

GRAFT COPOLYMERS AS SUBSTRATES IN COLUMN EXTRACTIONS

I. NON-CHROMATOGRAPHIC SEPARATIONS ON EXTRACTION COLUMNS*

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INTRODUCTION

Extraction chromatography, also referred to as reversed-phase partition chromatography, is a technique of broad application in analytical chemistry, particularly in the separation and purification of various elements in radiochemical analysis. Numerous papers describing various extraction systems which utilize a wide variety of column supports are listed in the bibliography by HEDRICK AND FRITZ¹. Recent papers in the literature favor the use of fluorocarbon polymers as column supports for inorganic applications²⁻⁶.

An initial attempt to adapt some of the liquid-liquid extractions routinely performed in radiochemical analysis at this laboratory to extraction columns using various standard column supports was unsatisfactory. The column supports that had high enough capacity for organic complexing agents to be of potential value in macro separations also required pressurization to attain practical flow rates. The primary purpose of converting the liquid-liquid extraction to a column operation was to simplify the handling of large numbers of radioactive samples, especially when working in a glove box. Under these conditions, restrictions due to space limitations and the reduced ability to manipulate apparatus make multiple extraction operations tedious and time-consuming. In addition, the probability of cross-contamination or loss of sample by spillage is enhanced. However, replacing the liquid-liquid extraction with a pressurized column does little to simplify the operation or reduce the time and attention required on the part of the operator. Complex liquid and gas flow systems are frequently needed, with attendant problems of maintenance, decontamination, etc. Pressurized columns require close attention on the part of the operator, particularly when different kinds of wash or eluting solutions must be added successively. Loss of liquid at the top of a column bed results in air blowing through the column, which destroys the column operation and requires abandoning the sample or dismantling the column to recover it.

Consequently, a program was undertaken to develop a column material which would behave in operation as do the ion-exchange resins in small columns, *i.e.*, flow freely by gravity feed and not run dry if the liquid at the top of the column is depleted. In addition, the material must be able to adsorb and retain relatively high loadings of organic complexing agents or solutions thereof and still be water-wettable to facilitate:

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the flow of aqueous solutions, must be stable to various extremes of chemical environment, and must not undergo large changes in volume as solution conditions change.

Various grafts of vinyl monomers to hydrophilic polymers were examined as possible column supports, and a new type of graft copolymer was developed with improved properties for column applications. The characteristics of extraction columns made from these materials and the adaptation of two extraction systems to column operation are reported in this paper.

EXPERIMENTAL

Reagents and equipment

Di-(2-ethylhexyl) orthophosphoric acid (HDEHP), Union Carbide Chemicals Company, 99 %, was purified in the following manner: the acid was dissolved by treating with excess 0.5 M NaOH and centrifuged to remove $\text{Fe}(\text{OH})_3$. The sodium salt was extracted with ether and the acid regenerated by stirring with dilute HCl. The ether solution was treated with activated charcoal, filtered and the ether evaporated under vacuum. The resultant HDEHP was stirred several times with an equal volume of ethylene glycol to remove mono-ester and the phases separated by centrifuging. 1 % tributyl phosphate was added to retard hydrolysis of the di-ester.

4-*sec.*-Butyl-2-(α -methylbenzyl)phenol (BAMBP) was used as received from Frinton Laboratories, South Vineland, N. J.

N,N',N''-Tri-*n*-hexyl phosphorothioic triamide (thio-THPA) was used as received from Regis Chemical Company, Chicago, Ill.

Carbowax 600, 1540, 6000, and Polyethylene Glycol Compound 20M were obtained from the Union Carbide Chemicals Company and used as received.

Kel-F 6061 moulding powder was obtained from the Minnesota Mining and Manufacturing Company. It was milled in a laboratory-size Wiley Mill and screened into appropriate fractions with standard sieves.

All other chemicals and solvents were reagent grade and used without further purification. In particular, the inhibitor was not removed from the styrene or divinylbenzene before irradiation.

The glass columns were 6 mm I.D. \times 9 cm long with a reservoir 17 mm I.D. \times 11 cm long at the top and a drip tip plugged with glass wool at the bottom (Fig. 1).

