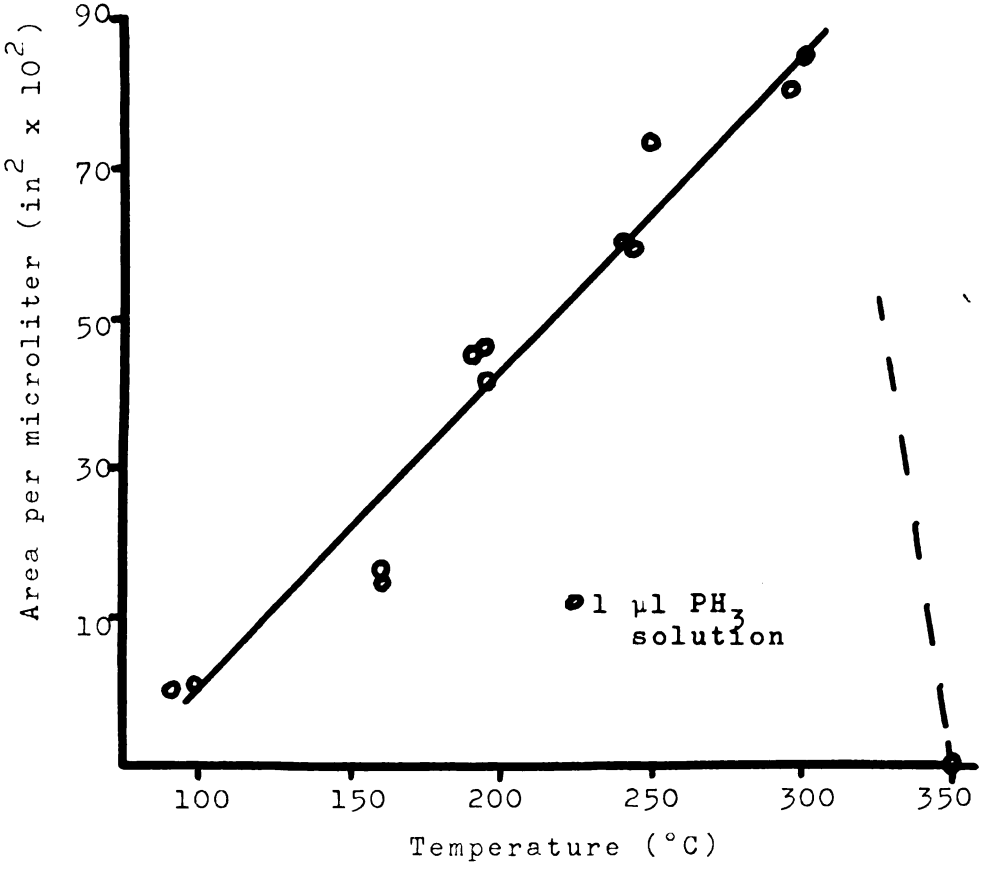
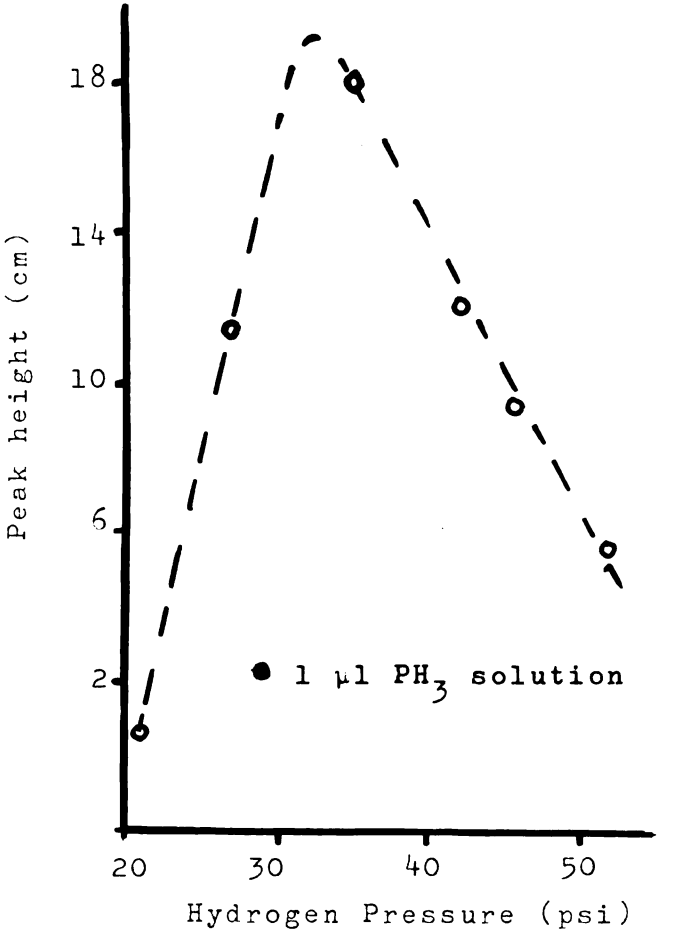


