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A countercurrent liquid-liquid extractor

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Abstract

A novel countercurrent liquid-liquid extractor is presented and illustrated with applications. The apparatus consists essentially of an assembly of mixer-settlers, feeders, reservoirs, and flow lines that are made of glass or other chemical resistant materials. In operation this multistage assembly rotates intermittently in one direction on a horizontal axis causing the immiscible phases to progress to opposite ends of the unit. Details for the construction of the extractor and its principles of operation are given. Extractors of this design are applicable to experimental work and to the preparation of pure compounds in quantity.

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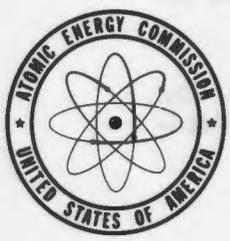
**A COUNTERCURRENT LIQUID-LIQUID
EXTRACTOR**

By
Harley A. Wilhelm
Raymond A. Foos

September 3, 1954

Ames Laboratory
Ames, Iowa

Technical Information Service, Oak Ridge, Tennessee



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by

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September 3, 1954

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
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ABSTRACT

A novel countercurrent liquid-liquid extractor is presented and illustrated with applications. The apparatus consists essentially of an assembly of mixer-settlers, feeders, reservoirs, and flow lines that are made of glass or other chemical resistant materials. In operation this multistage assembly rotates intermittently in one direction on a horizontal axis causing the immiscible phases to progress to opposite ends of the unit. Details for the construction of the extractor and its principles of operation are given. Extractors of this design are applicable to experimental work and to the preparation of pure compounds in quantity.

The applicability of the extractor is illustrated by extractions involving zirconium and hafnium, and niobium and tantalum. A fraction containing high purity hafnium and one containing high purity zirconium were obtained from a liquid solution containing roughly equal amounts of both. Another extraction produced zirconium of high purity from a mixture containing largely hafnium. Niobium and tantalum were also successfully separated.

INTRODUCTION

During the past few decades liquid-liquid extraction has become one of the principal methods of performing separations and purifications on both laboratory and commercial scales. Partial or complete separation or purification of rare earth mixtures (1-4), atabrine (5), penicillin (6), vitamins (7), normal fatty acids (8), higher fatty acids (9), bile acids (10), monoamino acids (11), antimony (12) and hafnium-zirconium mixtures (13) are only a few applications of this unit operation being investigated or employed today. Von Berg and Wiegandt (14) state that this principle is most widely employed in the petroleum industry for fractionation of oil mixtures although its use is gradually spreading to other industries to include many other types of recoveries and purifications. The role of extraction in general analytical chemistry has been discussed by Morrison (15) and Craig (16)

while Irving (17) limited his considerations to solvent extraction and its application to separations of inorganic compounds. The main objective of the present article is to present a novel apparatus for performing multistage countercurrent liquid-liquid extractions. Data obtained using this apparatus in the separation of zirconium from hafnium and tantalum from niobium are presented to demonstrate the practicability of this extractor.

Separation by liquid-liquid extraction in the cases discussed here depends largely on the differential distribution of the two inorganic solutes when placed in an immiscible or partially immiscible system of two liquid phases. It is apparent that when two or more solute components are present in such a liquid system a partial separation is possible if all of the components do not favor the same liquid phase to the same degree. The difference between the distributions of any two solute components in the phases indicates the effectiveness of liquid-liquid extraction as a means for their separation. When the solute components have similar distribution ratios a series of extractions operated countercurrent-wise is usually required for good separations. This operation becomes laborious and time consuming if carried out in equipment such as individual separatory funnels. To simplify this process many continuous and intermittent countercurrent flow liquid-liquid extractors have been designed to operate on a laboratory or on a commercial scale (14,18).

The continuous flow extractors include those in which the materials flow to and from the extractor in essentially continuous streams. The two phases may or may not be mutually in contact at all times. Various modifications of extraction columns, box type mixer-settlers and power driven extractors operate as continuous flow extractors. Intermittent flow extractors include those in which there is a flow of liquid only during a portion of each cycle which includes contacting, mixing, settling and separation of the two phases repeatedly through a series of stages. This type of operation is exemplified by extractors such as those of Compere and Ryland (19), Craig (20-22), Lathe and Ruthen (23), Fenske and Tegge (24), Nadel and Highhouse (25) and a series of separatory funnels.

The solutes to be separated in both the continuous and intermittent countercurrent flow type extractors can be introduced at an end or at some intermediate stage of the apparatus. They are generally in solution in one of the liquid phases which then constitutes the feed solution. Some extractors employ "limited-feed" in the sense that essentially only a limited amount of feed such as a single batch addition can be processed without completely reloading the equipment. The Craig machine (20-22) and the apparatus of Lathe and Ruthen (23) both employing "limited-feed" have applications in scientific investigations but are not directly adaptable to problems requiring continued output. Large scale single batch extractors can be employed essentially only on the simpler separations.

Other extractors may employ "unlimited-feed" either as a steady stream or as intermittent batches on a continuing basis. Many large scale production extractors employ "unlimited-feed" for continued output of product; many small capacity extractors employ similar feeding to obtain data on which to base larger scale operations. In extractors employing "unlimited feed" an essentially steady state develops which can be continuously maintained during prolonged operation.

Some data useful in countercurrent extractions can be obtained with equipment in which there is progressive movement of only one phase. The term "countercurrent distribution" employed by Craig (21) does not refer to an actual countercurrent flow of liquids through the equipment but merely to a method of operation which permits direct application of the binomial expansion to interpret the results. In describing the extractor presented in this article the term "countercurrent" has the meaning indicated by K. A. Vorteresian and M. R. Fenske (26) whereby the flow of the immiscible liquid phases in opposing directions through the equipment actually occurs.

The liquid-liquid extractor described here operates with intermittent countercurrent flow and with "unlimited-feed"; therefore, it can be operated under essentially steady state conditions giving continued output. Consequently this extractor has research, development and some production potentialities.

PRINCIPLES OF OPERATION OF THE EXTRACTOR

The extractor described here is one of a number of similar countercurrent liquid-liquid extractors that have been designed by the senior author (27). These extractors are being employed in liquid-liquid extraction studies and for actually making separations of chemically similar inorganic substances in quantity. The particular extractor described in detail in this report has been constructed with twenty stages; however, the design is such that any number of stages can be assembled and operated as a unit. Figures 1, 2 and 3 are photographs in which the 20 stage assembly is shown in three different positions of rotation on a horizontal axis. Each of the twenty stages in this extractor has a mixer-settler tube with two reservoirs, one for the light liquid phase and one for the heavy liquid phase. The stages are mounted side by side in an orderly fashion in a cradle that rotates about the horizontal axis. Since the laboratory scale extractors usually operate for only a limited number of cycles in order to obtain operational data, they have been designed to operate by manually turning the driving crank, 1 of Figure 1. As will be shown later, the feeding of liquids to the extractor and the collection of outputs

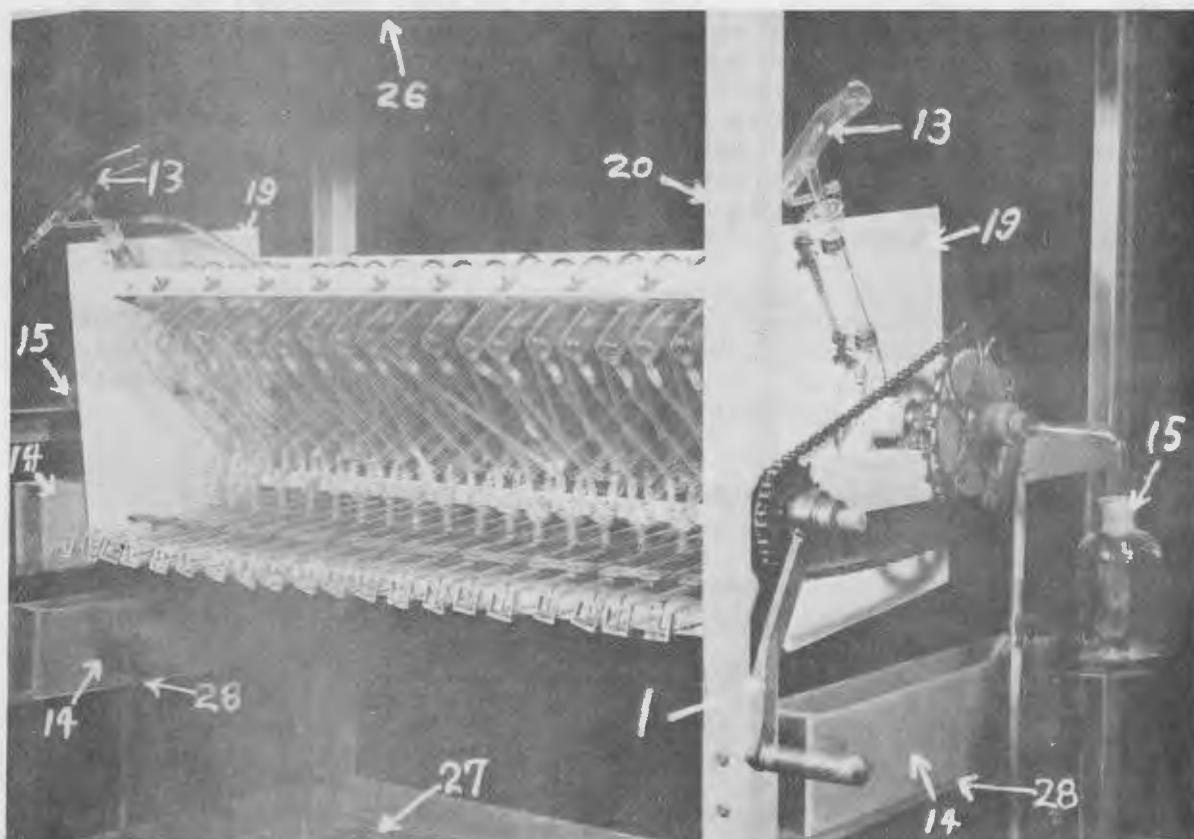


Fig. 1 - Extractor in Settling Position.

