



FLOW INJECTION REAGENT INTRODUCTION BY SUPPORTED LIQUID AND NAFION MEMBRANES: DETERMINATION OF PHOSPHATE

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Summary.—The use of membrane tubing for the introduction of reagents for the determination of phosphate in waters by flow injection analysis was studied. The use of membranes eliminates the need for confluence points in the design of flow injection manifolds. This increases the sensitivity of the manifold by providing a sufficient reagent excess for the reaction without diluting the sample. Methods for the introduction of acid, molybdate and hydrazine were devised for the determination of phosphate by the Molybdenum Blue method. Several membranes were examined and Nafion and Accurel (microporous polypropylene) were found to be most useful. Molybdate introduction was achieved using a supported liquid membrane (SLM). Calibration was linear and a detection limit of 12 ppb phosphate (4 ppb phosphorus) was obtained.

Flow injection analysis (FIA) is now well established as an automated method for common colorimetric determinations. The enclosed environment of a flow injection (FI) manifold allows reagent addition in a more reproducible and less time consuming manner. However, the necessity to add reagents inherently decreases the possible sensitivity of the manifold because of the dilution that occurs at the confluence point(s).

In a previous paper¹ it has been shown that each type of manifold configuration, single, double (mult) and reverse single line, has the same sensitivity when optimized. One of the results of this investigation showed that the optimal procedure for introduction of a reagent is to use the most concentrated solution of reagent possible. This provides the reagent excess necessary for the reaction yet minimizes the dispersion (or confluence point dilution) thus increasing sensitivity. Extrapolation of this finding indicates that reagent introduction without dilution (RIWD) should provide the best sensitivity. In this paper we approach the idea of RIWD by using membranes to deliver reagents.

Polymeric membranes have been used widely in FI for the separation of gas/liquid streams²⁻⁴

and permeation of gases analytes between liquid streams.⁵⁻⁸ They have also been used extensively to modify electrodes for better selectivity/specificity.⁹⁻¹³ Nafion cation exchange tubing has also been used in a method for the preconcentration of lead in sea-water.¹⁴

The FIA literature also contains examples of reagent introduction using membranes. Nieman and co-workers used Nylon 66 and Celgard 5511 to introduce glucose oxidase as a reagent for enzyme catalyzed determinations of sucrose and glucose, respectively.^{15,16} Porous PTFE has been used by Dasgupta *et al.*¹⁷ to introduce 4-(2-pyridylazo) resorcinol (PAR) in the determination of copper. However, in these papers the reagent was introduced by forcing a small bulk liquid flow ($\mu\text{l}/\text{min}$) through the membrane. Although this causes minimal dilution the procedure is similar to the use of a confluence point for reagent addition. True reagent introduction without dilution has been implemented in FI. Hwang and Dasgupta have used Nafion tubing for the pH control of FI streams by the introduction of ammonium ion from an ammonium hydroxide donor.^{18,19} Bruckenstein and Trojanek used a silicone rubber membrane for the introduction of bromine gas in the indirect determination of phenols.²⁰ In a different, but equivalent, manner reagent introduction using polymers has also

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Flow rates were measured by timing the effluent into a 10 ml volumetric flask. Membrane reactor flow rate integrity (estimation of any bulk flow through the membrane) was tested by weighing the acceptor/donor before and after pumping for a measured period of time. The weights were corrected for density changes and compared. In all cases when the membrane reactors were used the flow rates in and out were found to be equal within experimental error.

Membrane reactors were constructed as re-exchange tubing was used throughout.