Carrier solutions were made by dissolving the appropriate salts to obtain 10 mg/ml of metal ion and spiked with radionuclides (^{144}Ce , $^{152-154}\text{Eu}$, ^{137}Cs and $^{110\text{m}}\text{Ag}$) obtained from Oak Ridge National Laboratory.

Counting of radioactive solutions was done at fixed geometry in a scintillation counter with a one-inch NaI(Tl) crystal.

Preparation of graft copolymers

Cellulose-g-polystyrene, starch-g-polystyrene, poly(acrylic acid-g-styrene), poly(acrylic acid-g-methyl methacrylate) and poly(acrylamide-g-styrene) were obtained from Dr. A. J. RESTAINO, Atlas Chemical Industries, Inc. c/o Industrial Reactor Laboratories, Inc., Plainsboro, N. J. In some cases, these were screened through standard sieves before use and suitable fractions taken.

Poly(ethylene glycol-g-styrene) was prepared by dissolving 20 g of Carbowax 20M in a mixture of 45 ml styrene and 45 ml methanol, flushing with argon, and

irradiating with fission-product gammas at a rate of approximately 30,000 rads/h for a period of 15–20 h. The resultant material was dissolved in excess toluene and the product precipitated by slowly pouring the solution into rapidly stirred methanol. After filtering and washing with fresh methanol, the solids were dried at 60° to constant weight. Crosslinked material was prepared in a similar manner by adding given

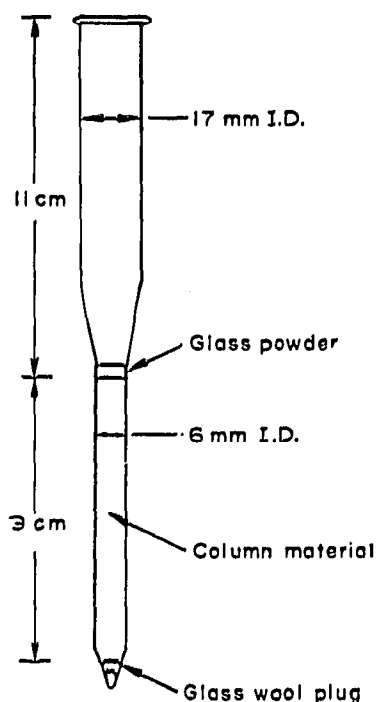


Fig. 1. Schematic diagram of extraction column.

amounts of divinylbenzene to the reaction mixture. The crosslinked product is not soluble; it was stirred overnight with toluene to remove ungrafted polymer, washed several times with fresh solvent, the toluene removed with a methanol wash, and the product dried as above.

Modified Kel-F was prepared by irradiating a mixture of 100 g of Kel-F powder of a given mesh size with 30–50 g of a syrup consisting of 21 wt. % Carbowax, 42 wt. % styrene, and 37 wt. % methanol at a dose rate of about 10,000 rads/h for about 50 h. The product was washed thoroughly with toluene, the toluene removed with a methanol wash, and the solids dried as above. Increases of weight in the range of 6 to 12 % were obtained. The product has greater capacity for adsorption of organic liquids than the ungrafted Kel-F and has sufficient water wettability to be used in a gravity-flow aqueous system, retaining interstitial aqueous solution by capillary action.

The process and the product are presently the subjects of patent action.

Preparation of columns

A weighed amount of graft copolymer was stirred with a known amount of complexing agent in a suitable volatile solvent (*e.g.*, toluene, chloroform, methanol, etc.), the solvent evaporated and the polymer thoroughly hydrated by stirring in excess water for several hours. The wet polymer was transferred in small increments to a column and pressed gently with a flat-ended stirring rod to remove voids and

pack uniformly within the column. A layer of glass powder, a few millimeters thick, was placed on top of the resin to prevent particles from swirling up or floating when solutions were added. It also helped to prevent the top of the resin bed from drying out if the liquid on top of the column was depleted. The column was flushed with several column volumes of aqueous solution of the same type as that to be used to transfer the sample.

