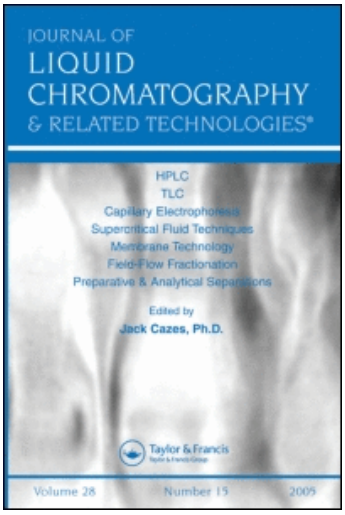

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The Separation of 12-Molybdophosphoric Acid from 12-Molybdosilicic Acid by Reverse Phase Liquid Chromatography

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THE SEPARATION OF 12-MOLYBDOPHOSPHORIC ACID FROM 12-MOLYBDOSILICIC ACID BY REVERSE PHASE LIQUID CHROMATOGRAPHY

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Abstract

The separation of 12-molybdophosphoric Acid (12-MPA) from 12-molybdosilicic (12-MSA) acid by reverse phase liquid chromatography is described with UV-visible detection. The system utilizes a commercially available styrene-divinylbenzene column (Hamilton PRP-1) and a acetonitrile-water mobile phase which is 0.1 F in $HClO_4$ and 1.2 X 10^{-2} in molybdate ion. In solutions with acetonitrile concentrations of between 30 and 35% (V/V), 12-MPA is completely retained on the column and 12-MSA has a capacity factor between 1.2 and .6. In solutions with acetonitrile concentrations of between 50 and 60% (V/V) 12-MSA is unretained and 12-MPA has a capacity factor between 2.2 and 1.6.

The detection limit is 5 X 10^{-7} M phosphate or silicate anion in 100 uL of injected sample. The linear dynamic range extends to 1.3 X 10^{-5} M for either anion. The relative standard deviation of the technique at the 5 X 10^{-6} M level is 2% for both silicate and phosphate. The analysis of phosphate in silicate rock is described.

INTRODUCTION

The quantitative analysis of phosphorus by spectrophotometric means is generally carried out by the method of Fisk and SubbaRow (1) or a derivative procedure thereof in which 12-molybdophosphoric acid (12-MPA) is formed in acidic molybdate solution and analyzed by spectrophotometry either in its initial or reduced state. These methods are simple, sensitive and require little expensive apparatus for their successful implementation. A major failing of this method is, however, the similar physical and chemical properties of the molybdoheteropolyacids of phosphate, arsenate, silicate and germanate which makes the analysis of one of these elements in the presence of others prone to positive interference.

The most common problem encountered is the analysis of phosphate in the presence of silicate. In matrices with moderate ratios of silicate to phosphate such as most fresh water samples this problem may be overcome by employing the formation of decamolybdodivanadophosphoric acid (DMVPA) (2,3) whose silicate analog is not formed under the analytical conditions specified. This method yields unacceptably high values (4) in samples containing large silicate concentrations due presumably to the competitive formation of silicate heteropolyacid at higher silicate concentrations whose absorbance is coincidental with the absorbance of DMVPA.

A second and more cumbersome approach to this problem is to either separate the silicate from the phosphate in the original

sample by solidifying the silicate under high temperature or to separate the 12-MPA from the 12-molybdosilicic acid (12-MSA) by schemes such as were proposed by Wadelin (5) and others (6,7) with subsequent analysis by spectrophotometry, atomic absorbance or x-ray fluorescence. Separations by ion chromatography are also possible for analyses of this type but must be preceded by sodium carbonate fusion in geological samples in order to remove transition metals which can poison the separator column (8).

This paper describes a novel solution to the above problem by utilizing a polystyrene-divinylbenzene column to separate a molybdophosphoric acid species from molybdosilicic acid and other possible interferences. The sample to be analyzed is digested by standard methods and mixed with mobile phase which is an aqueous solution 0.1 F $HClO_4$, 1.2 X 10^{-2} F in sodium molybdate and 55% acetonitrile. This mixture is then injected into a liquid chromatograph of standard design. The peak with retention time of 225 seconds is detected by spectrophotometry and calibrated with a standard calibration curve. Solvent composition effect on chromatographic retention times of molybdophosphoric acid and molybdosilicic acid is studied in order to ascertain the effect of varying acetonitrile, perchloric acid concentration and molybdate concentration. System response is studied as a function of perchloric acid and molybdate concentration. Linear range and limits of detection are determined. Actual analyses are performed on rock standards supplied by the USGS and the International Working Group of Geostandards. Effects of interferences are also investigated.