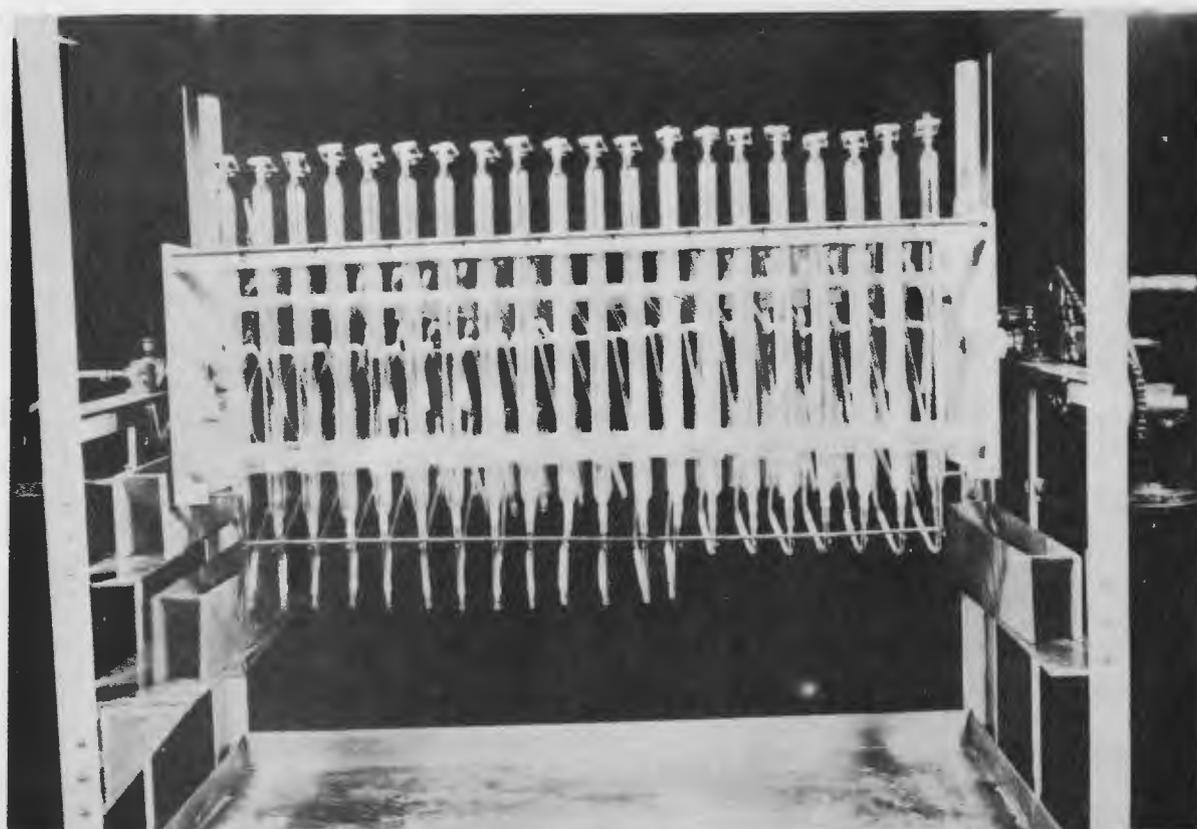


Fig. 2 - Extractor in Light Liquid Flow-Off Position.

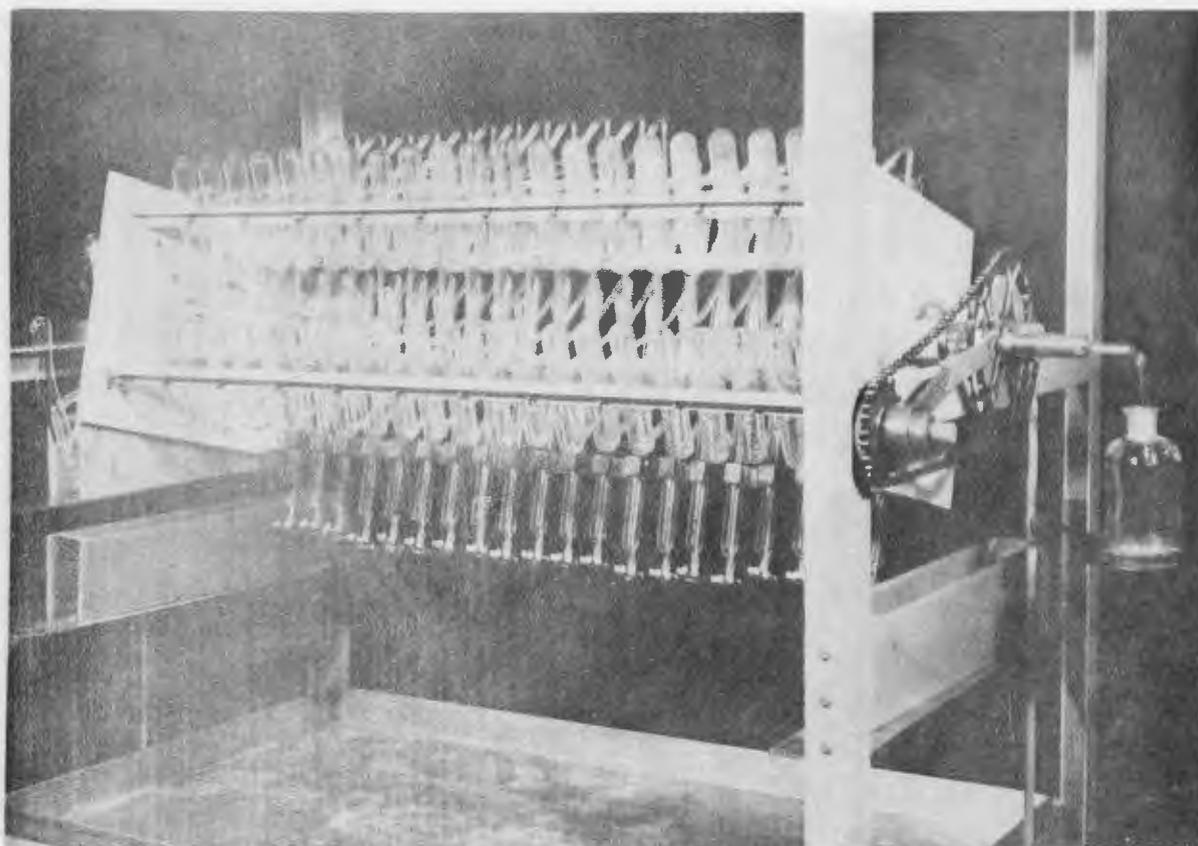


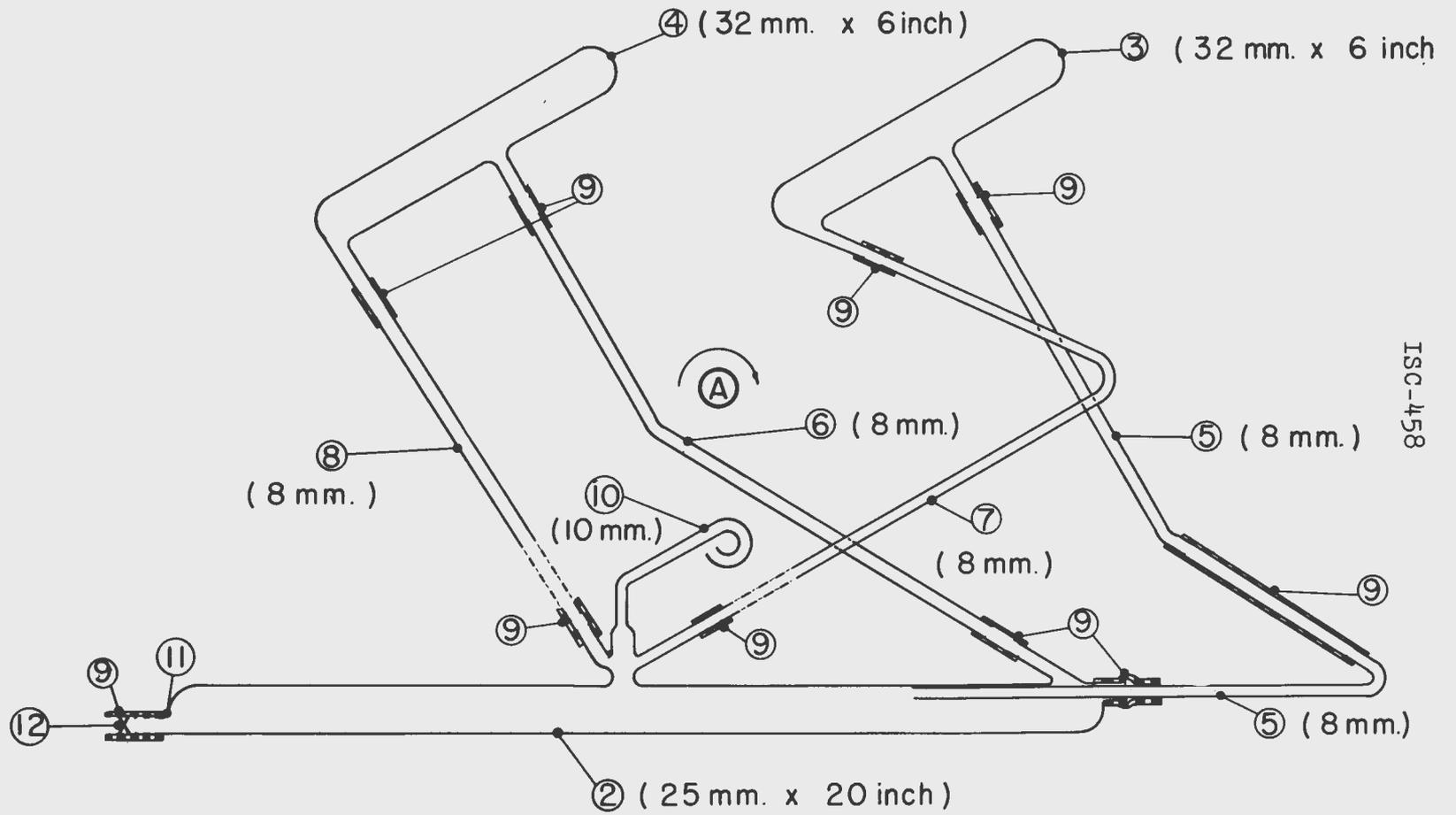
Fig. 3 - Extractor in Position after Liquid Pick-Up.

are essentially automatic with all sizes of this equipment. This extractor has been found to be quite useful as a research tool on a laboratory scale and the data obtained are directly applicable to larger scale separations. All parts of the apparatus that contact liquids have been constructed of glass or plastic.

A schematic drawing which represents the arrangement and connections for a single stage of the liquid-liquid extractor is shown in Figure 4. Rotation of this single stage clockwise through 360° around the axis, A, completes one cycle. During this cycle the light and heavy liquid phases, not shown in this figure, move from the mixer-settler, 2, to the reservoirs, 3 and 4, through tubes 5 and 6 respectively. From the reservoirs the phases flow through tubes 7 and 8 and back to mixer-settlers. The dashed sections of tubes 7 and 8 indicate that in a multistage unit these tubes are actually connected to the mixer-settlers of the stages on either side of a stage such as that shown in Figure 4. The position of the light liquid take-off tube, 5, in the mixer-settler tube is adjustable by movement through the plastic sleeve connection. Tube 10 is open to the outside at the curved end and serves as a breather tube. The curved section at the open end of this tube is necessary for returning to the mixer-settler tube any liquid that might get into the breather. The spout, 11, serves for adding and removing liquid from the mixer-settler tube when desired. A clamp or plug, 12, is used to close the short section of plastic tubing on this spout.

