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Richard H. Hanson

University of Arkansas at Little Rock

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By

Richard H. Hanson

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AN INVESTIGATION OF USING DERIVATION REACTION GAS CHROMATOGRAPHY TO MEASURE ANIONIC WATER QUALITY PARAMETERS

Richard H. Hanson
Department of Chemistry
University of Arkansas at Little Rock
Little Rock, Arkansas

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For Cathey DeFoggi, our secretary, a sincere appreciation for her skills and patience.

ABSTRACT

A new analytical method has been developed which provides researchers with another way to measure orthophosphate content in aqueous samples.

The reaction gas chromatographic system was capable of analyzing orthophosphate in the range from 0.25 - 5.0 micrograms of P in 50 microliters of aqueous sample. Flame ionization proved to be the most successful detector. The primary advantage of this technique was the small volume of sample required.

KEY WORDS: *orthophosphate,* reaction gas chromatography

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INTRODUCTION

A literature search in the Water Research Catalog, Vol. 8, 1973, listed only eight research projects involved in analytical method development for anions in water systems (1-8). All approaches by these investigators involved developing and evaluating electrochemical or spectroscopic methods. There was no evidence of any group testing chromatographic techniques applied to aqueous anion analysis.

Five reports (9-13) appeared in the literature between 1966 and 1968 describing the successful synthesis of a volatile trimethylsilyl (TMS) derivative of ortho-phosphate. These procedures were used primarily by biochemists analyzing nucleotides and carbohydrates. The volatile derivative was then separated from the reaction mixture and quantitatively determined by gas chromatography.

Silylation is the term given to the process of introducing the trimethylsilyl group, $-Si-(CH_3)_3$, into a molecule. This reaction involves the substitution of an active hydrogen (H on an alcohol, acid or amine) for the TMS group. Replacement of the active hydrogen by TMS reduces the polarity and decreases intermolecular hydrogen bonding. As a result, the derivative is more volatile and amenable for analysis by gas (vapor phase) chromatography. The original compounds can be easily regenerated by hydrolysis of the derivatives.

Butts (14) in 1970 reported the synthesis of volatile TMS derivatives of eight common anions and the subsequent gas chromatographic separation of the derivatives. Wu et.al. (15) added silicate to the list of anions studied by Butts. In the following year, Butts and Rainey (16) published a paper in which the ammonium salts of borate, carbonate, oxalate, phosphate, sulfate, arsenite, phosphite, vanadate and arsenate were reacted with bis(trimethylsilyl)trifluoroacetamide (BSTFA) using dimethylformamide as the solvent. A few microliters of this reaction mixture was injected into a gas chromatograph, separated and detected with either the flame photometric (for P) or the flame ionization detector. They established the molecular formulae of the derivatives with a mass spectrometer. Matthews et.al. (17) developed an analytical procedure for aqueous orthophosphate by extracting the phosphate into a nonaqueous solvent, exchanging the cation for a quaternary amine, forming the volative derivative and injecting into a gas chromatograph. More detailed discussions were found in the doctoral dissertations of Morrow (18) and Matthews (19) of work done with anions other than phosphate but not published in circulated journals. In 1972, this author published a paper (20) which greatly simplified the procedure developed by Matthews et.al., but was not capable of reaching their detection limits. The new approach, reaction gas chromatography, used the principle of performing the synthesis of the volatile derivative on the chromatographic column. The tedious extraction steps were replaced by a rapid vaporization step. The required sample size was reduced from 200 milliliters to 50 microliters. The ion exchange procedure was eliminated by simply adding an excess of an ammonium salt. Time and cost per analysis were both decreased.

At this point the TMS derivatives of the aqueous anions had been prepared. Two analytical precedures for orthophosphate had been published. The next logical step was to see if one generalized analytical procedure could be developed that would make it possible to analyze in one test, an aqueous sample, quantitatively and qualitatively for all anions present. Thus, this project.

The objectives of this project were stated to be:

1. to evaluate analytical derivative reaction gas chromatography as a possible method for analyzing carbonate, oxalate, phosphite, sulfate, arsenite, vanadate, arsenate, sulfite, nitrate, nitrite and pyro-phosphate.

2. to develop analytical reaction gas chromatographic methods for mixtures of the ions listed above.

3. to compare cost, ease of analysis and precision with standard analytical techniques now available.

4. to study matrix effects on this procedure due to other ions, molecules and particulates present in natural occurring water.

The plan was to first evaluate a procedure for orthophosphate using analytical reaction gas chromatography and the flame photometric detector and the flame ionization detector. Next, the eleven anions listed in 1 above would be studied using a similar technique as for orthophosphate. Different column packings, silylating reagents and oven conditions would be studied. Finally, natural water samples would be analyzed by this technique with possible interferences being observed and eventually eliminated.

PROCEDURES

The initial phase of this study was to design a reaction system compatible with a gas chromatograph equipped with either flame photometric (FPD) or flame ionization detection (FID). Both detectors are more sensitive than the one used by Wiese and Hanson (20) in the original reaction gas chromatographic approach to this problem. The thermal conductivity detector they used did not chemically alter the derivative or the other reagents present in the mixture during the detection process. Thus, a relatively primitive reaction precolumn system was designed and it proved to be successful. The fundamental idea behind this first design was to provide a chamber where the water solvent could quickly be vaporized from the phosphate sample. The gas flow in the system was routed around this chamber while a silylating reagent reacted with the sample. Finally, the mixture of derivative, excess reagent and by-products was swept onto the analytical column and separated.