Orthophosphate can be analyzed by the technique at the maximum rate of 12 samples per hour with a detection limit of 16.2 ppm P in the original mineral sample. A standard isocratic HPLC equipped with a spectrophotometric detector is the only specialized equipment necessary.

MATERIALS AND METHODS

Reagents

All solutions were prepared from high purity (greater than 99.7%) reagent grade chemicals. Deionized water used for all solution preparation was prepared with a HYDRO Model 1000 Reagent Water System (Hydro Service & Supplies, Inc., 3200 Sandy Creek Drive, Durham, N.C. 27705). All organic solvents used were HPLC grade. Glassware used in solution preparation was cleaned with a 50% (v/v) solution of HCl followed by multiple rinsings with deionized water and was isolated from other laboratory glassware to prevent contamination from laboratory detergents.

HPLC System

The HPLC used for this work was constructed in our laboratory using a Milton Roy Minipump Type NSI-33R HPLC Pump, a Rheodyne Model 7010 injection valve equipped with a 200 uL stainless steel injection loop, a stainless steel gauge adapter and pressure

gauge supplied by Rainin Instrument Co., Li-Chroma-damp II Pulse Damper (Handy and Harman Tube Co., Norristown, Pa.). All tubing is made of stainless steel with a .020 in. i.d. The detector is a Model LC-6 fixed wave length detector fitted with a 440 nm filter purchased from Bioanalytical Systems, W. Laffayette, Ind. The column is a Hamilton PRP-1 4.1 mm X 15 cm Analytical Column filled with 10 um packing. Peak heights were measured on a Fisher Recordall Series 5000 Strip Chart Recorder.

Mobile Phase Studies

A) Acetonitrile Concentration vs. Capacity Factor. Mobile phases 0.10 F in $HClO_4$, 5.85 X 10^{-3} F in $NaMoO_4$ and 25, 30, 35, 50, 55, 60, 65, and 70% acetonitrile were prepared. B) Sodium molybdate concentration vs. Capacity Factor. Mobile phases 0.10 F in $HClO_4$, 58% acetonitrile (for phosphate study) and 30% acetonitrile (for silicate study) and 0.01 0.05, 0.10 0.15 0.20 F in sodium molybdate were prepared. C) Perchloric acid concentration vs Capacity Factor. Mobile phases 1.2 X 10^{-2} in sodium molybdate, 58% acetonitrile (for phosphate study) and 30% acetonitrile (for silicate study) and 0.02, 0.03, 0.05, 0.08, 0.10 in $HClO_4$ were prepared. One additional concentration for the silicate study was included which was 0.04 F in $HClO_4$. D) Ionic strength vs Capacity Factor. An initial mobile phase was produced which was 5.85 X 10^{-3} F in sodium molybdate, 0.10 F in $HCLO_4$ and 55% or 28% v/v in acetonitrile. The ionic strength of this solution was 0.118.

Capacity factors for injections of phosphate or silicate standard diluted with mobile phase were recorded. The ionic strength of the measured volumes of mobile phase was then increased by additions of known quantities of solid sodium perchlorate to produce solutions with ionic strengths of 0.158, 0.258, 0.358, 0.458. In all of the above studies samples for injection were prepared by diluting 1.00 mL of 1 X 10^{-3} M silicate or phosphate stock solution with enough mobile phase to yield a final volume of 10.00 mL. Each point is the average of three injections.

A flow rate of 1 mL/min was used throughout this study which resulted in pressures less than 800 psi. It was not necessary to degas the mobile phase at this flow rate and pressure.

Sample Preparation

All samples must be treated in such a manner that when they are diluted 10:1 with mobile phase their final phosphorus concentrations are between 5.23 X 10^{-6} M (ten times the detection limit) and 1.3 X 10^{-5} M. All samples must be aged at least four hours after preparation.

Rock Analysis.

