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by

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A. Work since the last progress report dated September, 1968.

A.1. Personnel. Dr. Kazuko Shimomura continued as Postdoctoral Research Associate until mid-February, 1969. An undergraduate honors student, Miss Harovel Grays, was employed on an hourly basis from February to May, and Mrs. Nila Petrowski (B.S. in Chemistry) was employed as a laboratory technician from mid-April to mid-June.

A.2. Publications (reprints enclosed)

C00-499-18A. The manuscript "Thin-Layer Chromatography of Amines by Ligand-Exchange," by K. Shimomura and H.F. Walton, was published in Separation Science, 3, 493 (1968).

C00-499-19A. The manuscript "Metal Complexes of Squaric Acid," by P.H. Tedesco and H.F. Walton, was published in Inorganic Chemistry, 8, 932 (1969).

C00-499-20. The work of Fred Hilgeman (mentioned in our last report) was extended and published: "Ion-Exchange Chromatography of Metal Ions with Ethanolamine Eluents," by F. Hilgeman, K. Shimomura and H.F. Walton, Separation Science, 4, 111, (1969).

A.3. Papers Presented

The principal investigator attended the Latin-American Chemical Congress and presented the three papers mentioned in the last report, and a fourth paper on the work of Hilgeman and Shimomura (C00-499-20). Acknowledgement of AEC support was made.

Harovel Grays presented a paper on silver-lead separations by ion exchange (see below) at the joint meeting of the Colorado-Wyoming Academy of Sciences and the Southwestern Division of the AAAS, held in May. The abstract will appear in the Journal of the Colorado-Wyoming Academy, and a more detailed account will be submitted to Separation Science.

A.4. Unpublished Work

We still have not published some of the data in Dr. Shimomura's thesis because of their incomplete nature. We refer especially to the ligand-exchange chromatography of ethylene imine and its derivatives, ligand-exchange chromatography of polyhydric alcohols, and the attempts to apply the principle of ligand-exchange to gas chromatography.

We have spent much time trying to develop better methods of automatic column monitoring in liquid chromatography. We used the differential refractometer in two distinct ways; first, to record the difference in refractive index between influent and effluent solutions, and second, to record the gradient of refractive index against volume in the solution flowing from the column.

We purchased a liquid chromatography detector from the Varian-Aerograph Co. which works on the heat-of-adsorption principle. We tried hard to make this work, and finally sent the detector cell back to the manufacturers, who promised to send us a new cell of better design. Finally, we have worked on an ultra-violet flow cell for monitoring aromatic compounds.

Over half of Mrs. Petrowski's time was spent testing these techniques. We have little to show for it, but feel that this work must be continued; we cannot hope to make ligand-exchange useful as an analytical technique until we can overcome experimental difficulties and make it easy and automatic.

However, we can report solid, publishable progress in two areas:

(a) Silver-lead separations. Eluents containing mono- and diethanolamine selectively complex Cu(II) and apparently Ag(I). We have passed solutions containing silver along with lead and other metals, plus diethanolamine, through columns of cation-exchange resins and immediately washed out the silver while retaining lead and other metals on the column. The carboxylic resin Bio-Rex 70 works best, and we can quantitatively recover milligrams of silver from mixtures with gram quantities of lead.

(b) Ligand-exchange chromatography of drugs derived from phenethylamine.

The columns are sulfonic or better, carboxylic resins loaded with ions of nickel, copper or cadmium; the eluents are methanol-water mixtures containing ammonia. The order of elution of some typical substances is:

1. Ephedrine,	$C_6H_5 \cdot CHOH \cdot CHCH_3 \cdot NHCH_3$
2. Methedrine,	$C_6H_5 \cdot CH_2 \cdot CHCH_3 \cdot NHCH_3$
3. Benzedrine
(amphetamine)	$C_6H_5 \cdot CH_2 \cdot CHCH_3 \cdot NH_2$
4. Phenethylamine	$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot NH_2$

Epinephrine (adrenalin) emerges with ephedrine or sooner, but it strips metal ions from the resin.

