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THIN CATION-EXCHANGE FOILS

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## ABSTRACT

Treatment of commercial polystyrene sheets with fuming sulfuric acid produces a thin layer of cation exchanger. The ion-exchange capacity of the layer is measured by an isotope-dilution procedure which utilizes  $\text{Th}^{228}$  and  $\text{Th}^{232}$ . At the same time the thickness is found from the yield of  $\text{Ra}^{224}$  which escapes from the foils as  $\alpha$ -decay recoils.

A specific capacity of 5.7 milliequivalents per gram can readily be obtained, and the thickness can be varied from a few to several hundred micrograms/cm<sup>2</sup>. The foils have been used for simple and fast preparation of  $\alpha$  sources.

THIN CATION-EXCHANGE FOILS\*

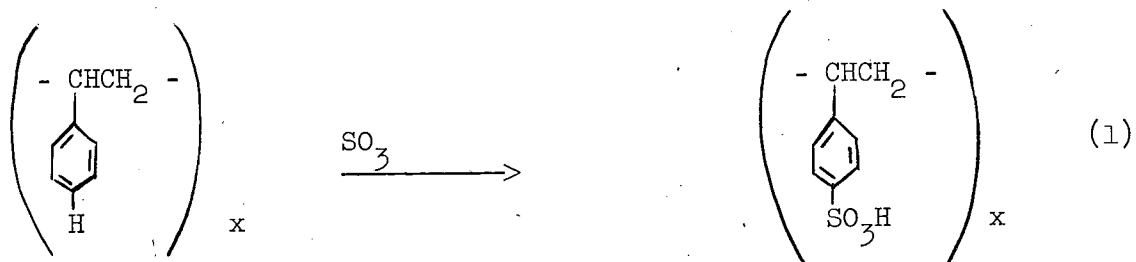
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1. Introduction

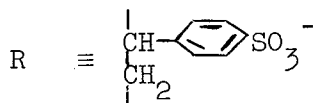
The cation-exchange properties of sulfonated polystyrene are well known from commercial ion-exchange resins. It has been suggested that sulfonation of polystyrene sheets may provide a simple method for producing thin uniform sources for  $\alpha$  and  $\beta$  spectroscopy.<sup>1</sup> A sulfonated surface layer of a desired shape and depth can be produced by the action of fuming sulfuric acid on a polystyrene sheet:



If a solution containing a radioactive cation is applied, hydrophilic action confines it to the sulfonated area, where it is chemically absorbed by the reaction



where



and

$\text{M}^{+n} \equiv$  the n-valent cation.

The pertinent properties of the sulfonated area are the thickness ( $\mu\text{g}/\text{cm}^2$ ) and the capacity [millimicroequivalents (m $\mu\text{eq}$ ) of exchangeable hydrogen per  $\text{cm}^2$ ], from which the specific capacity (meq/g) can be derived. The thickness determines the energy spread of radiation from the source. Capacity determines the maximum source strength for a given specific activity. High specific capacity implies high total capacity for a given thickness; in addition it helps to obtain quantitative absorption of cations, as can be seen from the equilibrium expression for the reaction (2):

