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RADIOCHEMICAL SEPARATION OF CADMIUM AND THE APPLICATION OF VACUUM DISTILLATION OF METALS TO RADIOCHEMICAL SEPARATIONS

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RADIOCHEMICAL SEPARATION OF CADMIUM AND THE APPLICATION OF VACUUM DISTILLATION OF METALS TO RADIOCHEMICAL SEPARATIONS

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ABSTRACT

The purpose of this research was to evaluate and develop radiochemical separation procedures of the elements. Radioactive tracer techniques were used to measure the degree of separation of the desired element from a large number of elements, which have been selected on the basis of their being representative of the groupings in the periodic table.

An evaluation of the radiochemical separations of cadmium was made by studying the separation by solvent extraction with dithizone in basic media, by ion exchange in hydrochloric acid solution, and by two precipitation methods, one with a complex inorganic precipitant, (Reinecke salt) and the other with an organic precipitant [2-(o-hydroxyphenyl) benzoxazole]. The separation by dithizone and ion exchange resulted in a yield of cadmium of 78% with decontamination factors of 10^3 for twenty elements. Although the organic precipitant appeared to be selective for cadmium, a poor separation was obtained as a result of occlusion of the contaminants on the gelatinous, flocculent precipitate. In contrast to this, the precipitate of cadmium Reineckate was very crystalline, and a separation of cadmium with a yield of 78% and decontamination factors of 10^3 for fifteen elements was obtained.

In order to determine the feasibility of radiochemical separations by vacuum distillation of the elemental state, an exploratory evaluation of the method was made. A simple vacuum distillation apparatus

was designed which consisted of a carbon rod furnace heated by induction. The apparatus produced an equilibrium pressure of 6×10^{-4} mm. of Hg after five minutes of evacuation. The radioactive distillate was collected on Teflon film which was wrapped around a liquid nitrogen cold finger.

The bimetallic systems Cd-Zn, and Cd-Ag were studied in order to measure the degree of separation of cadmium that could be obtained by distillation from various atom ratios of cadmium to zinc or silver. The separation that was observed with these metal systems was compared with the theoretical degree of separation when it was assumed that an ideal solution existed, and the discrepancy between theory and experiment was discussed.

Separation procedures which were evaluated include the separation of trace amounts of mercury by chemical reduction onto a copper foil with subsequent distillation of the mercury, and by electrolysis of cadmium (1 mg.) onto copper foil (or into a mercury cathode with volatilization of the macro mercury) followed by distillation of the cadmium. For the separations of cadmium the radiochemical reduction step resulted in limited separation; however, the distillation step improved the overall separation so that it was possible to obtain a degree of separation which was comparable to that which was obtained in the separations by extraction and ion exchange. The radiochemical reduction of mercury was selective in itself, and the distillation of the mercury resulted in an overall separation of mercury with a yield of at least 72% and decontamination factors of 10^4 for twenty elements.

A very useful application of the vacuum distillation technique was found in the separation of a volatile carrier free daughter from a macro amount of a less volatile parent metal, such as the separation of indium 113m from neutron irradiated tin. From this type of system, vacuum distillation can provide a method for preparing very thin high specific activity counting sources.

CHAPTER I

INTRODUCTION

In this age of world-wide interest in the radioactive atom, whether it be in the study of the radioactive fallout from atomic bombs or of the fission products of a nuclear reactor, considerable interest has evolved about the separation of this total resultant activity into its constituent parts. These separations are primarily for the purpose of aiding in the study of the radiation from a pure radioactive nuclide, and in the yield distribution of the products of a nuclear reaction. Ideally each individual nuclide with a given mass and atomic number would be separated from every other nuclide. Nuclides of a given atomic number (isotopes) can be physically separated by a mass spectrograph or can be electronically discriminated by observing radiation characteristic of and exclusive to each nuclide (e.g., beta particle or gamma ray spectometry). Chemistry can, of course, also be used to separate isotopes in the case of the low atomic number atoms due to the change in reaction rates with a change in mass number (isotope effect).

Radiochemical separation, which is the separation of the nuclides of different elements by virtue of their different chemical properties is to be considered in this thesis.

There are many possible applications of radiochemical separations. Through fission of uranium or plutonium many radioactive fragment nuclides are formed. The separation and characterization of these fission products constitutes a very large segment of nuclear research at the present time. In addition, there are a large number of other nuclear reactions which produce products that must be separated from the reactants in order to be studied. When analyzing for a trace constituent by activation analysis, other elements which also activate must frequently be removed to facilitate quantitative measurement of the activities associated with the amounts of each element.

The separation of a given radioactive element in a highly pure state enables one to use the element in various tracer experiments. As a side application, the high degree of purity obtainable through a combination of radiochemical procedures should be of interest to the transistor industry and others, where high purities are required.

This research continues a program of investigation of the radiochemical separations of the elements which was initiated in this laboratory. Since the radiochemical separations of cadmium are of general interest in fission product analysis, a detailed evaluation of the radiochemical separations of cadmium was made.

While studying the radiochemistry of tin, interest was directed toward the general method of separation by distillation. An investigation of the literature revealed that little attention has been paid to the application of distillation to radiochemical separations. In particular, the vacuum distillation of metals seemed to be very promising. Therefore, an exploratory investigation was conducted on the application of vacuum distillation of metals to the radiochemical separation. It is intended that this work will indicate new potentialities for the use of vacuum distillation as a radiochemical separation of the metallic elements.

CHAPTER II

RADIOCHEMICAL SEPARATIONS

A. Definition of a Radiochemical Separation

A radiochemical separation is the separation of radioactive atoms by virtue of their different chemical characteristics. Because of the high sensitivity of the counting instruments used to detect radioactivity, very small amounts of foreign activity can interfere in the measurement of the desired activity. Therefore, high purity which is greater than that which one routinely encounters in a quantitative analytical procedure is required. Many of the radioactive atoms (nuclides) which one encounters are short lived (minutes or hours) and the separation procedure must be rapid enough to assure a sufficient yield of the desired activity. In order to gain high purity of the desired activity in the shortest length of time, usually some of this activity is lost during the separation, and consequently less than quantitative separations are obtained. This creates no difficulty as long as the yield and its reproducibility are known.

Usually a radiochemical separation procedure is derived from either known facts about the analytical and physical chemistry of the element in question, or from a standard analytical procedure which has been used in the quantitative analysis of the inactive element. The radiochemical procedures are then built up from this information to conform to the requirements of the radiochemical separation. This requires a considerable amount of experimentation in the laboratory to find a set of conditions which will result in an optimum radiochemical separation.

B. Types of Radiochemical Separation

Two classes of separation are encountered which differ in the form of the desired activity after separation. The activity may be in the carrier free state (C.F.) which means that the specific activity disintegrations per unit time per unit weight of the total element present) is at a maximum. The usual units for specific activity are millicuries per milligram (3.7×10^7 disintegrations per second per milligram). Counters which are ordinarily used (Geiger-Muller, proportional, or scintillation well counter) do not count all of the disintegrations, but only a known percentage of them (called counting efficiency). Often one uses the unit of a quasi-specific activity which is counts per minute per milligram. This nomenclature for specific activity has the disadvantage of not being general from one counter to the other.

The highest specific activity which can be obtained by a given nuclide is the carrier free state in which all of the atoms of the particular element in question are radioactive. It is desirable to maintain the highest possible specific activity in a radiochemical separation, since it is difficult to increase it after it has once been lowered by dilution with inactive atoms.

The activity may also be present in a large amount (mg.) of the same inactive element (lower specific activity than C.F.). This may be the result of deliberately adding a given amount of inactive element (called carrier) to effect a separation.

To separate the desired activity in either class (carrier or carrier free) one has to transfer the desired radioactive atoms away from the undesired ones. When carrier is added the problem is simple.

The element can be precipitated as an insoluble compound or reduced to the elemental state and filtered to carry out the separation.

This cannot be done in the case of carrier free activity. Some sort of "carrying medium" must be supplied to effect the transfer of the activity. Many well known systems are used to do this, e.g., extraction into a water immiscible organic liquid, ion exchange onto a solid exchanger, electrolysis, or a type of surface effect such as surface adsorption, coprecipitation, or post precipitation of the activity on a macro amount of precipitate (often called scavengers in radiochemistry). It is, of course, also possible to use the methods of separation which are outlined for the carrier free state with the carrier state.

A carrier free separation which does not use a carrying medium in effecting the separation is the vacuum distillation of metals which will be presented in Chapter IV.

C. Evaluation of a Radiochemical Separation of an Element

Several of the more promising radiochemical separations or quantitative inactive analytical procedures reported in the literature were taken into the laboratory for experimental evaluation. The evaluation of the radiochemical separation was done in the following way:

The yield of the desired activity and the degree to which it can be separated from those radioactive elements which would be expected to contaminate (e.g., those which have similar chemical behavior) were studied. This is done by the use of radioactive (tracer) atoms of each element concerned. Only one element present in the mixture to be separated was made radioactive (tagged) in any given experiment. After conditions have been adjusted to give an optimum separation, the radiochemical separation was further evaluated to determine the degree of separation of the desired constituent from a large number of other elements.

Selection of the basic contaminating elements was made to gain a good representation of the elemental groups in the periodic table. Particular emphasis was placed on other additional elements which would be expected to contaminate by virtue of their chemical similarity. Table I gives a complete list of all of the tracer solutions which have been used in these evaluations of radiochemical separations. The list of basic contaminating elements which are used in these evaluations are denoted with an asterisk. The specific activity of the nuclide which is shown in parenthesis (middle column) is that value for the radioisotope as obtained from Oak Ridge National Laboratory before the nuclide has decayed appreciably.

Table II has been prepared in order to indicate the procedure used to form those isotopes which were produced in the University of Michigan Phoenix Reactor. The metal targets which are listed in Table II have been obtained from the following sources:

Gold	Hardy and Harman, New York, N.Y., Spectroscopic Analyzed 99.99% pure
Cadmium	Johnson, Matthey & Co., Limited 73/83, Hatton Gorden, London, E.C.I.
Copper	Baker & Adamson, Reagent (1621), Allied Chemical and Dye Corp., New York, N.Y.
Indium	Indium Corporation of American, Utica, N.Y., 99.9% pure

TABLE I

CHEMICAL CHARACTERISTICS OF TRACER SOLUTIONS

	Isotope	Source	Final Solution and (specific activity mc/gm)	For Carrier Tracer Exchange	Used as
1*	Ag^{110m}	ORNL $AgNO_3$ in HNO_3	3 $\underline{M}$ HNO_3 (300)	thorough mixing	Ag (I)
2	Au^{198}	Au metal irrad. in Michigan reactor	0.5 $\underline{M}$ HCl, 1.5 $\underline{M}$ HNO_3 (5)	a	Au(III)
3*	Ba^{140} La^{140}	ORNL $BaCl_2$ in HCl	1 $\underline{M}$ HCl (C.F.)	thorough mixing	Ba(II) La(III)
4	Bi^{210}	Atomic Energy of Canada, Ltd.[b]	0.1 $\underline{M}$ HNO_3 (C.F.)	a	Bi(III)
5*	Ce^{144} Pr^{144}	ORNL $Ce(NO_3)_3$ in HNO_3	3 $\underline{M}$ HNO_3 (C.F.)	thorough mixing	Ce(III) Pr(III)
6	Cd^{115m}	ORNL $CdCl_2$ in HCl	1 $\underline{M}$ HCl (400)	thorough mixing	Cd(II)
7*	Co^{60}	ORNL $CoCl_2$ in HCl	1 $\underline{M}$ HCl (400)	thorough mixing	Co(II)
8*	Cs^{134}	ORNL CsCl in HCl	0.1 $\underline{M}$ HCl (C.F.)	thorough mixing	Cs(I)
9*	Cr^{51}	ORNL $CrCl_3$ in HCl	0.2 $\underline{M}$ HCl (32,700)	thorough mixing	Cr(III)
10	Cu^{64}	$Cu(NO_3)_2$ irrad. in Michigan reactor	$Cu(NO_3)_2$ in H_2O (1)	a	Cu(II)
11*	Hg^{203}	ORNL $Hg(NO_3)_2$ in HNO_3	3.0 $\underline{M}$ HNO_3 (66)	thorough mixing	Hg(II)
12*	I^{131}	ORNL NaI in $NaHSO_3$	H_2O (C.F.)	thorough mixing	I(-I)
13	In^{114m}	ORNL $InCl_3$ in HCl	0.5 $\underline{M}$ HCl (90)	thorough mixing	In(III)
14*	Ir^{192}	ORNL $IrCl_6^{-3}$ in HCl	0.2 $\underline{M}$ HCl (98,000)	Ir oxidized with Cl_2 reduced with $NH_2OH \cdot HCl$	Ir(III)
15	Ni^{65}	Ni metal irrad. in Michigan reactor	0.1 $\underline{M}$ HNO_3 (0.2)	a	Ni(II)
16	Pd^{109}	Pd metal irrad. Michigan reactor	0.05 $\underline{M}$ HCl (0.2)	a	Pd(III)
17*	Ru^{106} Rh^{106}	ORNL $RuCl_3$ in HCl	2.0 $\underline{M}$ HCl (5000)	thorough mixing	Ru(III)
18*	Se^{75}	ORNL H_2SeO_3 in HCl	1.0 $\underline{M}$ HCl (250)	thorough mixing	Se(IV)
19*	Sb^{124}	ORNL $SbCl_3$ in HCl	3.0 $\underline{M}$ HCl (2900)	oxidize Sb^{+3} to Sb^{+5} with Br_2; reduce to Sb^{+3} again with hydrazine	Sb(III)
20	Sn^{113} In^{113m}	ORNL $SnCl_2$ in HCl	3.0 $\underline{M}$ HCl (7)	oxidize in excess NaClO	Sn(IV)
21*	Ta^{182}	ORNL $K_8Ta_6O_{19}$ in KOH	2.0 $\underline{M}$ KOH (4900)	HF with heat	Ta(V)
22*	Tl^{204}	ORNL $TlNO_3$ in HNO_3	1.0 $\underline{M}$ HNO_3 (160)	reduce with $NaHSO_3$[c]	Tl(I)
23*	Zn^{65}	ORNL $ZnCl_2$ in HCl	1.0 $\underline{M}$ HCl (1000)	thorough mixing	Zn(II)
24*	Zr^{95} Nb^{95}	ORNL Complex in oxalic acid	0.5 $\underline{M}$ oxalic acid (C.F.)	thorough mixing	Zr(IV) Nb(V)

(a) No additional carrier used.

(b) Bi^{210} is a decay product of Pb^{210} which was obtained as one millicurie per pound of $Pb(NO_3)_2$. The Bi^{210} was separated by extraction of a water solution of $Pb^{210}(NO_3)_2$ at pH- 2.5 into 0.5 $\underline{M}$ thenoyltriflouroacetone (TTA) in benzene, and then was back extracted into 0.1 $\underline{M}$ HNO_3.

(c) Excess of reducing agent must be present in order to assure that Tl remains in the +1 state.

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TABLE II

ISOTOPES PRODUCED IN THE UNIVERSITY OF MICHIGAN PHOENIX REACTOR

Isotope	Form of Target	Time^c irradiated at 10^{12} neut./cm^2/sec	Specific Activity mc./gm.	To Form Tracer Solution
Au^{198}	metal	2.5 hours	5	dissolve in hot aqua regia
Cd^{115m}	metal	120 days	0.3	dissolve in 1 $\underline{M}$ HNO_3
Cu^{64}	metal	6 hours	1	dissolve in 1 $\underline{M}$ HNO_3
In^{114m}	metal	60 days	3	dissolve in HBr^a
Ni^{65}	metal	1.5 hours	0.2	dissolve in 3 $\underline{M}$ HNO_3
Pd^{109}	metal	6 hours	0.2	dissolve in hot aqua regia
$Pt^{197,199}$	metal	4 days	2	dissolve in hot aqua regia
Se^{75}	metal	20 days	3	dissolve in $HNO_3{}^b$
Sn^{113}	metal	5 months	0.1	dissolve in HBr^a

(a) A radiochemical separation procedure used for purification, see Sunderman and Meinke(75)

(b) Dissolve the selenium metal in hot concentrated H_2SO_4. Pour the green solution into water to precipitate metallic selenium, wash and filter. Dissolve precipitated metal into a small amount of concentrated HNO_3.

(c) The days listed are operating days which comprise a period of about 7 hours operation per day.

Nickel	International Nickel Co., Inc., Bayonne, N.J., 99.997% pure
Palladium and Platinum	American Platinum Works, Newark, N.J., 99.9% pure
Selenium	Johnson, Matthey & Co. Limited, Spectrographic Standard
Tin	Baker and Adamson, Reagent (2390), Allied Chemical and Dye Corp., New York, N.Y.

All of the isotopes which have been used in the tracer experiments have been checked for radiochemical purity on a gamma scintillation spectrometer (see Chapter IV, Section C).

All of the radioisotopes which are listed in Table I and II were counted in a scintillation well counter with the exception of Tl^{204}. The absolute counting efficiency (defined as a factor which is multiplied by the disintegrations per minute to give the counts per minute in the counter) varies with the energy of the incident gamma ray for a given geometrical position relative to the scintillator. However, in these tracer experiments the same radioisotope is counted before and after the separation. Since the ratio of the activity before separation to the activity after separation is measured, the counting efficiency cancels. (See definition of decontamination factor, Chapter V). Therefore, the counting efficiency of a scintillation well counter is only important when it is so small that the sensitivity of the tracer experiment is lowered. The counting efficiency of a scintillation counter for a pure beta particle emitter (such as Tl^{204}) is very low and it is good practice to count it with a Geiger-Muller counter.

The advantages of a scintillation well counter over a G-M or proportional counter are found in the practical consideration involved in the experimental procedure. The sample is placed in the bottom of a glass test tube. Care is taken not to contact the sides of the counting tube with the activity. This tube is then inserted into a lusteroid protective tube which is inserted into the well in the scintillator. This well type of scintillator which is used for this work(76,77) is commercially available. This system affords an easily reproduced geometry ($< 0.5\%$) with respect to the scintillator. The same reproducibility can be obtained with the Geiger-Muller or proportional counter if special equipment is used and if the sample is in solution. It is usually quite difficult to obtain reproducible mounting of solid samples.