FIGURE VIII Detector Response vs. Hydrogen Pressure



recoated with sodium sulfate weekly.

The reference compound chosen for most of the work was triphenyl phosphine as it was readily available, easily purified by crystallization, and easily weighed. A standard curve was made with a series of solutions varying from 10 to 0.2 milligrams per ml of $\emptyset_3P$. The curve shown in Figure IX was obtained and, though not exactly linear over the entire range, the curve is still analytically useful if the unknown is compared to a standard of near the same response. Another standard curve using 0.010 molar solutions gave a linear response over this range of sample sizes as shown in Figure X and Table 1. A standard curve from 0.010 molar $TBPO_4$ is shown in Figure XI with its deviation from ideal response shown in Figure XII as response area per unit of $TBPO_4$ injected versus the total volume injected, sample plus flush solvent. Note the changes in the peak shape as the sample size is increased as in Figure XIII. These plots indicate the advisability of injecting samples of similar concentration to the standard being used. The detectability limit of the method has been ascertained to be on the order of 2 times 10^{-10} moles of $\emptyset_3P$.

Response variation from compound to compound has been noted as in Table 1. Ronnel almost invariably gives a slightly higher response than does $\emptyset_3P$, malathion, or $TBPO_4$.

FIGURE IX $\emptyset_3P$ Calibration Curve

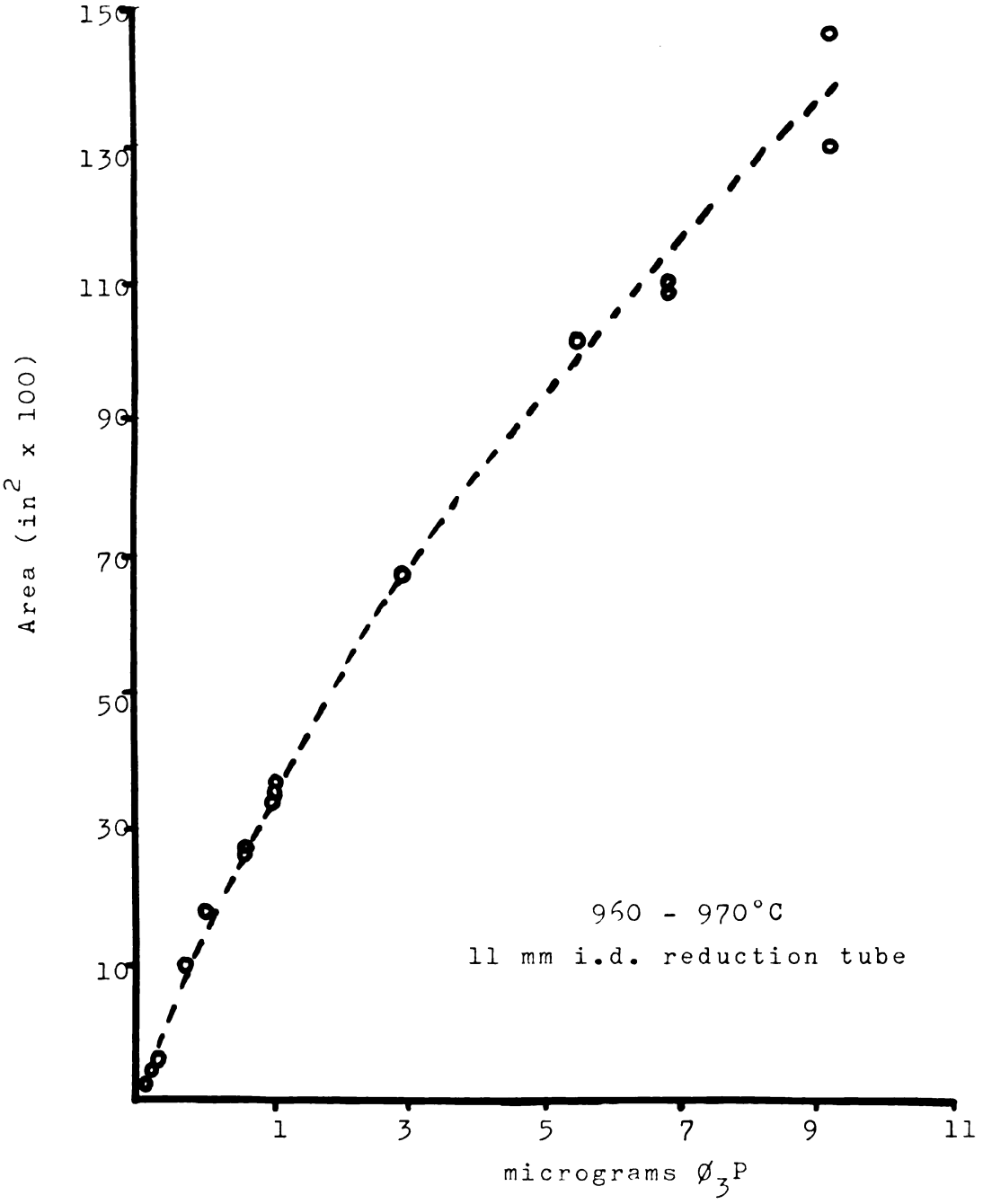


TABLE 1 Response to Various 0.01 M Solutions

945° ± 5

µl Injected	Sample (0.01 M)	Area x 100 in^2
1.01	$Ø_3P$	97
1.0	Malathion	96.5
0.95	$Ø_3P$	101
1.02	Ronnel	114
1.0	$Ø_3P$	98