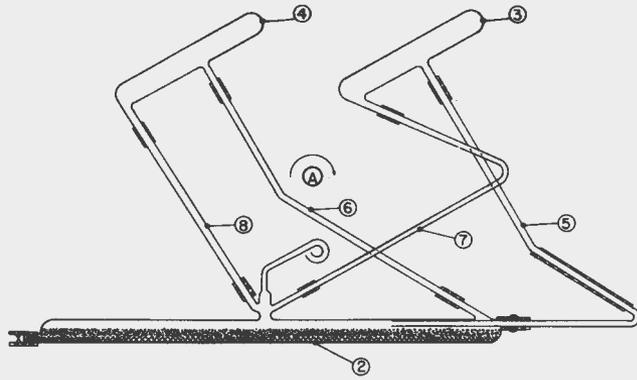
The principles of operation of the stages are further illustrated by the four positions of one stage shown in Figure 5. Suppose that the two immiscible liquid phases containing the solutes are mixed by a rocking action about the axis, A, and that they are then allowed to separate in the mixer-settler tube, as shown in Figure 5A. The dotted area represents the liquid having the lowest specific gravity and constitutes the top phase while the cross-hatched area indicates the bottom or more dense liquid phase. When the stage is rotated clockwise through 90 degrees the position and phase separation shown in Figure 5B result. During the slow movement to this position the less dense liquid flows into the light liquid reservoir through the light liquid take-off tube. The open end of the take-off tube is at or near the limit of the liquid-liquid interface which results on approaching position B of Figure 5. Another 90° of rotation to the position indicated in Figure 5C then causes the heavy liquid to flow into the heavy liquid reservoir. Rotating the stage through the next 90° causes the liquids to flow to the opposite ends of their respective reservoirs, see Figure 5D. Finally on completing the 360° cycle the light liquid phase and the heavy liquid phase flow from these reservoirs to their proper mixer-settlers.

In a multistage assembly the two separated phases from each of the stages actually flow from their reservoirs to separate mixer-settler tubes on opposite sides of and adjacent to the mixer-settler tube from which they came. This operation occurs in each of the

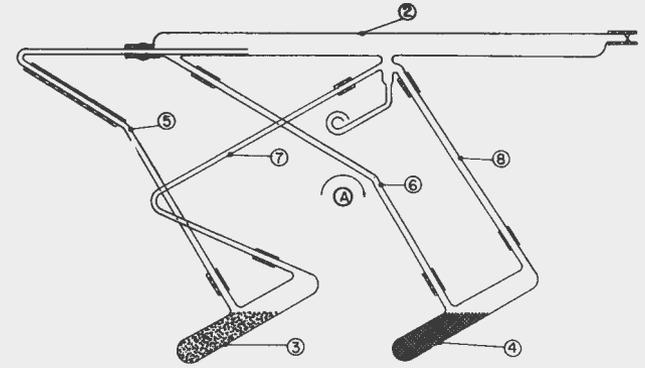


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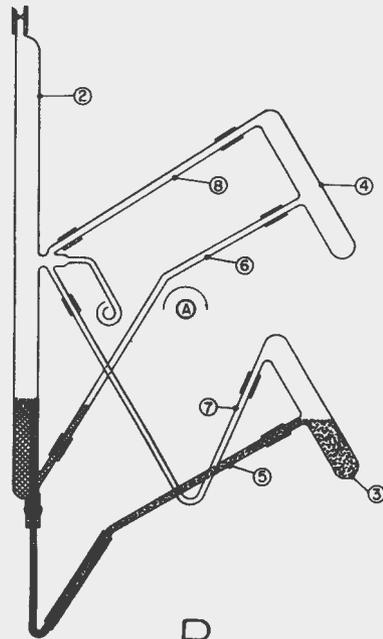
Fig. 4 - Design of a Single Stage, Adjustable Open-Tube Type.



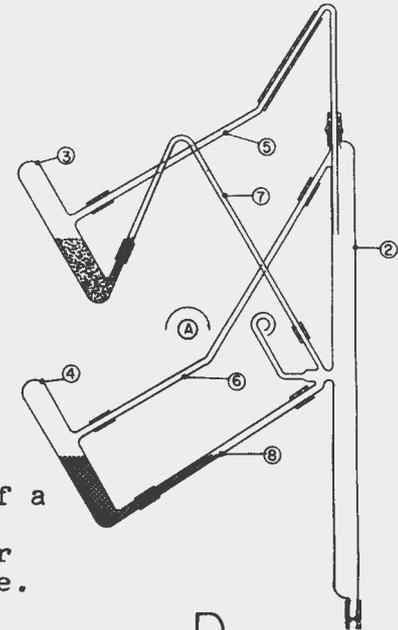
A



C



B



D

Fig. 5 - Positions of a Single Stage and Its Liquid Phases at Four Points during a Cycle.

stages in a multistage assembly for each rotation or cycle of the extractor. The pattern of flow of phases is the same for all stages of the assembly. The result of continued operation is therefore a countercurrent movement of the two liquid phases through the extractor. For each cycle of operation of a multistage assembly the mixing, settling, separation and countercurrent flow take place in that order and practically in phase for all of the stages.

Generally, in making fractional extractions with this apparatus, the two immiscible solvent phases are introduced at the stages at opposite ends. The solutes to be separated are dissolved in a portion of either phase and may be fed at any desired stage through a Y-connection inserted in the line between tube 7 or 8 and the mixer-settler tube of the stage. A feeder of one type employed for introducing a liquid phase to one of these extractors is shown at 13 of Figure 1. The three plastic troughs, 14 of Figure 1, contain the liquids to be introduced into the extractor. These troughs are located so that the feeders which rotate with the stage assembly will each pass through a trough and become filled with the proper liquid.

The product solutions are delivered from the end stages of the assembly to their receivers (15 of Figure 1). The delivery of a phase is made from the end stage reservoir to the receiver by means of a tube, 16 of Figure 6, that passes through the hollow end shaft of the cradle, described below. This tube is connected to a delivery spout, 17, by means of a rotary joint, 18.

SOME DETAILS OF THE EXTRACTOR DESIGN AND OPERATION

The twenty stage assembly is mounted and rotated in a cradle made of metal end plates, 19 of Figure 1, connected by four angle irons which also serve as stage supports. Each end shaft of the cradle has a flange that is bolted to an end plate. These shafts pass through bearings that are mounted on the cross bars of the support frame, 20. The large sprocket-wheel of a 1:2 ratio chain drive mechanism is securely mounted on an end shaft. The rotation of the cradle then is effected by means of the hand crank on the small sprocket-wheel which revolves on an axle mounted on the frame work. The larger wheel is a bicycle sprocket wheel with an even number of sprockets while the smaller wheel is specially made with one-half as many sprockets. With this ratio the position of the handle is the same for a certain point in any cycle. A metal plate with many holes is mounted on the frame and very close to the large sprocket-wheel. In order to secure the cradle in any position a metal pin is placed through this sprocket-wheel and into a hole in this stationary plate. A revolution counter which

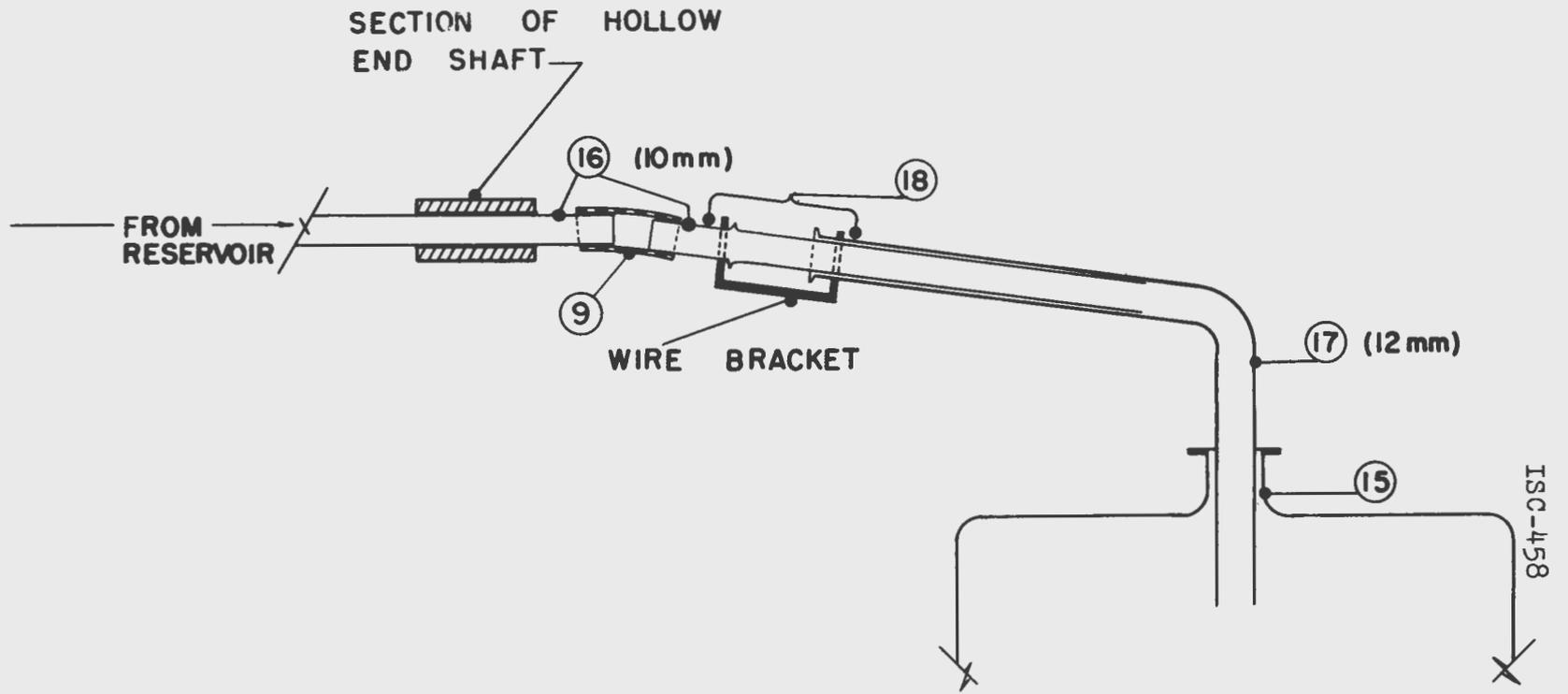


Fig. 6 - Delivery Line for a Product Solution.

is mounted on the frame engages a small arm protruding from the large sprocket-wheel on each cycle of operation. This counter does not show in Figure 1. The feeders, 13, are secured to the end plates by band clamps that are soldered on the ends of bolts. In Figure 1 only two of the three feeders are in view; the third feeder operates on a shorter radius and is obscured by the far end plate.