Some of the radioisotopes which are used have a radioactive daughter. Use of these radioisotopes requires in some cases a special procedure to gain decontamination information from them. In the case of Ce^{144} ($t_{1/2} = 280d$) which decays to Pr^{144} ($t_{1/2} = 17m$) much information can be gained by counting the tracer in equilibrium before separation, and then following the decay after separation. If the activity decays with the half life of Pr^{144} then the contamination is due to Pr^{144}. If it stays constant (2 hrs.) both Ce^{144} and Pr^{144} contaminate. If the decay curve indicates that both are present, it is usually possible to estimate the contamination due to each.

Unlike the above case, in Ba^{140} - La^{140} the chemical characteristics of barium and lanthanum are significantly different, and usually separation of the Ba^{140} from the La^{140} is necessary before the tracer experiment is done. The same applies to the system Zr^{95} - Nb^{95} because Nb^{95} has a half life of 90 hours, and thereby, the decay study becomes too time consuming. In the case of Ru^{106} - Rh^{106} it is not possible to determine the contamination of the Rh^{106} because it has too short a half life. (30 seconds) The decontamination data are then reported as due only to Ru^{106} with that of Rh^{106} unknown. The Sn^{113} - In^{113m} is allowed to reach equilibrium after separation (400 min.) before it is counted so that only the activity resulting from Sn^{113} contamination is measured.

CHAPTER III

RADIOCHEMICAL SEPARATIONS OF CADMIUM

A. Review of Literature on the Radiochemistry and the Radiochemical Separations of Cadmium

Separations of cadmium are gaining increased use as a result of interest in the fast fission reaction. While cadmium is of rather low yield in the thermal fission process, the yield increases significantly in the fast fission reaction.

There are several good reviews in the literature on the inorganic and analytical chemistry of cadmium.(28,46,71,30) In addition there are two general reviews of radiochemical separation methods which list the applications of these methods to cadmium.(59,21)

In attempting to modify quantitative analytical procedures so as to be useful in radiochemical separations it is helpful to consider the general chemistry which may be applied to the radiochemistry of cadmium. A thorough search of the literature has been made in order to determine the previous radiochemical separations, and the inactive quantitative separations which have been used for cadmium. This review is compiled by this author in a National Research Council Bulletin.(13)

B. Selection and Discussion of Radiochemical Methods to be Studied

A list of the nuclides of cadmium is given in Table III. A maximum time of separation for any given separation step was placed at thirty minutes since this time is sufficiently less than the half life of most of the cadmium nuclides which are of interest.

TABLE III

ISOTOPES OF CADMIUM

Isotope	Half Life	Type of Decay[1]	Method of Preparation[2]
Cd^{104}	59m	EC	
Cd^{105}	55m	EC, β^+, γ	$Pd^{102}(\alpha,n)Cd^{105}$ (33)
Cd^{106}	6×10^{16}y	-	1.22%
Cd^{107}	6.7h	EC 99% β^+ 0.3%	$Cd^{106}(n,\gamma)Cd^{107}$
Cd^{108}	-	-	0.88%
Cd^{109}	470d	EC	$Cd^{108}(n,\gamma)Cd^{109}$
Cd^{110}	-	-	12.4%
Cd^{111m}	48.6m	IT, γ	daughter of In^{111}(0.01%) $Cd^{110}(n,\gamma)Cd^{111m}$
Cd^{112}	-	-	24.07%
Cd^{113m}	5.1y	IT, β^-, γ	$Cd^{112}(n,\gamma)Cd^{113m}$ fission product
Cd^{113}	-	-	12.26%
Cd^{114}	-	-	28.86%
Cd^{115m}	43d	β^-, γ	daughter of Ag^{115}(9%) $Cd^{114}(N,\gamma)Cd^{115m}$ fission product
Cd^{115}	53h	β^-, γ	daughter of Ag^{115}(91%) $Cd^{114}(n,\gamma)Cd^{115}$ fission product
Cd^{116}	$> 10^{17}$y	-	7.58%
Cd^{117m}	3h	IT, γ	daughter of Ag^{117} fission product
Cd^{117}	50m	β^-, γ	daughter of Ag^{117} $Cd^{116}(n,\gamma)Cd^{117}$
Cd^{118}	50m	β^-	fission product
Cd^{119}	10m	β^-	--

[1] For detailed decay and reference to the data in this table see reference 74.
[2] Only a few of the common sources are listed here. This column also lists percent abundance of the stable isotopes.

Cadmium is not easily separated radiochemically pure, and most procedures involve time consuming sulfide precipitations.(5,44,86) Because of this, standard analytical methods were studied with a view towards modifying them for use as a radiochemical separation step.

From the information taken from the literature which is given above, four analytical quantitative separation procedures were modified so as to be useful in a radiochemical separation method and were then evaluated. These are two precipitation methods, an ion exchange and an extraction method of separation.

Many organic reagents have been used in the gravimetric determination of cadmium. Most of these suffer from a lack of specificity and selectivity. A reagent which is rather selective is 2-(o-hydroxyphenyl) benzoxazole.(49,84) A study was made of this reagent to determine its effectiveness in a radiochemical separation. Another selective precipitant for cadmium is Reinecke salt (ammonium Reineckate), $NH_4[Cr(NH_3)_2(CNS)_4]$. This reagent has been known for many years but only recently has it been used(61) with thiourea as a precipitant for cadmium. In view of its ability to separate cadmium from zinc this precipitant was also evaluated.

Very few radiochemical separations of cadmium have used solvent extraction techniques. In the literature there are, however, a large number of quantitative analytical methods which separate cadmium by solvent extraction with subsequent determination by colorimetric means for trace quantities or gravimetric analysis for semi-micro quantities. Saltzmann reports(63) that dithizone (diphenylthiocarbazone) extraction gives sufficient purity of cadmium for spectroscopic use while Sandell(64,65) has discussed in detail the use of dithizone in the analysis of rocks. The application of this extractant to high specific activity tracer solutions was studied in detail.

Kraus and Nelson(36) have indicated that cadmium can be separated from many elements by anion exchange. This procedure was also evaluated using high specific activity tracers.

C. Apparatus, Reagents, and Procedures

Apparatus. The apparatus used in these series of experiments is identical with that described previously by Sunderman and Meinke(76,77) with the addition of a glow transfer scaler, Model 162 A, made by the Atomic Instrument Company, Cambridge, Mass. Use of this instrument with the scintillation well counter made it possible to count up to one million counts per minute with less than 0.5% "coincidence" error.

Reagents.

Ammonium Reineckate, $NH_4[Cr(NH_3)_2(SCN)_4].H_2O$, Eastman Kodak reagent No. 3806, Solution, 4 gms/100 ml. water.

Anion exchange resin AG2-X8, 200-400 mesh, Bio-Rad Laboratories, Berkeley, Calif. Stored in 6 M hydrochloric acid until used.

Chloroform, commercial grade unpurified.

Dithizone (diphenylthiocarbazone), Eastman Kodak reagent No. 3092. Stock solution, 750.0 mg./100 ml. chloroform; working solution; dilute with chloroform to 0.75 mg./ml.

Hydrion pH paper (12-13.5).

2-(o-hydroxyphenyl)benzoxazole, $C_{13}H_9O_2N$, (HPBZ), Eastman Kodak reagent No. 6754. 0.1 gm. in 135 ml. of 95% commercial grade ethyl alcohol.

Thiourea, CSN_2H_4, Merck USP. Solution 5 gms./100 ml. water.

All other nonradioactive chemicals were of analyzed reagent grade. The preparation of most of the carrier solutions has been described previously [Table 1, Reference (76)]. All additional carriers used here (cadmium, zinc, mercury, thallium, indium) were made by dissolving their nitrate salts in water to give 10 mg. of the element per ml. of solution as Cd^{+2}, Zn^{+2}, Hg^{+2}, Tl^{+1}, and In^{+3} respectively.

The tracers which were used in these experiments are listed in Table I (Chapter II)

Procedures.

Dithizone Extraction Procedure. Add 1 ml. sodium tartrate solution (20%) to the extraction vessel. Add tracer of cadmium (for yield measurements), or add tracer of the contaminating element (without carrier) to measure decontamination, and dilute with distilled water. Adjust the pH to 13-13.5 with dilute sodium hydroxide using Hydrion pH paper. Total volume should be 10 ml. Add 10 ml. of dithizone solution and stir for two minutes. Draw off the chloroform layer into exactly 10 ml. of 0.1 M hydrochloric acid. Stir for two minutes, count aliquot of acid layer in well counter. Total time of separation is 10 minutes.

Anion Exchange Procedure. Equilibrate anion exchange column with 3 M hydrochloric acid. Pass tracers of the cadmium for yield measurements or tracers of the contaminating ion (without carrier) for decontamination measurements in 10 ml. of 3 M hydrochloric acid through the column. Wash with 10 ml. of 3 M hydrochloric acid. Elute with 0.1 M ammonium hydroxide. Discard the first one half ml. and collect the next 3 ml. of elute. Total time of separation is 15 minutes.

Reinecke Salt Precipitation. Add 10 mg. of carrier and tracer of the contaminating ion to a 15 ml. centrifuge cone and take the necessary steps to secure exchange. Add 10 mg. of cadmium carrier (as well as cadmium tracer when determining yield) and 2 ml. of thiourea solution (see discussion). Add 5 ml. of 2 M hydrochloric acid and dilute to 10 ml. Stir and add 2.5 ml. of Reinecke salt solution (see discussion). Stir for five minutes, centrifuge for five minutes, and remove supernate by a suction tube.(77) Wash the precipitate by adding 10 ml. of 1% thiourea solution in 1 N hydrochloric acid and stir for five minutes. Centrifuge and remove the supernate as before. Slurry the precipitate into a tube for counting in the well counter. Total time of separation is 30 minutes.

2-(o-hydroxyphenyl)benzoxazole(HPBZ) Precipitation. Add 10 mg. of carrier and tracer of the contaminating ion to a 40 ml. centrifuge cone and take the necessary steps to secure exchange. Add 10 mg. cadmium carrier (plus tracer when determining cadmium yield). Add 3 gms. of solid ammonium tartrate, heat to 60°C. Dilute with 20 ml. of distilled water, and adjust pH to 13 ± 0.5 with Hydrion paper, using sodium hydroxide. Heat again to 60°C and recheck pH. Slowly add 5.5 ml. of HPBZ, and stir for five minutes at 60°C. Centrifuge for five minutes and remove the supernate by suction. Dissolve the precipitate in hydrochloric acid, aliquot into a counting tube and count in well counter. Total time of separation is 28 minutes.

D. Discussion and Results

Yields of cadmium for the four procedures and decontamination factors (see definition in Chapter V) for a large number of tracer impurities are listed in Table IV. No carriers were added for the solvent extraction and anion exchange procedures, whereas 10 mg. amounts of cadmium and contaminants were present for the precipitation steps. In the ion exchange procedure where carrier was not added the decontamination factor obtained will vary with the amount of contaminant present (see Chapter V). Therefore, the weight of the elements used in the decontamination tests have been recorded in Table IV.

The 43 day Cd^{115m} was used in these experiments. Although this isotope decays by only 2% gamma emission, the bremsstrahlung from the high energy beta particles constituting the remainder of the decay is sufficient for this isotope to be measured with sufficient sensitivity in the scintillation well counter.

Extraction. Dithizone is known to react with a great many of the heavy metals, but cadmium is almost unique in being able to form a stable dithizonate in strongly basic solution. Charlot and Bezier(7) have included a graph of percent extraction vs. pH for most of the heavy metals which form dithizonates. The separation procedure outlined above has evolved from this information and experiments in the laboratory.

Of the twenty-three elements listed in Table IV only silver, copper, thallium and zinc contaminate the separation. Presence of 1 M ammonium hydroxide in the original solution satisfactorily complexes the silver preventing contamination, but contamination by the other three elements is not affected. When the basicity is increased to 0.5 M sodium hydroxide, the copper decontamination factor is increased to about 10^3. The increased basic strength often reduces the strength of the dithizonate bond. This is probably caused by increased solubility of the dithizone

TABLE IV

DECONTAMINATION FACTORS FOR CADMIUM SEPARATIONS[a]

Tracer	Extraction (No carrier added)[b]	Ion Exchange (No carrier added)[b]	Precipitation	
			(Carrier added)[c] Reinecke Salt	2-(o-hydroxyphenyl) benzoxazole
Cd^{115m}YIELD (%)	77 ± 1.7 (7μg)	80 ± 1.6 (7μg)	78 ± 1.5	80 ± 1.8
Ag^{110m}	50 (0.2mg)	1.1 (0.2mg)	1	25
Au^{198}	250 (0.5mg)	-	-	-
Ba^{140}	10^3 (C.F.)	3×10^3 (C.F.)	1.7×10^3	-
Bi^{210}	10^4 (C.F.)	-	-	-
$Ce^{144}Pr^{144}$	5×10^3 (5.6μg)	10^4 (3μg)	3×10^3	20
Co^{60}	3×10^3 (3.7μg)	1.4×10^4(3.7μg)	2×10^3	1.3
Cr^{51}	10^3 (0.7μg)	5×10^3(0.3μg)	5×10^2	25
Cs^{134}	1.2×10^3 (0.3μg)	1.4×10^4(0.3μg)	120	9.1
Cu^{64}	7.6 (4mg)	-	-	-
Hg^{203}	10^3 (26μg)	2.8 (26μg)	2.2	-
I^{131}	1.7×10^3 (C.F.)	10^3 (C.F.)	140	10
In^{114}	200 (0.1mg)	300 (16μg)	10^3	-
Ir^{192}	10^3 (0.003μg)	6.7×10^3 (0.003μg)	1.2×10^3	1.1
La^{140}	10^3 (C.F.)	3×10^3 (C.F.)	1.7×10^3	-
Ni^{65}	1.1×10^3 (17mg)	-	-	-
Nb^{95}	10^3 (2μg)	3×10^3 (2μg)	2.5	-
Pd^{109}	10^3 (15mg)	-	-	-
Ru^{106}	3×10^3 (2μg)	3.4×10^3 (1μg)	360	1.3
Sb^{124}	5×10^2 (0.6μg)	22 (0.6μg)	33	9.1
Se^{75}	10^4(3.5μg)	10^4(1.5μg)	1.08	17
Sn^{113}	300 (0.2mg)	300 (0.2mg)	120	20
Ta^{182}	170 (5μg)	2×10^4 (5μg)	1.7×10^3	10
Tl^{204}	1.1 (0.12mg)	1.4×10^4 (0.4mg)	1	25
Zn^{65}	1.6 (36μg)	1.3 (90μg)	170	12.5
Zr^{95}	10^3 (2μg)	3×10^3 (2μg)	2.5×10^3	

(a) Average of duplicate runs except for cadmium which is an average of quadruplicate runs. Errors are standard deviations.

(b) Weight of inactive element prior to separation indicated in parentheses.

(c) 10 mg. Cd, 10 mg. contaminant carrier added.

in the basic aqueous layer, thereby displacing the equilibrium toward dissociation of the dithizonate. Unfortunately the yield of cadmium is also reduced to about 50% by this step.

The contamination of thallium can be conveniently removed by utilizing a displacement reaction.(63) An equal volume of a solution made up with 0.1 gm. of cobalt nitrate, 5.0 gm. sodium acid tartrate, and 4.0 gms. sodium acid carbonate in one liter of water is agitated with a chloroform solution of the cadmium and thallous dithizonate. The cobalt displaces the thallium to form the dithizonate, but the cobalt will not displace cadmium. This procedure, therefore, results in a removal of the contamination by inactive cobalt. Subsequent removal of the cadmium in 0.1 M HCl results in removal of cadmium but very little inactive cobalt. The decontamination factor obtained from thallium by this method is 120 with a yield of Cd of 65%. Unfortunately, this displacement did not occur with zinc.

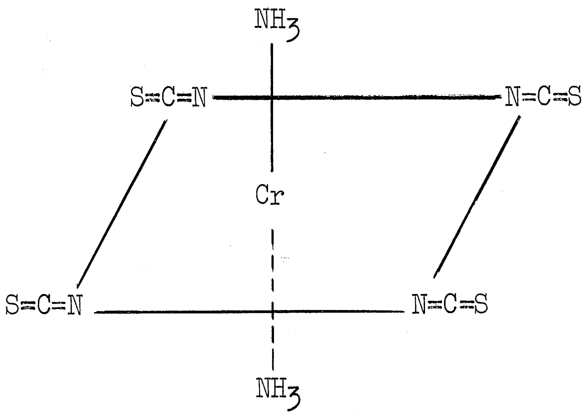
In many cases the radiochemist is interested only in pure activity. The presence of even large amounts of inactive foreign ions is unimportant. Therefore, this method of selective displacement of a persistently contaminating ion should be of use in many radiochemical separations by solvent extraction.

Ion Exchange. Since cadmium forms very slightly dissociated chloride complexes the anion exchange separation was of interest. Kraus and Nelson(36) have reviewed this method, while Hicks and coworkers(29) specifically tried Dowex II resin with a wide variety of elements in a hydrochloric acid media. The cadmium chloride complex will be held very strongly while many metals which do not form complexes can be washed through the column with dilute hydrochloric acid.

Experimental decontaminations from eighteen tracers are listed in Table IV. As would be expected all of those cations which form even moderately undissociated complexes with chloride ion remain on the column at high chloride ion concentration. The high acid concentration was used to prevent hydrolysis of cations which would then adsorb on the column and elute over a wide volume of eluant, causing contamination. Special care must be taken in the case of thallium to insure that it is all present in the +1 state. This is accomplished by heating the solution with 0.1 M sodium bisulfite.

Ion exchange can be used to separate zinc, mercury and silver from cadmium by replacing the ammonium hydroxide eluant with distilled water. In this case the water acts as a true chromatographic eluant. The impurities elute in the first 6 free volumes, while the cadmium does not elute until 9 free volumes have been collected. In this modified procedure the yield of cadmium was found to be about 55%, with a decontamination factor of 100, 200, and 330 for zinc, mercury and silver respectively.