0.500 g samples of finely ground rock were placed in 100 mL teflon beakers to which 45 mL of 50% HF and 15 mL of 16 M HNO_3 were then added. The samples were swirled in order to wet the

samples, covered, and placed in a 95 degree C hot water bath for 24 hours. The covers were removed and the samples evaporated to dryness. They should not be baked after this point. 1.0 mL of 16 M HNO_3 is added to the sample and swirled to thoroughly wet the residue and 50 mL of deionized water is added. 3.75 mL of 16 M HNO_3 and 6.25 mL of 12 M HCL are added and the solution is brought to a boil and evaporated to a volume between 25-40 mL. After cooling, the solution is diluted volumetrically to 50 mL and again 1:10 (9). One mL of this solution is diluted to a final volume of 10.00 mL with mobile phase and 100 uL is injected into the HPLC system.

The mobile phase for this analysis was 58% acetonitrile(V/V), 42% water 1.2 X 10^{-2} M in sodium molybdate and 0.1 F in $HClO_4$. The flow rate was 1.0 mL/min.

Pre-analyzed rock samples for analysis were obtained from the United States Geological Service (10) and The International Working Group of Geostandards (11,12).

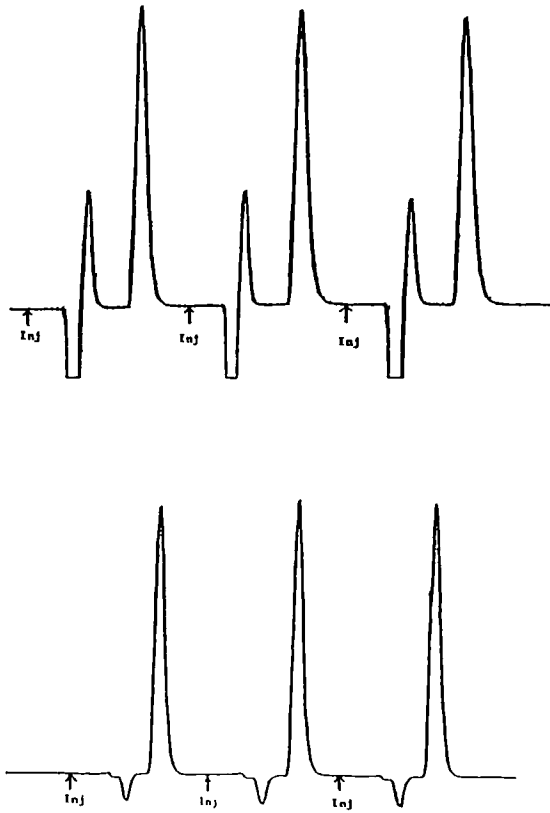
RESULTS AND DISCUSSION

Ohnishi and Mayer (13) first separated a phosphomolybdate species by affinity chromatography using a polyvinylpolypyrrolidone packed column. Unfortunately they made no attempt to study the chromatographic characteristics of their system. Braungart and Russel (14) also separated the heteropolyamine associates of Si, As, Ge, and P on a Nucleosil CN reverse phase column after solvent extraction with dichloromethane. Our system makes use of a commercially available HPLC column whose stationary phase is XAD-2

resin which has been ground to a uniform particle size of 10 microns. XAD-2 is a polystyrene-divinylbenzene polymer which can withstand the high ionic strengths (0.5N) and acidities (pH 1 to 13) required to make heteropolyacids. The high concentrations of molybdate anion and perchloric acid in the mobile phase prevent the dissociation on the column of the heteropolyacid.

Figures 1a and 1b are chromatograms obtained by injecting acidified solutions containing either phosphate ion and molybdate ion (Figure 1a) or silicate ion and molybdate ion (Figure 1b) on a PRP-1 column. In both cases a negative peak appears at the solvent front which is not reproducibly affected by solvent conditions. The last peak in both chromatograms is of analytical importance. In Figure 1a the height of this peak has a linear relationship to phosphate ion concentration in the injected sample measured at 440 nm by a UV-visible detector operated in the absorbance mode. In Figure 1b the last peak has a linear relationship to silicate ion concentration in the injected sample measured identically to the second peak in Figure 1a. Due to the above linear relationships and solvent conditions under which these compounds are known to form (15), we have tentatively identified these compounds as 12-molybdophosphoric (12-MPA) and 12-molybdosilicic (12-MPA) acids or their anions.

In Figure 1a the second positive peak appearing almost coincidentally with the solvent front is 12-MSA impurity which is poorly retained under solution conditions optimal for 12-MPA retention. This peak can be eliminated by careful choice of reagents and particularly containers.