To increase sensitivity, a FPD or FID system had to be used. The problem with these detectors and this chemical system was the formation of silicon oxides on burning the organic silicon compounds. This white powder quickly coated the detector electrodes (FID) or fogged the window (FPD) to the extent that the sensitivity of the method went down with each run and ultimately made the detector inoperable.

SYSTEM I - Figure 1 shows the first system that was tested. It was constructed of 1/8 inch brass and stainless steel tubing in such a way that the reactants and products came in contact with

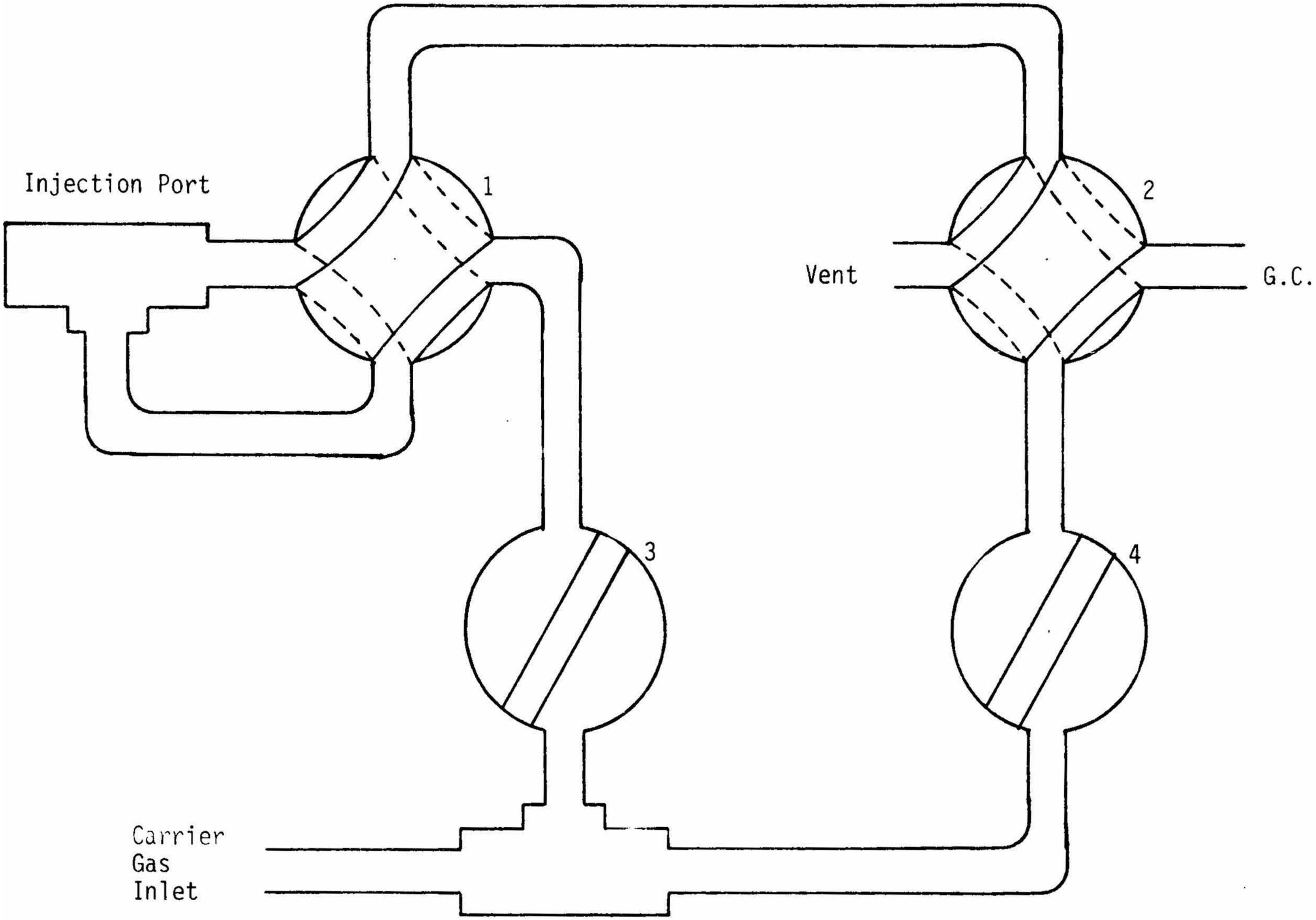

Figure 1: System I

only the stainless steel. The injection port was a Swagelok tee. Valves 1 and 2 were Valco High Temperature 4-way valves and 3 and 4 were Whitey toggle-operated forged-body valves. The entire system was mounted in a container lined with asbestos. Heating tape originally was used to heat the transfer lines between the injection port and gas chromatograph. Later nichrome wire was wrapped over the tubing, now insulated with asbestos paper, and temperature controlled with a Variac voltage regulator.

With the valves set so nitrogen carrier gas passed through valve 3, through the reaction loop on valve 1 and then to the vent port on valve 2, 50 microliters of the aqueous anion sample was introduced through the injection port with a Hamilton Syringe. At the temperature of the loop, 120°C, water vaporized and was vented to the atmosphere. The residue remaining was the ammonium salt of the anion and excess ammonium chloride. Valve 1 was then set so the gas flowed directly from valve 1 to valve 2, thus isolating the reaction loop. Approximately 1 microliter of silylating reagent, usually BSTFA, was injected over the deposited residue and allowed to react for five minutes. Valve 2 was turned so the gas flow would enter the gas chromatograph. Then valve 1 was rotated so the derivative and excess silylating reagent would go to valve 2 and then to the chromatograph.