Reinecke Salt Precipitation. The structure of the Reineckate anion is shown below:(78)



Most commonly the cadmium ion is complexed with thiourea (increasing the size of the cation) before precipitating the Reineckate. Cadmium as well as mercury and copper have been successfully precipitated without the thiourea, but a distinct advantage is derived by the complexation. A suitable colorimetric method has been used by Mahr(42) for these three elements using Reinecke salt. The manner in which the cadmium dithiourea complex cation is chemically bound to the Reineckate anion is believed to be closely related to the ionic type of bond.(61)

The effects of variation of the concentration of the thiourea, pH, amount of Reinecke salt added, and number of washes of the precipitate for the separation of cadmium from zinc is shown in Table V. The addition of too much thiourea (6.9%) evidently results in the formation of a complex with zinc and it contaminates the separation by forming a precipitate with the Reineckate anion. The decontamination data for 19 elements are listed in Table IV. Silver and thallium undoubtedly precipitate as the chloride. The use of nitric acid for these elements does not, however, improve the separation because they, along with mercury, also form insoluble Reineckates. Selenium is found to be reduced by the thiourea to the metallic state. Removal of thiourea will lower the contamination of selenium, but at the same time the overall decontamination factor may decrease because of the loss of crystallinity in the precipitate.

With thiourea the cadmium precipitate is rose in color and is very granular and crystalline, a fact which substantiates the postulated ionic structure. Ammonium Reineckate when dissolved in distilled water, slowly decomposes on standing to give the greenish blue chromium ammonium complex. Thus a solution of the ammonium Reineckate (5 ml. of 4 gm/100 ml.)

TABLE V

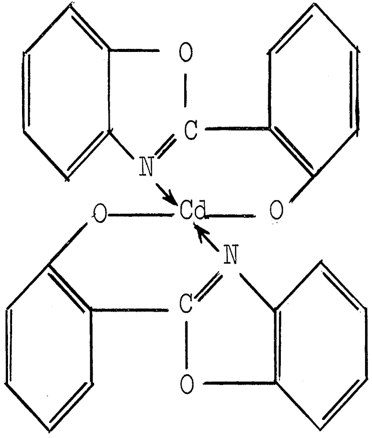
YIELD DATA FOR PRECIPITATION SEPARATIONS OF CADMIUM
(Ammonium Reineckate = R); (2-(o-hydroxyphenyl)benzoxazole = HPBZ)

Precipitating Solution	Condition Varied	Decontamination Factor of Zinc	Cd Yield Est. (%)
1.75 ml. of 4% solution of R;	pH 4 (HCl)	10^2	50
1% thiourea	pH 3 (HCl)	110	50
	pH 2 (HCl)	125	50
	pH 0 (HCl)	170	50
4% solution of R at pH 3;	1.75 ml. R	110	50
1% thiourea	2.5 ml. R	125	80
2.5 ml. of 4% solution of R; pH 3;	6.9% thiourea	4.8	70
	2.7% thiourea	55	70
	1.0% thiourea	71	70
	0.8% thiourea	59	70
2.5 ml. of 4% solution of R; ph3; 1% thiourea	0 wash (1% thiourea)	67	70
	1 wash (1% thiourea)	500	60
	2 wash (1% thiourea)	2.5×10^3	60
5.5 ml. of 1% HPBZ;	pH 9	1.2	90
10% $(NH_4)_2C_2O_4$	pH 10	1.7	90
	pH 12	12.5	90
	pH 13	12.5	90
5.5 ml. of 1% HPBZ;	5 gms. $(NH_4)_2C_4H_4O_4$/100 ml.	5.3	90
pH 13	10 gms. $(NH_4)_2C_4H_4O_4$/100 ml.	9.1	90
	15 gms. $(NH_4)_2C_4H_4O_4$/100 ml.	12.5	90
1% HPBZ; pH 13; 15%	5.5 ml. HPBZ	12.5	90
$(NH_4)_2C_2O_4$	4.0 ml. HPBZ	25	60
	2.5 ml. HPBZ	50	40
5.5 ml. of 1% HPBZ;	0 wash (ammoniacal ethyl alcohol)	12.5	90
pH 13; 15% $(NH_4)_2C_2O_4$	1 wash (ammoniacal ethyl alcohol)	25	90
	5 wash (ammoniacal ethyl alcohol)	25	90

- -

was unable to precipitate 10 mg. of cadmium in 5 ml. of water 72 hours after preparation. The precipitation was quantitative, however, if the reagent was used during the first 24 hours after preparation and if a 10% excess of reagent was used.

HPBZ Precipitation. Cadmium presumably forms a complex similar to the structure below:



Cadmium 10 mg/ml will not be precipitated by HPBZ at a pH less than two nor in a concentration of base of greater than 1.0 M NaOH. In order to use this precipitant the easily hydrolyzable metals were complexed with ammonium tartrate. The separation of cadmium from zinc was used to measure the systematic variation of the pH, amount of "HPBZ", concentration of ammonium tartrate, temperature of the precipitation, and time of stirring on the efficiency of separation (Table V). The large increase in the decontamination factor above a pH of 10 is probably due to the increasing amount of tartrate anion formed with increasing pH.

As seen from Table IV the decontamination factor is small for all elements. With the exception of cobalt and ruthenium the small decontamination factor is probably due to occlusion and surface adsorption. This is indicated by the fact that washing the precipitate with ammonical 50% ethyl alcohol increased the decontamination factor for zinc from 12.5 to 25, but continued washing of the same precipitate did not further increase this value. Heating the precipitate at 60°C for five minutes reduces the gelatinous nature of the precipitate, and facilitates centrifugation.

Combination of these separation steps can provide a procedure to suit many types of samples. Table VI shows the overall decontamination which could be obtained if the extraction, ion exchange and Reinecke salt precipitation separations were conducted in that order. The least separation is that from silver. Extraction is the only one of the three procedures which gains any separation from silver, so that a single repetion of this separation step could give a decontamination factor of 10^4. The same applied to the Reinecke salt separation from zinc.

This work has been published in a more concise form.(14)

TABLE VI

TYPICAL RADIOCHEMICAL DETERMINATION OF CADMIUM

Cd, Ag, Ba, Ce, Co, Cr, Cs, Hg, I, In, Ir, Ru, Sb, Se, Sn, Ta, Tl, Zn, Zr

1. Add 1 ml. tartrate solution
2. Adjust pH to 13 with NaOH. Total volume 10 ml.
3. Add equal volume dithizone in $CHCl_3$; stir for 2 minutes
4. Re-extract with equal volume 0.1M HCl; stir for 2 minutes

Decontamination factors:
1-10 Zn, Tl
10-10^2 Ag
10^2-10^3 Cr, Hg, In, Ir, Sn, Ta, Zr, Ba, Sb
10^3-10^4 Ce, Co, Cs, I, Ru, Se

Dithizone extraction of cadmium — Yield 77%

5. Add concd. HCl until solution 3M HCl
6. Pour through Dowex II column; wash with 10 ml. 3M HCl
7. Elute with 0.1M NH_4OH; discard first 0.5 ml. Collect next 3 ml.

1-10 Zn
10-10^2 Ag
10^3-10^4 Hg, Sb
10^4-10^5 In, Sn, Tl
10^6-10^7 Cr, I, Ir, Ru, Ta, Zr, Ba
10^7-10^8 Se, Cs, Co, Ce

Anion exchange separation of cadmium — Yield 62%

8. Add 10 mg. of carriers of Cd and contaminating ions
9. Add 0.1 g. of thiourea in solution. Also add HCl and dilute to make 10 ml. of 1M HCl
10. Add Reinecke salt solution. Stir for 5 minutes
11. Centrifuge for 5 minutes; remove supernate
12. Wash ppt. with 10 ml. 1% thiourea in 1M HCl. Stir for 5 minutes
13. Centrifuge and remove supernate

10^2 Ag
10^2-10^3 Zn
10^3-10^4 Hg
10^4-10^5 Tl, Sb
10^6-10^7 Sn
10^7-10^8 Se, In
10^8-10^9 Ru, I
10^{10}-10^{11} Ta, Zr, Ir, Cs, Cr, Co, Ce, Ba

Reineckate precipitation of cadmium — Yield 48%

14. Mount precipitate for counting with Geiger tube or dissolve in hot 3M HCl and count in scintillation well counter

CHAPTER IV

APPLICATION OF VACUUM DISTILLATION OF METALS TO RADIOCHEMICAL SEPARATIONS

A. Introduction and Review of the Literature

The principle of separation of inactive substances by distillation is a very useful one. In spite of the fact that industrial non-radiochemical methods have been employed successfully in countless examples for many years (e.g., fractionation of organic compounds), very limited work has been done on the radiochemical separation by distillation. The vacuum distillation of metals was found to be desirable for this exploratory experimentation for reasons which will be discussed below.

A limited amount of interesting work has been done in the radiochemical separations by vacuum distillation. Sherwin(69) has reported that it is possible to separate Sr^{90} from its daughter Y^{90} (as the carrier free chloride) by vacuum distillation using a unique apparatus which has a counter within the distillation apparatus. Decontamination factors for Y^{90} of 10^4 were found. There are a large number of examples of separation of the non-metallic elements and the chloride compounds of the elements by distillation. The separation of polonium has been done by vacuum distillation.(19) Other carrier free separations involved the distillation of cadmium isotopes from a bombarded Ag target.(1,32) In this case the cadmium is evaporated and collected on a suitable surface. For compounds a good compilation of these methods with an extensive bibliography is given in Wahl and Bonner, Table 6-D.(83)

Kidson and Elsdon(35) have devised a procedure in which an irradiated platinum target is purified from gold isotopes by volatilizing the lower boiling gold. Radioactive lithium(4) can be volatized from a number of other elements (Al, Ba, Cu, Mg, and Si). Weinstein, <u>et al</u>.(85) discuss the selective evaporation of K, Tl, Ni, Ba, Zn, Cd, and Bi.

There are other investigations which use radioisotopes as a means of tracing the effect of a distillation phenomenon. Frauenfelder(23) has used isotopes to determine surface processes occurring on the vapor condensing surface. In this paper one of the first suggestions was made pertaining to the application of vacuum distillation of metals for the radiochemical separation of the shortlived nuclides.

The investigation of the degree of concentration of volatile impurities from a non-volatile matrix of solid material has been done with the use of radioactive impurities.(6,20). By heating the base material to 0.55 to 0.60 of its melting temperature (°C), almost quantitative volatilization of the more volatile impurities have been observed. In some cases it has been found convenient to transform the matrix to the oxide to decrease its volatility.

Radioactive tracers have also been used to measure the vapor pressure of metals and other substances of low volatility which require a sensitive technique.(48)

In addition, Merines(47) has found that vacuum distillation is very suitable for the preparation of homogeneous even layers of radioactive substances which can be used as standard counting samples.

There are a large number of references dealing with the development of commercially feasible vacuum distillation processes. Kroll(37,38,39) has presented a very complete review of the application of vacuum distillation to the separation of metal alloys on a commercial scale. Other good references reviewing vacuum distillation of metals are References (67) and (81). One of the most common industrial procedures which uses vacuum distillation is the evaporation of alloys containing zinc.(10,55,3,79) In addition, some work has been done on the separation of Pb and Sn.(52,67)

Preuss(53) has measured, by the use of radioactive tracers, the degree of separation that can be obtained from the commercially adaptable vacuum distillation of some alloys.

Another recent application of the vacuum distillation involves the distillation of trace amounts of metals from large amounts of the base metal.(41,54,80) This is analagous to the method of concentration of trace impurities for subsequent spectrographic analysis.(25,34,87) From this work pertaining to industrial processes and the limited amount of work which has been done using radioactive metals, an exploratory evaluation of the application of vacuum distillation of metals to radiochemical separations has been made.

B. General Discussion of the Vacuum Distillation of Metals

The vapor pressure of a metal follows the Clausius-Clapeyron expression:

$$\log p = \frac{-\Delta H}{2.3\ RT} + C$$

where

ΔH = heat of vaporization,

R = ideal gas constant,

T = temperature, °K,

C = constant.

A list of the temperatures for various partial pressures of the elements is given in Table 3.8 of Reference (57). Some of these data appear in Figure 1 in which the logarithm of the vapor pressure (P) is plotted against the reciprocal of the absolute temperature (°K). If ΔH is not a function of the temperature but remains constant, the plot should give a straight line. Within the sensitivity of the plot a straight line was obtained. The temperature range is above 200 °K where the heat capacity for most of the metals does not change appreciably with further increase in temperature. It can be seen from Figure 1 that the best separations for a given metal takes place at the low temperatures. This is one reason why it is advisable to conduct the distillation in a vacuum. The vacuum enables a significant amount of the metal to evaporate at a lower temperature in a shorter period of time. There are a number of factors which tend to lower the degree of separation. These will be discussed later.

There are many factors which must be considered when designing a suitable vacuum evaporation system. One has to consider the species of metal vapor. It is possible to work with ions, atoms, and clusters of atoms. If ions are produced the vapor stream can be very conveniently controlled almost in any desired direction by a magnetic field. Also, an oppositely charged surface acts as a very efficient collector. The problem of forming these ions is a rather difficult one. Many attempts have been made to do this by intersecting, in perpendicular paths, an atomic beam with a high speed electron beam. In most cases, however, only a few percent of the atomic beam becomes ionized.

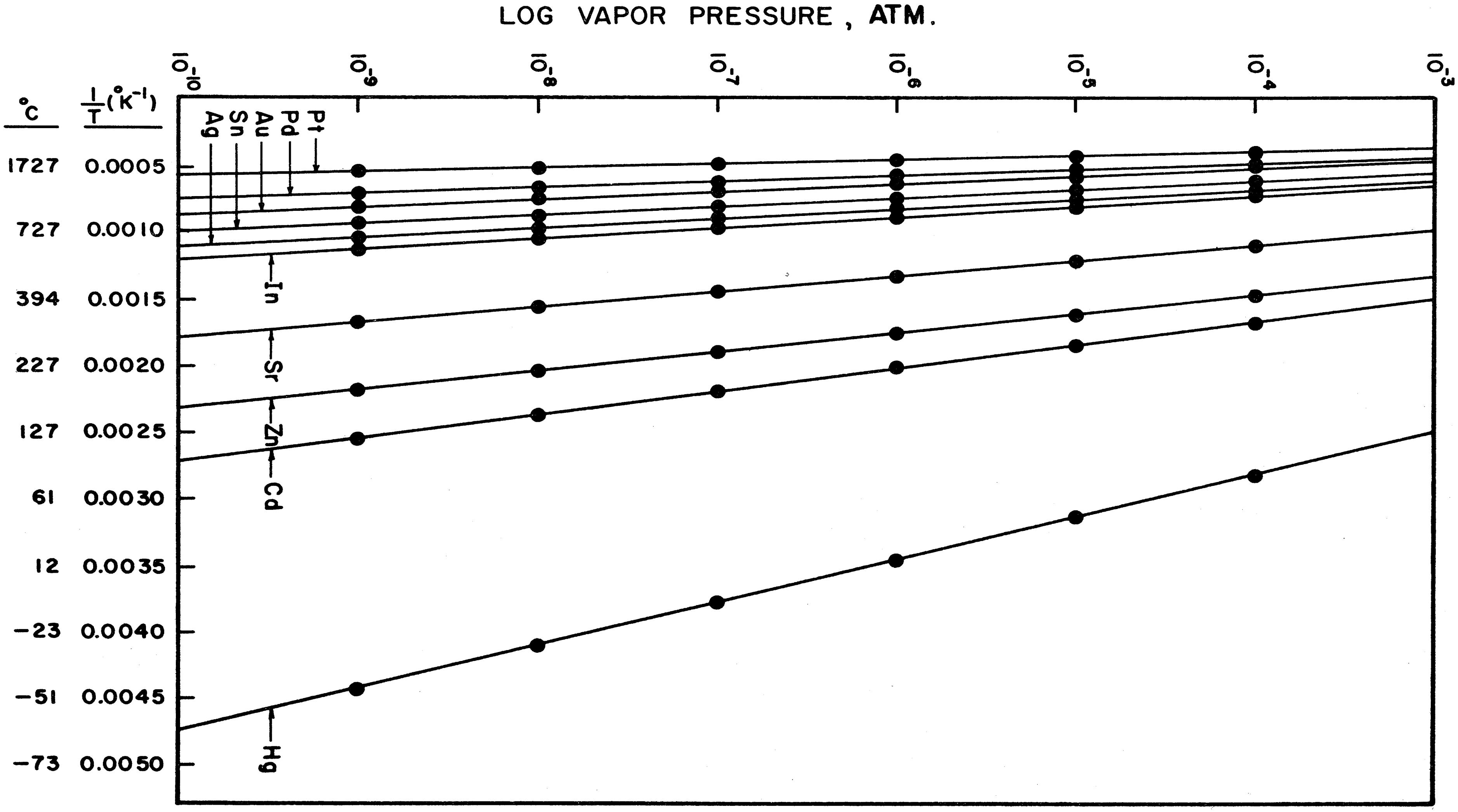


Figure 1. Logarithm Vapor Pressure of Metal vs. Reciprocal of Absolute Temperature.

Using the uncharged atom results in a difficult but at least feasible method of handling the distillate. The problem of the trajectory of the atoms after vaporization is an important one. Ramsey in his book on molecular beams(58) has a good discussion of this problem. There exists a certain amount of angular distribution of the atoms from the evaporated sample. The intensity of the atoms varies directly with the cosine of the angle (θ) between the perpendicular and the plane of the orifice which have slit jaws of negligible thickness. Therefore, one must design the equipment to collect at least 80-90% of this total beam integrated over the angle θ. An important assumption in this angular dependency is that the slit width be very much less than the mean free path of the atoms. This removes the possibility of secondary collisions, and therefore presents added necessity for operating the evaporation in a vacuum.

There are many methods of heating the metal charge to the desired temperature. The most direct method is to wrap a tungsten wire into the form of a helix which makes a basket onto which berylium oxide or alundum is baked.(51) The basket, which accommodates the charge, is then heated by electrical resistance. This procedure has also been used successfully with a tantalum boat.(62) Another useful type of material is carbon.(17,60) It has a low vapor pressure at the experimental temperatures. (< 1100 °C)

Another useful method of heating is to use an induction coil external to the evacuated apparatus. The induced current in the furnace heats by electrical resistance. A large number of designs for induction heaters are presented in the literature.(26,43,70)

Another important consideration in obtaining a relatively constant vacuum in a short time is the degree of outgassing which the furnace undergoes at the operating temperature. It is desirable to have the furnace made of a material which will not outgas when the charge is being evaporated.