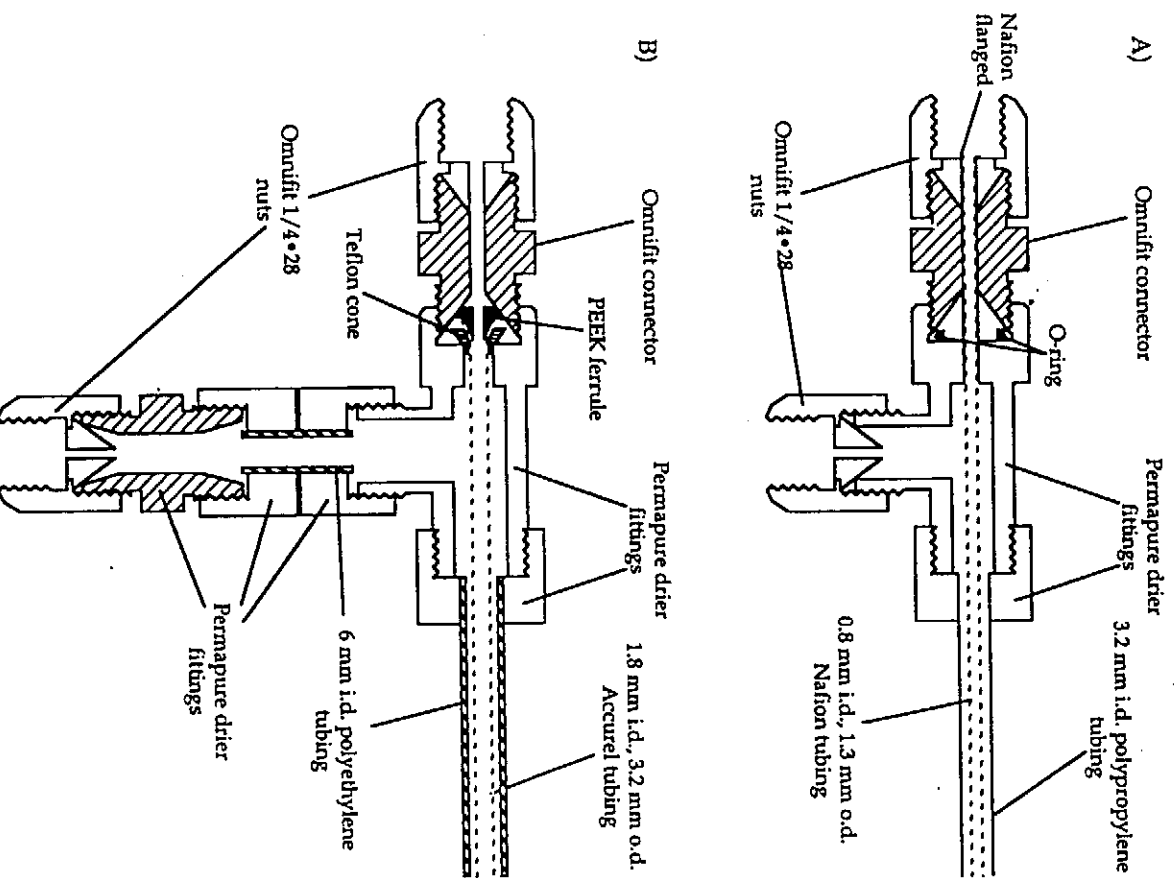


Fig. 2. Tubing connections for Nafion and Accurel membrane reactors. (A) A PermaPure Nafion membrane drier was modified to allow use of liquids as both the acceptor and donor. The Nafion tubing expands when wet and forms a tight seal against the Omnifit connector. (B) PermaPure drier fittings were used to produce an Accurel reactor. The Accurel tubing was crimped between a cone and a ferrule to provide a water tight seal when the fitting was tightened down.

indicates that the kinetics of the donor/ membrane equilibrium are slow compared to the release of protons into the acceptor stream. Increasing the ionic strength of the acceptor stream increased the acidity of the acceptor stream for the same donor stream only when the ionic strength of the acceptor was high enough for substantial ion exchange. However, even with water as the acceptor the acceptor stream acidity increased. This, and the difference that the type of acid had on the acidity resultant in the acceptor indicates that a Donnan breakdown process allows HCl to pass through the membrane.¹⁶ This was verified by the detection of chloride in the acceptor stream.

Concentrated hydrochloric acid was also tried as a donor solution; however, this caused bulk flow through the membrane from acceptor to donor, presumably as a result of osmosis.