The feeders are constructed essentially of glass according to the design illustrated in detail in Figure 7. The support arm, 21, furnishes a means for mounting the feeder. The combination of this arm and the adjustable band clamps allows proper positioning of a feeder scoop on an end plate of the extractor cradle. A cup, 22, on the feeder support arm is designed to catch liquid which adheres to the outside of the feeder scoop and tends to run down the support arm while in the top position. The radius of operation of a feeder scoop is adjusted so that the scoop passes near the bottom of its trough. As the feeder chamber, 23, passes below the liquid level in its trough during a cycle, liquid enters the chamber through a hole near the leading end. On further rotation of the assembly the excess liquid overflows through the volume control tube, 24, and returns to the trough. The portion of liquid retained in the scoop is delivered later in the cycle to the proper mixer-settler tube through the side arm, 25.

The inlet end of the feeder chamber is so designed to prevent dripping of any residual liquid from this chamber when it is inverted during the cycle. The feeder volume control tube, 24, is open at one end and closed at the other. However, near the closed end and on one side there is an overflow opening. The excess liquid that flows back to the trough during rotation of the unit does so as this volume control tube approaches a vertical position in the cycle shortly after filling. This volume control tube should be turned so that the overflow opening faces the axis of rotation of the extractor for delivery of more reproducible volumes. The actual volume fed to the extractor is controlled by the adjustment of the volume control tube through the plastic sleeve joint at 9 of Figure 7.

Figure 1 shows a diagonal view of the countercurrent liquid-liquid extractor with the mixer-settlers in the settling position as shown for a single stage by Figure 5A. If the stage assembly is rotated 90° clockwise from this position as observed from the sprocket end, the light phase take-off position shown by the front view in Figure 2 results. This position of the stages corresponds to that for a single stage represented in Figure 5B. Another 180° of rotation results in the position shown in Figure 3. This is a position for drainage of excess liquid from the feeders which have emerged from the feeder troughs and also corresponds to the position for a single stage in Figure 5D. On completing this cycle by another 90° of clockwise rotation, a return to the position shown in Figure 1, deliveries of the phases from the many reservoirs and feeders to the proper mixer-settler tubes or to the

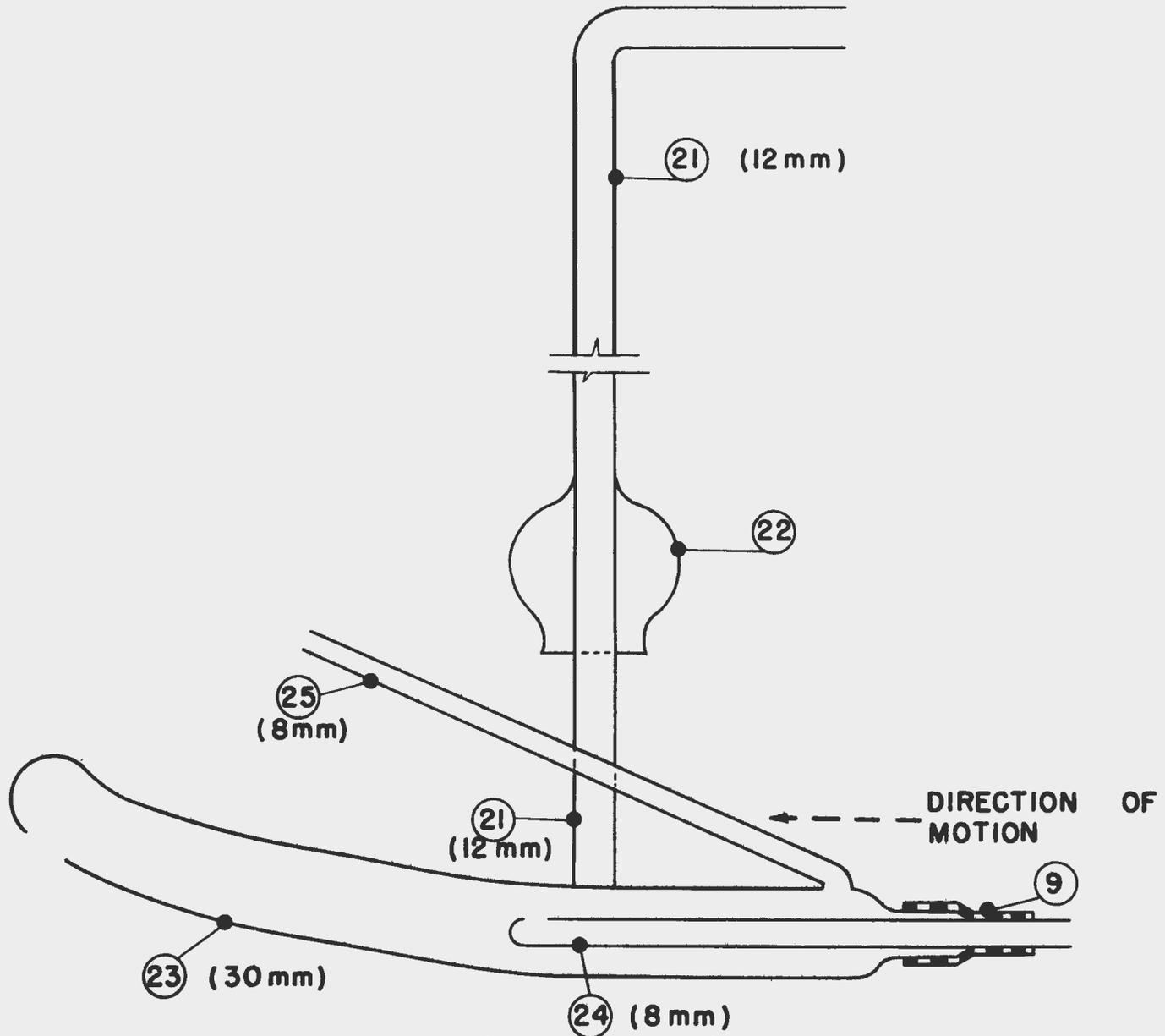


Fig. 7 - Design of a Feeder.

two product receivers occur. It is apparent that for each 360° of rotation of the assembly there is one addition of each of the liquids to the extractor and a delivery of each of the product phases from the extractor. The time necessary to complete a cycle will be discussed later, since it depends largely on factors associated with the particular system employed.

The extractor support frame, 20 of Figure 1, is made of two-inch angle iron with welded construction. This stationary frame is 60 in. high, 53.5 in. across the front (front view in Figure 2) and 34 in. on the side. A wooden platform, 26, on top of this frame protects the extractor and serves as a shelf. The drip tray, 27, is 12 in. from the floor; it is made of 20 gage sheet stainless steel and is 2.5 in. deep, 30 in. wide and 50 in. long. Its purpose is to catch the liquids in case of accidental spillage. The three trough supports, 28, are adjustable shelves that are bolted to the frame, 20. These shelves are made of 1/4 in. stainless steel and have arms with slotted bolt holes for making proper height adjustments.

Plastic, in 1/4 in. thick sheet, was employed for construction of the feeder troughs, 14. These plastic troughs are three in. wide and 4 in. high over-all. The two lower troughs are 22 in. long while the over-all length of the upper one is 17 in. Each trough has a curved floor, the radius of curvature being approximately that for the arc through which the feeder scoop, 13, moves in passing through the trough. These three troughs contain supplies of the various liquids employed in the extraction. With proper flow lines from the feeders, deliveries can be made to the desired stages of the extractor. In selecting the material of construction for these troughs, full consideration must be given to possible attack on the material by the liquids. Some plastic materials are quite chemical resistant, readily available and easily fabricated to shape. Polyethylene appears to be a material that is quite generally useful either alone or as a coating material. Lucoflex has been found to resist the action of most acid aqueous solutions but it is attacked by some organic solvents.

All of the glass used in this extractor is Pyrex while both polyethylene and Tygon tubing have been employed in short lengths for making connections. Tygon, which has greater flexibility, has been employed but only at certain points because it has been found to be less resistant to attack by some of the organic chemicals employed in liquid-liquid extraction studies. Since polyethylene is somewhat rigid at room temperature and quite flexible at 100°C it was softened by heating in boiling water in order to make connections. If subsequent adjustment is to be made at a plastic-to-glass connection, a bit of lubricant such as silicone stopcock grease may be required.

Table 1 contains a summary of the nomenclature used in describing the various numbered parts for all figures of the apparatus

Table 1

Extractor Parts and Material of Construction

Part Number on All Figures	Part	Material of Construction
1	Driving crank	Steel
2	Mixer-settler tube	Glass
3	Light liquid reservoir	Glass
4	Heavy liquid reservoir	Glass
5	Mixer-settler light liquid delivery tube	Glass
6	Mixer-settler heavy liquid delivery tube	Glass
7	Reservoir light liquid delivery tube	Glass
8	Reservoir heavy liquid delivery tube	Glass
9	Sleeve connection	Plastic
10	Breather tube	Glass
11	Mixer-settler spout	Glass
12	Closure	-----
13	Feeder	Glass
14	Feeder troughs	Plastic
15	Product receivers	Glass
16	Product delivery tube	Glass
17	Product delivery spout	Glass
18	Rotary joint	Glass
19	Cradle end plates	Steel
20	Extractor support frame	Steel
21	Feeder support arm	Glass
22	Cup	Glass
23	Feeder chamber	Glass
24	Feeder volume control tube	Glass
25	Feeder delivery tube	Glass
26	Extractor cover	Wood
27	Drip tray	Stainless steel
28	Feeder trough supports	Stainless steel
29	Mixer-settler side arm	Glass
30	Mixer-settler side arm	Glass
31	Piston	Glass
32	Tap-off volume control tube	Glass

together with the materials of construction. Dimensions of some of the glass parts in this laboratory scale apparatus are indicated with the part number on some of the figures. The positions, sizes and forms of the parts of the entire assembly relative to one another have some flexibility without causing improper flow of liquids.

A PROCEDURE FOR STARTING THE EXTRACTOR

A systematic procedure for starting a countercurrent liquid-liquid separation with this extractor is required for efficient operation. The connections should first be made between the feeders and the desired mixer-settler tubes and between the proper reservoirs and the receivers to give the required number of stages and proper flow. Each feeder and trough combination is positioned to give proper movement of the feeders through the troughs. In the particular examples that are presented here for the separation of two inorganic compounds, an aqueous feed is introduced at some intermediate stage while an aqueous scrub and an immiscible, less dense, organic liquid enter at stages at opposite ends of the extractor. The two product phases are discharged according to countercurrent flow at the reverse ends.

The selection of flow rates (volumes of liquids introduced into the extractor per cycle) is made on the basis of single stage or other data and the extractor cradle is placed in approximately the position indicated in Figure 3. Measured flow-rate volumes of the liquids are placed in the chambers of their respective feeders. The feeder volume control tubes are then adjusted down to deliver only these volumes to the extractor as the cradle is turned slowly clockwise. The rotation is continued to a position for complete charging with the aqueous phase. This position is attained when the mixer-settler tubes point up with their spout ends at about 30° from horizontal.