Once the atoms in the solid have been converted to the vapor state another series of problems involving the collection of the vapor become important. There are a number of collection methods that can be used. If the atomic or molecular vapor is allowed to impinge upon a tungsten wire heated to at least 2500 °C, the atom or molecule becomes a positive ion. It can then be collected on a negative plate.

This method is restricted to only a few elements such as the alkali metals and a few others such as indium and gallium.(58) A similar application as mentioned above utilizes a high speed electron beam with a cathode collector. This gives the same increased application of the method to elements such as silver and gold.

A much more simple system uses the principle of condensation of the neutral atoms on a cooled uncharged surface. As early as 1924, it was recognized that there exists a critical temperature above which no visible deposit forms, and a critical intensity of the atom beam below which there is no deposit.(15,22,24) Cockroft(9) found that the critical temperature while dependent upon the type of atom or molecule condensing, was independent of the kind of condensing surface. He attributed this to the adsorption of a gas on the surface. Considerable understanding of this process was brought about by Appleyard(2), Levinstein(40), and Stahl(72) who studied the properties of thin films of condensed metals.

The atoms in most of these films show a tendency to migrate and agglomerate when of the order of a few atoms in thickness. Out of this work was developed an explanation of the critical temperature and intensity. An atom impinging on a surface transfers some of its kinetic energy to the surface, but it retains a sufficient amount to allow it to migrate over the surface. If it has sufficient energy it may desorb from the surface in a very short time. If there is, however, another atom approaching the surface, it could in effect strike it back onto the surface. This means then that the greater the flux the more likely the atoms will adhere to the surface.(50) This implies that there may be a critical intensity above which deposition of the metal is allowed.

By reducing the temperature of the surface the energy transfer on the collision of an atom is greater and the probability of desorption is less. This indicates the presence of a critical temperature. Frauenfelder(23) and Devienne(11,12) have used radioactive tracers to study this surface process and have shown that the terminology "critical", referred to the formation of a visible condensate. They have redefined the terminology because by counting the radioactivity in the condensate they had been able to detect less than visible amounts of condensate on a surface. They refer to what is now known as the accomodation coefficient which is the fraction of energy given off by an atom, and the coefficient of adherance which is the probability that an atom remains on the surface for a length of time greater than a specified amount.

The above indicates, therefore, that even carrier free amounts of activity can be collected. It is still necessary however, to have a sufficiently low temperature and high flux to cause a significant percentage of the vapor to condense (e.g., a yield of 50-70%), and in this sense the meaning of critical temperature and intensity is still useful. It has been found that by degassing the condensing surface, it is possible to gain condensation at a higher temperature than when a gas is adsorbed on the surface.(23) This substantiates Cockroft's findings.

It is also seen that the amount of metal charge in the furnace as well as other factors which will be discussed below, affect the efficiency of condensation.

C. Apparatus, Operating Procedures, and Calibrations

Apparatus. An all glass apparatus was chosen because of the ease of fabrication, the absence of surface defects in the glass, and the fact that the condensation of the vapor could be observed visually. A diagram of the apparatus is given in Figure 2. It consists of a cylindrical container which has a top which seals by a dessicator type of ground glass fitting. This allows an easily accessible opening to the furnace. The furnace consists of a carbon cylindrical rod 6 mm. in diameter and 5 cm. in length. A 4 mm. diameter hole is drilled concentric with the long axis of the rod to a depth of 3 cm. The charge which is to be distilled is placed at the bottom of this hole in the carbon rod. This carbon rod furnace is held in the cylindrical bottom section (120 mm. length) by a Vycor holder (Figure 3), which sits on a ledge made by a pyrex glass tube of 45 mm. diameter as shown in Figure 3. The carbon rod is then heated by placing induction coils externally around the outside of the evacuated chamber opposite to the length of the carbon rod furnace.

The vapor is collected on a cold finger which extends down from the top of the apparatus as shown in Figures 2 and 3. The top is fitted

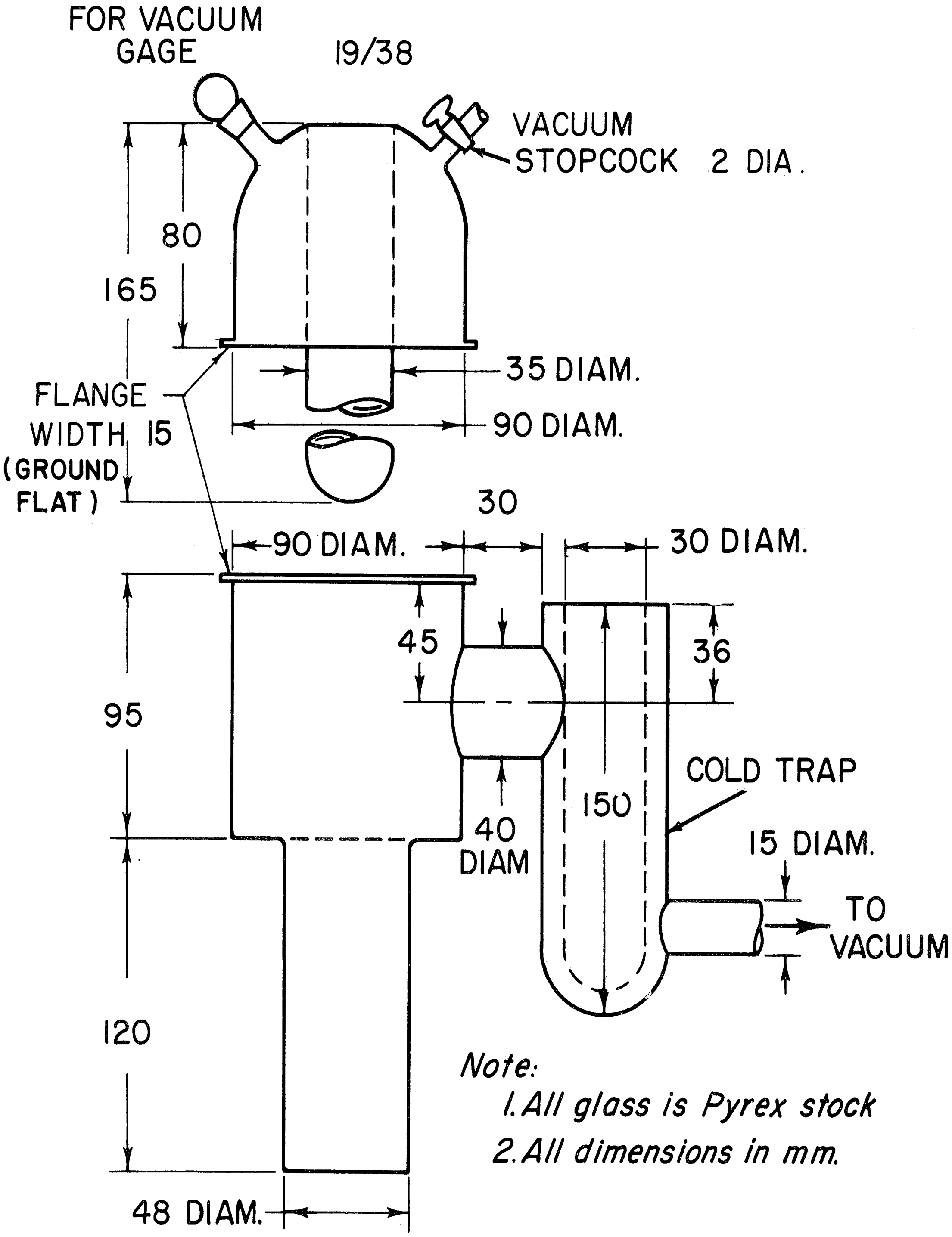


Figure 2. Distillation Apparatus.

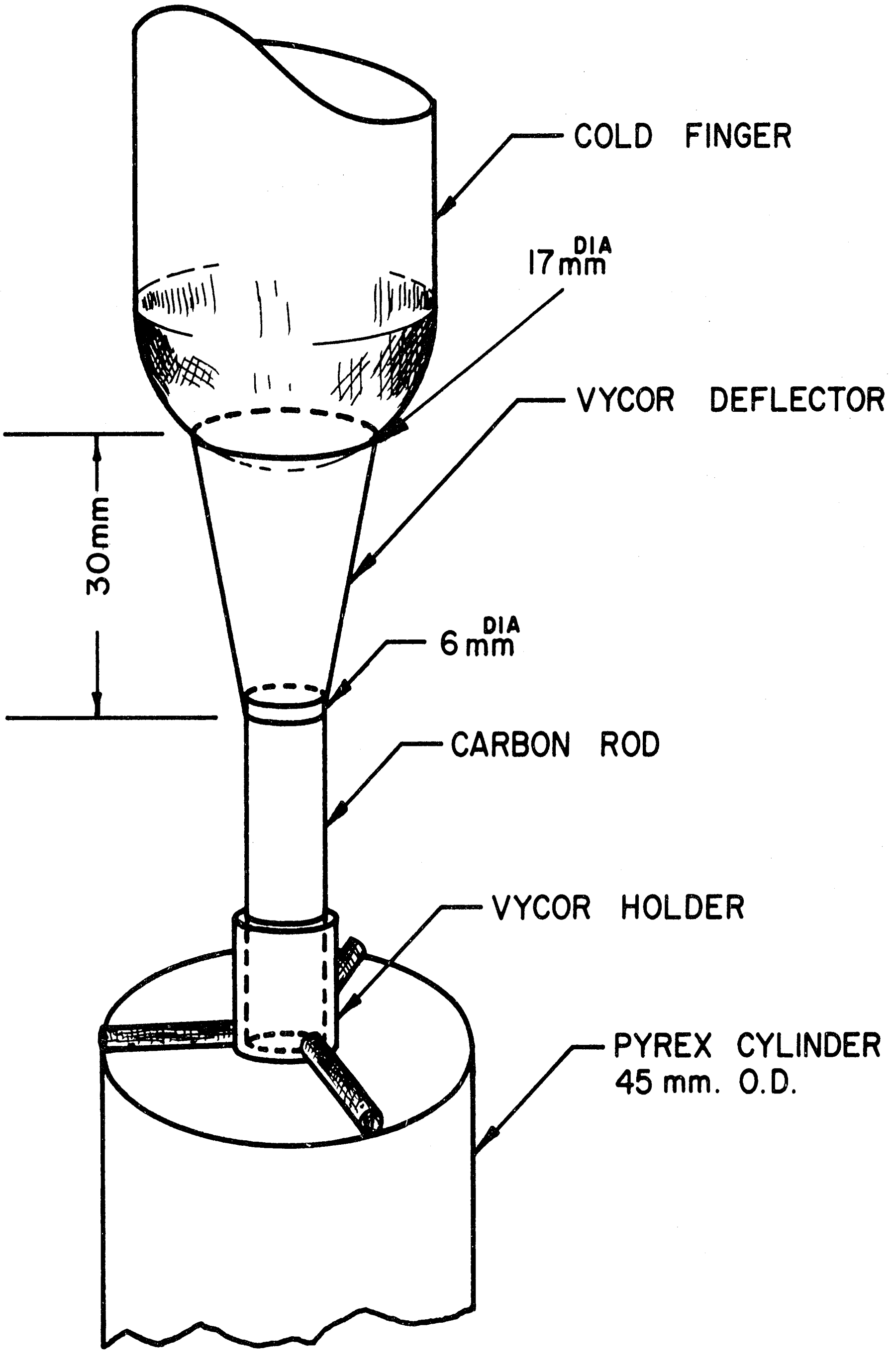


Figure 3. Detailed Sketch of Furnace and Collector.

with two openings to accommodate an ionization type vacuum gage, and a stopcock for vacuum release. Connected into this vacuum chamber through a cold trap is a Welch Duo-Seal vacuum pump. The complete arrangement of the apparatus can be seen in Figures 4 and 5.

In order to obtain sufficient collection of microgram and carrier free quantities of vapor, it was necessary to insert a deflector between the carbon rod and the surface of the cold finger. This deflector which is made of Vycor sits directly on the top of the carbon rod. The deflector is wrapped with a piece of (0.001") tantalum foil which becomes heated by induction, and the foil then heats the deflector. This prevents adsorption of metal vapor on the surface of the deflector. The top of the deflector is then aligned with the cold finger at the time of sealing the vacuum. This is done by allowing the cold finger to contact the top of the deflector (Figure 3).

In order to remove conveniently the condensed metal vapor a thin (0.001") teflon film is wrapped around the cold finger and is held in place by a ring of copper wire. The teflon can be easily handled if the static charge is removed by wiping the film with Anstac M. The vapor condenses on this film which can then be easily removed.

The holder for the carbon furnace is made so that when placed in the distillation apparatus the carbon rod and its deflector line up with the cold finger (Figure 3).

The following is a list of specialized equipment used in the distillation experiments:

1. Induction heater, 300 watts designed and built by Ronald W. Shideler, University of Michigan. For schematic see Figure 6. For layout see Figure 7, and for parts list see Table VII.

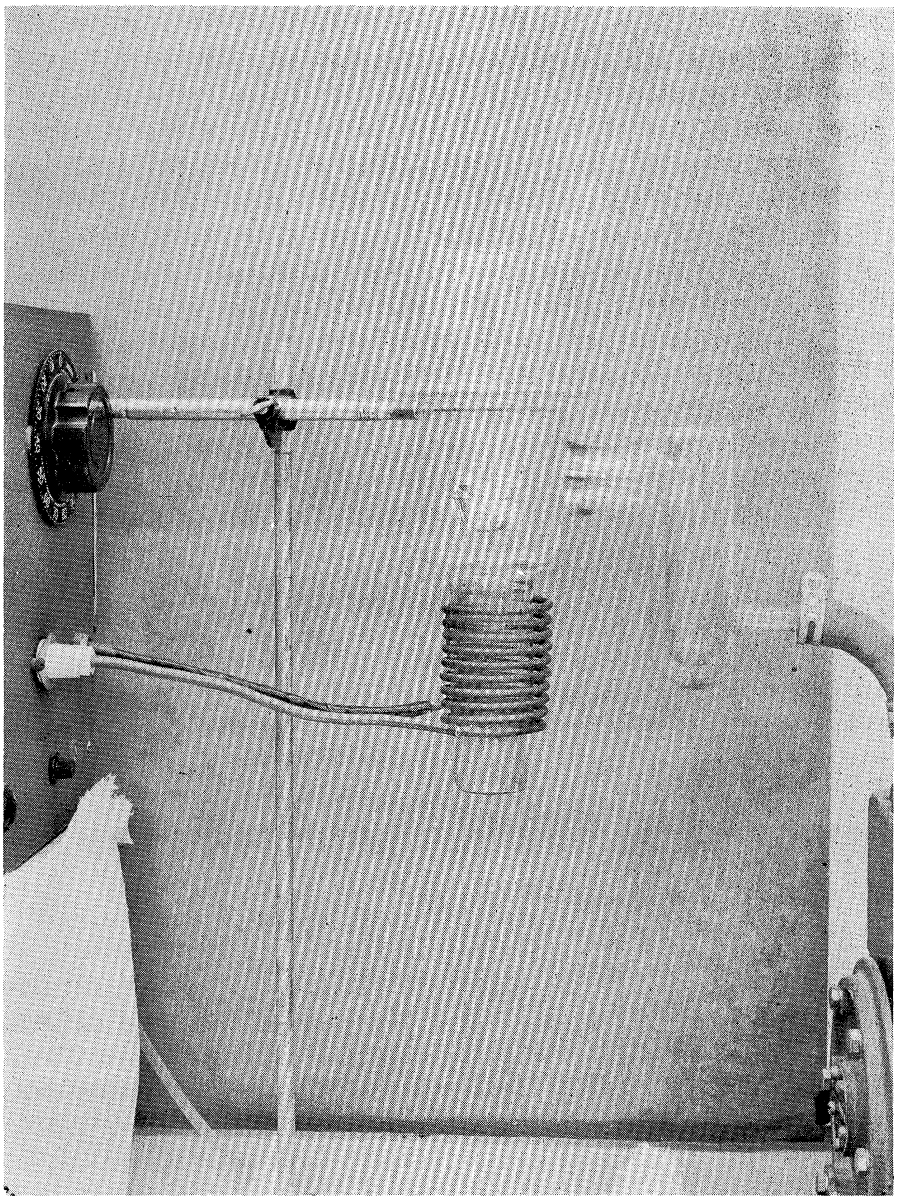


Figure 4. Photograph of Distillation Apparatus.

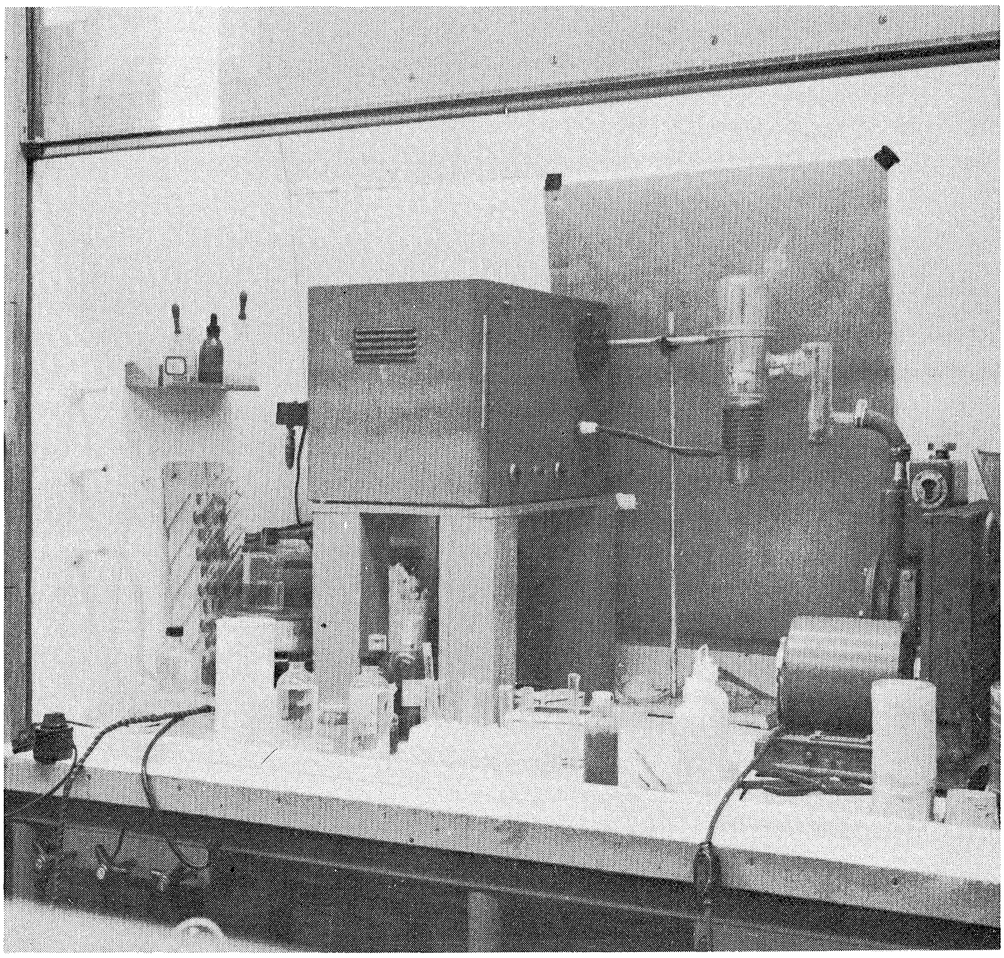


Figure 5. Photograph of Complete Distillation Apparatus in Hood.