975

1.0	$Ø_3P$	68
2.0	$Ø_3P$	110
2.7_3	$Ø_3P$	152
0.45	$Ø_3P$	43.5
0.95	$Ø_3P$	62.5
1.0	$Ø_3P$	68.5

FIGURE X Response to 0.01 M Solutions

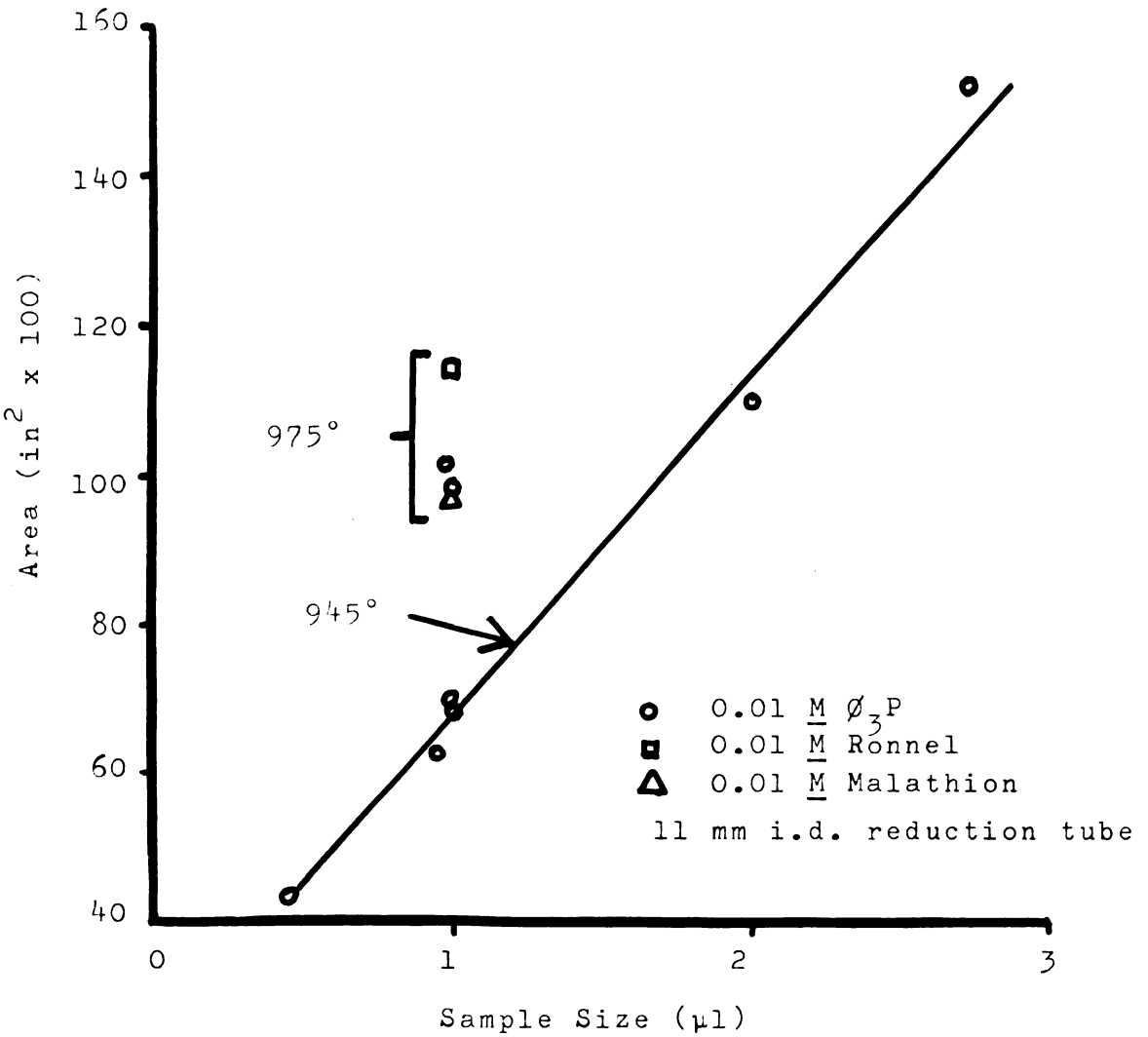


FIGURE XI Response to $TBPO_4$

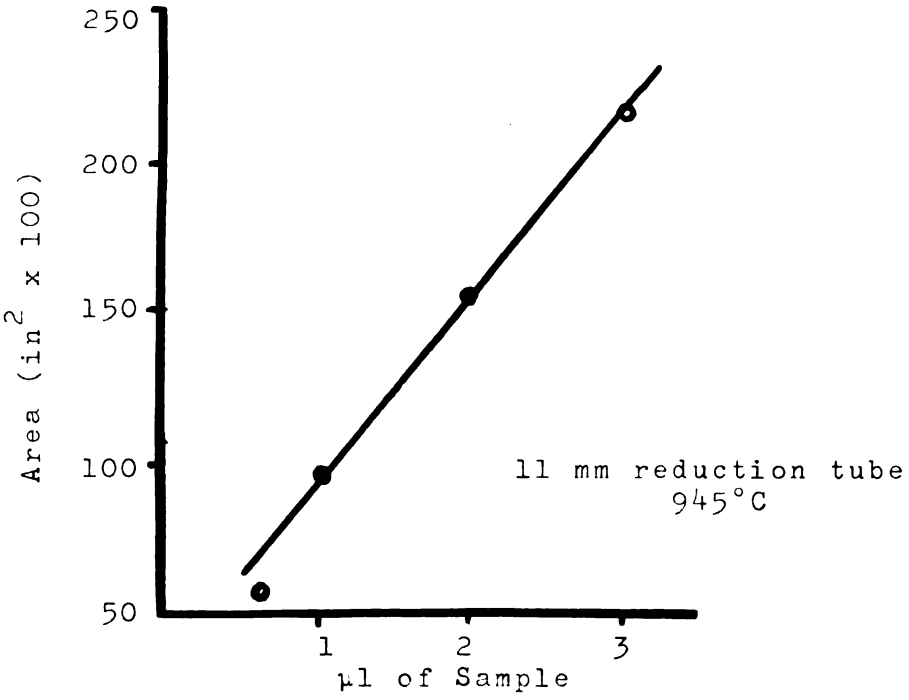