At this new position the closures, 12, (see Figure 4) are released and the required volumes of the aqueous phase for the stages are added to the mixer-settler tubes through the spouts, 11. Sometimes the aqueous scrub liquid serves for all of these aqueous phase additions in starting up the extractor. The extractor assembly is then further rotated clockwise to the position indicated in Figure 2. Here the volume control tubes are adjusted down in the mixer-settlers until their open ends are slightly above the level of the aqueous phase, as shown in Figure 5B. The cradle is then slowly rotated counterclockwise back to the position employed above where additions of aqueous phase were made to the stages. At this position the required volume of organic liquid is added to the stages through the spouts, 11. These spouts are then closed. The feed troughs are then filled with their respective liquids. The cradle is now slowly rotated about 30° counterclockwise to the position represented in Figure 1. The mixer-settler tubes should contain at this time the proper amounts of the liquids for starting continuous operation.

Mixing of the phases in the mixer-settler tubes is next achieved by an oscillatory movement of the cradle through a total arc of roughly 40° about the position shown in Figure 1. The phases are then allowed to separate with the mixer-settlers in a horizontal position. Rotation of the stage assembly through 360°

in a clockwise direction according to the sequence of operation described for passing through the positions illustrated by Figure 5 completes the first cycle. The feeding and delivery of liquids are essentially automatic during subsequent cycles. All further rotations of the assembly are made in a clockwise direction except during the mixing operation for each cycle.

If the stage assembly is initially charged with feed solution at only the feed stage, a number of cycles will be required before delivery of solutes will be observed. The liquid-liquid extraction system ordinarily does not closely approach a steady state of operation until a number of cycles have been completed. Consequently, it will usually be desirable during the early cycles of operation to make minor readjustments of the positions of the light liquid take-off tubes in the mixer-settlers. It is essential that each of these take-off tubes be kept in such a position so that a small amount of the light liquid phase flows to the heavy liquid reservoir and not vice versa.

SEPARATION OF SOME INORGANIC SALTS

Countercurrent liquid-liquid extractors are employed in this Laboratory largely for the separation and purification of inorganic salts. By use of extractors of the type described in this article a number of compounds with purities adequate to serve as base materials for the preparation of standards for spectrographic analysis have been obtained in quantity. Although other mixtures have been studied, some experiments on separations of zirconium from hafnium and of tantalum from niobium will be presented to demonstrate practical use of these extractors. In each case the operating conditions employed in the multistage extractions were selected from single stage data.

1. Separation of Zirconium from Hafnium

It was reported earlier by workers in this Laboratory (28) that tributyl phosphate preferentially extracts zirconium from an aqueous nitric-hydrochloric acid solution containing both hafnium and zirconium. Two countercurrent liquid-liquid extractions employing this system are reported here; the first was carried out on an intermediate composition mixture which contained about equal proportions by weight of the two elements while the second extraction employed a mixture that was primarily hafnium containing only a few per cent of zirconium.

In the analysis of the solutions involved in the extractions the zirconium and hafnium were quantitatively precipitated by additions of excess ammonium hydroxide. Acetone was added to the organic phase before this precipitation in order to facilitate filtration. After filtering and calcining the precipitates at 600°C

for at least two hours the resulting oxides were assayed for relative percentages of zirconium and hafnium with minor impurities disregarded. Analytical data are reported on the basis of hafnium and zirconium elements only; i.e., the sum of the hafnium and the zirconium contents equals 100 per cent. The spectrographic methods of Fassel and co-workers (29) were employed for analyzing these mixtures containing hafnium and zirconium.

a. Separation of Zirconium from Hafnium in An Intermediate Composition Mixture

The separation of zirconium from hafnium employing a mixture in which both are present in approximately equal amounts is of very limited practical interest; however, such a separation is presented here as an example of the performance of this extractor.

A mixture of hafnium and zirconium oxychlorides containing 43 w/o hafnium (and 57% zirconium) relative to the total hafnium and zirconium content was dissolved in nitric acid. The resulting solution, or aqueous feed, was 6.75 molar in nitric acid and contained the equivalent of 172 g. of the combined oxides per liter. Twenty-five milliliters per cycle of this feed solution was introduced at stage 14 of the 20 stage extractor shown in Figure 1.

The aqueous scrub liquid which consisted of 6.75 molar nitric acid was introduced at stage one. Its flow rate was 15 ml per cycle. A mixture of 40% by volume of dibutyl ether in tributyl phosphate constituted the organic phase. This solution was introduced at stage 20 at the rate of 40 ml per cycle.

Operation of the extractor with these solutions was started according to the procedure described above. The products from every tenth cycle of operation were analyzed for hafnium and zirconium to determine the approach to essentially steady state. These analyses indicated that about 100 cycles were required to obtain this steady state operation. After 130 complete cycles of operation the extraction was discontinued and the liquids collected from each of the stages to obtain stagewise analytical data for the phases at steady state. A material balance, calculated on the average volumes, concentrations and analyses of the two product phases from the last 30 cycles indicated that about 50 w/o of the total oxides of hafnium and zirconium was delivered by the organic product phase.

The stagewise analyses for all 20 stages of the extractor after 130 complete cycles appear in Table 2. It is apparent from these data that the aqueous phase product, ready for delivery from stage 20, contained hafnium with 0.7% zirconium. The organic phase product, ready for delivery from stage one, contained zirconium with only 150 ppm hafnium. It is also

Table 2

Stagewise Data for the First Zirconium and Hafnium Extraction

Stage Number	Organic Phase		Aqueous Phase	
	Grams Oxide/ Liter	Per Cent Hf	Grams Oxide/ Liter	Per Cent Hf
1 aqueous scrub enters	68.8	0.015	15.5	-----
2	71.0	0.018	22.6	-----
3	71.5	0.028	28.1	0.24
4	72.1	0.015	32.1	0.15
5	75.6	0.043	35.9	0.76
6	79.4	0.042	40.8	0.77
7	76.3	0.052	43.7	1.28
8	76.6	0.13	48.4	1.19
9	80.4	0.13	53.4	1.48
10	83.7	0.12	57.4	2.53
11	89.8	0.58	63.5	6.37
12	91.4	1.48	69.9	12.3
13	91.0	3.39	81.0	25.4
14 aqueous feed enters	92.7	9.92	124.0	56.4
15	82.7	23.7	111.9	80.4
16	67.0	68.6	91.5	96.1
17	49.3	85.5	76.0	98.0
18	30.0	95.0	54.2	98.1
19	12.8	96.1	45.8	98.1
20 organic enters	1.58	96.1	50.7	99.3

apparent from these stagewise data that the oxide concentrations were at maxima in both the organic and aqueous phases at stage 14, the feed stage. It is to be noted that in general the stagewise percentages of hafnium and zirconium progressively changed through the extractor. The minor deviations from this trend were probably caused by sample contamination or operative errors in analysis. This recovery of two high purity products from a binary mixture of roughly equal amounts of closely related compounds demonstrates the adaptability of this extractor to separations by countercurrent liquid-liquid extractions.

b. Separation of Small Amounts of Zirconium from Hafnium

Although removal of small amounts of zirconium from a mixture that is largely hafnium is not considered important industrially, it is employed here as a further demonstration of the applicability of these extractors to liquid-liquid purification processes. In this second multistage extraction only 15 stages of a 20 stage extractor were employed for making the separation. The liquid-liquid system used to effect the removal of the zirconium was the same as that employed in the multistage extraction above except for concentrations and flow rates.

The analysis of the inorganic salt mixture employed in preparing the aqueous feed solution gave about 3.2 w/o zirconium and 96.8% hafnium relative to their total weight. The feed contained the equivalent of 380 g. of the combined oxides per liter and was 3.16 molar in nitric acid. Twenty milliliters of feed was added at stage 7 for each cycle of operation.

A 3.14 molar nitric acid solution constituted the aqueous scrub liquid for this multistage extraction. For each cycle of operation 5.0 ml of this aqueous scrub was added at stage one. The organic phase, introduced at stage 15 at a rate of 25 ml per cycle, was a solution consisting of 40 volume per cent dibutyl ether and 60 volume per cent tributyl phosphate. This organic solution was also 2.68 molar in nitric acid.

Analysis of the products from every tenth cycle showed that essentially steady state conditions were reached at about the 40th cycle. The extraction was discontinued after 100 complete cycles and the phases from the odd numbered stages were analyzed. These stagewise data appear in Table 3 while Figure 8 indicates the variation of these analyses with stage number.

It is apparent from Table 3 that the aqueous phase product from stage 15 was about 99% hafnium while the organic phase product from stage one was 99.93% zirconium. Approximately 70% by weight of the total zirconium containing only 700 ppm hafnium was recovered in the organic phase product. The loss of hafnium in this organic product amounts to less than 0.002% of the total hafnium. Most of the zirconium remaining in the aqueous product phase could be recovered and a higher purity hafnium could be

obtained by a subsequent multistage extraction employing similar conditions. However, by properly varying the operating conditions, a more nearly quantitative separation could likely be affected in only one multistage extraction.

Table 3
Stagewise Data for the Second Zirconium and Hafnium
Extraction

Stage Number	Organic Phase		Aqueous Phase		E_{Zr}	E_{Hf}	β Separation Factor
	Grams Oxide/ Liter	% Zr	Grams Oxide/ Liter	% Zr			
1	10.8	99.93	22.2	98.9	0.491	0.0321	15.3
3	21.4	99.6	37.0	93.5	0.611	0.0337	18.2
5	25.1	92.9	52.5	47.5	0.878	0.0606	14.5
7Feed	34.1	51.5	340	2.82	1.71	0.0465	36.8
9	30.4	50.0	336	2.44	1.74	0.0432	40.1
11	28.5	51.8	340	2.53	1.60	0.0387	41.4
13	22.5	37.1	337	1.57	1.48	0.0405	36.7
15	18.1	31.3	321	0.95	1.79	0.0375	47.5

In the organic scrubbing section of the extractor, or stages 15 to seven inclusive, the relative flow rates were approximately five volumes of the aqueous phase to four volumes of the organic phase. The relative flow rates in the aqueous scrubbing section, stages one to six inclusive, were about four volumes of the organic phase to one volume of the aqueous phase. Figure 8 indicates that the greater over-all change in zirconium (and hafnium) percentage in either phase occurred in the aqueous scrubbing section of the extractor. According to the data in Table 3 the organic phase extracted considerable hafnium as well as zirconium in the feed stage. Although most of this hafnium was back extracted by the aqueous scrub solution in stages three to six, minor amounts remained in the organic product phase delivered from stage one. A larger relative volume of aqueous scrub would have decreased the amount of hafnium reaching stage one and increased the purity of the