Evaluation of graft copolymers as column supports

The conversion of a liquid-liquid extraction to a column operation has several distinct advantages apart from the possibility of obtaining chromatographic separations, particularly in handling of large numbers of samples or in working in a confined enclosure such as a glove box. The elimination of stirring apparatus and separatory funnels can considerably reduce the problems of spillage, splashing and cross-contamination so easily encountered in an operation of this type. In addition, the problem of poor phase separation, with which one is occasionally plagued, is also eliminated.

Three solvent extractions which are routinely in use at this laboratory and which could profitably be converted to column operation for certain types of samples are: extraction of Ce(IV) from 4 *M* HNO₃ with HDEHP, extraction of Cs from 1 *M* NaOH with BAMBP, and extraction of Ag from dilute HNO₃ with thio-THPA. Generally, twenty milligram quantities of carriers are involved and the standard size column used in most operations, as described above and illustrated in Fig. 1, has a bed volume of about 2.5 ml. Consequently, the development program was directed to obtaining a column material which would adsorb enough complexing agent to extract a 20 mg sample in 2.5 ml of swollen resin, maintain water wettability and remain free flowing in various aqueous media without undue changes in volume.

Preliminary investigation

In order to determine the feasibility of using graft copolymers as column supports, several types of grafts on various hydrophilic polymers were obtained from Dr. A. J. RESTAINO, Atlas Chemical Industries, Inc., and tested for swelling ratios in organic solvents and aqueous solutions. Some of these were made into columns containing adsorbed complexing agents and examined for capacity, retention of organics, and general adaptability to the solvent extraction systems of interest. A summary of the information obtained in the preliminary study is given in Table I.

As indicated in Table I, none of the graft copolymers are sufficiently stable chemically to be used in the Ce(IV)/HNO₃ system. Oxidation of the organic substrate by the Ce(IV) ion results in gas evolution and the formation of tiny bubbles which eventually stop liquid flow through the column.

Columns made from grafted poly(acrylic acid) can be used for some purposes in acid solutions but the substrate swells tremendously in aqueous alkali and is completely unacceptable in systems which go from acid to base. Large changes in volume also occur with variations in the ionic strength of the aqueous solution. This is true of the polyacrylamide and starch based grafts as well, both of which suffer from the additional disadvantage of hydrolyzing and degrading in strong acid or base. The styrene-grafted cellulose can be used with dilute nitric acid solutions but degrades on prolonged exposure to hydrochloric or nitric acid greater in concentration than three

TABLE I

PRELIMINARY EVALUATION OF GRAFT COPOLYMERS AS COLUMN SUPPORTS

Type of graft	Adsorbed organic solution	Mobile phase	Observations
Poly(acrylic acid-g-styrene)	HDEHP/CCl ₄	4 M HNO ₃	Stopped flowing when Ce(IV) put on column.
	BAMBP/CCl ₄ thio-THPA/CCl ₄	1 M NaOH 1 M HNO ₃	Stopped flowing before Cs was adsorbed. Good flow rate, good capacity; Ag completely adsorbed but column stopped and support swelled to seven times its original volume on treating with ammoniacal solution to elute the silver.
Poly(acrylic acid-g-methyl methacrylate)	—	—	Excessively solvated by toluene or CCl ₄ ; could not be made into a column through which aqueous solution would flow.
Poly(acrylamide-g-styrene)	—	—	Hydrolysis of the acrylamide portion of the molecule in strong acid or base resulted in excessive aqueous swelling during use.
Starch-g-polystyrene	HDEHP/CCl ₄	4 M HNO ₃	Stopped flowing when Ce(IV) put on column.
	BAMBP/CCl ₄ thio-THPA/CCl ₄	1 M NaOH 1 M HNO ₃	Stopped flowing before Cs could be eluted. Stopped flowing when NH ₄ OH solution put on column.
Cellulose-g-polystyrene	HDEHP/CCl ₄	4 M HNO ₃	Flow rate dropped to as little as 1 ml/h when Ce(IV) put on column.
	BAMBP/CCl ₄	1 M NaOH	Flow rate slow (10 ml/h) with poor retention of Cs.
	thio-THPA/CCl ₄	1 M HNO ₃	Good flow rate (20–30 ml/h) but poor retention of Ag.