Introduction of molybdate

Molybdate chemistry in aqueous solution is complex and not fully understood.³⁷⁻³⁹ An aqueous solution of ammonium heptamolybdate has a pH close to 6 and consists of mainly the heptamolybdate ion. Use of an anion exchange membrane was unsuccessful for the introduction of molybdate probably due to the size of the heptamolybdate ion. Basification of an ammonium heptamolybdate solution (pH 10) produces molybdate (MoO_4^{2-}) as the major species. A small concentration of molybdenum was produced in the acceptor stream, with this solution and the anion exchange tubing, but it was not high enough for practical use. The transport of hydroxide across the membrane also made this setup unfavorable.

If an aqueous molybdate solution is acidified (below pH 2) then precipitation and redissolution of MoO_3 occurs. The molybdenyl ion, MoO_2^{2+} , now becomes the dominant species in solution. A Nafion membrane reactor was tried with a 0.01M ammonium heptamolybdate solution of 6M HCl. A small concentration of molybdenum was seen in the acceptor stream but not enough to be useful.

Attention turned to the use of a supported liquid membrane as a method of introducing molybdate into the acceptor stream. A common method for separation of molybdenum (VI) from other metals is extraction with an organic amine or oxygenate.⁴⁰⁻⁴⁵ Of the extractants investigated tri-*n*-butyl phosphate (TBP) has the highest extraction efficiency.^{46,47} The distribution ratio a 6M HCl solution of molybdate

(molybdenyl) and TBP is 316⁴⁶ in favor of the organic phase. As the aqueous phase acidity decreases the extraction into TBP is much less favored due to the lower concentration of molybdenyl which is extracted as $[\text{MoO}_2^{2+} \cdot 2\text{Cl}^-]$ into TBP.

A silastic grade silicone membrane with a mixture of TBP and methyl isobutyl ketone (another good molybdenyl extractant) in the membrane was found to swell to almost double its size. However, transport of molybdenyl using this arrangement was slow, and did not produce a high enough acceptor stream concentration.

Three different configurations (Fig. 3) of a microporous polypropylene supported SLM were examined and the results are detailed in Table 2. First the membrane was used as a stabilizer for an organic/aqueous interface between a 50% TBP/MIBK extract of ammonium molybdate/6M HCl and a 0.3M HCl acceptor. Increasing the concentration of molybdenum in the donor stream increases the acceptor concentration produced. Changing the flow rate of the acceptor also has an appropriate effect on the concentration and it is interesting to note the slow kinetics of the re-extraction indicated by the decrease in the extraction rate with increasing acceptor flow rate. This configuration was the least stable of the three studied.

An SLM of TBP between two aqueous phases produced higher concentrations of molybdenum in the acceptor stream. It was also more stable than the organic/aqueous interface and showed the same kinetic limitations of re-extraction.

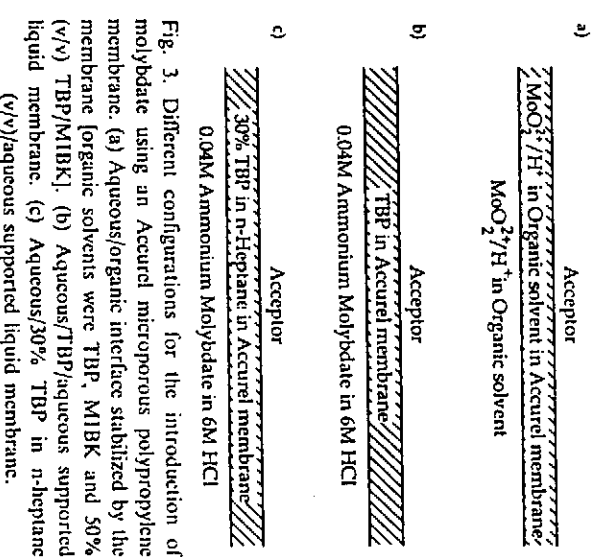


Fig. 3. Different configurations for the introduction of molybdate using an Accurel microporous polypropylene membrane. (a) Aqueous/organic interface stabilized by the membrane [organic solvents were TBP, MIBK and 50% (v/v) TBP/MIBK]. (b) Aqueous/TBP/aqueous supported liquid membrane. (c) Aqueous/30% TBP in n-heptane (v/v)/aqueous supported liquid membrane.