The chromatographic column was operated in the temperature program mode using the flame ionization detector. Three different columns were used to separate the derivative from the other reagents. The first was 6 feet by 1/8 inch outside diameter (o.d.) stainless steel packed with 3% SF-96 in 60/80 mesh Chromosorb W. The second was a 6 feet by 1/4 inch o.d. glass column packed with 3.8% UCW-98 coated on 60/80 Chromosorb W. Finally, a 6 feet by 1/4 inch o.d. glass column coated with 3% OV-1 on 60/80 mesh Chromosorb W was tested.

A derivative of orthophosphate formed, but not quantitatively under the conditions described. Some of the sample particles were probably swept down the tube during the vaporization step and only a relatively small excess of silylating reagent was present. The derivative peak under the conditions specified was on the shoulder of the peak from excess silylating reagent. Larger quantities of silylating reagent completely obscured the derivative peak. Sulfate formed a complex mixture of derivative and decomposition products. The large dead volume of the system made derivative peaks that were broader than observed if the derivative was injected directly into the chromatograph. This problem was present in all systems and thus made the separation more difficult.

SYSTEM II - Figure 2 shows the second system. It was constructed so that the derivative was prepared and moved to the chromatograph in glass tubing. This was done in hopes of minimizing the decomposition of sulfate discussed above. The glass reaction chamber, 12 centimeters long, was packed with particles of 60/80 mesh Chromosorb W coated with 10% OV-17. The packing would decrease the dead volume, physically prevent any sample particles from being swept away and provide a liquid solvent system that would possibly dissolve the reactants. The entire system was mounted on a metal rack and the temperature controlled with nichrome wire wrapped around the tubing.

The sample was injected into the system with the valves, the same as described in System I, set so gas flowed from valve 4,