TABLE II

ADSORPTION PROPERTIES OF STYRENE-GRAFTED POLYETHYLENE GLYCOLS

Sample designation	Mol. wt. range of the PEG	Irradiation conditions	Total dose (Mrad)	Grams of solvent per gram of dry polymer	
				Water	Toluene
2A	570–630	50% solution in styrene	0.5	0.9	Soluble
2B	1300–1600	Powder in excess styrene	0.5	0.9	Soluble
2C	6000–7500	Flakes in excess styrene	0.5	3.4	Soluble
2D	15000–20000	Flakes in excess styrene	0.5	4.4	Soluble
2E	15000–20000	21% solution in 1:1 styrene-methanol	0.5	1.1	Soluble
2F	15000–20000	Same as E with 5% DVB	1.1	0.67	3.4
2G	15000–20000	Same as E with 7.5% DVB	1.1	0.40	2.3
2H	15000–20000	Same as E with 10.0% DVB	1.1	0.36	1.8
2I	15000–20000	Same as E with 12.5% DVB	1.1	0.43	1.9
2J	15000–20000	Same as E with 15.0% DVB	1.1	0.79	2.1

to four molar. An extended study of the characteristics of columns made from styrene-grafted cellulose was undertaken and is reported in a separate paper⁷.

Graft copolymers of polyethylene glycols

The principal disadvantages of the polymers examined in the preliminary study were essentially due to the chemical characteristics of the hydrophilic substrates (*i.e.*, the lack of chemical stability and the excessive swelling in aqueous media). The Carbowax polyethylene glycols are water-soluble polymers that range in molecular weight from a few hundred to twenty thousand, are heat stable and inert to many chemicals. It appeared that grafting styrene to a polyethylene glycol would improve the chemical stability of the hydrophilic substrate and possibly reduce the aqueous swelling characteristics. The latter effect could be expected since the low molecular weight of the starting material would result in a graft copolymer with a much lower ratio of hydrophilic to organophilic portion (assuming the molecular weight of the polystyrene side chain did not vary substantially from that obtained on the other grafts to cellulose, starch, etc.). Consequently, mixtures of styrene and various representative polyethylene glycols (Carbowax 600, 1540, 6000 and 20M compound) were irradiated with gamma rays from a used fuel element in the Livermore LPTR facility and the products recovered as described above. The uncrosslinked graft and polystyrene are similar in solubility characteristics; therefore, no attempt was made to separate homopolymerized styrene from the product. Irradiation of similar solutions that did not contain polyethylene glycol indicated the rate of homopolymerization was much less than the rate of grafting and it was concluded that the presence of a small amount of homopolymer in the graft would have a negligible effect on its properties as a column support.

Graft copolymers that are not soluble in organic solvents were prepared in a similar fashion by incorporating various amounts of divinylbenzene in the reaction mixture before irradiation. Swelling properties of the crosslinked grafts and some of the uncrosslinked material are given in Table II. Samples 2B, 2C and 2D demonstrate the increasing aqueous capacity of the graft with increasing molecular weight of the hydrophilic substrate. The same effect is observed in comparing the samples irradiated in solution (2A and 2E).

With reference to the crosslinked materials, both aqueous and organic adsorption values indicate a minimum at 10 % divinylbenzene content. It is not certain that the effect is real, and no satisfactory explanation for it can be given at this time.

Columns were made from several of the materials listed in Table II for the three systems of interest. As with the previous grafts tested, degradation by Ce(IV) ion in nitric acid solution was sufficient to slow down and eventually stop column flow before a separation could be attained. However, functioning columns were fabricated with adsorbed BAMBP and thio-THPA, on which it was possible to adsorb and elute milligram quantities of cesium and silver, respectively.

The kinetics of adsorption-desorption are similar to that found for the cellulose-styrene grafts so that the resolution of peaks is highly dependent on the particle size of the column support⁷. In addition, the low density of the graft copolymer renders it difficult to handle in a slurry or to make columns since it has a strong tendency to float. In an effort to minimize both of these problems, a new polymer system was developed by grafting styrene to the surface of powdered Kel-F in the presence of polyethylene glycol. The product is a modified Kel-F which has a high capacity for adsorption of organic liquids and is water-wettable as well.