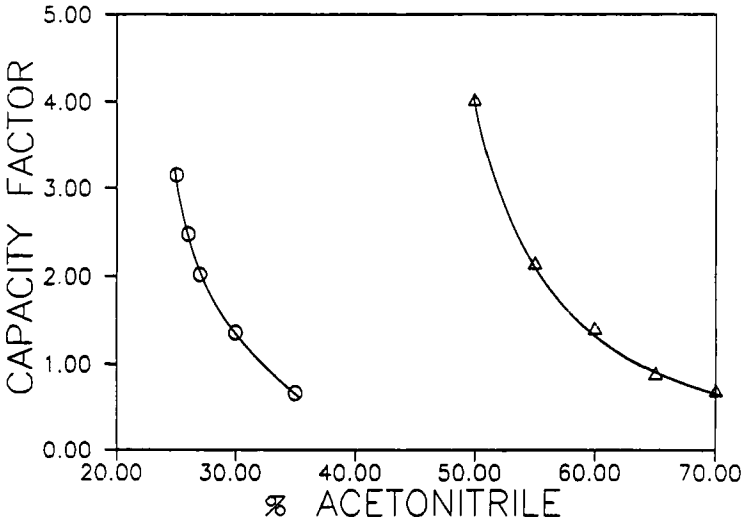
1. a) Molybdophosphoric acid (12-MPA) chromatogram: $1x10^{-4}$ F in orthophosphate, $5.04x10^{-2}$ F in sodium molybdate, 0.1 F in perchloric acid, and 58% (v/v) acetonitrile. Three replicates.

   b) Molybdosilicic acid (12-MSA) chromatogram: $1x10^{-4}$ F in silicate, $1.2x10^{-2}$ F in sodium molybdate, 0.08 F in perchloric acid, and 30% (v/v) acetonitrile. Three replicates.

Capacity Factor and Response Studies

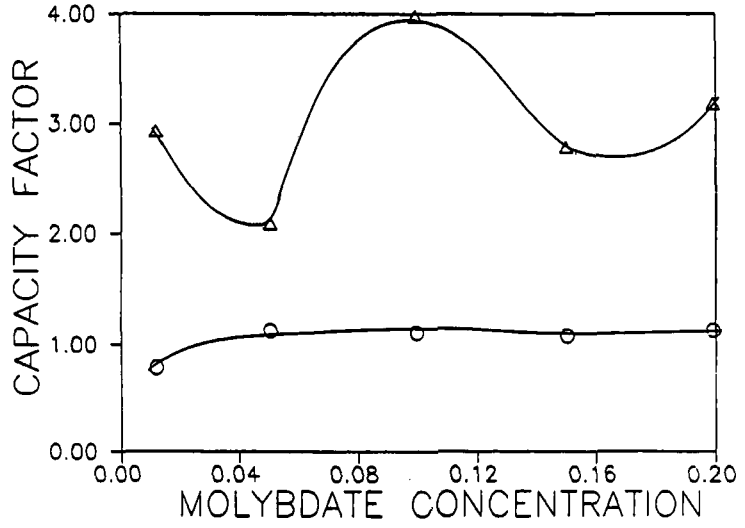
The effects of varying the concentration of sodium molybdate, perchloric acid and acetonitrile on the capacity factor of 12-MPA and 12-MSA was studied by varying the concentration of each under conditions of constant concentration of the others. Reagent concentration ranges were limited to values which would not exceed the column manufacturer's recommendations for pH or ionic strength limits. The initial concentrations of molybdate and perchloric acid for this series of experiments were chosen arbitrarily from concentrations found to give satisfactory initial results.

Figure 2 is a plot of capacity factor vs. % acetonitrile for injections of 12-MPA and 12-MSA. It is evident from this plot that the capacity factors of both are highly dependent upon the acetonitrile concentration and that their separation can be affected by the proper choice of acetonitrile concentration. This behavior is analogous to the retention behavior of organic compounds in classical reverse phase separations. In solutions with acetonitrile concentrations between 30 and 35%, 12-MPA is completely retained on the column allowing the unambiguous analysis of 12-MPA. At acetonitrile concentrations greater than 50%, 12-MSA species are essentially unretained allowing the unambiguous analysis of 12-MPA. A concentration of 58% (v/v) acetonitrile was chosen for other experiments involving phosphate analysis parameter maximization and 30% (v/v) acetonitrile for those same experiments involving silicate analysis.

