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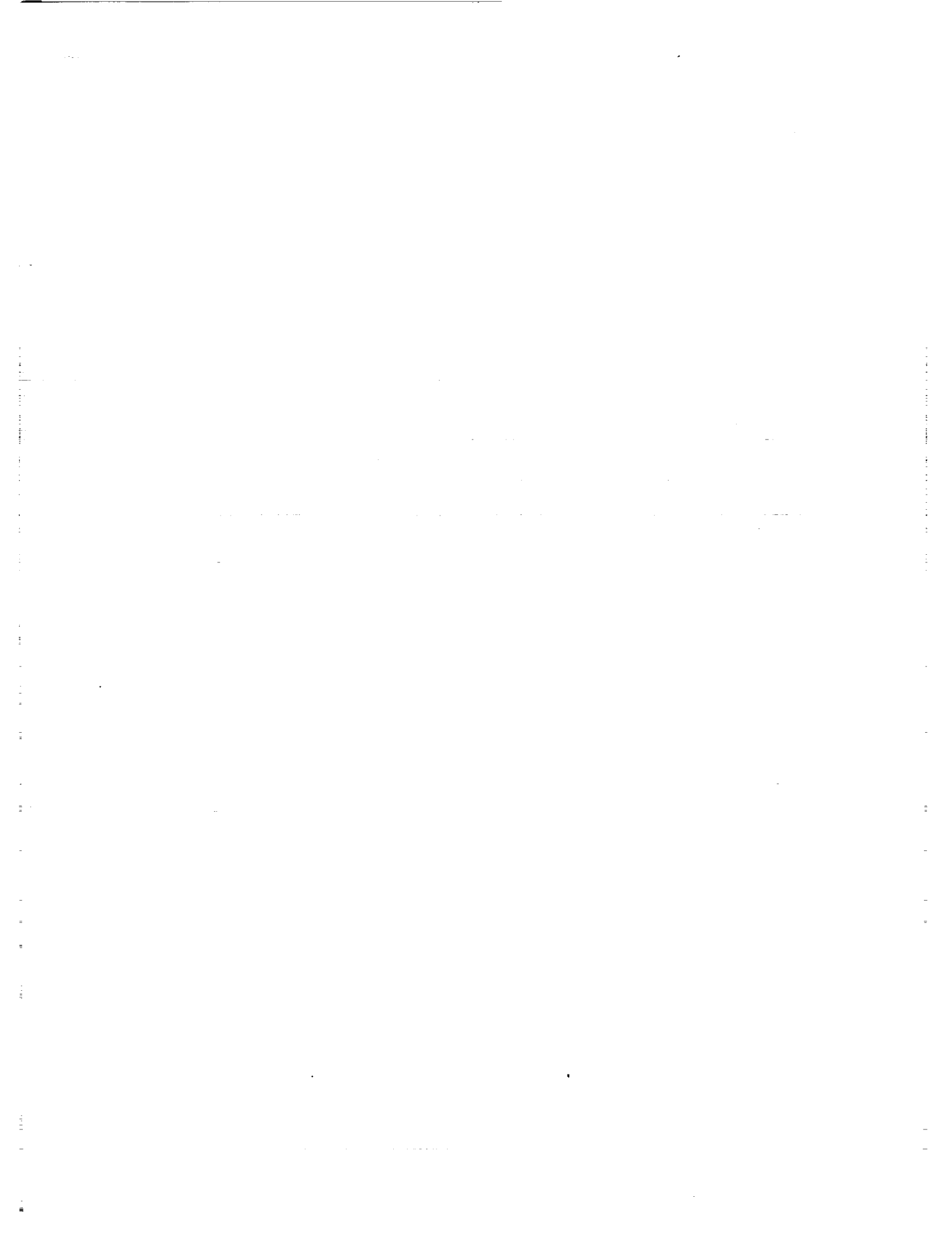
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Recovery and Separation of Precious Metals From Space**H. Freiser and S. Muralidharan****Strategic Metals Recovery Research Facility****Department of Chemistry****University of Arizona****Abstract**