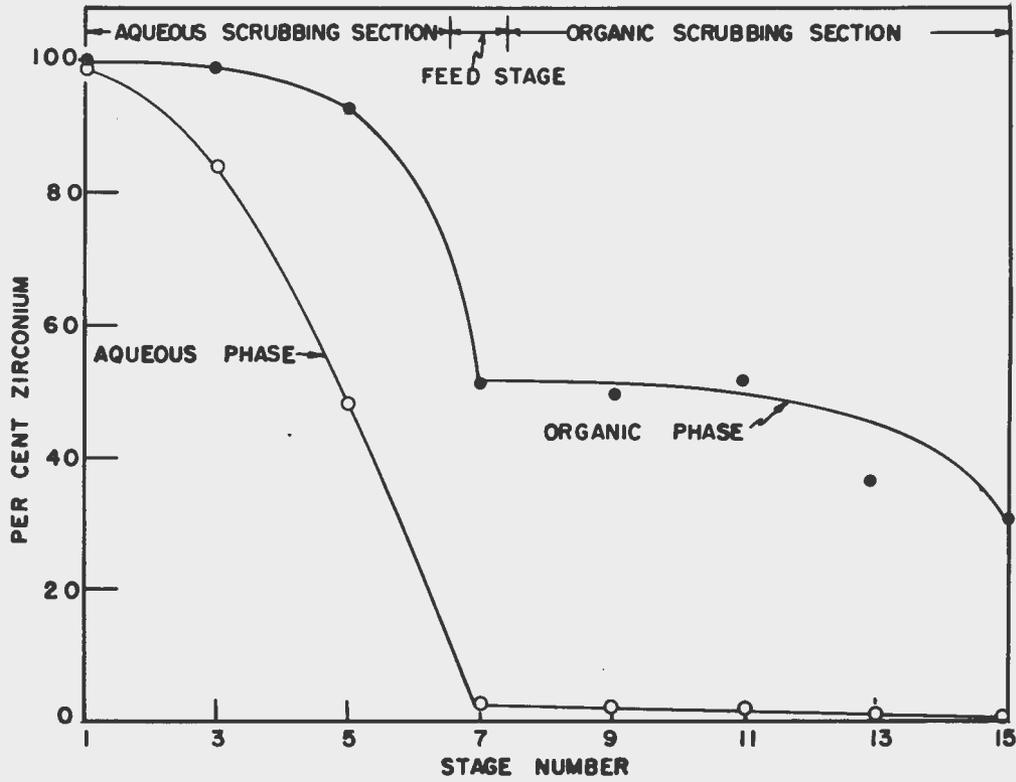


Fig. 8 - Plot of Analytical Data of Table 3.

zirconium delivered but the amount of zirconium recovered would have been less. Similarly a relatively larger volume of the organic phase would have increased the recovery of zirconium while decreasing its purity. Changes in the number of stages employed and in the position of the feed stage as well as variations in relative flow rates would have effectively altered the separations obtained by this extractor with this particular liquid-liquid system.

The distribution ratios for zirconium and hafnium, E_{Zr} and E_{Hf} respectively, and their separation factors also appear in Table 3. The distribution ratio here is the ratio of the total concentration of a constituent in the organic phase to its total concentration in the aqueous phase. The separation factor is defined as the ratio of the two distribution ratios for a stage in equilibrium. Large separation factors are desirable for making separations but proper mass distribution between the phases must also be considered.

It can be seen from Table 3 that the separation factors for the liquid-liquid system employed have considerably different values in the organic and aqueous scrubbing sections of the extractor. Since the acid concentrations in the respective solutions delivered to the extractor and in the corresponding solutions delivered from the extractor were essentially the same, it is assumed that there was no appreciable variation of acid concentration in either phase throughout these sections. The distribution ratio for zirconium in the organic scrub section appears then to be influenced by the presence of large amounts of hafnium. This particular extraction of zirconium from hafnium illustrates some of the operational data which can be readily obtained by employing an extractor of the design described here.

2. Separation of Tantalum from Niobium

Earlier work in this Laboratory (30) showed that tantalum could be readily separated from niobium by extractions involving their aqueous hydrofluoric acid solutions and certain immiscible organic liquids. Since this system contained free hydrofluoric acid it was not practical to use glass equipment for continued separation work. Therefore, other effective liquid-liquid systems for the separation of tantalum from niobium were developed in an effort to obtain conditions of extraction that would permit prolonged use of glass equipment.

It was found that tantalum could be easily extracted from an amine-hydrofluoric acid salt solution containing both niobium and tantalum. The addition of the amine to the hydrofluoric acid solution forms this salt and markedly reduces the attack of the solution on glass. A multistage extraction employing this resulting solution is used to further demonstrate the utility of extractors of the design presented here.

The aqueous feed solution was prepared by dissolving a mixture of niobic and tantalic acids in a minimum amount of concentrated hydrofluoric acid. After dilution with water this solution contained the equivalent of 130 grams of niobium and tantalum pentoxides per liter. A sodium hydroxide titration of an aliquot of this solution indicated acid equivalent to 4.06 moles per liter. Sufficient phenyl ethyl ethanolamine was added to the hydrofluoric acid solution of niobium and tantalum to saturate the solution. The resulting solution which had a pH of about 5 and a concentration equivalent to about 110 grams of niobium and tantalum pentoxide per liter constituted the feed solution for the multistage extraction. The oxide was composed of about 51% tantalum oxide and 49% niobium oxide relative to their total pentoxide weight. For each cycle of operation 10.0 ml of this aqueous feed solution was added at stage four. Only 10 stages of a 20 stage extractor were used in this experiment.

The aqueous scrub solution was diluted hydrofluoric acid which had been saturated with phenyl ethyl ethanolamine giving a fluoride salt concentration of about 0.5 molar and a pH value of about 4. Five milliliters of this solution was added per cycle at stage one. Pure diethyl ketone constituted the organic phase in this extraction and was introduced at stage ten at the rate of 30 milliliters per cycle.

The product phases for every fifth cycle of operation were analyzed for their total oxide contents and for relative percentages of the niobium and tantalum oxides. After 55 complete cycles the process was discontinued, the liquids collected from the stages and oxide analyses performed on both phases from each stage. In these analyses excess ammonium hydroxide was added to the aqueous and organic phases to precipitate niobium and tantalum. Acetone was also added to the organic phase to facilitate the precipitation and filtration. The precipitates were calcined at 600°C for at least two hours to form the pentoxides. The percentages of niobium and of tantalum oxides are expressed relative to their total oxide contents in the samples with all impurities disregarded. For samples containing between two and 98% tantalum oxide an x-ray fluorescence technique (31) was employed, while for less than two and above 98% tantalum oxide the spectrographic methods of Fassel and Krotz (32) were used.

The cycle analyses indicated that about 20 cycles were required to reach essentially steady state conditions. The data also showed that tantalum was not detected in the niobium of the aqueous product although the lower limit of detection of tantalum in niobium by the spectrographic method employed was about 300 ppm. This high purity of the niobium product is substantiated by the data for the aqueous phase of stages nine and ten in the stagewise analyses appearing in Table 4. The purity of these niobium oxide samples is seen to be 99.97% or better.

The cycle analyses showed that for the first 50 cycles of operation only about 100 ppm niobium oxide was present in the tantalum oxide from the organic product. However, the stagewise data of Table 4 indicate that the oxide delivered in the organic phase from stage one should have contained 0.054% (540 ppm) niobium oxide. A new supply of aqueous scrub was employed for the last few cycles of operation and it is possible that this scrub contained a small amount of niobium. A slight contamination of the scrub with niobium would also explain the lower percentages of niobium in both phases in stage two with higher niobium percentages in stage one. Since the laboratory is also used for other problems involving these elements this contamination is not unlikely. This contamination effect has been met previously in other work here in attempts to prepare very pure compounds; however, when special precautions were taken on recheck experiments it was found possible to eliminate these minor contaminations.

The data in Table 4 also show that the maximum oxide concentrations of both the aqueous and the organic phases were in stage four, the feed stage. It is also apparent that very little material was extracted into the organic phase in stages nine and ten. The over-all material balance, based on average analyses, concentrations and volumes of products indicated that the organic product phase from stage one and the aqueous product phase from stage ten contained about 51% and 49% respectively of the total weight as tantalum and niobium oxides.

Figure 9 shows the variation of the oxide composition, expressed as niobium pentoxide percentage, with stage number for both the organic and aqueous phases. It is apparent from the data that very little niobium transferred to the organic phase in any stage. Since the large variation in niobium percentage in the aqueous phase is due mainly to the distribution of tantalum to the organic phase, the separation then depends essentially on the selective transfer of tantalum. Consequently, the prime operation factor in this separation is the organic scrubbing of tantalum from the aqueous feed solution.

In this extraction an equivalent of approximately a 50-50 mixture of niobium and tantalum oxides was quantitatively separated into a tantalum oxide fraction containing 100 ppm niobium pentoxide and a niobium fraction spectrographically free of tantalum. This experiment further demonstrates the possibilities of this extractor for obtaining useful data on liquid-liquid extractions. For large scale separations of tantalum and niobium more economical liquid-liquid systems than the example presented have been developed in this Laboratory.

Table 4

Stagewise Data for the Niobium and Tantalum Extraction

Stage Number	Organic Phase		Aqueous Phase	
	Grams Oxide/Liter	% Nb ₂ O ₅	Grams Oxide/Liter	% Nb ₂ O ₅
1	19.0	0.054	10.8	0.84
2	15.8	0.030	40.9	0.080
3	18.8	0.17	47.2	1.78
4 Feed	19.8	0.24	51.2	64.0
5	5.27	0.50	47.0	72.3
6	2.24	1.42	40.2	90.0
7	1.20	*	38.4	97.5
8	0.97	*	37.5	99.1
9	0.038	*	36.1	<99.97
10	0.12	*	37.7	<99.97

*Insufficient sample for analysis by x-ray fluorescence; per cent Nb₂O₅ outside range for the spectrographic calibrations employed. Values for stages 8, 9, and 10 estimated at above 2.5% Nb₂O₅.

MODIFICATIONS OF THE EXTRACTOR

Several modifications in design have been made on the extractor presented above. Figure 10 is a schematic drawing which illustrates some of the modifications in a single stage. The stage shown here and the one presented in Figure 4 are quite similar. Essentially the only variations in design and operation of their multistage assemblies are connected with the removal of the light liquid phase from the mixer-settlers.