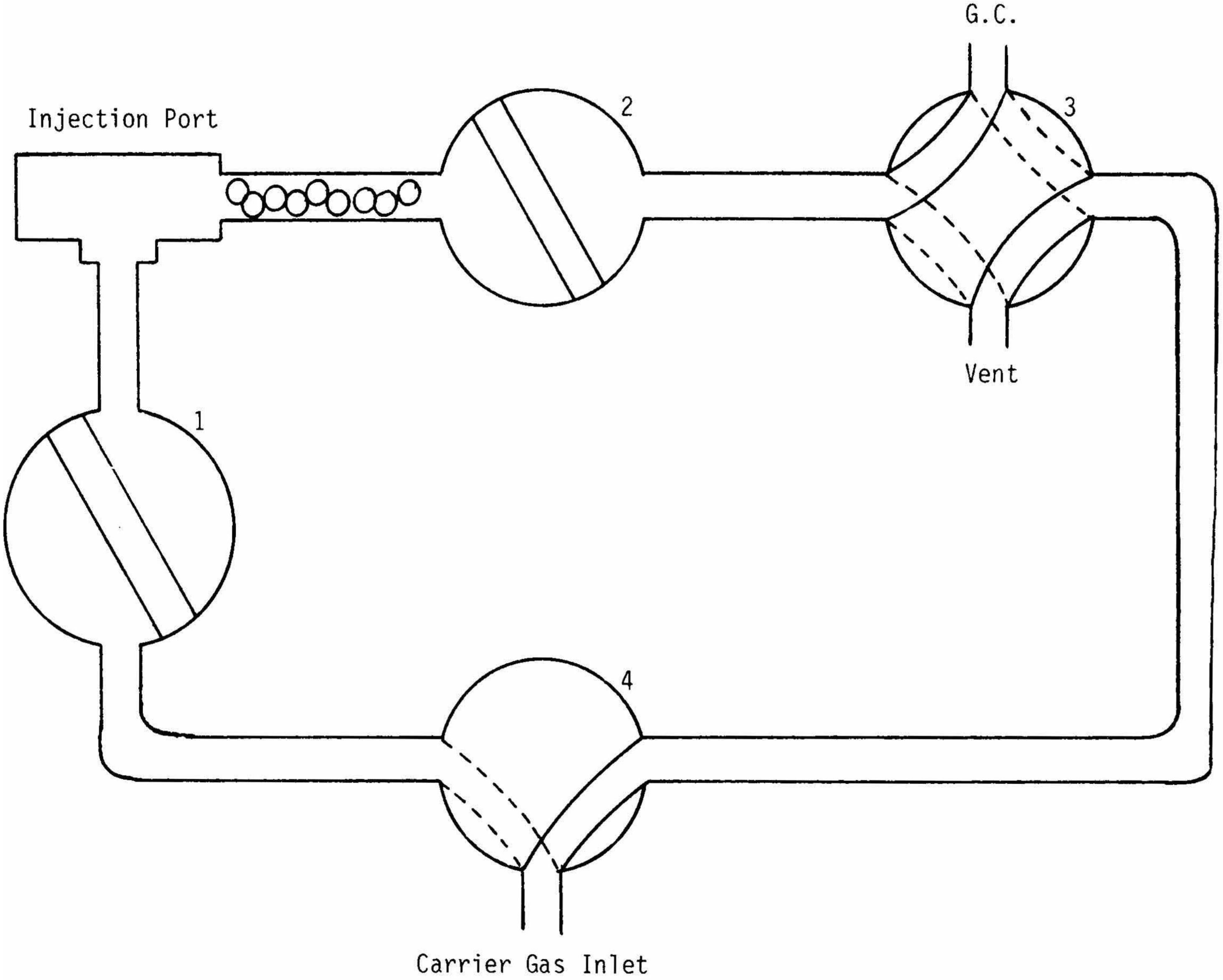

Figure 2: System II

through 1 and 2, and then to the vent in valve 3. After the water had been removed, the flow through valve 4, was sent directly to valve 3 and to the chromatograph. Valves 1 and 2 were closed. The reaction chamber was now isolated from the system and carrier gas was flowing through the gas chromatograph and stabilizing the flame detector. Silylating reagent was injected into the reaction portion of the system and allowed to react. Derivative and excess reagent were swept onto the analytical column when valves 1 and 2 were opened. Two columns, one a 6 feet by 1/4 inch o.d. glass 3% OV-1 on 60/80 mesh Chromosorb W and the other of identical dimensions, but packed with 10% OV-17, were used. The conditions of the chromatograph were similar to those described for System I except an 8 minute post injection hold was used before the temperature of the column was increased. A temperature was found where the orthophosphate derivative would not move through the column, but excess silylating reagent (BSTFA) would. This would separate most of the BSTFA from the derivative, hopefully removing the peak from the shoulder.

Results obtained from System II were much better than those from System I. By using the 8 minute post-injection hold, most of the excess BSTFA was separated from the derivative. Longer hold times made the separation better, but the time per analysis was getting too long and the derivative peaks were becoming too broad. The derivative peak from orthophosphate still appeared on the shoulder of the excess reagent.

Reproducible quantitative results were obtained with orthophosphate in the concentration range of 1 to 100 parts per million as P when 50 microliters of aqueous sample were reacted with 1 microliter of BSTFA. However, the system was not worthy of evaluation as an analytical method because of problems introduced by using the glass tubing. Slight movement in the system caused the glass tubing-stainless steel fitting connections to crack and leak. Also, excess ammonium chloride and other decomposition products were accumulating in the reaction chamber. The time required to clean and repair the system could not be justified for the quantity of samples analyzed.

SYSTEM III - Figure 3 shows the third generation. It is of much simpler design and provides better temperature control in the reaction chamber.

A second injection port was purchased and modified to serve as the reaction chamber. Glass inserts, packed with either 20% OV-1 or 10% OV-1 on 60/80 mesh Chromosorb W, were put into this second injection port and served as the reaction chamber. The rest of the path to the gas chromatograph was stainless steel heated with nichrome wire. This design eliminated the glass-stainless steel connections that broke so frequently in System II and yet kept a glass surface where most needed - at the point of vaporization. These inserts could be changed in thirty seconds and the two major objections to System II were overcome. All other operating conditions remained the same as in the two previous systems.

Aqueous samples were injected into the injection port at 110°C and the gas flow such that nitrogen from valve 1 flushed the water vapor from the port, back through valve 1 and to the vent in valve 2.

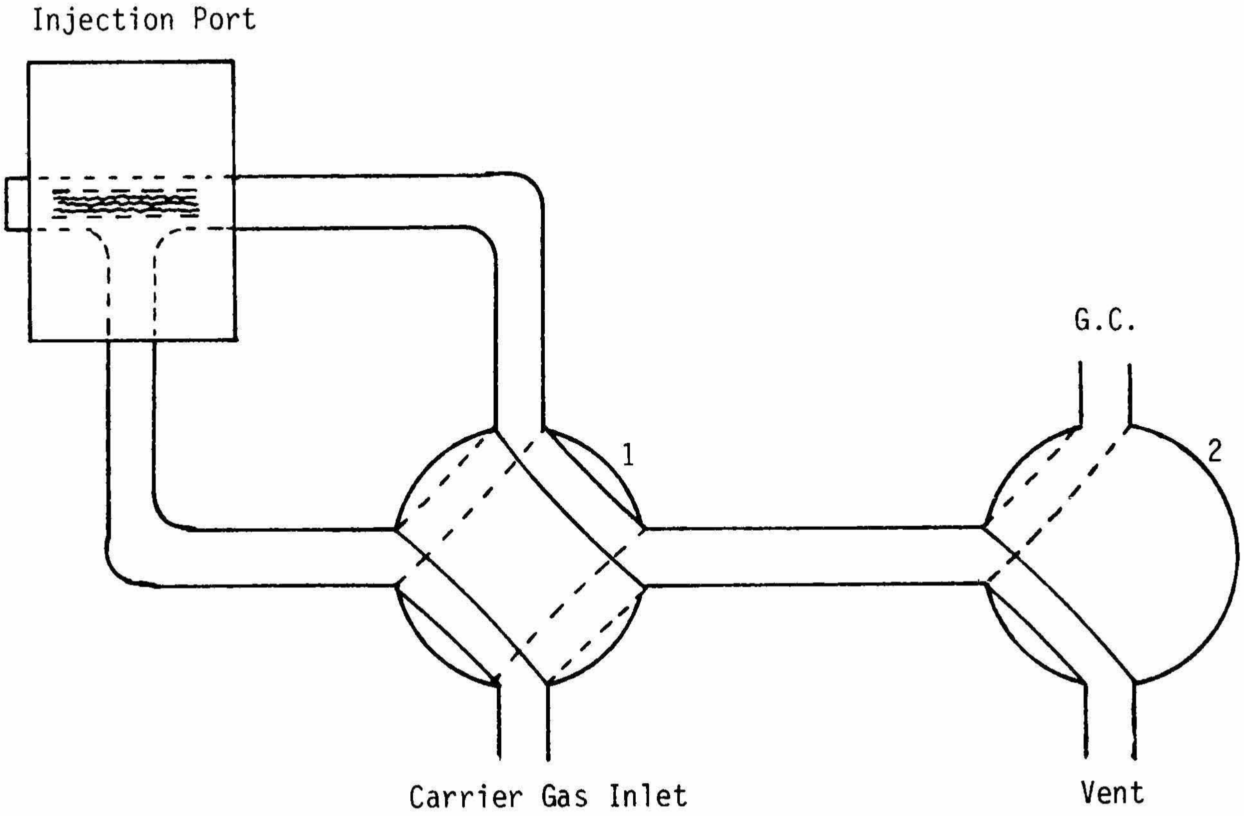

Figure 3: System III

During the derivative formation step, gas was routed directly from valve 1 to valve 2. The sample mixture was moved to the gas chromatograph by setting valve 1 back to its original position. An eight minute post-injection hold was used and then the column temperature increased. 10% OV-17 on 60/80 mesh Chromosorb W in a 6 feet by 1/4 inch o.d. glass tube served as the analytical column.