The modified (surface-grafted) Kel-F is an excellent support for extraction

columns and is presently being used in a program to develop new separations of radiochemical interest based on extraction chromatography (*e.g.*, the separation of alkali metals on a column containing adsorbed BAMBp/HDEHP). A comparison of the adsorption properties of several such modified polymers is given in Table III. As indicated in Table III, 11 % graft is sufficient to increase the aqueous capacity by as much as 80 % and organic capacity by 190 % over the unmodified Kel-F. For samples of approximately the same percent graft, decreased capacities are observed with decreased particle size of the substrate.

TABLE III

ADSORPTION PROPERTIES OF SURFACE GRAFTED POLYTRIFLUOROCHLOROETHYLENE

Sample designation	% Graft ^a	Mesh size	Composition of grafting solution before irradiation	Grams of solvent per gram of dry polymer ^b	
				Water	Toluene
3A	0.0	100-115	Unirradiated Kel-F	0.38	0.28
3B	0.0	100-115	Toluene + methanol (1:1)	0.45	0.34
3C	5.9	100-115	Styrene + methanol (1:1)	0.61	0.47
3D	6.2	100-115	Standard grafting solution ^c	0.64	0.63
3E	10.9	100-115	Standard grafting solution ^c	0.69	0.82
3F	12.7	115-150	Standard grafting solution ^c	0.67	0.75
3G	12.0	250-325	Standard grafting solution ^c	0.58	0.74
3H	11.7	-325	Standard grafting solution ^c	0.56	0.61
3I	18.4	-325	Styrene-enriched solution ^d	0.58	0.70

^a $\frac{\text{Final wt. minus initial wt.}}{\text{Initial wt.}} \times 100.$

^b A 10 g portion was soaked for several hours in excess solvent, centrifuged in a tared 40-ml cone, and wet weight determined.

$$\text{Grams of solvent per gram of dry polymer} = \frac{\text{wet wt. minus dry wt.}}{\text{dry wt.}}$$

^c 42 wt.% styrene, 21 wt.% Carbowax, 37 wt.% methanol.

^d 53 wt.% styrene, 17 wt.% Carbowax, 30 wt.% methanol.

The Kel-F based material is significantly denser than the styrene Carbowax grafts described in the previous section. Consequently, it is much easier to handle in slurries with aqueous solution and in making up columns, having little tendency to float. The high capacity for organic liquids combined with the virtual absence of swelling in aqueous solutions gives rise to a higher concentration of complexing agent per unit of bed volume than can be attained with some of the other grafts examined. There is also a greatly decreased sensitivity of the swollen resin volume to the ionic strength of eluting solutions.

Examples of column extractions performed on columns made from Carbowax grafts and modified Kel-F are given in Figs. 2-4.

CONCLUSIONS

From the observations made, graft copolymers based on hydrophilic substrates which are easily hydrolyzed or display excessive swelling characteristics in aqueous solutions are unsatisfactory as column supports in the extraction chromatography of

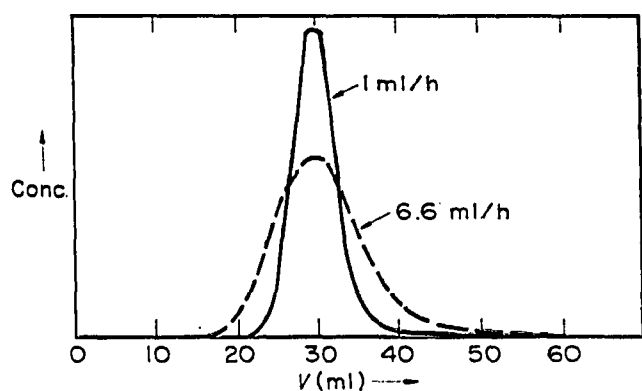


Fig. 2. Elution of carrier-free $^{152-154}\text{Eu}$ with 0.5 M HCl from a $20\text{ cm} \times 0.17\text{ cm}^2$ column.