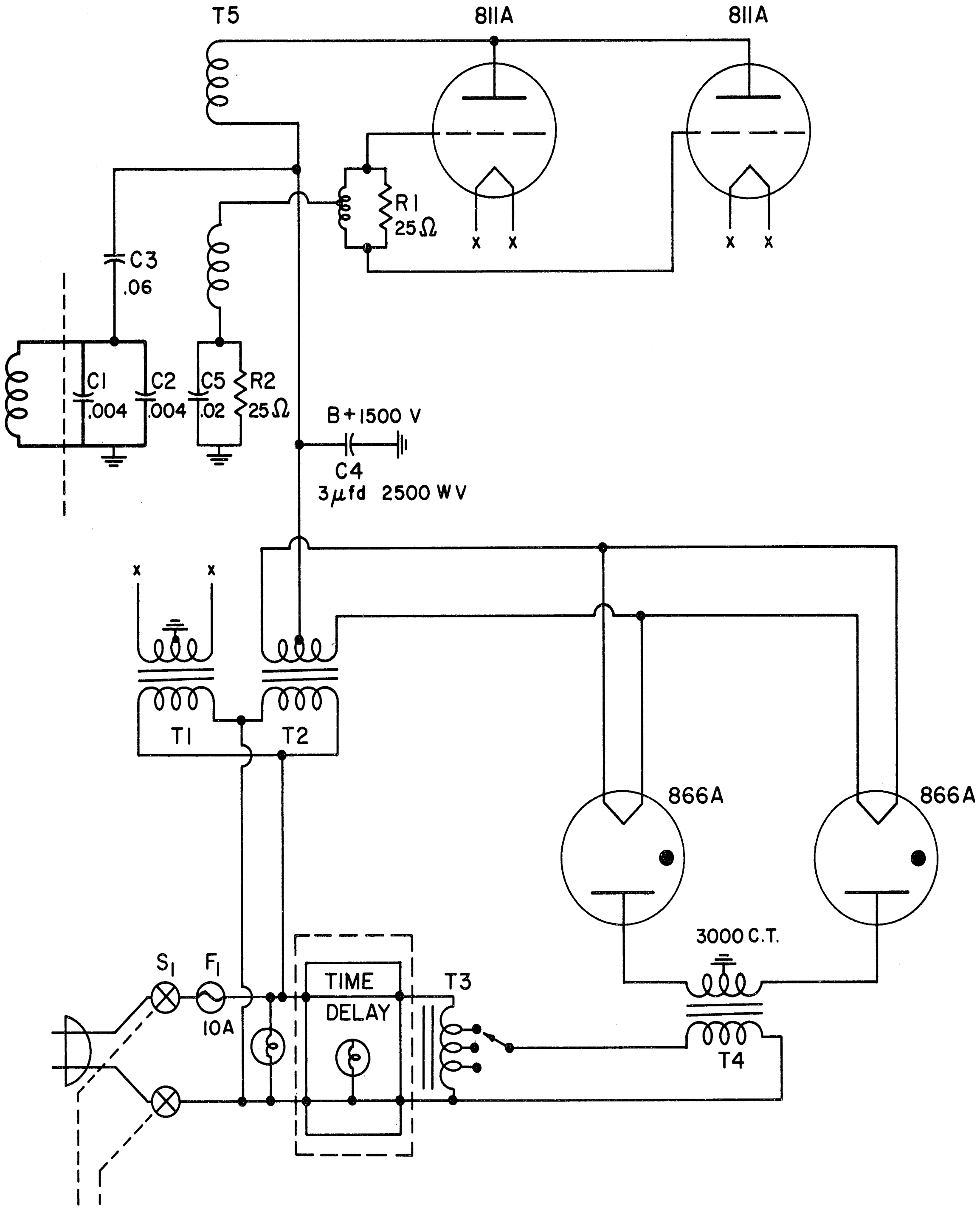


Figure 6. Schematic of 300 watt Induction Heater.

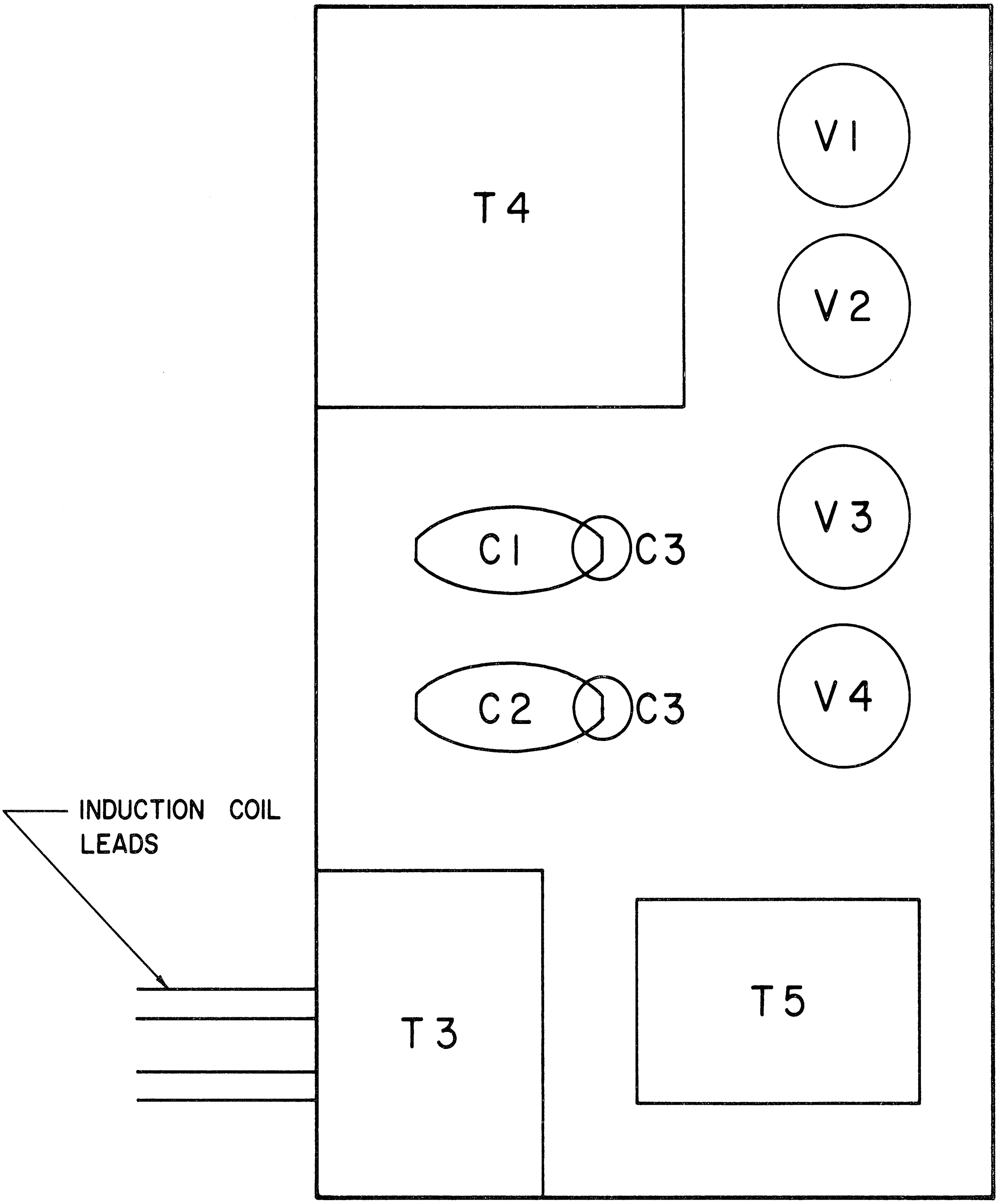


Figure 7. Lay-out of 300 watt Induction Heater.

TABLE VII

PARTS LIST FOR 300 WATT INDUCTION HEATER

Part	Quant.	Specifications
R1	1	25 ohm, 2 watt carbon resistor with 6 turns of # 16 wire wound around the resistor
R2	1	2K 10 watts wire wound
C1,2	2	0.004 mfd. 6 KV capacitor Sprague #MX-60
C3	6	0.01 mfd. 2500 V working mica cap.
C5	2	0.02 mfd. 2500 V test mica CD #9-21020
C4	1	3 μfd 2500 V oil filled cond.
S1	1	D.P.S.T. toggle switch 12 a., 125 v. Arrow H&H
Lt1,2	2	Dial lamp assembly for 6 watt 110v bulb Drake 10c jewels #408 pilot Lite Bracket
Pg1	1	A.C. plug and cord
T1	1	Filament transformer 6.3v, 6a Thordarson T19F98
T2	1	Filament transformer 2.5v, C. T., 5a Thordarson T21F00
T3	1	Variable transformer 115v, 5a General Radio 200c
T4	1	Plate transformer, 3000v C. T. 300 ma. U.T.C. No. 547
T5	1	R.F. Transformer, primary has 85 turns of No. 20 enam. wire on 2" coil form, secondary has 30 turns of polyethylene insulated wire.
Heating Coil		See Drawing
V1,2	2	866 mercury vapor half wave rectifier
V3,4	2	811 H.F. Transmitting triode
F1	1	10a fuse 3AG size, Buss
Time delay relay		Cramer

2. Welch Duo-Seal Vacuum Pump, Model 1405H, W. M. Welch Scientific Company, Chicago, Illinois.

3. Ionization Vacuum Gauge, Type DPA-38, Ionization gauge tube VG-1A, Consolidated Electrodynamics Corp., Rochester, New York.

4. Teflon, "Flouro-Film" cast, 2 inch width, 0.00025" thick, Dielectrix Corp., Farmingdale, Long Island, New York.

5. Anstac "M", Chemical Development Corp., Danvers, Mass.

6. Carbon Spectroscopic Graphite Electrode, United Carbon Products Company, Inc., Bay City, Michigan.

7. Optical Pyrometer, Serial No. 1183667, Cat. No. 8622, Leeds Northrup Co., Philadelphia, Pa.

8. Dual Memory 100 Channel Analyzer (used with gamma ray scintillation detector). Complete description of the analyzer is given by W. W. Meinke.(45)

The rest of the equipment consists of readily available commercial apparatus. A detailed specification of this apparatus including all of the counting equipment which was used is listed in References (75), (76), (77), and in Chapter III.

Operating Procedures and Calibrations. The carbon rod which holds the charge to be distilled is placed in the holder. The deflector is placed on the carbon furnace and this whole assembly is then placed in the distillation chamber on the ledge created by the glass cylinder. The cold finger in the top is covered with a Teflon film. After coating the ground glass surface with a thin film of Apiezon (class M), the top is inserted in place so that the contact with the furnace assembly is made as indicated in Figure 3. The vacuum pump is turned on while liquid nitrogen is placed in the cold trap and in the cold finger in the top of the apparatus. The system is tested for leaks around the ground glass seal with a Tesla coil. Five minutes are allowed for the pressure to come to equilibrium (see pressure change with time below). Then the induction heater is turned on and the distillation is carried out. Operating instructions for the induction heater are as follows:

1. Check power level control for OFF position.

2. Turn master switch ON.

3. If unit is to be used for extended periods of time (5 minutes), the field coil must be water cooled.

4. Place material in the field region.

5. Wait one minute (for time delay switch, red indicator lamp ON) after turning unit on. Power may now be applied by turning up power level control. Power should be advanced slowly to prevent overheating the material.

After the distillation is completed the Teflon film is removed. The area upon which the metal has condensed is cut out and placed in a counting tube for counting in the well scintillation counter.

A temperature calibration curve for the induction heater is shown in Figure 8. The temperature can be adjusted with an error of ± 20 °C (three standard deviations). Experiment has shown that equilibrium temperature is reached after 2 minutes. A new calibration curve was made every month. A check on the calibration at the higher temperatures was made with the use of an optical pyrometer. The calibration at lower temperatures was done by checking the melting points of pure metals. The values obtained in this way were within the error mentioned above. The temperature limit of this apparatus is about 1100 °C.

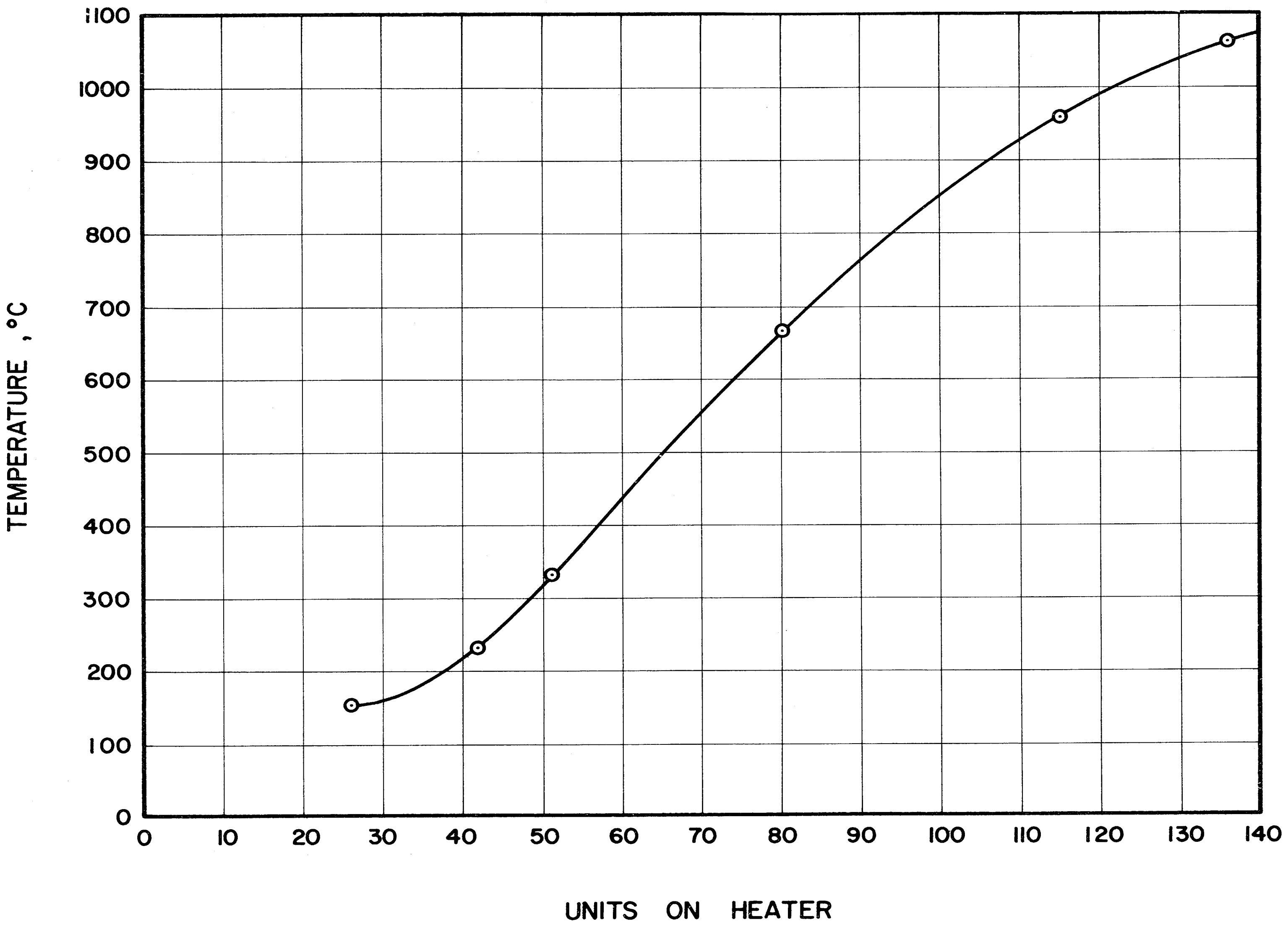


Figure 8. Temperature Calibration of Induction Heater.

The pressure of the system was measured with an ion gauge. The change of pressure in the system with time after turning on the vacuum pump is shown in Figure 9. At the times indicated in Figure 9, the temperature of the carbon rod was increased from room temperature to 720 °C. The carbon rod which had been previously outgassed at 1000 °C, caused little increase in pressure when heated to 720 °C even though it had been exposed to the atmospheric pressure for 15 minutes. The carbon rod which had not been outgassed caused a 100 fold increase in pressure when heated to 720 °C. Therefore, an added requirement is that the carbon rod furnace be outgassed for five minutes at 1000 °C before the distillation is to be carried out. When this is done the time rate of pressure change becomes small after five minutes and the equilibrium pressure is found to be between 5×10^{-4} and 7×10^{-4} mm. Hg.

D. Experimental

Since this work was largely an exploratory investigation of the use of vacuum distillation of metals, a number of different types of experiments were made. In this way a complete survey of the application of this method to the radiochemical separation can be attained.

The method of developing the radiochemical separation procedure was identical with that done in Chapter III. The conditions of the separation were adjusted to give the best separation with the particular type of system which was used.