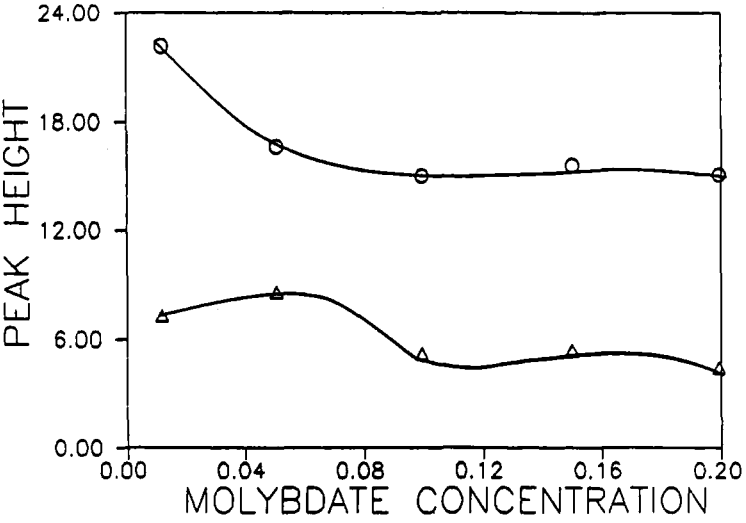


2. Plot of capacity factor vs. % acetonitrile concentration for 12-MPA ( ) and 12-MSA ( ). Acetonitrile concentration varied between 25% and 70% (v/v). Solutions for 12-MPA are $1x10^{-4}$ F in orthophosphate, $1.95x10^{-3}$ F in sodium molybdate, and 0.1 F in $HClO_4$. Solutions for 12-MSA are $1x10^{-4}$ F in silicate, $5.85x10^{-3}$ F in sodium molybdate, and 0.1 F in $HClO_4$.

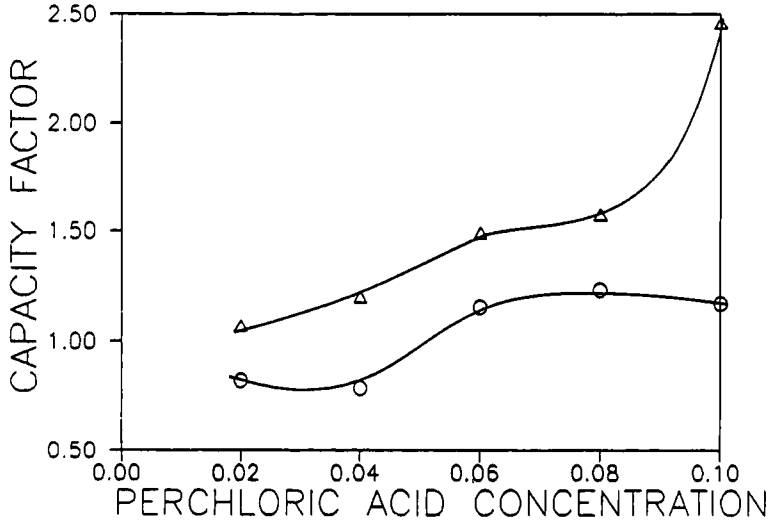
The effect of varying mobile phase molybdate concentration on the capacity factor and peak height of 12-MPA and 12-MSA may be seen in Figures 3 and 4. Concentrations of molybdate below 1.2 X 10^{-2} M result in serious peak broadening and lack of first order dependence on phosphate or silicate concentrations whose concentrations are above the 1.3 X 10^{-5} M level. This minimum ratio of 24:1 excess of molybdate over the analyte anion present may be maintained for analysis of higher concentrations of analyte ion by increasing molybdate ion concentration in the mobile phase. At lower concentrations of molybdate an additional problem is encoun-



3. Plot of capacity factor vs. molybdate concentration for 12-MPA ( ) and 12-MSA ( ). Sodium molybdate concentration varied between 1.2×10^{-2} to 0.2 F. Solutions for 12-MPA are 1×10^{-4} F in orthophosphate, 58% (v/v) acetonitrile, and 0.1 F in $HClO_4$. Solutions for 12-MSA are 1×10^{-4} F in silicate, 30% (v/v) acetonitrile, and 0.1 F in $HClO_4$.