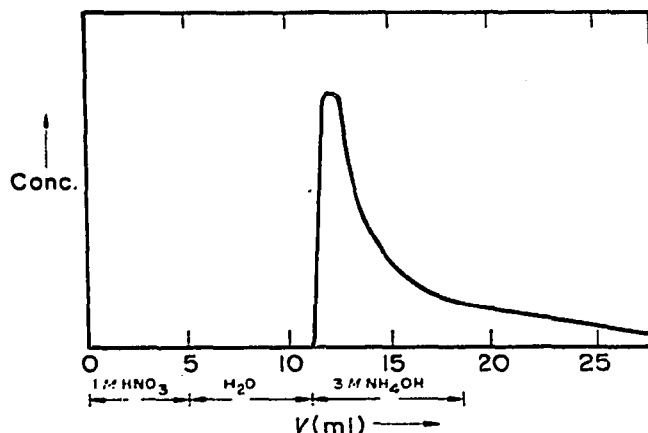


Fig. 3. Elution of 10 mg Ag from a $9\text{ cm} \times 0.3\text{ cm}^2$ column.

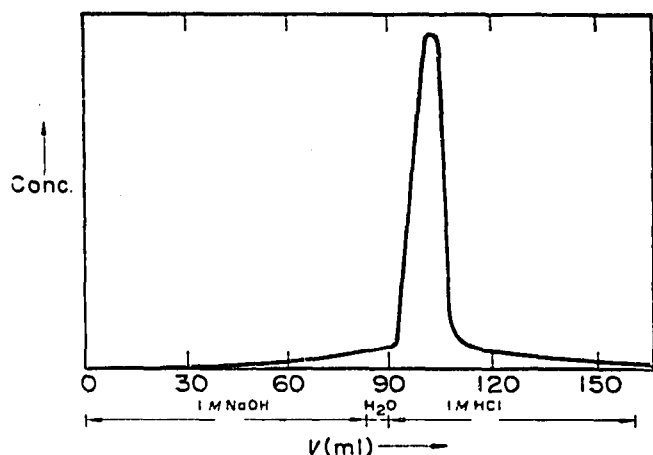


Fig. 4. Elution of carrier-free ^{137}Cs from a $16\text{ cm} \times 0.71\text{ cm}^2$ column.

inorganic materials. In particular, polymeric systems based on acrylic acid, acrylamide or starch are especially limited in such an application, while those based on cellulose can be used in extraction systems which do not require strongly oxidizing conditions or strongly acidic or basic solutions.

Satisfactory column supports can be obtained by grafting styrene to the Carbowax polyethylene glycols (*i.e.*, water-soluble polymers obtained by condensing ethylene oxide) as long as strongly oxidizing media (*e.g.*, Ce(IV) in HNO_3) are avoided. Aqueous swelling characteristics of the Carbowax grafts can be minimized so that only negligible volume changes occur as the ionic strength of the eluting solution is changed. Thus, styrene containing 10% divinylbenzene can be grafted to Carbowax compound 20M to give a product which takes up approximately 40% by weight of water and 180% of its dry weight of toluene and still retains its water-wettable character.

The product obtained by grafting styrene to powdered Kel-F in the presence of dissolved Carbowax is a highly useful column support in that it has more than twice the capacity of ungrafted Kel-F for adsorbing organic solvents but is water-wettable. Therefore, it can be made into columns through which aqueous solutions flow with

ease and which will not run dry, retaining interstitial solution by capillary action. Columns made from this support with suitable adsorbed organic complexing agents are extremely useful in adapting liquid-liquid extractions to column operation under conditions where one wishes to avoid pressurized columns or devices to prevent the columns from running dry if not constantly attended.

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SUMMARY

Liquid-liquid extractions based on systems consisting of an aqueous solution and an organic complexing agent have been adapted to column operation by the use of graft copolymers which are both hydrophilic and organophilic as column supports. Columns have been made and evaluated using graft copolymers of styrene and various hydrophilic polymers as substrates with complexing agents such as di-(2-ethylhexyl) orthophosphoric acid (HDEHP), N,N',N''-trihexyl phosphorothioic triamide (thio-THPA), and 4-*sec.*-butyl-2-(α -methylbenzyl)phenol (BAMBP) as the adsorbed organic species.

An improved column support has been developed by irradiating polytrifluoro-chloroethylene (Kel-F) in a slurry with a styrene-methanol solution of polyethylene glycol compound.

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