1. Two Metal Component Systems

In order to find out how different atom ratios of a two metal system behave, cadmium-zinc and cadmium-silver systems were investigated. The cadmium was distilled and condensed leaving most of the zinc or

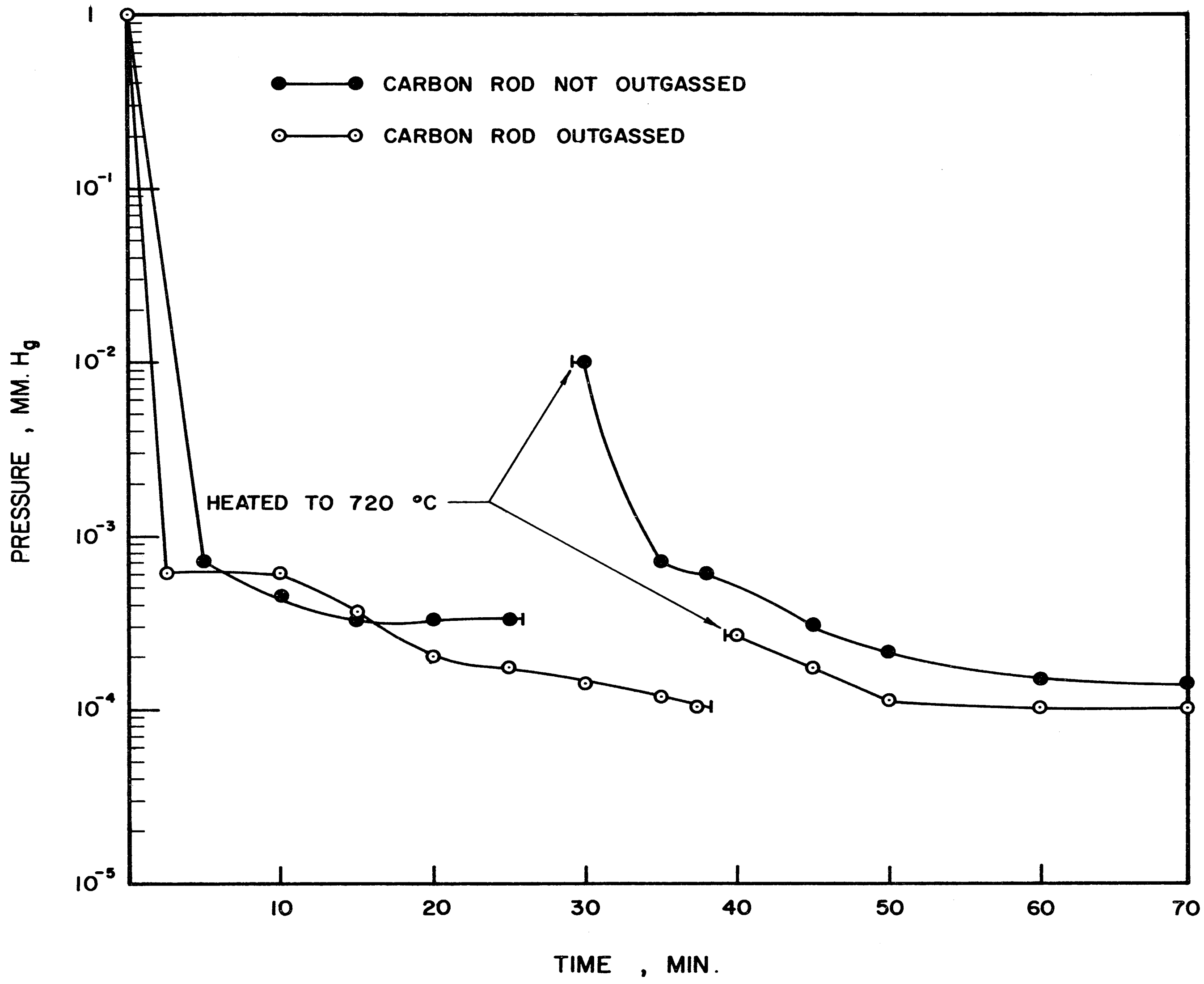


Figure 9. Internal Pressure as a Function of Time After Starting Vacuum Pump.

silver behind in the carbon furnace. It is convenient to work with small amounts of tracer (less than 1 mg.) so it was decided that a convenient way of obtaining these mixtures would be to electrolyze them simultaneously from solution into mercury. By transferring the entire electrode into the furnace 1 mg. amounts of the mixture could be easily handled. The mercury cathode was used in order to avoid possible preferential interaction between the metal components and the metal cathode. The mercury containing the deposited metal mixture was then evaporated off leaving the residual metal mixture virtually free from mercury. The experimental procedure is as follows:

1. Make a simple mercury electrolysis cell by sealing a platinum wire into the bottom of a 5 ml. pyrex test tube.

2. Put one half gram of mercury metal in the bottom so that the end of the platinum wire is not exposed.

3. Add the necessary amount of carrier solution of each metal component. Conduct two experiments in which each metal component is labeled with radioactive tracer, while the other is inactive.

4. Add sufficient H_2SO_4 to give a final solution of 2 ml. 0.1 $\underline{M}$ H_2SO_4, and electrolyze at 6 volts for 45 minutes. (According to previous experiment this procedure removes the highest concentrations, quantitatively.)

5. With the current still on, remove the electrolyte in the cell and wash three times in acetone to dry.

6. Transfer the mercury drop to a pyrex tube which is connected through a cold trap to a vacuum of one micron. Heat to 140 ± 20 °C for 15 to 30 minutes until the macro amount of mercury appears to have evaporated. Allow to cool under vacuum to room temperature.

7. Transfer the charge to the carbon furnace and distill at 180 °C for five minutes.

The results of these experiments are recorded in Tables VIII and IX. Note that in Table VIII the decontamination factor was normalized to the specific activity in the experiment using 0.04 mg. of Zn. The atom ratio in the vapor is also recorded in addition to the decontamination factor.

2. Autoreduction of Trace Amounts of Mercury by Copper

It has been known for a long time that copper metal will plate mercury from solution on the copper metal surface in accordance with the equation: $Cu^{o} + Hg^{+2} = Hg^{o} + Cu^{+2}$. If it is possible to evaporate the mercury from the surface of the copper metal, then it would make a good radiochemical separation. Trace amounts (μgm) of mercury can be separated by this means by using the following procedure:

1. To a 50 ml. round bottom centrifuge cone, add carrier free Hg^{203} tracer solution, or to measure decontaminations, use an equivalent amount of inactive mercury plus tracer of the contaminant.

2. Add sufficient acid to bring total volume to 2 ml. of 0.15 N HNO_3.

3. Prepare an 8 mg. Cu foil, 0.5 cm^2 (10 mils thick), by washing in 4 N HNO_3 to clean the surface; rinse with distilled water, and add to the centrifuge cone.

4. Stir slowly for about 20 minutes, and wash six times with distilled water and once with acetone.

5. Transfer to a carbon rod furnace, and heat to 100 °C for three minutes.

TABLE VIII

DISTILLATION OF CADMIUM FROM VARIOUS CONCENTRATION RATIOS OF CADMIUM AND ZINC

Expt.	Initial Cd(mg.)	Amount Zn(mg.)	Atom Fract. Cd	Yield Cd(%) in total condensate	Decontamination Factor Zn	Normalized Decont. Factor Zn	Atom Ratio Cd/Zn in total condensate	Amount Zn (gm - atom x 10^{-7}) in total condensate
1	0.5	0	1.0	96	-	-	-	-
2	0.5	0.04	0.88	75	1.7	1.7	9.5	3.6
3	0.5	0.16	0.64	70	18	4.5	2.2	1.4
4	0.5	0.64	0.31	65	44	2.7	13	2.2
5	0.5	2.56	0.10	63	53	0.87	3.5	7.8
6	9.3 µg.	0.50	0.01	42	65	5.2	0.29	1.2

TABLE IX

DISTILLATION OF CADMIUM FROM VARIOUS CONCENTRATION RATIOS OF CADMIUM AND SILVER

Expt.	Initial Cd(mg.)	Amount Ag(mg.)	Atom Fract. Cd	Yield Cd(%) in total condensate	Decontamination Factor Ag	Atom Ratio Cd/Ag in total condensate	Amount Ag(gm.- atom x 10^{-7} in total condensate
1	1.0	0	1.0	94	-	-	-
2	1.0	3μg	0.997	90	20	6×10^3	1.4
3	1.0	0.1	0.91	96	661	6×10^3	1.4
4	0.5	0.1	0.82	78	3.8×10^3	1.5×10^4	0.24
5	0.1	0.1	0.49	68	500	330	1.8
6	9.3μg	0.1	0.08	38	1.7×10^3	55	0.55
7	16μg	1.0	0.02	77	3.5×10^3	46	2.6
8	0	0.1	0	-	7×10^2	-	1.3

6. Collect the mercury on Teflon film. Cut out the area where collection occurs, and count in a scintillation well counter.

The yields of mercury which were obtained using about 16 μgms. in 0.15 N HNO_3 were as follows:

Chemical Separation, av. of 5 runs	78%
Distillation Separation, av. of 5 runs	93%
Overall yield	72%

The decontamination factors for a number of elements are listed in Table X. In order to show that the presence of a foreign metal with the mercury did not appreciably affect the yield of the mercury which was distilled, tracer mercury was separated with the equivalent amounts of inactive contaminant that was used above. The results are shown in Table XI. In addition the effects of various electrolytes on the mercury yield were measured. These results are also tabulated in Table XI.

3. Electrolysis of Cadmium Onto Copper

In order to test more adequately the separation by distillation it was decided to electrolyze a metal onto copper foil. Since copper has a moderately high hydrogen overvoltage a number of elements should plate out. It was decided to separate cadmium metal in order to compare the separation by vacuum distillation to the wet chemical methods done in Chapter III.

The following procedure was found to give a good radiochemical separation:

1. To a solution which is 0.1 to 0.2 N in either HCl or HNO_3 with the radioactive contaminant present, add 1 mg. of Cd to give a total volume of 2 ml.

TABLE X

DECONTAMINATION FACTORS FOR THE SEPARATION OF MERCURY ONTO COPPER AND THE DISTILLATION OF MERCURY

		Decontamination Factors		
Contaminant	Amount(μg)	Chemical Redn.	Distillation	Total
Ag^{110}	200	1.2	2×10^4	2×10^4
Ba^{140}	C.F.	3×10^2 (2.3×10^5)	3.3×10^2	10^5 $(.8 \times 10^7)^{*5}$
Au^{198}	220	40	4×10^3	1.6×10^5 *2
Ce^{144}-Pr^{144}	C.F.	1.2×10^3	2.3	3.8×10^3
Cd^{115m}	190	1.6×10^2	3.4 *3	5.4×10^2
Co^{60}	7.4	10^5	5	5×10^5
Cr^{51}	5	2.5×10^3	6	1.5×10^4
Cs^{134}	2.5	3×10^3	2.3	7×10^3
Cu^{64}	65	1.2×10^2	1.4×10^2	1.7×10^4
In^{114}	4.6	10^5 $(2 \times 10^7)^{*4}$	10^2	$10^7$$(2 \times 10^9)$
Ir^{192}	0.2	2×10^4	1.4	2.5×10^4
Nb^{95}	8	3×10^3	10	3×10^4
Pd^{109}	50	1.4	1.8×10^5	2.5×10^5
Ru^{106}	2	32	350	1.1×10^4
Se^{75}	3.5	6.5	2.8×10^3	1.8×10^4
Sb^{124}	0.6	2.8×10^2	4.7	1.3×10^4
Sn^{113}	500	1.3×10^3	10	1.3×10^4
Ta^{182}	4	-	-	- *1
Tl^{204}	400	4×10^4	2.5	10^5
Zn^{65}	180	4.3×10^3	4.7	2×10^4
Zr^{95}	8	2.7×10^3	14	3.6×10^4

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1. HF interferes with the mercury yield.
2. Mercury comes off at 350°C.
3. Mercury comes off at 220°C.
4. Start with 5×10^6 and (4×10^8)(C/M resp.
5. Start with 1.9×10^6 and (1.9×10^9) C/M resp.

TABLE XI

MEASUREMENT OF THE INTERFERENCE ON THE MERCURY YIELD

Substance	Amount with Mercury	Overall Yield of Mercury(%)
Ag	0.2 mg.	74
Au	0.22 mg.	76
Cd	0.19 mg.	70
Pd	50 µg.	68
Ru-Rh	2 µg.	55
Se	4 µg.	72
Sb	0.6 µg.	65
Sn	0.5 mg.	73
Zn	0.18 mg.	75
HNO_3	0.15 N	72
HNO_3	0.3 N	63
HNO_3	1.0 N	51
HNO_3 5 ml vol.	0.15 N	34
HCl	0.3 N	71
HCl	0.5 N	72
HCl	2.0 N	74
NaCl	0.2 N	74
NaCl	0.5 N	74
NaCl	1.0 N	74
NaCl	5.0 N	71
$NaCl-HNO_3$	0.2 - 0.15 N	71
$HClO_4-HNO_3$	0.15 - 0.15 N	66
$H_2SO_4-HNO_3$	0.15 - 0.15 N	65
$NH_4NO_3-HNO_3$	0.2 - 0.15 N	71
HNO_3-HCl	0.15 - 0.15 N	62
HF	0.5 N	0

2. Insert a platinum wire anode and a copper foil (1/2 cm. wide by 10 mils thickness) cathode into the solution to a depth of about 1 cm.

3. Electrolyze at 6 volts (negligible current) for 1 hour. Stir the solution with bubbling air.

4. Remove the copper foil. Cut off the area of the foil which appears plated, and place in the furnace of the distillation apparatus.

5. Heat the furnace to 180 °C for five minutes after equilibrium vacuum pressure is obtained (five minutes).

6. Cut out the area of the Teflon film upon which the metal has condensed and place in a tube for counting in the scintillation well counter.

The overall cadmium yield for this procedure is 74% ± 3% (standard deviation). The decontamination data are listed in Table XII.

A few interference measurements were made. It was found that chloride ion seemed to cause a considerable decrease in the yield of the cadmium. It has been found that greater than 0.1 M NaCl reduced the yield by a factor of 2. In some cases it was found necessary to convert the contaminating ion to the sulfate in order to maintain a sufficient yield of cadmium.

4. Electrolysis of Cadmium into Mercury Electrode

Another technique is to electrolyze 1 mg. of cadmium into a mercury cathode. The macro mercury is removed and the cadmium is distilled and collected.

TABLE XII

DECONTAMINATION FACTORS FOR ELECTROLYSIS OF CADMIUM ONTO COPPER AND THE DISTILLATION OF CADMIUM

	Amount	Decontamination Factor		
Contaminant	(μg)	Electrolysis	Distillation	Overall
Ag^{110}	32	2.5	1.5×10^2	380
$Ce\text{-}Pr^{144}$	C.F.	3	10^4	3×10^4
Cs^{134}	10	10^3	30	3×10^4
Co^{60}	7	3.8	10^3	3.8×10^3
Ir^{192}	6	3	3.5×10^3	10^4
Nb^{95}	30	10	3×10^3	3×10^4
Se^{75}	14		2×10^3	2×10^3
Ru^{106}	8 *	5	2×10^3	10^4
Tl^{204}	360	1.5	40	60
Zn^{65}	360	4.6	75	370
Zr	30	80	10^4	8×10^5

* Solution of chloride converted to sulfate so that final concentration is 0.1 N H_2SO_4

The following procedure which closely follows that procedure in Section D.1 above was used:

1. Place 1/2 gm of mercury metal into the mercury cathode cell which was described above (Section D.1).

2. Place 1 mg. of cadmium as a carrier solution in the cell with trace amounts of the radioactive contaminating element (or with radioactive cadmium tracer added if yields are to be determined).

3. Add sufficient 1 N H_2SO_4 to bring the total volume to approximately 1 ml.

4. Electrolyze the solution for 30 minutes at 6 volts.

5. Remove the electrolyte by means of a suction tube, and discard. Wash the mercury drop five times in distilled water and three times in acetone, and transfer to a pyrex tube. Evaporate the mercury off as described above (Section D.1). Transfer the residue to a carbon rod furnace and distill the cadmium off between 160 °C and 180 °C at about one micron of pressure until no visible deposit forms when a fresh collecting surface is used after successive five minute distillations.

6. The area on the Teflon film which contains the deposit is placed in a counting tube and counted in a scintillation well counter.

A preliminary experiment in order to evaluate the general procedure was done by attempting the separation of cadmium from the fission products of uranium. Uranyl acetate (0.100 gm.) was irradiated in the Phoenix reactor for 10 minutes at 10^{12} neutrons per cm^2 per sec. Three hours after irradiation the solution was dissolved in 1 N H_2SO_4 containing 1 mg. of cadmium carrier, and was electrolyzed for 30 minutes. This procedure removed 97% of the fission product activity from solution.

After separating off the macro mercury and distilling off the cadmium at 180 °C in the vacuum distillation apparatus, detectable amounts of Cd^{115} and Cd^{117m} were found. (1000 c/m using a 3" x 3" potassium iodide scintillator gamma ray spectrometer). Estimation of its purity indicated that the decontamination factor for the total activity in the fission products was 10^5. Data from a detailed investigation of the separation is given in Table XIII. The cadmium yield for this separation is 93.5% ± 2.5% (standard deviation).

5. Distillation of Carrier Free Indium 113m from Tin Metal

This experiment and those to follow involve the irradiation of a target material to produce a carrier free product of a nuclear reaction. The target materials used in these experiments are metal foils.

In this particular experiment granular tin metal (Baker and Adamson, A.R., see Chapter II) was irradiated in the reactor for 150 days at a neutron flux of 5×10^{12} neutrons/cm^2/sec. An operating day for the reactor is about six hours. Since there are only five operating days per week there is considerable cool off time interspersed between the irradiation time. When this metal is removed from the reactor and allowed to decay for a few hours the following nuclides with their most characteristic radioactive emission are found:

Nuclide	Half life	Characteristic radiation
Sn^{113}	120d	EC. 0.025 Mev Sn X-Ray
Sn^{117m}	14d	0.16 Mev (high convers.) Sn X-Ray
Sn^{119m}	250d	0.065 Mev
In^{113m}	104m	0.392 Mev (0.024 Mev In X-Ray)

TABLE XIII

DECONTAMINATION FACTORS FOR ELECTROLYSIS OF CADMIUM INTO MERCURY CATHODE AND THE DISTILLATION OF CADMIUM

Contaminant	Amount (μg)	Decontamination Factor Electrolysis	Distillation	Overall
Ag^{110}	8	2	10	20
$Ce\text{-}Pr^{144}$	C.F.	1.5×10^3	20	2.2×10^4
Co^{60}	7	1.1	1.1×10^3	1.1×10^3
Cs^{134}	3	1.1×10^3	20	2.2×10^4
Hg^{203}	840	3	194	590
Ir^{192}	0.05	4.4	230	10^3
Ru^{106}	3.6	7	10^3	7×10^3
Sb^{124}	5	1.5	20.8	31
Se^{75}	400	26	1.7	45
Sn^{113}	1,540	1.9	208	400
Tl^{204}	580	1.7	4.1	7.1
Zn^{65}	50	1.6	20	32
Zr^{95}	0.8	3	27	81

It was possible to resolve all of the above peaks including the 0.024 Mev X-Ray on the gamma ray scintillation spectrometer.