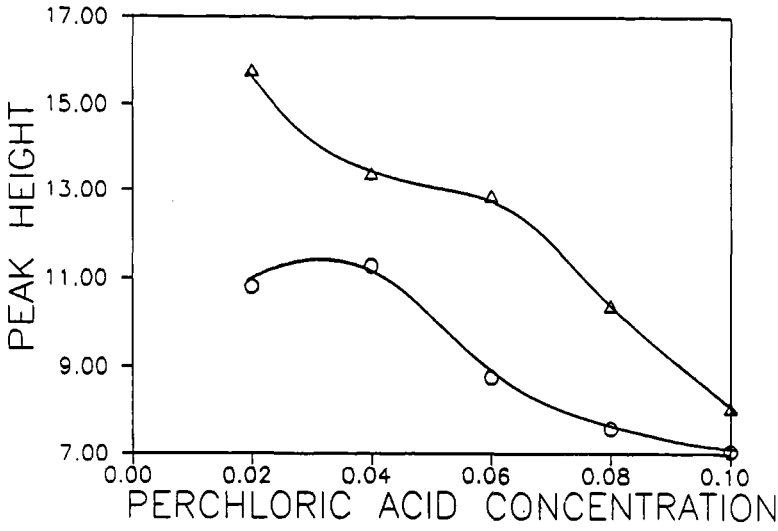
4. Plot of peak height vs. molybdate concentration for 12-MPA ( ) and 12-MSA ( ). Sodium molybdate concentration varied between 1.2×10^{-2} to 0.2 F. Solutions for 12-MPA are 1×10^{-4} F in orthophosphate, 58% (v/v) acetonitrile, and 0.1 F in $HClO_4$. Solutions for 12-MSA are 1×10^{-4} F in silicate, 30% (v/v) acetonitrile, and 0.1 F in $HClO_4$.



5. Plot of capacity factor vs. perchloric acid concentration for 12-MPA ( ) and 12-MSA ( ). Perchloric acid concentration varied between 0.02 to 0.10 F. Solutions for 12-MPA are $1x10^{-4}$ F in orthophosphate, $1.2x10^{-2}$ F in sodium molybdate, and 58% (v/v) acetonitrile. Solutions for 12-MSA are $1x10^{-4}$ F in silicate, $1.2x10^{-2}$ F in sodium molybdate, and 30% (v/v) acetonitrile.

tered with silicate samples due to the extremely slow formation of the silicate heteropolyacid. Since only small improvements in capacity factor and peak height can be obtained by varying molybdate concentration past the amount necessary to achieve first order dependency on phosphate concentration, a molybdate concentration of 1.2 X 10^{-2}M was chosen for further work. The molybdate concentration should be kept to as small a value as is possible to lessen incidences of clogging the small orifices and filters of the HPLC system.

Figures 5 and 6 are plots of peak height and capacity factor vs. perchloric acid concentration for 12-MPA and 12-MSA.



6. Plot of peak height vs. perchloric acid concentration for 12-MPA ( ) and 12-MSA ( ). Perchloric acid concentration varied between 0.02 to 0.10 F. Solutions for 12-MPA are $1x10^{-4}$ F in orthophosphate, $1.2x10^{-2}$ F in sodium molybdate, and 58% (v/v) acetonitrile. Solutions for 12-MSA are $1x10^{-4}$ F in silicate, $1.2x10^{-2}$ F in sodium molybdate, and 30% (v/v) acetonitrile.

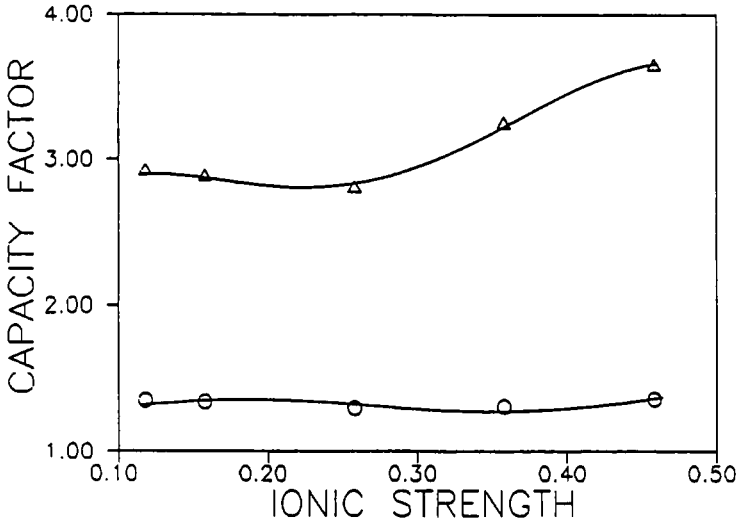
Use of concentrations less than 0.04 F in $HClO_4$ were not practical for normal analysis since at these acid concentrations the solution has low buffer capacity and maintaining constant hydrogen ion concentrations is difficult. The effect of acid concentration on capacity factor is quite pronounced. Peak widths at half height for both compounds are approximately constant from 0.10 F to 0.03 F. At lower concentrations this parameter increases rapidly indicating not only that the peak height is increasing due to chromatographic effects but also due to an actual increase in absorbing species. Any $HClO_4$ concentration from 0.04 F to the