Two new problems arose with this design. Not all the phosphate was converted to the derivative during the synthesis step. Doing the procedure again, but leaving out the sample injection step, gave a response that indicated some sample was still in the system from the previous run. This memory could not be entirely eliminated. However, it was minimized when the glass insert was packed with silylated glass wool instead of Chromosorb W. Second, a problem of detector sensitivity developed for the first time. Successive injections of the same sample of the phosphate derivative prepared on the bench gave smaller signals, suggesting the silicon oxide coating on the electrodes was changing the detector characteristics.

SYSTEM IV - It was decided at this point that some prior separation of excess silylating reagent had to be accomplished. System III was modified slightly by putting a 6 inch by 1/4 inch o.d. glass tube between valve 1 and 2. This tube was packed with various column packings. Temperature was controlled with a Variac and nichrome wire wrapped around the column. An additional step in the procedure was added so excess silylating reagent would pass through the tube while the derivative remained condensed in the liquid phase of the coating. As the mixture was swept from valve 1 to valve 2, the more volatile BSTFA would move to valve 2 which was set in the vent position. The column would then be warmed, moving the derivative on to valve 2 now set so the gas would enter the gas chromatograph. The analytical column would then have to separate only residual silylating reagent from the derivative.

A second change in the procedure was to use the flame photometric detector. This detector would respond only to the phosphorous-containing derivative and not to the BSTFA.

Burning silicon-containing compounds in the FPD gave the same problem as the FID with respect to loss of detector sensitivity. The silicon oxide coated the windows to the photomultiplier tube. Residual phosphorous-containing compounds condensed in the detector and gave a large background signal so that frequent cleaning was necessary. Replicate analyses gave irreproducible peak areas. In addition to the detector changing sensitivity, some of the derivative was venting with the excess silylating reagent. Temperature control of the condensing column was very critical. A temperature, which on one day would hold the derivative back, would allow it to pass on another day. This change in the characteristics was probably due to slight bleed of the liquid phase, thus requiring a different temperature to accomplish the desired effect.

Three other systems were built and tested that showed no promise. The basic idea behind all three was to, as nearly as possible, create conditions in the chromatographic system similar to those when the reaction was run in a vial on the bench.

SYSTEM V - Figure 4 shows the system that was developed and proved to be successful. Figure 5 is a typical chromatogram from that system and Figure 6 shows a calibration curve for orthophosphate. Details of the successful method are given below.

A Hewlett-Packard 5750 gas chromatograph was equipped with dual flame ionization detectors. The analytical column was 6 foot, 1/4 inch glass packed with 5% OV-225 on 60/80 mesh Chromosorb W, DMCS treated and acid washed. The flame detector was operated at 250°C, the injection port at 150°C and the column at 135°C. Nitrogen carrier gas flow was 60 milliliters per minute at 50 psi. The precolumn was the commercially available Pyrolysis Sampling System from Hamilton Company. This accessory, though designed as a pyrolysis attachment, was easily adapted for the reactive part of the system. The controlled temperature zone nearest the opening of the process tube, the furnace, area 2 in Figure 4, was not packed. The oven zone, area 1 in Figure 4, closer to the heated line and downstream of the first zone, was packed with the same material as the analytical column. A heated transfer line, marked 6 in Figure 4, connected this assembly from the oven line to the injection port of the gas chromatograph.

Phosphate standards were prepared from ammonium monohydrogen phosphate or from sodium phosphate. N,O-bis(trimethylsily)-trifluoroacetamide with 1% trimethylchlorosilane was obtained from Regis Chemical.

A glass tube, 3 millimeters o.d. and 80 millimeters long, was used to introduce the sample, in the ammonium or acid form, into the precolumn reaction system. The tube was prepared by rinsing with 1:3 nitric acid, distilled water, and then silylated.