FIGURE XII Response Variation with Sample Volume

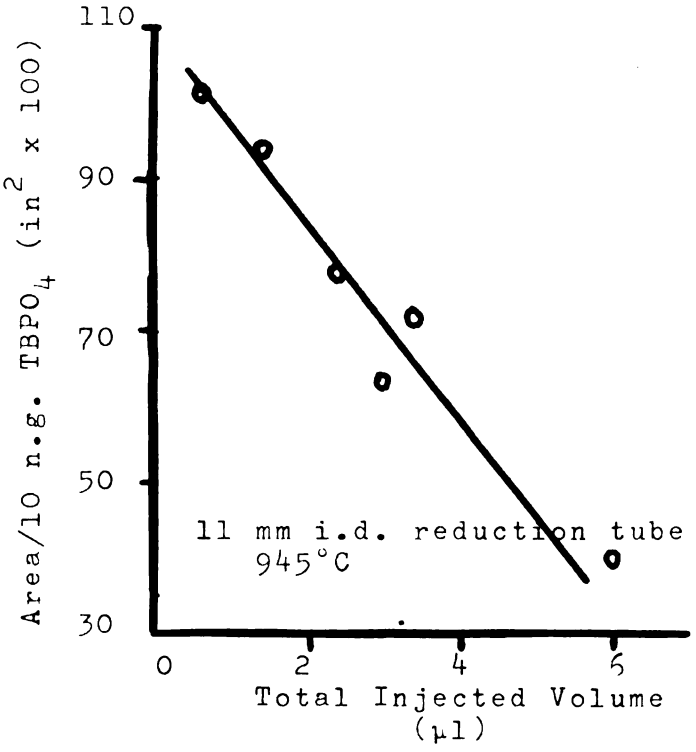
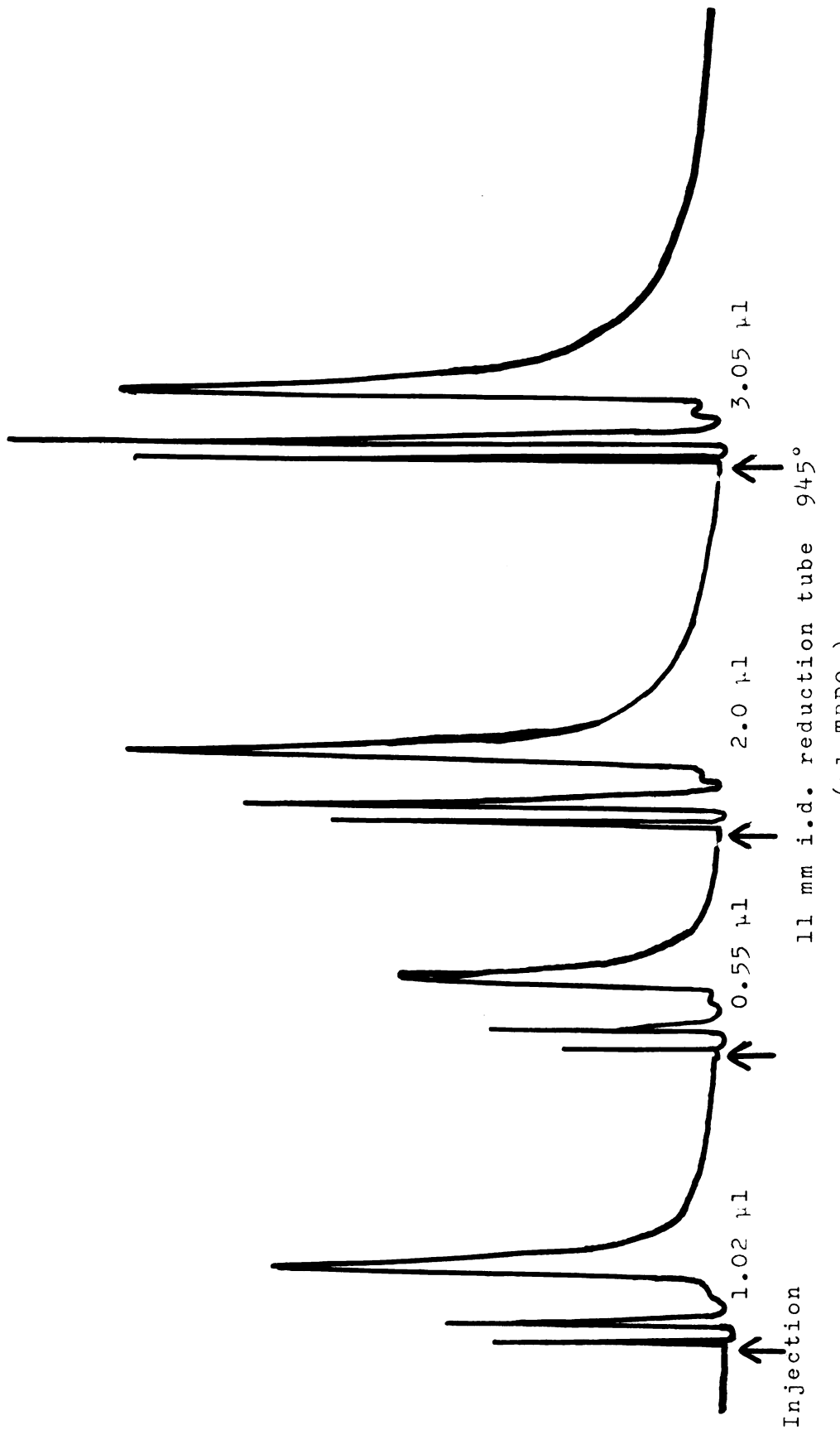