We have developed during the past year a viable procedure centered around centrifugal partition chromatography (CPC), a multistage liquid-liquid partitioning technique for the separation of precious metals (Pt, Pd, Rh, Ir, Os, Ru). We have identified stable and inexpensive ligands that can be readily recycled to achieve the separations of the precious metals. The separation methods developed so far yield three separate fractions: Pt, Pd, and Rh-Ir. The Rh-Ir pair can be separated in a subsequent run. The total amount of precious metals separated in a single experiment varied from 1 to 50 mg. The factors affecting the efficiencies of these separations have been studied. The kinetics of the decomposition of the complex and the ion pair have a major bearing on these efficiencies, with slow kinetics resulting in poor efficiencies. The methods for the improvement of the efficiencies have also been investigated. For example, significant improvement in the efficiencies and separation times for Pt and Pd have been achieved by the use of chloride gradient in the mobile phase.

Two papers were published and talks were presented on our work at the FACSS meeting in Anaheim, October 1991, and at the Pittsburgh Conference in New Orleans, March 1992.



Overall Research Objectives

Our major overall objective in this project is to develop efficient and economical large-scale separation and recovery methods for the metals of the platinum group and other precious metals that are suitable for use in space. Our analysis of the problem has led us to the use of multistage separation processes involving two liquid phases as the optimum direction to pursue. The relatively novel separation technique known as Centrifugal Partition Chromatography (CPC), has been selected as the most promising of the various types of chromatography, particularly from the point of view of scale up, as well as the strong scientific support provided by analogies to solvent extraction, an area of great strength in our group.

Progress to Date

Centrifugal Partition Chromatography (CPC), a recently introduced countercurrent liquid-liquid distribution technique, used mainly for the separation of a broad spectrum of organic compounds, has now been applied to the separations of metal ions. We were the first to demonstrate the efficient separation by CPC of adjacent lanthanides, including the separation of both light and heavy lanthanides in a single run using gradient pH elution.

With NASA support, we were the first to achieve the separation of palladium(II) from the other PGM with CPC using a mixed complex, $\text{Pd}(\text{TOPO})_2\text{Cl}_2$. These studies revealed that, under comparable conditions, CPC efficiencies for metal ions separations were significantly lower, by a factor of 4-5, than those regularly seen for organic compounds. Another anomaly that occurs with metal ion separations is that unlike the behavior of organic compounds, column efficiency depends on the distribution ratio of a given metal species. Although not commented on in the literature, similarly low efficiencies and their dependence on the distribution ratios of the extracted metal species can also be observed in the separation of metals by derivatized solid supports. Generally, in chromatography the column efficiency is constant for a given set of operating conditions, exhibiting no dependence on the distribution ratios of the species being separated. Possibly, because separations of metal ions by CPC involve formation and dissociation of extractable complexes using suitable ligands, chemical factors may be responsible for the differences. During the last project period we undertook systematic investigation to determine whether, and in what manner, chemical factors, in contrast to simple solvation and desolvation as well as mass transfer factors, were responsible for the differences in CPC efficiencies for metals and organic separations. CPC studies coupled with

solution kinetic studies using stopped flow has allowed us to clearly establish the influence of chemical kinetics on CPC column efficiencies and correlate them to the half-lives of the chemical reaction responsible for the lowered chromatographic efficiencies.

In work to date, we have focused our efforts on finding optimal solutions to problems of reagent systems affording great selectivity and sufficiently rapid kinetics to eliminate threats to separation efficiency. First, we developed a CPC procedure which served to separate Pd(II) from the rest of the platinum group metals (PGM). We used our experience here to uncover the chemical factors limiting selectivity and efficiency of separation because we learned that for many metal separation systems, these outweighed the mass transfer factors governing most multistage separations. This study led us to an investigation of the chemical kinetics of extractable complex formation and dissociation reactions and the testing and evaluation of appropriate new systems. During this past project period, we have been successful in separating Pd(II) and Pt(II) from each other and from the remaining PGM.

Nature of Research Proposed

Our current research is directed toward applying the principles we have discovered to the separation and recovery of all of the individual members of PGM and scaling up the best of the systems we find. Finally, we will address the problems of adapting our processes to conditions in space. Before the end of this project period, we expect to apply the separation and recovery schemes to the production of fractions of the individual PGM from the carbon monoxide-treated residue of iron meteorite sample(s) to be made available to us by Dr. John Lewis.