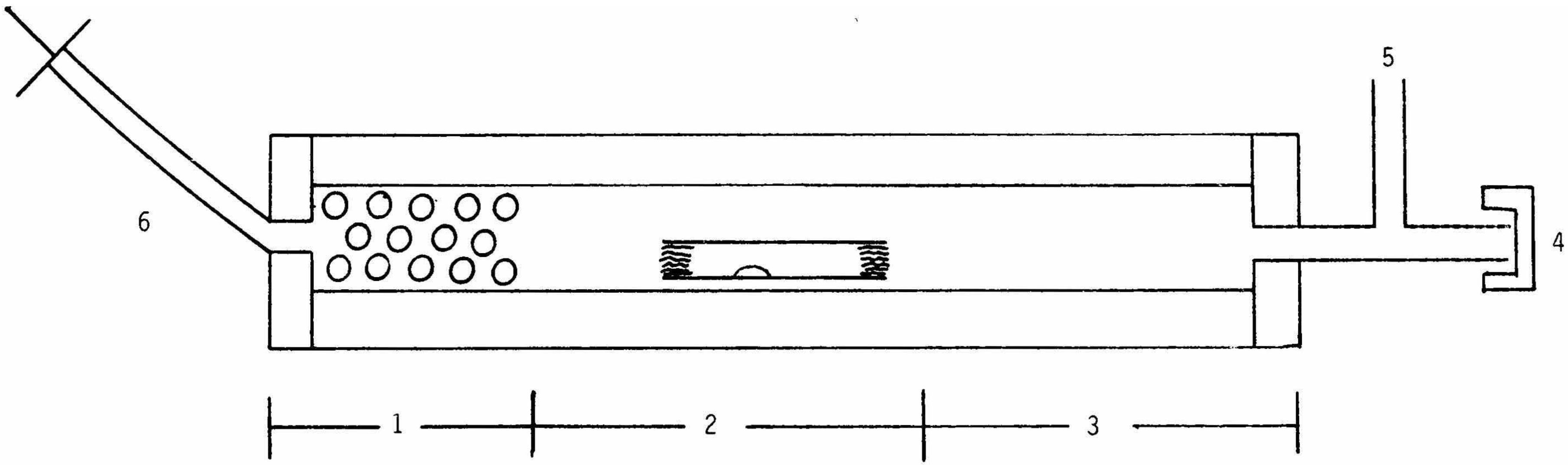

Figure 4: System V

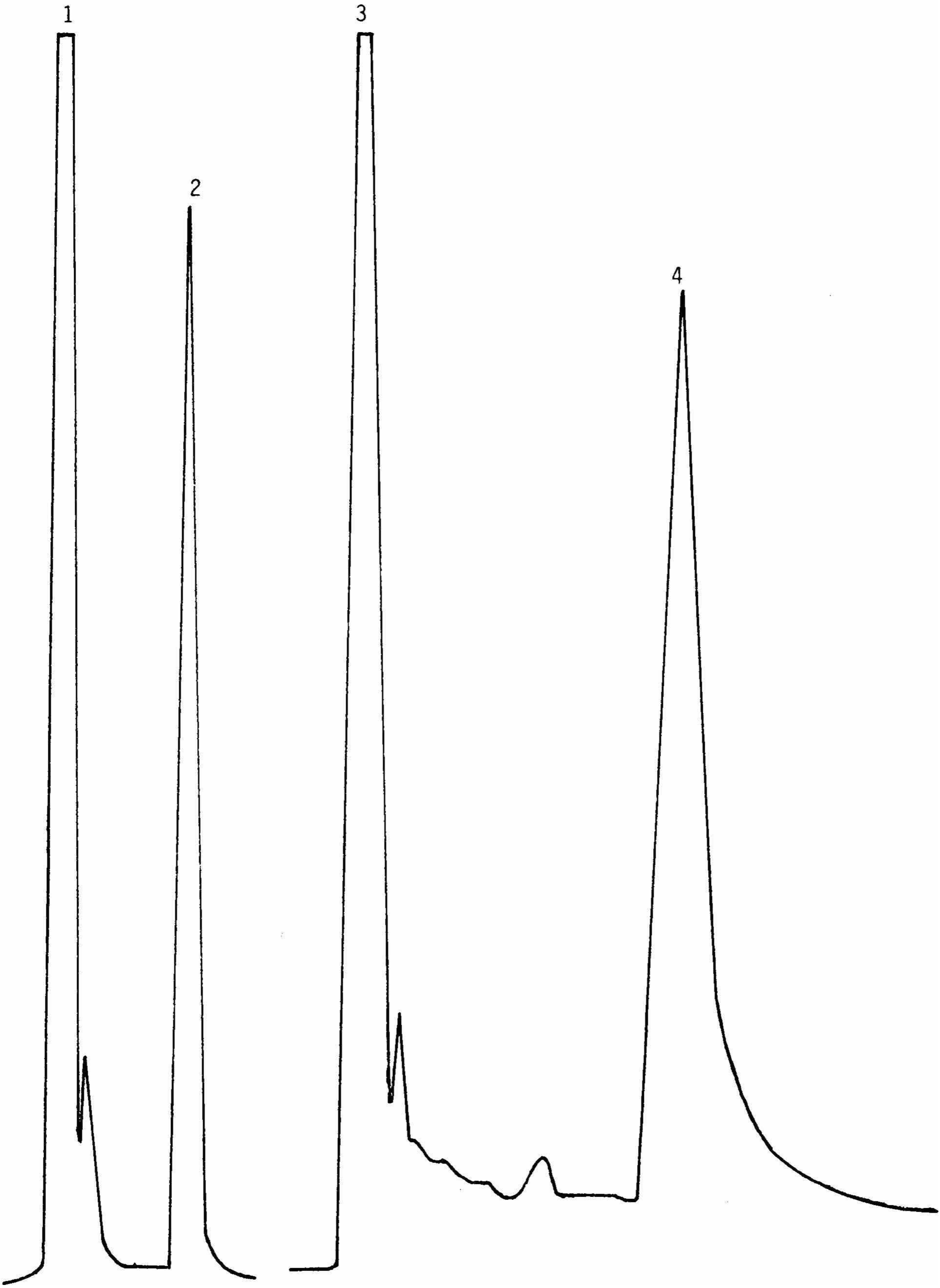

Figure 5: Typical Chromatogram

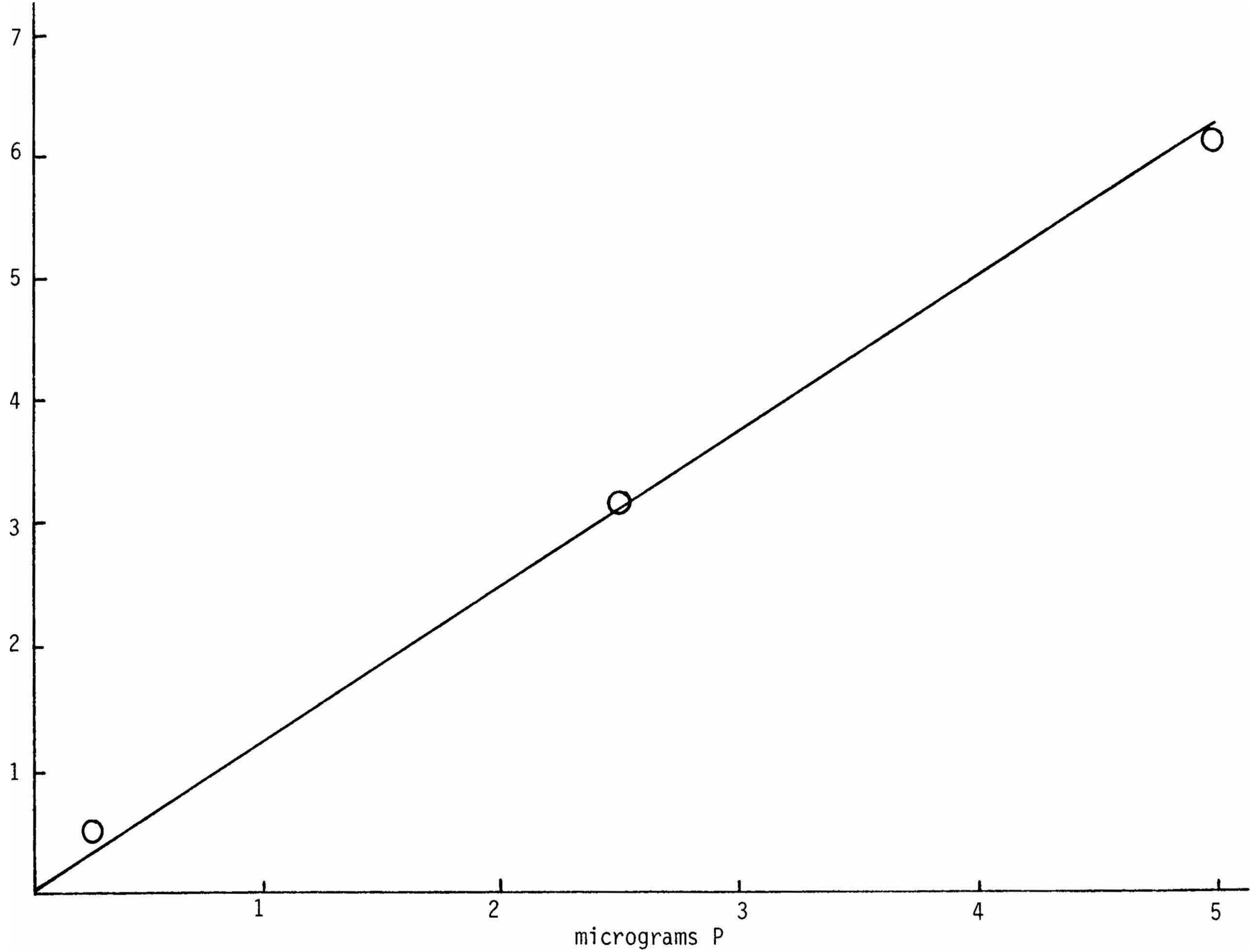

Figure 6: Calibration Curve

A plug of silylated glass wool was put in both ends, leaving the center portion empty. Five microliters of the sample were deposited on the wall inside the tube with a Hamilton syringe. The tube was then placed in a vacuum oven at 98°C and the pressure reduced 24 psi. Water from the sample vaporized in about 3 minutes. Eighty microliters of BSTFA-1%TMCS were added to the tube, now at room temperature, so that the deposited sample was covered with reagent. The tube was put into the larger process tube of the Pyrolysis Sampling System through the port, 4 in Figure 4, and moved into the furnace zone, 2, at 80°C. Reaction at this temperature occurred for 15 minutes. The temperature was next increased to 140°C for 5 minutes. All of this was done with the carrier gas flow off. Carrier gas was then swept through the small system, and the phosphate derivative condensed on the packing in the oven area, 1, at 45°C, while excess BSTFA-1%TMCS and some reaction by-products passed through the oven and heated transfer line, 6, and were vented to the atmosphere. The venting step required 10 minutes. During this time, the tubing upstream of the furnace, area 3 in Figure 4, was heated for 3 minutes with a hot air gun to remove any condensed silyl compounds. Carrier gas flow was stopped and the oven temperature increased to 140°C. The heated transfer line, at 150°C, was injected into the injection port of the chromatograph and the carrier gas flow again resumed. The derivative was thus introduced into the analytical column for separation from residual silylating reagent and reaction by-products. In three minutes the derivative hit the detector. If the sample was not in the ammonium or hydrogen form, a 45 molar excess of ammonium chloride or hydrochloric acid was added to the sample prior to the start of the analysis.

Figure 5 shows the form in which the data was collected. The ratio of the orthophosphate derivative peak, 4, to the standard 2-octanol peak, 2, was taken as the response for the phosphate. Peak 1 was solvent for the 2-octanol and peak 3 excess silylating reagent.