limits of the column (0.1 F) is usable for analysis since, in this concentration range, solution hydrogen ion concentration may be maintained constant. An $HClO_4$ concentration of 0.10 F was chosen for further work in this paper. More sensitivity may be gained by choosing concentrations of about 0.05 F. The capacity factor may then be increased by slightly lowering the acetonitrile concentration.

Ionic Strength Studies

The effects of changes in mobile phase ionic strength upon retention of the analytical peak are illustrated in Figure 7 for molybdophosphoric and 12-molybdosilicic acids. The plot of 12-molybdophosphoric acid capacity factor vs. mobile phase ionic strength is similar to the curve predicted by the "solvophobic theory" of Horvath and coworkers (16) as applied to organic ion retention on octadecylsilica bonded columns. The minimum found for our data at I = 0.26 is quite close to the minimum of I = 0.3 predicted by Horvath's theoretical treatment for monovalent ions.

The less pronounced minimum of the analogous 12-molybdosilicic acid plot in Figure 7 along with its substantially different retention behavior as a function of acetonitrile concentration is suggestive of a different retention mechanism than that of 12-molybdophosphoric acid. This is an unexpected finding since both 12-MPA and 12-MSA are thought to be composed of a central XO_4 tetrahedron surrounded by twelve MO_6 octahedra arranged in four



7. Plot of peak height vs. ionic strength for 12-MPA ( ) and 12-MSA ( ). Ionic strength varied between 0.12 to 0.46. Solutions for 12-MPA are $1x10^{-4}$ F in orthophosphate, $5.85x10^{-3}$ F in sodium molybdate, 0.1 F in $HClO_4$, and 55% (v/v) acetonitrile. Solutions for 12-MSA are $1x10^{-4}$ F in silicate, $5.85x10^{-3}$ F in sodium molybdate, 0.1 F in $HClO_4$, and 30% (v/v) acetonitrile.

groups of three edged-shared octahedra, M_3O_{13} (Keggin structures)(17) . It would seem unlikely that compounds with the same structure which are so monopolized by MO_6 octahedra would exhibit such different retention behavior based solely on the physical or chemical characteristics of their central octahedron. Since the 12-MSA ion is readily eluted by a more aqueous mobile phase than 12-MPA it may be reasonable to believe that at perchloric acid concentrations of 0.1 F and below the tetraprotic12-MSA is more ionized than the triprotic 12-MPA. This however does not explain the small effect of ionic strength on capacity factor which is exhibited by 12-MSA.

Interference Studies

A number of inorganic species such arsenate and germinate, which form heteropolyacids with molybdate are possible interferences with this method. The retained heteropolyacid made from arsenate ion and molybdate ion was found to behave identically to the 12-MPA discussed above. Since all attempts to separate the two have been futile to this date, arsenate must be identified as a serious interference in this method. Similarly germanate and silicate anion behave almost identically in chromatographic systems we have studied causing them to also be serious mutual interferences. Efforts to separate the above mentioned pairs continues in our laboratory.

Since Cu^{+2}, Fe^{+3} and Al^{+3} are quite likely found in geological sample the effect of their presence on the above analysis was tested by preparing solutions with ratios of interference to orthophosphate between 0.1 and 100. These solutions were injected into the HPLC system and the signals compared with the signal produced by a standard phosphate solution. The percent enhancement or attenuation achieved for each species at the various ratios appears in Table 1, as well as the standard deviation computed for each value by standard error propagation techniques.

Even though all signals appear to be attenuated in this table the lack of an upward or downward trend with increasing ratios of a particular interference as well as the sizes of the standard deviations infers that the apparent attenuation is coincidental.