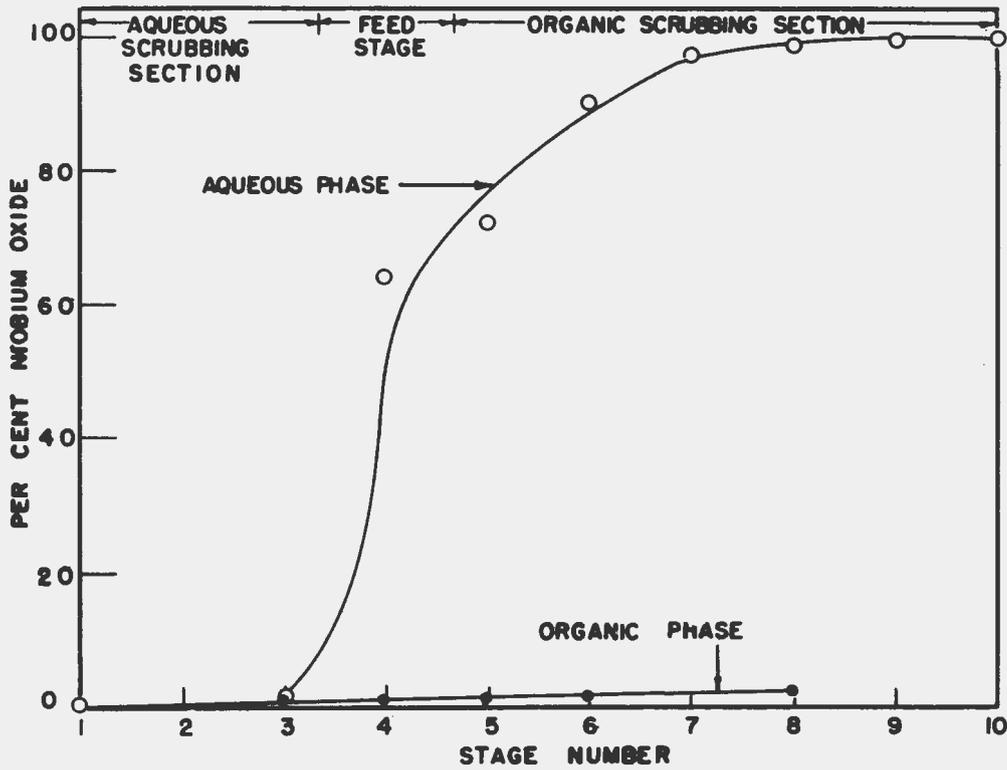


Fig. 9 - Plot of Analytical Data of Table 4.

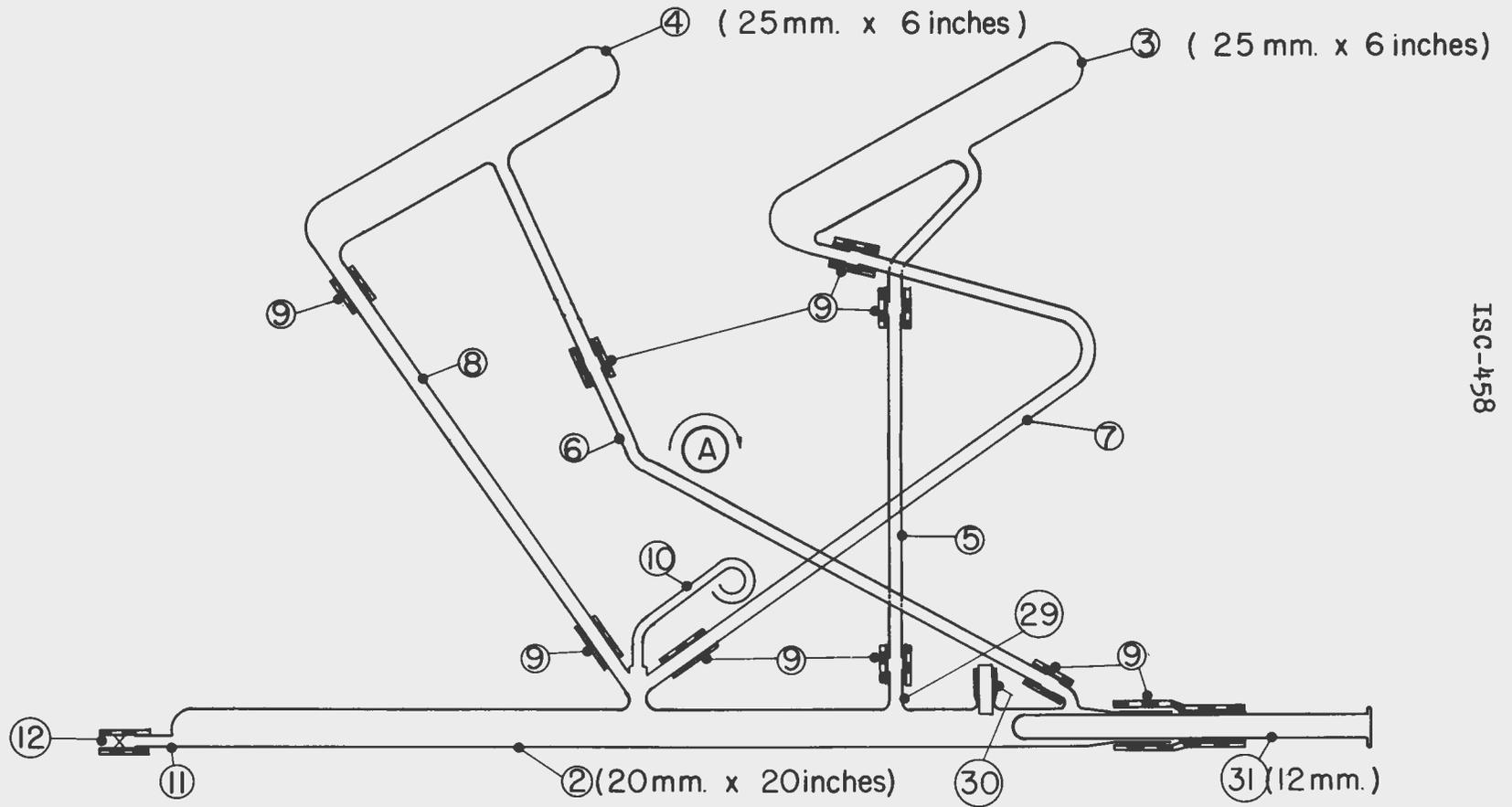


Fig. 10 - Design of a Single Stage, Adjustable Piston Type.

If we substitute for the single stage of Figure 5B, the design of stage shown in Figure 10, then the light liquid phase would be delivered from the mixer-settler tubes through the side arm, 29. The side arm, 30, is employed for delivery of the light liquid phase when the volume of the heavy liquid phase is small. For the extractor size presented here a volume of about five milliliters or less of the heavy phase requires the use of the side arm, 30. The side arm which is not in use is usually closed by a glass or plastic plug. It is evident from Figure 10 that for the use of side arm 30 an interchange of positions of plug and end connection of tube 5 is required.

The piston, 31, is adjusted through its sleeve joint, 9. This adjustment regulates the position of the liquid-liquid interface for proper flow of the light liquid phase to its reservoir. For small diameter (less than 24 mm) mixer-settler tubes this piston-type adjustment usually affords a better control of delivery of the phases to the proper reservoirs; however, for larger (greater than 24 mm) diameter mixer-settlers the adjustable open-tube type shown in Figure 4 has advantages.

Figure 11 shows a 20 stage piston type liquid-liquid extractor in a position corresponding to that of the open-tube type extractor shown in Figure 3. The procedure for starting and operating these two extractors is essentially the same. The first hafnium-zirconium extraction described above was carried out in the open-tube type extractor while for the second hafnium-zirconium extraction and for the niobium-tantalum extraction the piston type extractor was used.

Occasionally in liquid-liquid extraction work it is desirable to remove a portion of a phase at some intermediate stage. A special reservoir designed for this extractor permits this removal. The details for this tap-off reservoir appear in Figure 12. It can be seen in this figure that a tap-off volume control tube, 32, is inserted at the delivery end of the reservoir. This tap-off device consists essentially of a tube which by a sliding adjustment through its sleeve connection regulates the amount of liquid removed from the reservoir and the extraction system. A portion of either phase can be removed from any desired stage by merely substituting this special reservoir in place of a regular reservoir. The liquid which is removed from the extractor by means of a tap-off reservoir can either be delivered into a receiver collecting a product phase or into a special receiver. This device can be employed in extractions involving what is often referred to as reflux. The reflux takes place as that portion of the product solution stream not removed by the tap-off device passes on through subsequent stages where solute is extracted by the scrub liquid. This tap-off reservoir has been successfully employed in this Laboratory for obtaining on a continuing basis a portion of a phase from an intermediate stage containing desirable product. Some extractions might require more than one of these special reservoirs in one extractor.