RESULTS AND DISCUSSION

The on-column silylation process had been studied by several authors prior to this study. Esposito (21) showed that by using an on-column synthesis technique, it was possible to silylate compounds dissolved in a reactive solvent such as water. He used sample concentrations in the one to ten percent range and did not comment on whether the conversion was quantitative. Morrow (18) constructed a precolumn assembly where solvent vapor was purged to the atmosphere prior to silylation. All volatile reaction products were swept onto the column and analyzed. Conversion to the orthophosphate derivative was less than fifty percent with a 48 microgram sample. Matthews (19) was able to lower the detection limit on orthophosphate to 1 microgram, but was unable to reproduce peak areas. The peaks were poorly shaped with serious tailing. Wiese and Hanson (11) quantitatively silylated orthophosphate in a precolumn in the 10-100 microgram range.

The technique developed in this study was used to quantitatively analyze aqueous orthophosphate in the 0.25 to 5.0 microgram range using a precolumn reaction system. Derivative peaks were very sharp with little tailing. The factors contributing to irreproducibility were located and controlled.

Quantitative conversion to the volatile derivative was accomplished when the sample was mixed with a large excess of silylating reagent and reacted near the latter's vaporization temperature. Experiments where injections of sample and silylating reagent were put directly on the analytical column above the vaporization temperature of the silylating reagent gave irreproducible and nonquantitative conversion to the derivative. This confirms Esposito's (21) data that the reaction is more quantitative in the condensed phase. His results showed that the reaction gave higher yields if the liquid phase load on the column was higher, thus dissolving more silylating reagent. He interpreted this to mean the reaction occurred in the liquid phase of the coating. In the technique presented in this report, no liquid coating was required to dissolve both sample and reagent. The reagent, kept near its vaporization temperature, dissolved the sample and allowed the reaction to occur.

Detector sensitivity continued to change even though only very little of the silicon-containing compounds was actually burned. Thus, prior to introducing the derivative into the analytical column, 5 microliters of Freon 113 were injected into the gas chromatograph, followed by 1 microliter of 1 percent 2-octanol in acetone. The response to the 2-octanol was taken as a reference and the ratio of this response to that of the derivative calculated.

Introducing the phosphate and silylating reagent into the gas chromatographic system in the 3 by 80 millimeter glass tubes proved to be far superior than injecting the aqueous sample and silylating reagent through a septum onto a packing. There was no buildup of excess ammonium chloride in the reaction chamber since it was removed after each run. Also, there was no buildup of decomposed material that forms when silylated compounds vaporize. This method provided more intimate contact for the solid sample to react with the liquid reagent. The solid ammonium phosphate is soluble in silylating reagent, so it dissolved prior to reacting.

Vaporizing the water from the aqueous sample was a critical procedure. Care was taken so some of the sample did not bump out of the tube at the elevated temperature. This was minimized when glass wool was tightly packed in both ends.

The other critical part of this technique was the temperature control in zone 1 of Figure 4. All of the derivative must stay in this condensing column while most of the excess silylating reagent passes through. A 2 °C difference from the correct temperature allowed the derivative to pass through. The correct temperature had to be checked daily because of slight changes in the packing material. The longer a packing stayed in the condensing column, the more the liquid phase bled. A buildup of a black residue accumulated on the particles from decomposition of the silyl chemicals. Fresh packing material was found to retard the derivative at lower temperatures than did more conditioned material.

In order to get the 0.25 micrograms to 5 micrograms of sample introduced into the system, 5 microliters of 50 ppm to 5 microliters of 1,000 ppm phosphate were injected into the small tube. By simply increasing the tube volume to accommodate enough solution to have 0.25 micrograms of sample or by some prior concentration step, less concentrated samples could be handled. For example, 50 microliters of 5 ppm phosphate would provide the 0.25 micrograms of phosphate.

Phosphate in any form other than hydrogen or ammonium gave no conversion to the volatile derivative. A large molar excess, 45 times, of ammonium chloride or hydrochloric acid relative to phosphate, was added to the samples prior to analysis and conversion became complete. A 5 microgram sample of sodium phosphate was treated with hydrochloric acid and another with ammonium chloride. The first response was 3.92 relative units and the second 4.20 units, the average being 4.06 ± 3.5%. Memory checks with 50 to 1 micrograms of phosphate gave no response. Reproducibility studies with 50 micrograms of the same phosphate sample gave results that were within 1 percent relative error. Tests where sodium phosphate was treated with excess ammonium chloride gave results that were consistently slightly lower than the corresponding concentration of phosphate made from diammonium hydrogen phosphate. Analysis of samples, whether in the sodium, ammonium or hydrogen forms, could be accomplished with an accuracy estimated to be ± 7 percent.

Sulfate, vanadate, carbonate, oxalate, sulfite, borate and arsenate were tested using the technique for phosphate. Only sulfate gave any response, irreproducible however, indicating a derivative formed. No derivative of the others ever reached the detector. Either no derivative formed, highly unlikely since they are known to form under similar conditions, or it vented to the atmosphere with the excess BSTFA. Of these ions tested, the phosphate derivative has the largest retention time except for arsenate. This means the derivatives of these other ions move through the columns more rapidly than the phosphate or arsenate derivatives if conditions are kept constant. At a temperature where the phosphate compound condensed, the others moved through to the atmosphere. If the temperature of the condensing column was reduced to hold back the other derivatives, excess BSTFA also condensed and stayed behind. In short, the condensing column, critical to the phosphate analysis, did not separate the derivatives of the other ions from excess silylating reagent. A longer column would improve the separation and increase the necessary vent time. However, the ten minute vent step already is too long.

This approach still offers promise of being able to simultaneously analyze complex mixtures of anions. A more efficient method of separating large quantities of silylating reagent from small amounts of derivatives must be found.

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