This irradiated tin metal was then placed in the carbon furnace and the pure In^{113m} was volatilized and collected. The temperature was increased until tin contamination could be significantly detected. Table XIV indicates the temperatures at which the various characteristic photoelectric peaks are observed. Since 270 °C is the maximum temperature to which the tin may be heated to give good purity, another experiment was made to see if the yield could be increased. The granular tin was heated for varying lengths of time. The results of this experiment is shown in Figure 10. A maximum of 4.5% of the total In^{113m} present in the target can be volatilized and collected in twenty minutes. In addition to this a 0.001" thick tin foil was heated for varying lengths of time. This curve is shown on the same graph. In this case the yields are much higher.

6. Separation of Carrier Free Gold^{199} from Platinum Metal

The same procedure which was used above was able to satisfactorily separate pure Au^{199} from platinum foil (see Chapter II) with its associated Pt^{199}. When platinum metal is irradiated with neutrons for five hours Pt^{199} is formed along with negligible amounts of Pt^{193m} and Pt^{191}. The Pt^{199} decays with a 31 minute half life to Au^{199} which has a 3.14 d half life.

The following isotopes were found in the platinum five hours after irradiation in the reactor for five operating days at 5 x 10^{12} neutrons/cm^2/sec.

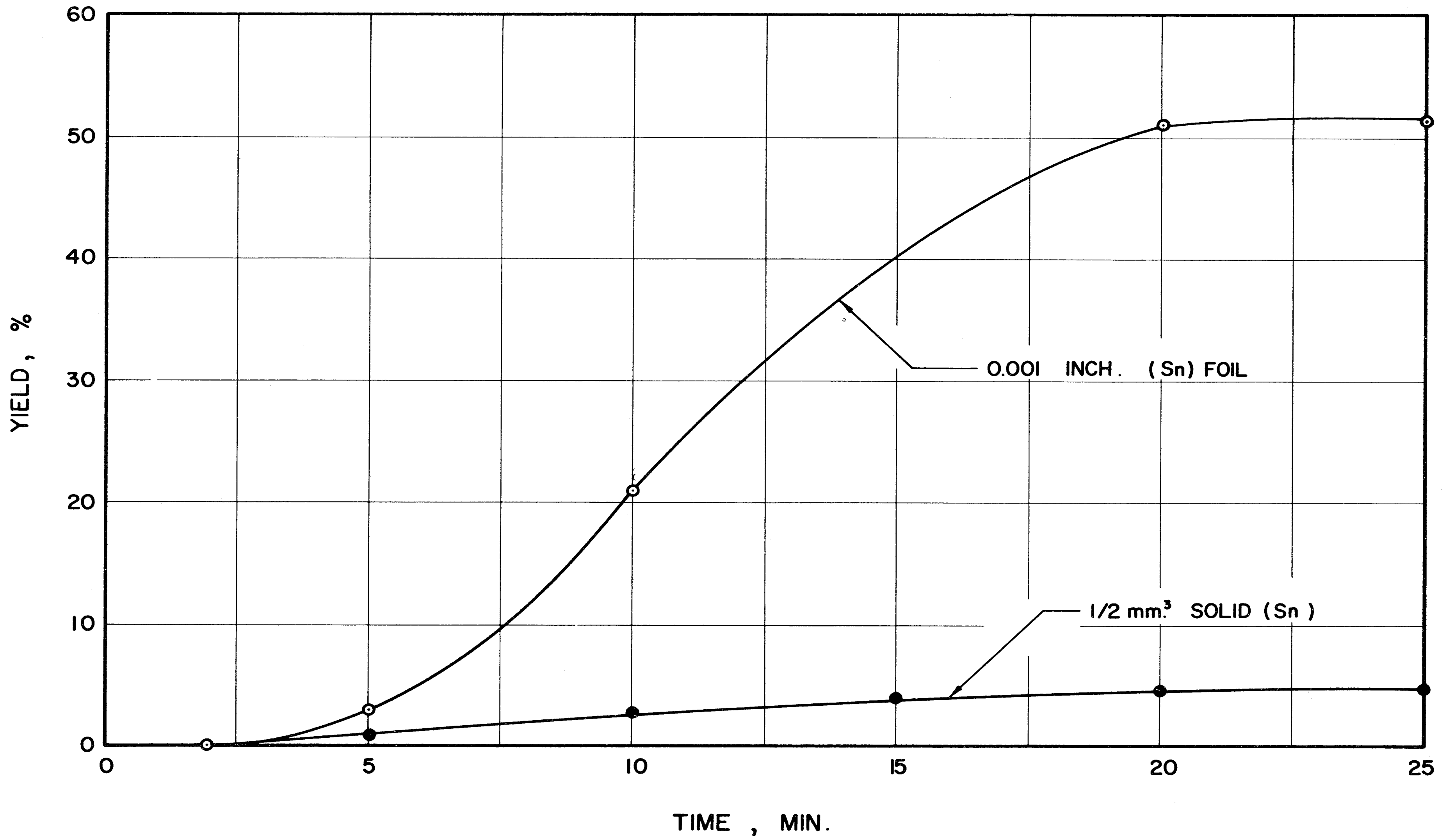

Figure 10. Yield of Carrier Free In^{113m} vs. Time of Heating at 270°C.

TABLE XIV

DISTILLATION OF CARRIER FREE In^{113m} FROM TIN AT VARIOUS TEMPERATURES

Temperature °C	Activity in the Photoelectric Peaks c/m				Percent Contam.	Decontam.
	0.024 Mev Sn^{113}	0.065 Sn^{119m}	0.160 Sn^{117m}	0.39 In^{113m}	0.39 Mev peak	Factor
165	-	-	-	-	-	-
180	-	-	-	-	-	-
190	-	-	-	27810	0	-
220	-	-	20	37800	0.05	10^4
270	-	-	100	68000	0.15	3.4×10^3
320	3000	15	50	178000	1.7	3×10^2
440	36500	1000	950	179000	21.5	5

Nuclide	Half life	Characteristic gamma radiation
Au^{199}	3.14d	0.208, 0.158 Mev (0.067 Mev X-Ray)
Au^{198}	2.7d	0.411 Mev
Pt^{199}	31m	0.074, 0.197, 0.246, others, Mev
Ir^{192}	74d	0.32, 0.63 Mev
Ir^{188}	41.5h	0.47 Mev

The platinum foil (0.002") was heated in the distillation apparatus up to 840 °C without any evidence of activity on the collector. In the range of 840 °C to 1100 °C, Au^{199} was detected. If any impurity was present it was below the limit of sensitivity 50 c/m of the gamma ray spectrometer. The yield at 1100 °C is less than 1% for a five minute heating. The impurity in this distillate was less than 0.1%.

7. Separation of Carrier Free $Silver^{109m}$ from Palladium Metal

By irradiation of palladium (0.005") in thickness, (see Chapter II) with neutrons of the same flux as indicated above, for four hours one finds very little gamma activity. The main gamma ray comes from Ag^{109m} (39s) which is the beta decay product of Pd^{109} (13.5h). Negligible amounts of Pd^{103} (17d) and the Ag^{111} (7.6d) daughter of Pd^{111} (22m) were found. This foil was placed in the furnace and heated for one minute after a two minute period to allow for temperature equilibrium. Ag^{109m} which was in equilibrium with Pd^{109} distilled off and was collected. The collected Ag^{109m} was counted by quickly removing the collector and mounting the sample (30 sec.) which was placed in the well counter. The count rate was then corrected for decay to the time of separation. By allowing the sample to decay out after one hour any Pd^{109} contamination present would be indicated by its daughter Ag^{109m} gamma activity. There remained a measureable amount of activity which corresponded to the total decontamination factors which are listed at the several temperatures as follows:

Temperature °C	Yield %	% Contamination of Pd^{109} in Ag^{109m}	Decontamination Factor
780	0.07	11	1.4×10^4
880	0.14	3	2.3×10^4
980	1	0.18	5.2×10^3

E. Conclusion and Discussion of Results

1. The Degree of Separation

Theoretical expression. Metals are known to form metallic solutions which obey the general characteristics that are observed for other types of solutions.(82) It is of interest to gain some idea of the separation which will be obtained in the distillation of an ideal solution of two metals (A and B). Suppose that B is to be distilled from A. The decontamination factor, as defined in Chapter V is

$$D.F. = \frac{A'_A}{A_A}$$

where

A'_A = activity of contaminant A initially present with B

A_A = activity of contaminant A present with B in distillate

For the separation by distillation this decontamination factor for a given specific activity of A takes the form:

$$D.F. = \frac{m_{as}}{m_{av}}$$

where

m_{as} = moles of component A in the solid

m_{av} = moles of component A in the vapor

By assuming that the vapors are behaving like an ideal gas,

$$D.F. = \frac{m_{as}\ K}{P_A}$$

where

P_A = pressure of A above solid solution

and

$$K = \frac{RT}{V}$$

R = ideal gas constant

T = temperature, °K

V = volume.

Using Raoult's law $P_A = P_A^o\ N_A$ (27,56), where N_A = mole fraction of A in the solid, and P_A^o = vapor pressure of pure A at the temperature of the experiment, one obtains:

$$D.F. = \frac{m_{as}\ K}{P_A^o\ N_A} = \frac{(m_{as} + m_{bs})K}{P_A^o}$$

m_{bs} = moles of B in the solid.

This decontamination factor can be calculated only if the volume of the system is accurately known. Since this volume is difficult to measure, it may be more convenient to express variables which are measured more easily by experiment.

Let us define an enrichment ratio (E.R.) as:

$$E.R. = \frac{A'_A}{A'_B} \bigg/ \frac{A_A}{A_B} = \left(\frac{A'_A}{A'_B}\right) \left(\frac{A_B}{A_A}\right)$$

where

A'_B = activity of B (the desired component), initially

A_B = activity of B in the vapor after distillation

Since the specific activities of A and B will again cancel, the enrichment ratio for A can be expressed as (using the same nomenclature as above):

$$E.R. = \left(\frac{m_{as}}{m_{bs}}\right) \left(\frac{m_{bv}}{m_{av}}\right)$$

Again substituting the ideal gas expression gives:

$$E.R. = \left(\frac{m_{as}}{m_{bs}}\right) \left(\frac{P_b}{P_a}\right)$$

From Raoult's law:

$$E.R. = \left(\frac{m_{as}}{m_{bs}}\right) \left(\frac{P_B^o}{P_A^o}\right) \left(\frac{N_b}{N_a}\right) = \frac{P_B^o}{P_A^o}$$

The enrichment ratio for A is not dependent on the initial concentrations of the components and is equal to the ratio of the vapor pressures of the desired component to that of the contaminant.

It is useful to look at the values of the enrichment ratio which are obtained from the theoretical expression for the Cd-Zn and Cd-Ag separations. Substituting for the vapor pressure of the pure components which are obtained in Figure 1 the following values are calculated:

$$E.R. = \frac{P_{Cd}^o}{P_{Zn}^o} = 250 \quad E.R. = \frac{P_{Cd}^o}{P_{Ag}^o} = 10^{15}$$

These values are to be compared with the experimental values of E.R. which are calculated by means of the above definition, using the data in Tables VIII and IX. These values are given below:

Experimental Enrichment Ratio

Experiment	Cd-Zn	Cd-Ag
2	1.3	18
3	13	634
4	29	3×10^3
5	33	340
6	27	600
7		3×10^3

The difference between experimental and theoretical values is enormous, especially in the case of the Cd-Ag system.

Comparison of theory with experiment. In view of the large difference between experimental and theoretical values, it is important to compare the assumptions that are inherent in this expression for the enrichment ratio to the actual experimental conditions. The assumptions and discussions are as follows:

Assumption 1. The atom fraction of the components in the residue does not change during the distillation. This assumption is not even approximated in experiment. It can be seen from Table VIII and IX that the atom fraction varies for each experiment from the initial value to a much smaller value after the distillation as indicated by the high yields of cadmium. If all of the assumptions which are discussed in the following paragraphs are duplicated in the experiment, it would be possible through suitable differential equations relating the change in composition of the vapor to the change in composition in the residue, to compare the theoretical to the experimentally observed enrichment factors.

Assumption 2. The metal systems form an ideal solution at all atom fractions at the temperature of the experiment. At the temperature and pressure of the experiment the phase diagram for the Cd-Ag system shows six different solid phases. The experimental measurement of the extent of deviation from Raoult's law has been made by Schaefer and Havorka(66) in the very dilute region. At the more concentrated regions the deviation was very large and unpredictable, presumably because the solid phase changes with composition. In the case, of the Cd-Zn system the complete activity (thermodynamic) vs. atom fraction of zinc curve was measured.(18,31) This curve shows a positive deviation from Raoult's law which indicates that there is more intra-atomic attraction than inter-atomic attraction. Positive deviation is the usual case in many of these metal systems.(68)

The extent of deviation from an ideal solution was very great for the Cd-Ag system while the deviation for the Cd-Zn system was small. This may partially explain the very large difference between the experimental and theoretical value of the enrichment ratio for the Cd-Ag system.

Assumption 3. The solid phase is at all times homogeneous. It is hard to visualize that a concentration gradient would not be formed due to a finite diffusion rate of the atoms to the surface of the solid residue. Use of radioactive tracer techniques should be valuable in studying this mechanism. This factor may be important in the rate of evaporation of metal from the solid phase. Dushman(16) states that the rate of evaporation is proportional to the vapor pressure. However, Stranski(73) reports several cases in which a component with the lowest vapor pressure has the highest rate of evaporation. He has found that this anomalous effect is dependent upon the temperature of the system. This suggests that the relative rates of diffusion of the atoms of the components is a possible cause of this effect.

Along with this it is important to realize that the amount of A which evaporates is also dependent upon the rate at which a satisfactory yield of B is obtained. This effect can be seen in the data of Tables VIII and IX. All of these bimetal mixtures are heated for the same length of time. The number of atoms vaporized in this length of time depends upon their availability to the surface. As the atom fraction of cadmium decreases the availability of cadmium decreases and that of silver or zinc increase. This would mean that the yield of cadmium decreases and the decontamination factor for zinc or silver decreases. The decrease in the yield is evident with the Cd-Zn system and with the exception of experiment 7 in Table IX, it is true for the Cd-Ag system. The decrease in the decontamination factor for the Cd-Ag system is not evident but is shown in experiments 3, 4, and 5 of Table VIII for the Cd-Zn system. Note that the decontamination factors were normalized to the specific activity of zinc which was used in experiment 2. If this is not done, a steady decrease in the decontamination factor of the zinc covers up the real effect. This effect is more clearly shown in the atom ratios of cadmium to silver and zinc.

Assumption 4. Equilibrium between the solid and the vapor state exists at all times. The experimental procedure was designed to measure the degree of radiochemical separation which could be obtained in a short time (10 minutes). Therefore, this is a dynamic system which would not be expected to yield equilibrium conditions.

Assumption 5. The temperature and pressure of the system are constant throughout the distillation. The temperature is maintained within ± 20 °C but there must exist a pressure gradient decreasing outward from the solid system. This deviation is essentially the same idea as that in Assumption 4. The pressure of the chamber is maintained constant at 6×10^{-4} mm. Hg.

The most significant difference between the experimental and theoretical results probably occurs in the extent of non-ideality of the system. If the solution deviates from the ideal case to such an extent that there is a maximum in the temperature vs. composition curve, an azeotropic mixture may distill out, thereby causing a large decrease in the decontamination factor. Note that in most of the separation methods which were used, carrier of the desired constituent was added in order to shift the atom fraction of this component close to 1.0 [e.g., 1 mg. of cadmium plus trace (microgram) amounts of contaminants). This procedure essentially avoids the problem of non-ideality and the formation of azeotropic mixtures.

Particularly in the case of the carrier system, there is still another factor which may be as important as that of the non-ideality. The vapor of the desired constituent may carry along with it some of the atoms of the contaminant (e.g., Ag with Cd). A qualitative correlation might possibly be made with the Cd-Zn and Cd-Ag systems. In experiment 1 the enrichment ratio or decontamination factor is much lower than would be expected. In fact it would be expected that in this experiment at atom fraction of cadmium close to 1, the decontamination factor would be the highest. In view of this it appears that no other explanation can satisfy the low decontamination factor at such a high atom fraction, quite as well as the concept of a carrying of the atoms of the contaminant by the large excess of atoms of the more volatile component (Cd).

If any of the macro amount of metals, (the mercury or carrier amounts of cadmium) are heated too strongly, they will vaporize in a way which resembles a mild explosion which is usually caused by the rupture of an impervious refractory like film (e.g., oxide) over the surface of the solid. When this is done some of the macro metal which contains contaminants is carried out of the furnace and onto the collector without actually vaporizing.

The advantage of using carrier of the metal which is desired to be volatilized as stated above, is offset to a small extent by the carrying of contaminants by this type of mechanism.

It is apparent from comparison of the assumptions used in the theoretical derivation, with the actual experimental conditions, that the theoretical enrichment ratio can serve only as a very inexact approximation to the experimental enrichment ratio.

In spite of these difficulties it can be seen from all of the data that the degree of separation experimentally obtained is comparable with the methods used for cadmium in Chapter III.

2. Carrier and Trace Distillation

The fact that chloride and flouride both interfered with the experiments involving mercury and cadmium on copper foil is probably the result of complex formation with the mercury and copper. High acid concentrations had to be avoided in order to prevent the dissolution of the copper foil. Interference from other electrolytes was negligible. Also the effect on the mercury yield of the contaminating elements in the reduction step was small. This indicates that there were either contaminants plating out on the mercury and cadmium or that there was excess surface area available on the copper.