Table 3. Hydrazine acceptor concentrations using a 40 cm Nafion cation exchange membrane reactor

Donor stream				Acceptor stream		
Hydrazine concentration (ppm)	Acid (HCl) concentration (M)	Flow rate (ml/min)	Composition	Flow rate (ml/min)	Hydrazine concentration produced (ppm) [permeation rate (µg/min)]	
50	0.01	0.58	Epure water 0.0001M HCl	0.47	0 0.01 (0.0047)	
			0.001M HCl		2.12 (1.00)	
			0.01M HCl		28.8 (13.5)	
			0.1M HCl		37.7 (17.7)	
			0.1M HCl	0.47	35.7 (16.8)	
	0.0001	0.58	0.1M HCl		35.9 (16.9)	
	0.0001				35.6 (16.7)	
100			0.1M HCl	0.47	53.6 (25.2)	
200					112.0 (52.6)	
300					169.0 (79.4)	
50		0.58	0.1M HCl	0.47	35.6 (16.7)	
					26 (28.6)	
					2.2 (44.0)	
					3.3 (46.2)	
					4.4 (44.0)	
					5.5 (41.3)	
					6.6 (39.6)	

380 nm. Comparing the sensitivities of the calibrations obtained it seems likely that the product is a molybdophosphate-TBP adduct as the sensitivity decreased with decreasing availability of TBP (interface > TBP > TBP/heptane).

Following the encouraging calibration results, water samples were analyzed and compared with those of an EPA colorimetric method (365.2) for phosphate. The EPA results were 10 times less than the results obtained from the SLM system indicating that this method is not specific to phosphate.

Determination of phosphate by the Heteropoly Blue reaction

It was important to find out if TBP had an effect on this reaction and it was not found to interfere below the 0.02% (v/v) level. However, a shift in the absorption maximum was observed (to 818 nm) when compared with previous results.²³

The final manifold that was used for this determination is shown in Fig. 4. As can be seen complete reagent introduction without dilution

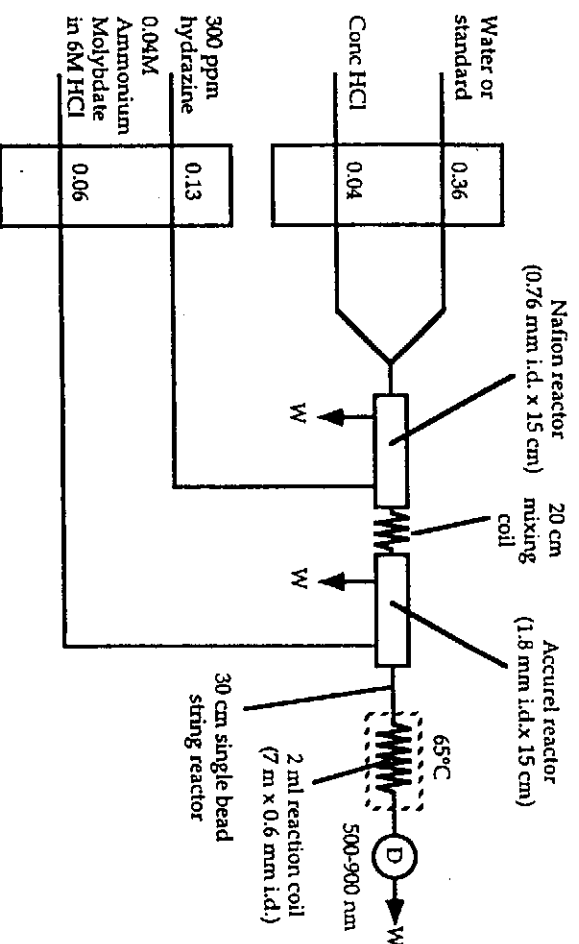


Fig. 4. Final manifold configuration for the determination of phosphate using reagent introduction without dilution of molybdate and hydrazine. Numbers above the flow lines represent flow rates in ml/min. A silicone oil bath was used as the heater. W is waste.

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