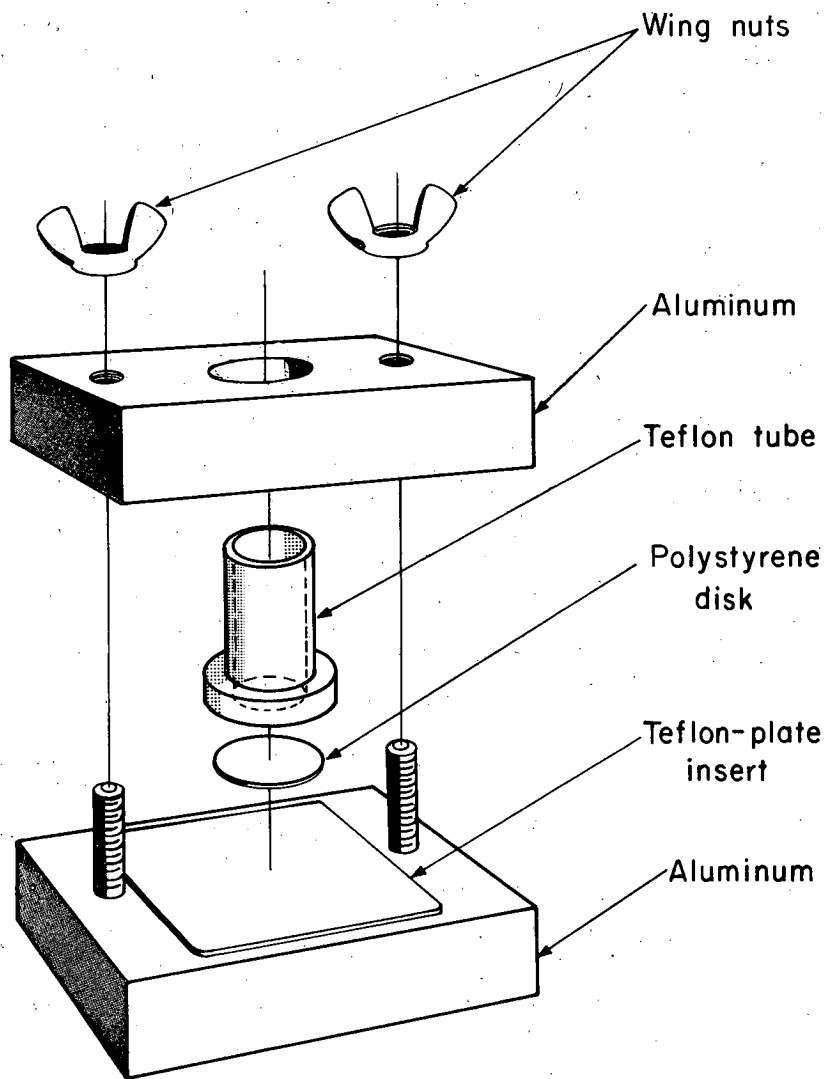


where K is the equilibrium constant.

The absorption depends on the acidity of the applied solution through the factor  $[H^+]^n$ . The dependence of  $[H^+]^n$  makes it possible to absorb polyvalent ions selectively in the presence of considerable excesses of lower valent ions and neutral contaminants. Considering the absorption equilibrium (2) more generally, it should be kept in mind that all cations present in the solution will compete for the resin sites. The factor  $[H^+]^n$  should then be replaced by a weighted sum of all ionic impurities. In practice, trivalent and higher-valent ions can be absorbed with good yields from solutions that are 0.001 to 0.1M in monovalent ions.

## 2. Procedure

The foils are made by clamping polystyrene disks in a press (see Fig. 1). The thickness of the polystyrene was 2, 5, or 10  $\text{mg}/\text{cm}^2$  (1, 2.5, or 5 mils). The press confines the sulfonated area and eliminates the effect of absorption.



MU-25013

Fig. 1. Expanded view of the sulfonation apparatus.



of water vapor during sulfonation. The sulfonating agent is made by diluting fuming sulfuric acid with concentrated sulfuric acid. Control of  $\text{SO}_3$  concentration is important. Because there are variations in the stock reagents, it is desirable to titrate the final solutions.

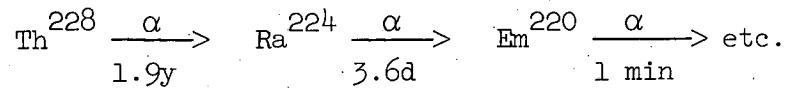
The fuming acid is poured into the Teflon tube for a measured length of time, poured out, and ice-cold sulfuric acid (concentrated reagent to which five volume-percent water has been added) is immediately poured in and swirled. A second rinse with sulfuric acid is followed by two with iced ethanol. The foil is then removed from the press, washed with ethanol, and allowed to dry.

When the foils are used for source preparation they are first moistened with 10 to 20  $\mu$ liter of distilled water. The hydrophilic action makes the water spread in a thin layer and confines it completely to the sulfonated area. The radioactive solution is then added, often directly as the effluent from a small ion-exchange column, with HCl as the eluant. The solution is evaporated to near-dryness under a heat lamp to eliminate hydrogen ions. Water is again added, and 5 to 30 min are allowed for the absorption equilibrium to be established. The solution is then drawn off, and the foil is washed once or twice with ethanol.

### 3. Measurements

The capacity of the foils is measured by saturating them with thorium from a 0.1M solution of  $\text{Th}^{232}$ -chloride, to which  $\text{Th}^{228}$  is added as a tracer. The amount of thorium absorbed, assumed to be in the form  $\text{R}_4\text{Th}$ , is determined by comparison of the  $\text{Th}^{228}$   $\alpha$  activity on the saturated foil with that of an aliquot of the stock solution, the  $\alpha$  activity of  $\text{Th}^{232}$  being negligible.

Decay of  $\text{Th}^{228}$  is by the chain



A grid ionization chamber coupled to a pulse-height analyzer is used to resolve the  $\text{Th}^{228}$   $\alpha$  group from those of the daughter activities.

The thickness of the layer can be obtained at the same time by observing how many of the recoiling  $\text{Ra}^{224}$  atoms, produced by the  $\alpha$  disintegration of  $\text{Th}^{228}$ , are able to escape from the foil. The recoil range is taken to be  $7 \mu\text{g}/\text{cm}^2$ .<sup>2</sup> By setting the recoil efficiency from an infinitely thin layer equal to unity, and assuming homogenous distribution throughout the sulfonated volume, one uses geometrical integration to obtain

$$t = \begin{cases} 2r(1-e) & \text{if } e \geq 0.5 \\ r/2e & \text{if } e \leq 0.5 \end{cases}$$

where

$t \equiv$  thickness, in  $\mu\text{g}/\text{cm}^2$ ,

$\mu \equiv$  recoil range:  $7 \mu\text{g}/\text{cm}^2$ ,

and  $e \equiv$  recoil efficiency.