The mercury cathode electrolysis of carrier amounts of cadmium was done to show an additional application of the method. Since many metals plated into the mercury, this method was also an interesting test of the distillation process. When the macro amount of mercury is evaporated there is considerable danger in oxidation of the desired cadmium distillate. The evaporation was first carried out in a flowing nitrogen atmosphere, but experiments showed that about 60% of the cadmium is oxidized.

When the evaporation was carried out in the carbon rod, under vacuum in an apparatus similar to the distillation apparatus it was found to be slow (1 to 2 hours), but a pure cadmium metal residue could be obtained. The process was slow because the maximum temperature to which the mercury could be heated was about 140 °C at one micron of pressure. Higher temperatures cause the mercury to bump out of the furnace. If carrier (1 mg.) is added it is possible to evaporate the mercury off in a pyrex tube and then transfer the residue to a carbon rod furnace without loss of residue. In this case the temperature can be raised to 180 °C and the evaporation of the mercury is accelerated. Care must be taken to assure that the vacuum is approximately one micron, since rapid oxidation occurs at higher pressures. It is also necessary to watch the charge in the pyrex tube to see when all of the mercury has been evaporated. Otherwise, some loss of cadmium will result.

3. Carrier Free Distillation

It is not apparent from theoretical considerations of metal solutions, just what the properties of a carrier free component are in a macro metallic component. This certainly nears the concept of infinite dilution. It can be seen from these experiments that a carrier free lower boiling daughter can be separated from a macro parent element by vacuum distillation. The yields however, are not high, and the rate at which the carrier free daughter is distilled is probably controlled by its diffusion to the surface of the parent metal. In the distillation of In^{113m} from macro tin the difference in the thickness of the macro tin appears to be important. The 0.001" thick tin foil produced ten times the amount of In^{113m} than the droplet of tin. The values expressing the degree of separation are based upon the resolution of the gamma ray and X-Ray peaks with the scintillation spectrometer, and are given as a percent contamination. From the percent yield, and from the activity of the contaminants in the tin before distillation, the decontamination factor can be determined.

Note that the temperature at which In^{113m} comes off in quantity with only 2% contamination, is about 0.23 of the temperature at which macro tin boils at the pressure of the system. It is also about 0.3 of the normal boiling point of pure macro amounts of indium metal.

The thickness of palladium and platinum foils may have been great enough to result in low yield. The maximum temperature to which these foils were heated was about 0.5 and 0.4 of the boiling points of Pt and Pd. These temperatures approximate the boiling points of macro gold and silver. This was near the maximum output of the induction heater. Even if higher temperatures were available, there is little indication that high yields could be obtained. One possible explanation would exist in the presence of a surface film such as an oxide or sulfide layer which prevents evaporation of the carrier free component.

4. Design of Apparatus

The use of the induction heater eliminates the glass to metal seals which would be needed for other methods of heating. By using a small power induction heater with a relatively small furnace (10 gms.) the temperature of the carbon rod furnace under vacuum reaches equilibrium (at 1200 °C) in two minutes. Lower temperatures require even shorter time. The sensitivity for temperature change is about 20 °C. This is sufficient because in a radiochemical separation very high purity is required. This necessitates a large difference in vapor pressure (or large difference in boiling points) between the metals to be separated. Therefore, very accurate temperature control is not required, particularly when the pressure control is very good.

The vacuum system was selected for its simplicity, coupled with the fact that it can supply a satisfactory vacuum in a very short time (five minutes). The equilibrium pressure when the carbon furnace is previously outgassed is $6 \times 10^{-4} \pm 10^{-4}$ mm.Hg.

From the pressure versus time curves (Figure 9) it can be seen that there is a decided advantage in outgassing the carbon rod before use. The equilibrium pressure is maintained over a longer period of time than for the carbon rod which has not been outgassed. When operating temperatures are below 300 °C outgassing is not necessary.

The most difficult problem to solve was the satisfactory control of the vapor. Control of the vapor means to pass it from the furnace almost quantitatively onto a collector. The vacuum which was used gave a sufficiently high mean free path, so that few collisions of residual gas with the vapor occurred, thereby eliminating vapor deflection. The long narrow cylindrical carbon furnace served to collimate the vapor into a beam.(8) Collection was found to be difficult at room temperature, presumably because adsorbed gases on the surface prevented close surface contact with the vapor as mentioned above. The easiest solution is to cool the surface of the collector, and when this is done the condensation efficiency is virtually independent of the kind of surface used.

By using the above system milligram amounts of metals were quantitatively collected. When using trace elements only 20% was collected. There are several possible explanations for this. The vapor may lose its collimation into a beam at low flux for reasons which are not apparent at this time. The flux may not be sufficient to prevent the vapor from desorbing from the cold surface after once striking it. The prevention of desorption would be the result of incoming atoms colliding with desorbed atoms and pushing them back onto the collecting surface. The actual cause is probably a combination of these, but since the problem of this thesis involves the evaluation of distillation, a simple remedy was found in the use of the deflector as described in the experimental section. It was experimentally verified that the presence of the deflector did not increase the pressure in the furnace.

The holder for the carbon rod furnace was designed in such a way that there was minimal obstruction of gas in order to facilitate rapid evacuation. This method allowed rapid and accurate centering of the furnace. Experimentation showed that adjustment of the carbon rod as much as 1/4 inch off center of the induction coils did not affect its heating characteristics.

5. Improvement in Design

The flange type of seal commonly used on dessicators is not satisfactory because it is difficult to get the surfaces ground flat. It is important if this seal is necessary (as was the case here in order to allow full access to the evacuated chamber) to have a wide flange which will allow a certain amount of warping under pressure in order to seal itself. In general it is better to use tapered joint openings into the evacuated chamber.

A rectangular slit is considered better than a circular opening because a higher intensity beam can be formed with a given furnace temperature and pressure.(58)

Since the vacuum distillation method of separation seems to have promise, a more advanced apparatus, such as that indicated in Figure 11, might be of interest. The apparatus consists of a tube which has two access joints (A and B) at either end, one of which (B) leads

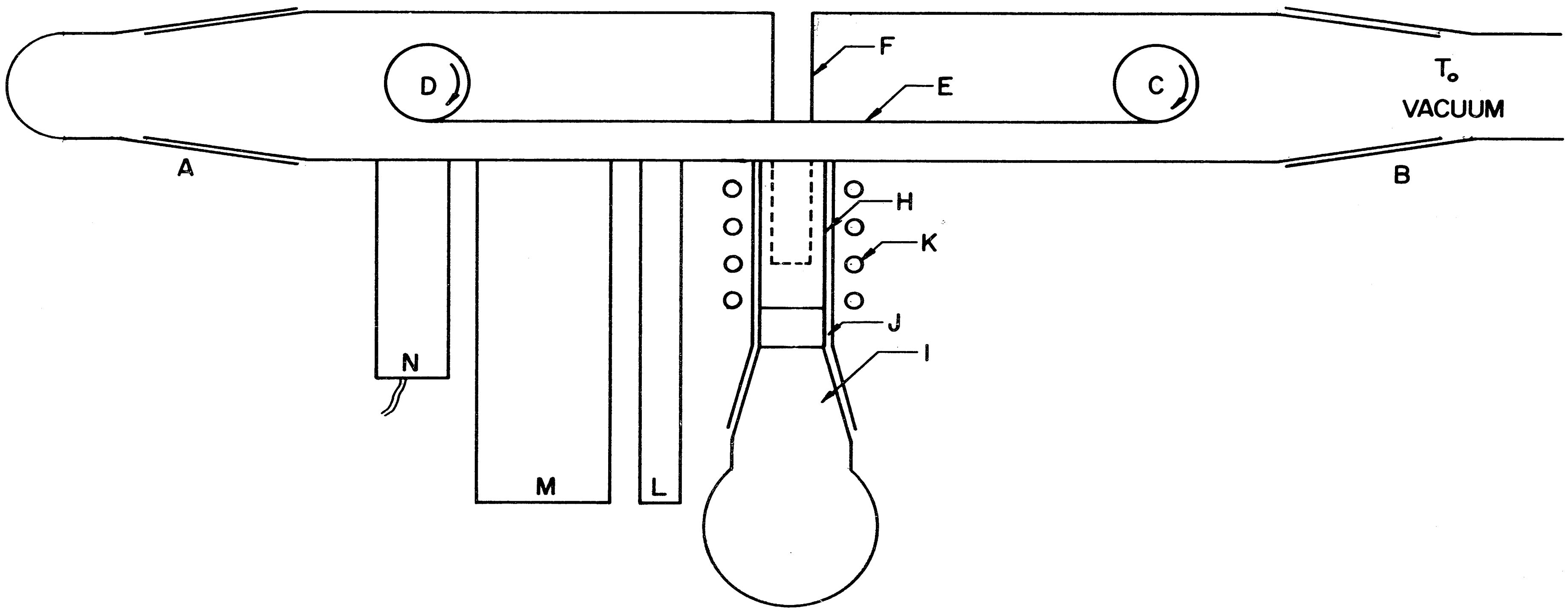

Figure 11. Design of Improved Distillation Apparatus.

to the vacuum pump. Inside of this tube are mounted two drums (C and D) which can be rotated from the outside at a constant angular velocity by means of magnets attached to a motor, which is external to the evacuated chamber.

A thin film strip (E) with suitable tensile strength which is wound around drum C makes contact with the bottom of the cold trap F, and is wound onto drum D. The carbon rod H is inserted and atmospheric pressure on the tapered joint holds it in place. The jacket around this carbon rod would have to be made of Vycor or some special high temperature ceramic. The top of the male tapered joint would be insulated from the carbon rod with a piece of ceramic J. The induction coils K are then placed around this. With liquid nitrogen in the cold finger, the strip is slowly moved over the cold surface while the temperature of the carbon rod furnace is gradually increased. Presuming that the metals of lower volatility can be completely removed, the various metals would deposit along the strip in order of their boiling points. The various areas of pure activity can then be cut out of the strip to complete the separation. In order to prevent cross contamination this procedure would be applicable to the metal which had a vapor pressure at room temperature of at least a factor of 100 less than the vacuum. The distance of drum (D) to the cold finger would depend on the number of components to be separated and their rate of distillation. Except in the carrier free separation it would appear unlikely that the film could bend without loss of deposit.

In order to measure short lived isotopes a lead shield, M, would screen out radiation from the furnace and collector and prevent it from actuating a counter N.

CHAPTER V

EXPRESSING THE DEGREE OF SEPARATION OBTAINED IN A RADIOCHEMICAL SEPARATION

At the present time there has been no consistent method for reporting the degree of separation obtained from a radiochemical separation. In fact there has been little attempt to define the various terms which have been used. This is probably due to the fact that most of the terms seem self explanatory at first glance. However, it appears that improperly defined terms have resulted in misinterpretation of separation data. The various possible methods of expressing the efficiency of a radiochemical separation are listed in Table XV. These definitions in Table XV have been made with the intention of paralleling as closely as possible the meaning intended in previous reports.(59,75,76) The percent yield is also listed in Table XV.

It is difficult to express adequately the degree of separation obtained in a radiochemical separation. The most logical approach to solving this problem would be to note the applications of most radiochemical separations as described in Chapter I. The amount of activity of the contaminant which is measured with the desired activity is the most important consideration. Therefore, one would expect that the efficiency of the separation should be expressed as a percent contamination. Usually the method of reporting the data should be as general as possible. In each case the activity will be counted with some type of counter (scintillation, Geiger-Muller, or proportional counter). Referring to Table XV it can be seen that the A_A and A_B refer to two entirely different radioactive nuclides which would ordinarily have different counting

TABLE XV

METHODS OF EXPRESSING THE DEGREE OF SEPARATION THAT CAN BE OBTAINED IN A RADIOCHEMICAL SEPARATION

1.	Decontamination Factor	A'_A/A_A
2.	Percent Contaminant Carried	$(A_A/A'_A)100$
3.	Percent Yield	$(A_B/A'_B)100$
4.	Percent Contamination	$(A_A/A_B)100$

A'_A	activity (c/m) of contaminant present initially
A_A	activity (c/m) of contaminant present with desired constituent after separation
A'_B	activity (c/m) of desired constituent initially
A_B	activity (c/m) of desired constituent after separation

fficiencies for the emitted radiation when using any given type of counter. The percent contamination changes with the type of counter used because the counting efficiency of a given nuclide would be different for each type of counter. Therefore, this method of reporting data is not very general.

If the data are reported as a decontamination factor, or percent carried (all involving the same variables) the difficulty involving changes in counting efficiency, and counter are removed because the same nuclide is measured before and after the separation. There are, however, two additional difficulties which arise. The decontamination factor will not "a priori" to actual experimentation indicate whether the radiochemical separation will be good enough to remove the contaminants to a level below the sensitivity of the counting instrument which will be used, or to a level below which no interference results. This is not a serious difficulty because the decontamination factor still gives a general indication of the degree of the separation which may be obtained. In any given experiment it may be necessary to repeat the separation procedure to get the total desired degree of separation.

The second difficulty is more serious because it affects the generality of the data. The decontamination factor is dependent upon the concentrations of the contaminant of a given specific activity.

In the case of a precipitation method of separation where the precipitate of the desired component is less soluble than the contaminant, the decontamination factor for the contaminant would be as follows:

Take the reaction $A^+ + X^- \rightarrow AX$ which is the precipitating reaction for the contamination of the desired component (BX). Since the specific activity of A cancels in the following formula one obtains:

$$\text{D.F.} = \frac{A_A^i}{A_A} = \frac{A_o}{A_o - [A^+]} = \frac{A_o}{A_o - \frac{KSP_{AX}}{[X^-]}} = \frac{A_o[X^-]}{A_o[X^-] - KSP_{AX}}$$

where

A_o = initial molar concentration of A

$[A^+], [X^-]$ = equilibrium molar concentration of A, X, respectively.

KSP_{AX} = solubility product constant of AX

The decontamination factor is a function of the original concentration of the contaminant as well as a function of the equilibrium concentration of the precipitant which is of course dependent on the original amount of B and X before separation. Usually loss of generality is avoided by adding a constant amount (e.g., 10 mg.) of inactive carrier of both contaminant and desired constituent in each separation, and by specifying the amount of precipitant which is added. This lowers the specific activity of both components.

If $A_o[X] \ll KSP_{AX}$, the decontamination factor has no meaning from a solubility standpoint. Let us assume, however, that some contamination exists and that it is due to adsorption of A on the surface of the precipitate BX. Suppose that the surface adsorption is of the form indicated by the Freundlich isotherm. $Y = Kc^{1/n}$(56), where Y = mass of contaminant adsorbed per unit mass of adsorbent, C = concentration (moles per unit volume) of contaminant in the medium in which the absorber exists, and n, K = empirical constants. The decontamination factor per unit mass of adsorbent per unit volume of the medium is expressed as $\mathrm{D.F.} = \frac{C}{Y} \cong \frac{Y^n}{K^{n+1}C^{1/n}}$ or if $C \cong A_o$ in terms of the above:

$$\mathrm{D.F.} = \left(\frac{m'_A}{m_{BX}}\right)^n \frac{1}{K^{n+1}A_o^{1/n}}$$

where

m'_A = mass of A adsorbed on BX

m_{BX} = total mass of BX

From this it is clear that if $n > 0$ the decontamination factor is dependent on both the concentration of desired constituent (B, or the mass of absorbant BX) and the contaminant. ($A°$). An example of a surface adsorption effect has been found in the copper foil experiment where copper is used to reduce trace amounts of mercury onto copper (Chapter IV). Data which were taken from Table X, Chapter IV that show this effect are listed in Table XVI. These data represent only a few examples of the effect. Since neither barium nor indium will be reduced by copper, the contamination which is observed is due to some other factor, such as surface adsorption. These data clearly show the dependency of the decontamination factor on the concentration of the contaminant. The concentration of the desired constituent, mercury, is a constant in these experiments.

Ideally, to unambigously express the degree of a separation recourse must be taken to discuss inactive atoms or molecules on a mole fraction basis or mole percent contamination. For a radiochemical separation, this has no meaning unless the specific activity of each component is known before the separation (e.g., in a carrier free separation).

At present for radiochemical separations the most generally accepted method of expressing the degree of the separation is with the decontamination factor or its associated percent contaminant carried. When the mechanism of the separation as explained above indicates dependency of the decontamination factor on the concentration of the components, such concentrations must be recorded.

TABLE XVI

CHANGE IN THE DECONTAMINATION FACTOR WITH INITIAL CONCENTRATION OF THE CONTAMINANT FOR THE SEPARATION OF MERCURY WITH COPPER (Taken from Table X, Chemical Reduction)

Contaminant	Activity of Contam. Added Before Separation	Amount of Contam. Before Separation	Activity on Copper c/m After Separation	Decont. Factor
Ba^{140}	1.9×10^6	C.F.	5,700	3×10^2
Ba^{140}	1.9×10^9	C.F.	8,000	2.3×10^5
In^{114}	4.8×10^6	4.6 μg	48	10^5
In^{114}	4.4×10^8	0.5 mg	19	2×10^7

CHAPTER VI

FUTURE INVESTIGATIONS

The study of the radiochemical separations of the individual elements (such as cadmium in this thesis) has of course proven beneficial to the nuclear industry for reasons stated in the Chapter I. In addition to this such investigations lead to new methods of radiochemical separations. Several new techniques have been found one of which is the vacuum distillation of metals which is discussed in this thesis. The method which is used for evaluation of the radiochemical separations can be improved. Future investigations should include experiments which determine the combined interference effect on the overall separation of 20 or 30 elements.

The radiochemical separation by vacuum distillation has proven to be useful. This thesis has presented numerous possibilities of the method. From the theoretical aspect, experiments might be devised to determine the extent that the experimental conditions deviate from the ideal conditions. Also, future research should be done on the volatilization and collection of three or four components in a stepwise manner from the more to the less volatile component. This will prove whether or not an instrument such as described at the end of Chapter IV is feasible.

While the decontamination factor seems to be the best method of expressing the degree of purity obtained in a radiochemical separation, it is far from being completely satisfactory. It appears that no one general term can be used to express the degree of separation obtained for all separation methods. Another program of future study which should result from the investigations described in this thesis would be to attempt to find better expressions for the degree of purity which is obtained in a radiochemical separation.

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