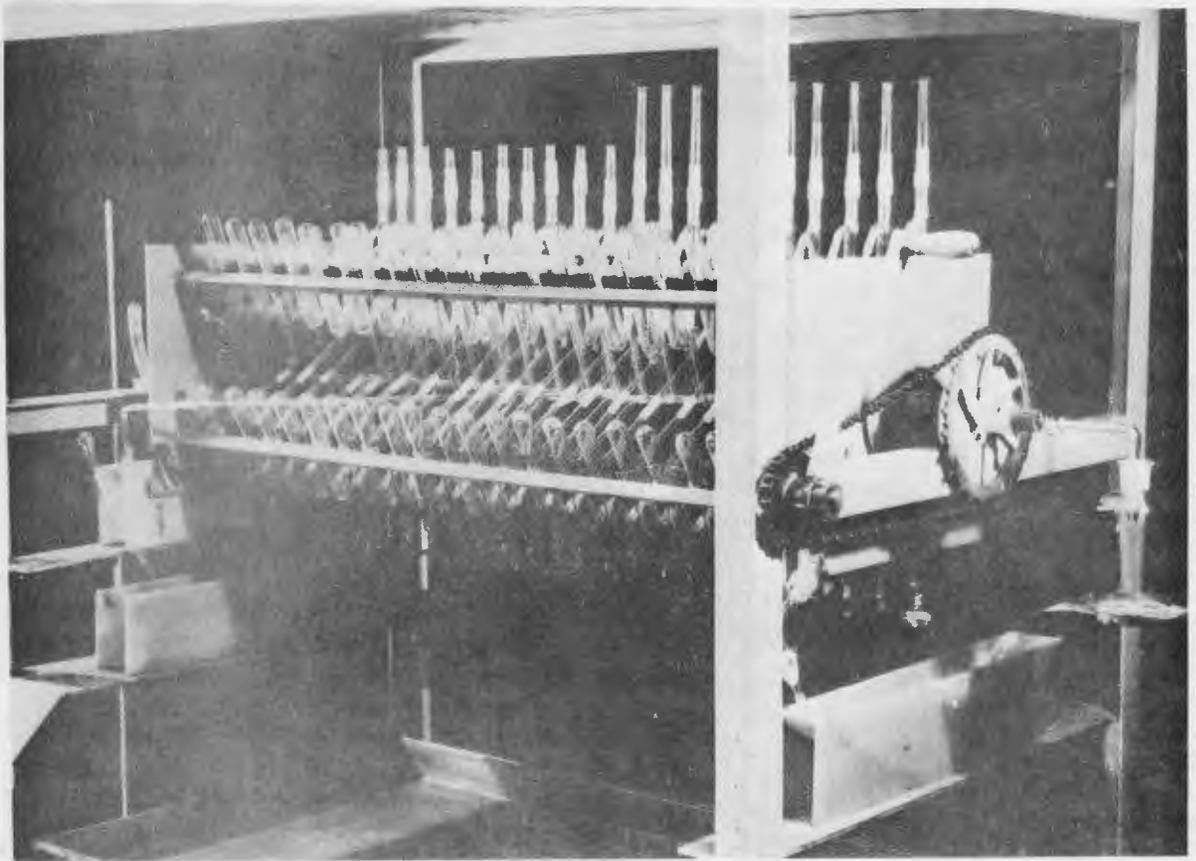
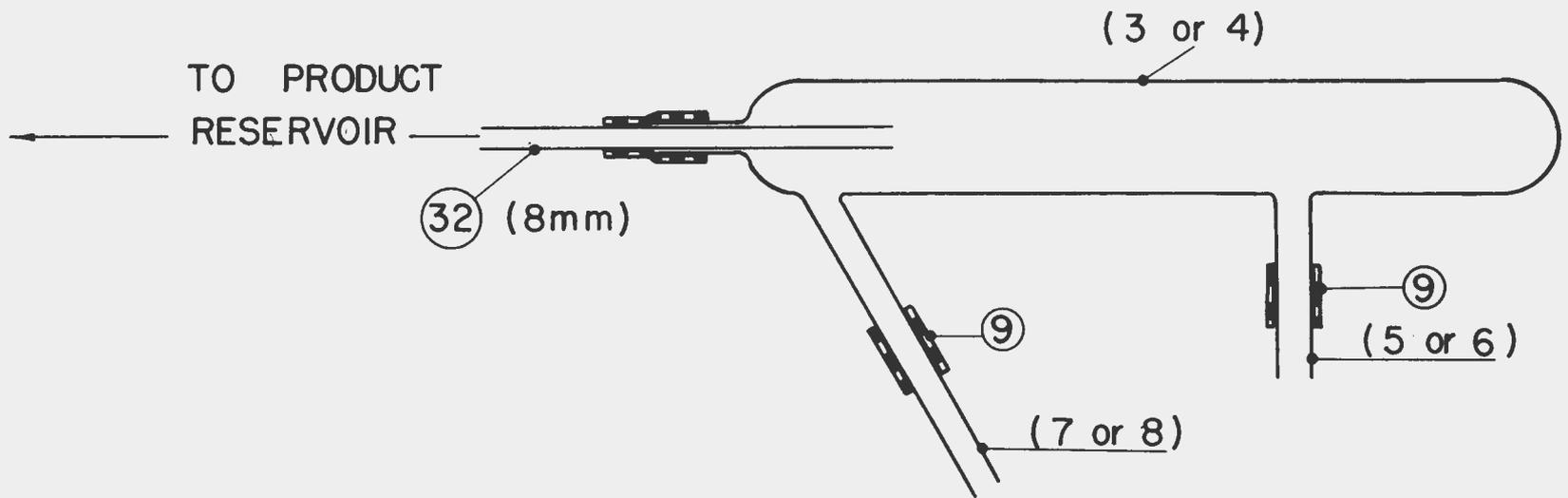


Fig. 11 - Twenty Stage Extractor with Adjustable Pistons.



ISC-458

Fig. 12 - Tap-Off Reservoir.

DISCUSSION

The extractor presented here has been demonstrated to give efficient operation in effecting separations by liquid-liquid systems. An analysis of the sequence of events in connection with the movements of the phases through the extractor shows that the operation and results are effectively those of a true multiple-contact countercurrent extractor. Since a phase portion moving into any one stage does not contact the portion of the other phase which earlier in the same cycle moved out of that stage, there arises a question as to the actual interpretation of the extraction pattern.

To clarify this matter, let us suppose that one employs all 20 stages of this extractor, and that the aqueous phase enters only at stage number 1 and leaves from stage 20, while the immiscible organic phase enters at stage 20 and leaves from stage 1. During the operation, each portion of aqueous phase that enters will, on succeeding cycles, be mixed with a portion of the organic phase in each of the 20 stages. Similarly each portion of the organic phase that enters the extractor will contact a portion of the aqueous in each stage. It is to be noted, however, that at any one time the portions of the aqueous and the organic phases in the odd numbered stages will not, on passing through the extractor, contact those portions of the opposite phases that are at that time in the even numbered stages and vice versa.

Consider a portion of aqueous phase that is at one time in stage number 1. This portion will contact the portions of organic phase that are at this time in stages 3, 5, 7, 9, 11, 13, 15, 17 and 19 when on further operation this particular portion of aqueous phase moves to stages 2, 3, 4, 5, 6, 7, 8, 9 and 10 respectively. The portions of organic phase to be contacted by this particular portion of aqueous phase when it passes through stages 11 to 20 inclusive are not yet in the extractor when this portion of aqueous phase is in stage number 1.

During the cycle that moves this aqueous portion from stage 1 to stage 2, a new portion of aqueous phase enters at stage 1. The new portion has the same number schedule for contacts with organic phase as was outlined above for the preceding portion of aqueous phase. This new aqueous portion will not, however, on passing through the extractor contact the same portions of the organic phase as the preceding portion of aqueous phase since on completing this cycle those portions of organic phase pointed out above all move to even numbered stages. In effect then the extractor operates as two supplementary countercurrent extractors, that receive and deliver liquids on alternate cycles. The net effect is that in this type of extractor an assembly employing mixer-settlers simulates a 20 stage continuous countercurrent extractor. A similar extractor

to be discussed in a later paper operates with all portions of the organic phase contacting all portions of the aqueous phase that pass through in a multicontact countercurrent liquid-liquid extraction. For similar systems the stagewise data have been found to be essentially identical when employing either type extractor.

The liquid-liquid extractors presented here can give effective separations and are applicable to the study of many liquid extraction problems. Larger capacity extractors of this type are in use in this Laboratory for preparing pure materials in quantity. Extractors of this design could also be constructed on a smaller scale for laboratory table use with smaller amounts of liquids. The lower limit of size would be determined by interfering capillary effects of the liquids in the tubing employed.

The design of this extractor permits its operation to be interrupted repeatedly at the convenience of the operator without losing continuity in an extraction. This allows samples to be taken of the phases in the stages and permits alterations in the extraction as desired.

In operation of this extractor it makes no difference which phase has the greater specific gravity. Extraction systems have been employed in this Laboratory in which sufficient carbon tetrachloride was added to tributyl phosphate to make the specific gravity of the organic phase greater than its contacted aqueous phase. The extractor functioned effectively in making separations with this type of system.

The phase separation time is a factor to be considered in the operation of any liquid-liquid extractor. For the extractor presented here it is especially important in determining the time required for a cycle of operation. Organic diluents have been found to be useful for decreasing the phase separation times. Any liquid-liquid system that upon mixing forms an emulsion which is not easily broken would be impractical to use in this extractor. Since phase separation time is usually the most time consuming step, its control is very important when considering the rate of product delivery or time required to carry out an experiment. The use of a 40 volume per cent dibutyl ether and 60 volume per cent tributyl phosphate organic solution for extracting zirconium from hafnium in a 6.0 molar nitric acid aqueous phase changed the phase separation time from 90 sec. for pure tributyl phosphate to 30 sec. for the mixed organic solvent phase. The initial aqueous and organic phases were mixed to about the same extent in both experiments. With a 30 sec. phase separation time a cycle can be completed easily in two minutes.

It is believed that the extractor presented here would be useful in research or quantity production in a great many problems involving separations, purifications or recoveries.

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REFERENCES

1. D. F. Peppard, J. F. Faris, P. R. Gray and G. W. Mason, *J. Phys. Chem.* 57, 294 (1953).
2. B. Weaver, F. A. Kappelmann and A. C. Topp, ORNL-1408 (1952).
3. A. C. Topp, ORNL-1409 (1952).
4. J. Bochinski, M. Smutz and F. H. Spedding, ISC-348 (1953).
5. L. C. Craig, *J. Biol. Chem.*, 150, 33 (1943).
6. L. C. Craig, G. H. Hogeboom, F. H. Carpenter and V. DuVigneaud, *J. Biol. Chem.*, 168, 665 (1947).
7. R. E. Cornish, R. C. Archibold, E. A. Murphy and H. M. Evans, *Ind. Eng. Chem.*, 26, 397 (1934).
8. Y. Sato, G. T. Barry and L. C. Craig, *J. Biol. Chem.*, 170, 501 (1947).
9. E. H. Ahrens and L. C. Craig, *ibid.*, 195, 299 (1952).
10. *Ibid.*, 195, 763 (1952).
11. A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, 35, 91 (1941).
12. C. E. White and H. Rose, *Anal. Chem.*, 25, 351 (1953).
13. E. M. Larsen and G. Terry, *J. Am. Chem. Soc.*, 75, 1560 (1953).
14. R. L. VonBerg and H. F. Wiegandt, *Chem. Eng.*, 59, No. 6, 189 (1952).
15. G. H. Morrison, *Anal. Chem.*, 22, 1388 (1950).
16. L. C. Craig, *ibid.*, 21, 85 (1949); 22, 61 (1950); 23, 41 (1951); and 24, 66 (1952).

17. H. M. Irving, *Quart. Revs.*, 5, No. 2, 200 (1951).
18. U. S. Mareello and N. Poffenberger, *Ind. Eng. Chem.*, 42, 1021 (1950).
19. E. L. Compere and A. Ryland, *Ind. and Eng. Chem.*, 45, 1682 (1953).
20. L. C. Craig, *J. Biol. Chem.*, 155, 519 (1944).
21. L. C. Craig and O. Post, *Anal. Chem.*, 21, 500 (1949).
22. L. C. Craig, W. Hasmann, E. H. Ahrens and E. J. Harfenist, *ibid.*, 23, 1236 (1951).
23. G. H. Lathe and C. R. Ruthen, *Biochem. J.*, 49, 540 (1951).
24. M. R. Fenske and B. R. Tegge, *U. S. Pat.* 2,580,010.
25. E. M. Nadel and F. Highhouse, *Chemist Analyst*, 43, No. 1, 25 (1954).
26. K. A. Varteressian and M. R. Fenske, *Ind. and Eng. Chem.*, 28, 1353 (1936).
27. H. A. Wilhelm, (a) ISC-155 (Jan. 24, 1951), (b) ISC-144 (May 1, 1951), (c) ISC-203 (March 31, 1952).
28. H. A. Wilhelm, K. Walsh and J. V. Kerrigan, *Patent Application Serial Number 382,496*, (August 18, 1953).
29. (a) V. A. Fassel and C. H. Anderson, *J. Opt. Soc. Am.*, 40, 742 (1950).
(b) V. A. Fassel and L. Gray, forthcoming publication from this Laboratory.
30. H. A. Wilhelm, L. Cass and J. V. Kerrigan, *ISC-220* (March 10, 1952).
31. W. J. Cambell and H. F. Carl, *Anal. Chem.*, 26, 800 (1954).
32. V. A. Fassel and L. Krotz, forthcoming publication from this Laboratory.