A striking feature of these results is the large effect of methyl groups on the elution volume; the differences between methedrine, benzidrine and phenethylamine are very marked. A similar effect was noticed with ethylene imine and hydrazine derivatives.

B. General review of the work supported by this contract since 1957.

Accomplishments have been in the following areas:

B.1. Distribution and equilibrium data for the cation exchange of metal ions.

We started with lead, uranium, thorium and barium ions, exchanged against hydrogen ions in sulfonated polystyrene resins, and found selectivities that increased with increasing metal-ion loading, with crosslinking, and with temperature. We made more detailed thermodynamic studies (not all of them published) of univalent-divalent exchanges, especially of Ba^{++} , Sr^{++} , Ca^{++} , and Mg^{++} against H^+ and Na^+ , and we measured water content and swelling. Our general conclusion was that the activities of the metal-resin combinations were more nearly proportional to equivalent fraction in the resin than to any other variable, and that the entropy effect, rather than enthalpy, governed the equilibrium. Indeed, entropy and enthalpy often worked in opposite directions.

We did some work with inorganic exchanges of the molecular-sieve type (Linde A) and confirmed the existence of different types of exchange sites in these materials. We also concluded that ion-pairing occurs between the fixed and mobile ions.

B.2. Co-ion uptake or Donnan Equilibrium.

We spent a whole year trying to adapt a kinetic approach with flow through a shallow bed of resin to the determination of co-ions retained by resin beads at low external salt concentrations, using radioactive bromide and chloride ions as tracers. We gave up this work and never published the results. First results were encouraging, but it became evident that we could not control the hydrodynamics of the flow system.

B.3. Cation exchange of organic ions.

We measured the distribution of cations of aromatic and non-aromatic amines between cation-exchange resins and mixed aqueous-nonaqueous solvents,

with and without excess of acid. We observed the very strong interaction between a polystyrene resin matrix and aromatic compounds, especially those containing the benzyl group, and the noted the adsorption of aniline and benzylamine bases is excess of the exchange capacity.

B.4. Stability of metal-amine complexes with cation-exchange resins.

We found that in sulfonic acid resins, cationic complexes such as CuB_4^{++} were neither more nor less stable than in aqueous solution if B were ammonia or an aliphatic amine of low molecular weight. With larger molecules, and especially 1, 2- and 1, 3- diamines, great differences in stability existed, and the nature of the resin matrix and fixed ions was important too. It was this work that led us into ligand-exchange chromatography, which has turned out to be the most fruitful area of our work.

B.5. Chromatography of organic acids by anion exchange.

Only one paper was published on this topic, but it listed some effective and simple separations and showed the use of a differential refractometer in liquid chromatography.

B.6. Ligand-exchange chromatography

We have published five papers in this area and have accumulated much unpublished data. The technique would seem specially applicable to basic substances that are not conveniently analyzed by gas chromatography by reason of their instability, chemical reactivity or low volatility. Such substances are ethylene imines, hydrazines, diamines, polyamines and amino-alcohols, aromatic amines and a whole range of natural products, hormones and drugs. We have demonstrated that the technique works, and are just beginning to exploit its practical applications. As to how it works, we know that many factors are involved, and would like to explore the theory of ligand exchange chromatography when we get time.

B.7. Coordination chemistry of "squaric acid."

This work, which is new, was indirectly supported by the subject contract through the use of equipment and materials.

C. Side-effects of the contract.

The principal investigator is active in undergraduate and graduate education and in exposition; he has written textbooks and contributed chapters to cooperative works such as Meites' Handbook of Analytical Chemistry, Heftmann's Chromatography and Wainerdi and Ukem's Modern Methods of Geochemical Analysis (in press); he has written the biennial review on ion exchange chromatography for Analytical Chemistry three times, and is about to write the fourth such review. He has become involved in international education, particularly in South and Central America. In all these activities he has drawn on experience gained by this contract.

D. Acknowledgement

Finally he would like to express warmest thanks to the AEC for eleven years of support, and the understanding way in which it has borne with various frustrations and delays. Particularly he thanks Mr. David M. Richman for his personal interest.