TABLE 1

% Signal Enhancement (+) or Attenuation (-) from Interfering Ions in the HPLC Analysis of Phosphate as 12-MPA in 1.20×10^{-2} M Molybdate, 0.1 F $HClO_4$, and 55% (v/v) Acetonitrile.

Ratio of interfering species concentration to PO_4^{-3} concentration:	% signal enhancement or attenuation			
Interfering Species	0.1	1.0	10	100
Silicate	-0.83 ±0.78	-3.31 ±2.60	-0.28 ±0.92	-2.48 ±2.32
Cu(II)	-0.42 ±0.98	-1.38 ±1.23	-0.28 ±1.23	-0.55 ±0.92
Aluminum	-1.38 ±0.92	-1.93 ±1.23	-0.83 ±0.78	-0.83 ±0.78
Fe(III)	-1.38 ±1.23	-0.83 ±0.78	-0.83 ±1.83	———

Iron (III) ratios greater than 10:1 (6.45×10^{-5} M iron (III)) caused the precipitation of an iron molybdate compound. Samples containing large amounts of iron must be pretreated to remove iron before analysis by this method.

Calibration Curves.

Plots of peak height as a function of orthophosphate and orthosilicate concentration were found to be linear up to a concentration of 1.3×10^{-5} M in the injected sample at the molybdate

concentration of 1.2×10^{-2} previously discussed. At higher concentrations of analyte the curve deviates negatively from linearity since the ratio of molybdate to phosphate is too low at this point to force more complete formation of the required heteropoly species. It is possible to extend the linear dynamic range by increasing molybdate concentration, but this will result in the more frequent clogging of the HPLC system.

Linear regression analysis of calibration curves produced correlation coefficients typically of 0.999 for both orthophosphate and silicate. Predicted intercepts of the response axis were less than one standard deviation from zero. The detection limit of 5×10^{-7} M in a 100 uL injection was calculated by a method reviewed by Miller and Miller (18) which estimates the standard deviation of the blank and the actual value of the blank from statistical values calculated from the calibration curve. The limit of detection is defined as the concentration corresponding to:

$$y_B + 3s_B$$

where y_B is the best fit absorbance value of the blank calculated by regression analysis and s_B is the calculated standard deviation of the absorbance of the blank.

Replicate responses at the 5×10^{-6} M level (10 times the detection limit) can be made with a relative standard deviation of 2% for both silicate and phosphate.

Rock Analysis.

In order to test for any systematic difference between phosphate concentrations derived by the chromatographic method and accepted values given for standard rocks, 6 standard rock samples were analyzed and these values compared to values supplied by the United States Geological Service or the International Working Group on Geostandards. The amount of silicate in these samples ranged from 59.25% to 69.90%. The results of this comparison appear in Table 2. The average of these differences was found to lie outside of the 95% confidence interval estimate of the average difference in results between the two methods and so a small negative systematic error must be excepted with that amount of confidence. A systematic error cannot be accepted with 99% confidence. The average relative error of all the above results is 4%.

CONCLUSION

The ability to analyze for orthophosphate by HPLC on a commercially available reverse phase column was assessed. This assessment indicates that phosphate may be accurately and precisely analyzed in the presence of a large amount of silicate and other interferences. The simplicity and economy of this method should make it highly desirable for use in a large number of laboratories. The feasibility of silicate analysis is also supported by the data in this paper. The separation of completely

TABLE 2

Comparison of HPLC and USGA Methods of Phosphate Analysis In Rock Samples.

Sample	% P_2O_5 HPLC analysis (Xa)	USGA analysis (Xb)	Xa-Xb
GA-GRANITE	0.12	0.12	0.00
GS-N GRANITE	0.27	0.28	-0.01
AGV-1	0.47	0.48	-0.01
STM-1	0.15	0.16	-0.01
G-2	0.13	0.14	-0.01
QUARTZ LATITE	0.23	0.26	-0.03

$X = -0.012 \pm 0.016$ for a 99% Confidence Level.

inorganic species has been achieved by reverse phase liquid chromatography without resorting to association with organic species.

The negative aspects of this method center around the problem of iron (III) and arsenate interferences which is discussed above. The additional problem of a possible negative bias and its causes will be a topic of continuing research in this laboratory. Additional work is now being performed in our laboratory on the use of other separable heteropolyacids for oxyanion analysis.

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