FIGURE XIII Peak Profile Variations with Increased Sample Volume



Also, aqueous inorganic phosphates give a larger response than equimolar organic phosphate compounds in organic solvents. Whether this is a solvent effect or more efficient reduction has not yet been ascertained.

Conclusion

The method as described has shown itself to be useful for the analysis for elemental phosphorus in a wide variety of phosphorus compounds in several different oxidation states. The procedure is straightforward and rapid and the analysis time per sample, using the disc integrator for peak area measurement, is well under 5 minutes. Although the full analytical range has not been determined, the range equivalent to 1 to 10 micrograms of triphenyl phosphine per sample puts the method routinely at the sensitivity limit of classical methods, with sensitivity capabilities down to the nanogram level. Assuming a one-microliter sample size, the present limit of accuracy is $\pm$ 10% for the 10-microliter syringe used for this work. Improvement of sample introduction, combined with speed, sensitivity, and versatility already attained, should give the method rapid acceptance for phosphorus analysis.

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Appendix I

Operation Procedure

I. Detector Conversion as described in the Experimental Section

II. Reduction - subtraction tube preparation

A. Reduction tube

1. Clean the reduction tube in H_2SO_4-dichromate solution; rinse and dry.
2. Insert a 1/2-inch pledget of quartz wool in the center of the reduction tube.
3. Insert white silicone septum in injection port.

B. Subtraction tube

1. Insert brown silicone septum in septum socket.
2. Insert needle stock connector.
3. Insert glass wool plug.
4. Add 2 - 4 cm of alumina.
5. Vibrate adsorbent and plug with glass wool.

C. Junction of reduction and subtraction tubes

1. Warm both halves of the spherical joint in Bunsen flame.
2. Touch male portion to stick of black wax, join to female, and rotate. Check for even seal.
3. Attach screw clamp and snug down.
4. Let cool.

III. Attachment into Instrument

1. Height of furnace is adjusted so reduction tube is in line with injection port.
2. The reduction-subtraction tube assembly is placed in position.
3. Needle stock connector is pushed through double septums in the chromatograph injection port.
4. Heat shields are attached between furnace and spherical joint.
5. Entire assembly is clamped securely into position.
6. Carrier gas inlet line is connected to the inlet tube and securely wired.
7. Chromatograph temperature settings: injection port, 100°C; column, off; and detector, 255°C.

IV. Operation CAUTION-Beware of hazardous hydrogen leaks.

A. Initial

1. The furnace turned on for one hour warm-up for temperature stabilization.
2. Carrier gas (nitrogen) turned on and set at 30 psi gauge pressure and 0.5 needle valve setting.
3. The chromatograph hydrogen and air supply are turned on 28 and 40 psi respectively.

4. Detector flames ignited.
5. The reduction hydrogen supply is turned on, 40 psi gauge pressure and 1.5 needle valve setting.
6. When hydrogen through reduction system will support combustion, turn off chromatograph supply to Column A.
7. Adjust the sodium flame using chromatograph carrier flow controller until it burns smoothly and extends 3/8 to 1/2 inch above the adapter.
8. Allow 45 minute detector warm-up.
9. Turn on electrometer and recorder for 15 minutes warm-up.
10. Balance the electrometer.
11. Set range setting at 10^4 and attenuation at 1, note stability of base line.
12. If base line is stable, set at 10^2 x 50.

B. Sample introduction

1. Fill syringe several times with solvent and flush.
2. Draw in about 1 µl of air ahead of plunger then 0.4 µl solvent, another microliter of air then the sample solution.

3. Draw the sample completely into the barrel for volume determination.
4. Inject through white silicone septum into the reduction tube.
5. Note size of peak and make necessary adjustments of range and attenuation.

C. Shutting down

1. Turn off hydrogen gas at tank, let excess burn off.
2. Turn off electrometer and recorder.
3. Turn off furnace.
4. Turn off chromatograph hydrogen and air supply.
5. Reduce nitrogen pressure and turn on oven to about 200°C to flush out solvent adsorbed on column.