The foil is placed 1 mm from a large aluminum collector plate in vacuum for a measured time. The amount of  $\text{Ra}^{224}$   $\alpha$  activity on the plate is subsequently recorded in the ionization chamber. The recoil efficiency can be determined after suitable half-life corrections.

The specific capacity, in milliequivalents per gram (meq/g), is obtained from the known capacity and thickness.

4. Results

Table 1 gives the results of a series of measurements in which the sulfonation time and the concentration of fuming sulfuric acid have been varied. The numbers are averages of several determinations, the errors indicating the reproducibility of the sulfonation process.

Table 1

Thickness, Capacity, and Specific Capacity of Sulfonated Foils						
Sulfonation agent			Sulfonation time <sup>c</sup>	Thickness ( $\mu\text{g}/\text{cm}^2$ )	Capacity ( $\text{m}\mu\text{eq}/\text{cm}^2$ ) <sup>d</sup>	Specific capacity ( $\text{meq}/\text{g}$ ) <sup>e</sup>
Fum. $\text{H}_2\text{SO}_4$ <sup>a</sup> : conc. $\text{H}_2\text{SO}_4$ <sup>b</sup>	Normality (eq/liter)					
1 : 3	35.7±0.1	4 min	2.8±1	0.29±0.08	0.11±0.02	
		12 min	3.5±1	0.35±0.08	0.11±0.02	
		25 min	3.7±1	0.42±0.08	0.12±0.02	
1 : 1.8	36.9±0.1	2 min	3.8±1	0.86±0.2	0.23±0.04	
		5 sec	9±3	39±15	4.3±1.0	
1 : 1	38.0±0.1	15 sec	14±3	82±20	5.7±0.4	
		1 min	23±5	130±30	5.8±0.4	
		2 min	52±10	280±60	5.4±0.4	
		5 sec	13±4	80±20	5.8±0.4	
2 : 1	39.1±0.1	15 sec	16±4	90±30	5.5±0.4	
		1 min	39±8	200±40	5.2±0.4	
		2 min	88±18	490±100	5.6±0.4	

The polystyrene is an ordinary biaxially oriented product, Trycite, made by extrusion of pure polystyrene with no plasticizer (manufactured by Dow Chemical Co., USA).

<sup>a</sup> Fuming sulfuric acid: 30 to 33%  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$  by weight; reagent grade.

<sup>b</sup> Concentrated sulfuric acid: 96%  $\text{H}_2\text{SO}_4$  by weight; reagent grade.

<sup>c</sup> At room temperature.

<sup>d</sup>  $\text{m}\mu\text{eq} = 10^{-9} \text{ eq} = 6 \times 10^{14}$  sulfonic acid groups.

<sup>e</sup> It is assumed that thorium is absorbed as a quadrivalent cation.

The specific capacity reaches a saturation value of 5.7 meq/g when the volume ratio is 1 : 1 or more. This capacity corresponds to an equivalent weight of 175, or to the introduction of one sulfonic acid group per benzene ring (1), and compares favorably with that of commercial cation resins. By scanning the surface of the saturated foil with a small collimator and an  $\alpha$  counter, the capacity per unit area was shown to be constant within 20%.

Foils are easily produced with thicknesses between 8 and 200  $\mu\text{g}/\text{cm}^2$ . Thinner foils may be obtained by lowering the temperature or by diluting the sulfonating agent. Thicker foils show an increasing tendency to peel off. (This tendency might be less pronounced if polystyrene containing a plasticizer were used.)

Selective absorption of thorium in preference to radium was seen in the  $\alpha$  spectra. The activity ratio of  $\text{Th}^{228}$  and  $\text{Ra}^{224}$  in the applied solution was 1 : 1, whereas the foils of 5.7 meq/g absorbed thorium preferentially in a ratio 20 : 1. It may also be worth noting that 90% of the emanation was pumped off in vacuum.

The foils have been used to prepare  $\alpha$  sources of curium, californium, einsteinium, and fermium in a matter of 20 to 30 min with yields of 70 to 90%. Selective absorption was manifest in a number of cases.

## 5. Conclusion

Cation-exchange foils of various thicknesses and capacities are easily made. The only special requirements are a simple press and standardized fuming sulfuric acid solutions. With these foils, radioactive sources of a predetermined shape and thickness can be made from a solution of the activity in a matter of minutes. The sources are uniform, and polyvalent cations can be absorbed selectively with good yield.

FOOTNOTES AND REFERENCES

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Copenhagen.

1. T. Westermark, Acta Chem. Scand. 6, 1194 (1952).
2. E. W. Valyocsik, Range and Range Straggling of Heavy Recoil Atoms,  
Lawrence Radiation Laboratory Report UCRL-8855, November 1959 (unpublished).

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