THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

RADIOCHEMICAL SEPARATIONS AND ACTIVATION ANALYSIS

Progress Report 7
November 1957 - October 1958

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The following is a report of the work completed on Project No. 7, Contract No. AT(11-1)-70 during the year of November 1, 1957 to October 31, 1958.

Previous progress reports are listed below:

Progress Report 1	November 1952
Progress Report 2	November 1953
Progress Report 3	November 1954
Progress Report 4 (AECU-3116)	November 1955
Progress Report 5 (AECU-3375)	November 1956
Progress Report 6 (AECU-3641)	November 1957

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I FACILITIES

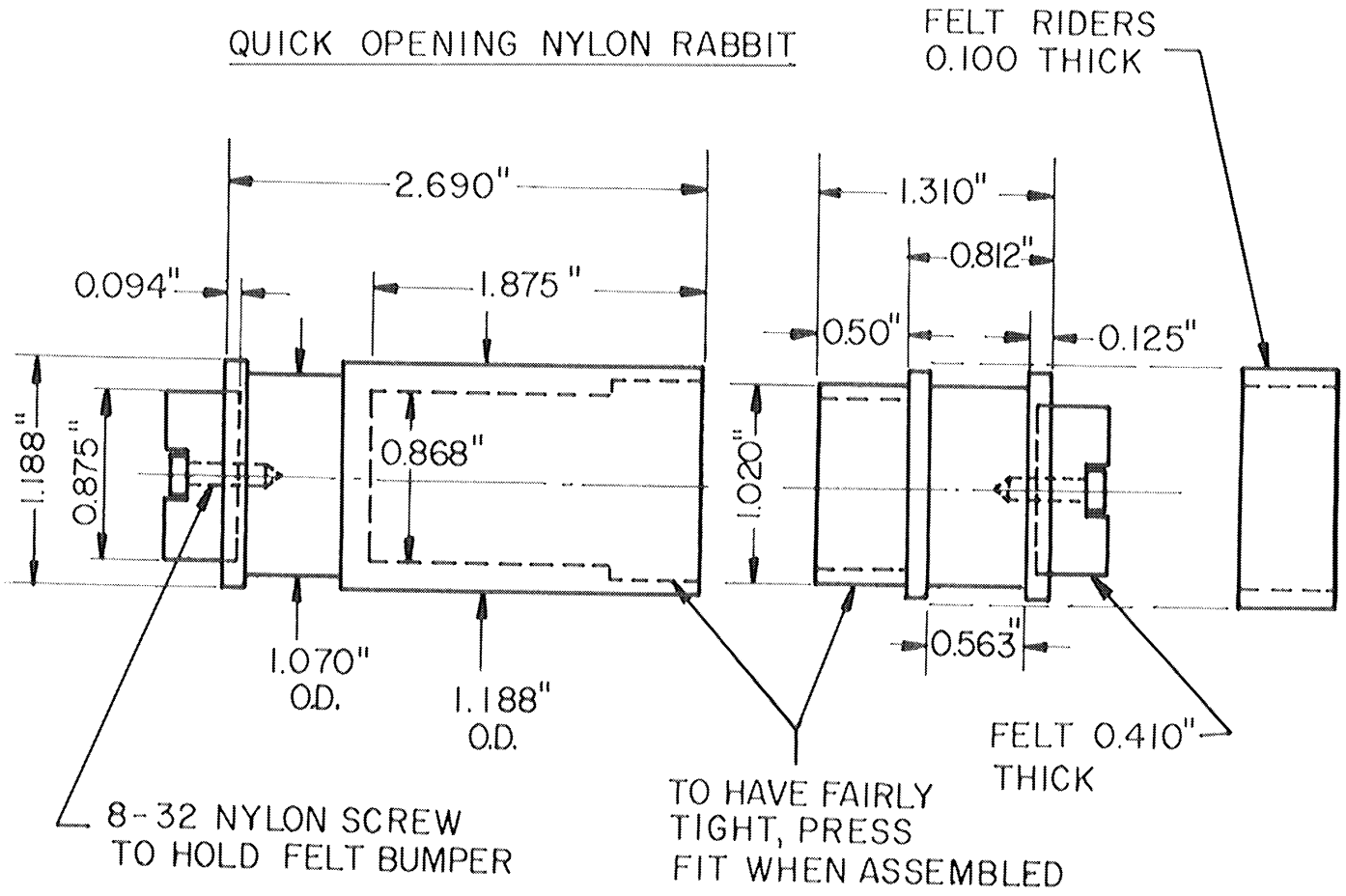
A. Michigan Reactor

Calibration of the Ford Nuclear Reactor (1) at the 10-watt level was completed by early spring and from April on the reactor operated at powers up to 100 kw and a flux of about 10^{12} n cm^{-2} sec^{-1}. The reactor is used in the nuclear engineering teaching program as well as for research and hence does not operate every day at full power. Since April, however, it has been possible for our group to obtain high flux irradiations on an average of two to three 8-hour days per week.

Late in August permission was received from the AEC to operate at a power of 1 megawatt and a flux of 10^{13} n cm^{-2} sec^{-1}, and much of the recent operation has been at this level.

The pneumatic tube system described in the last progress report (1) has operated routinely during the past year with few problems. Samples are received in the hood in the Chemistry Laboratory 3 seconds after the end of irradiation. Although several types of rabbits machined from many different materials have been tried in the past, we now prefer a quick opening nylon rabbit. These rabbits are machined from nylon rod and gasketed with felt, giving a low level of induced radiation. The press fit of the top is tight enough to prevent opening in the pneumatic tube yet the rabbit can easily and rapidly be "uncorked" to remove the sample. Fig. 1A gives the shop drawing for the rabbit while Fig. 1B pictures the nylon rabbits as well as the lusteroid rabbit mentioned below.

Experimental dose rates recorded at the surface of the nylon



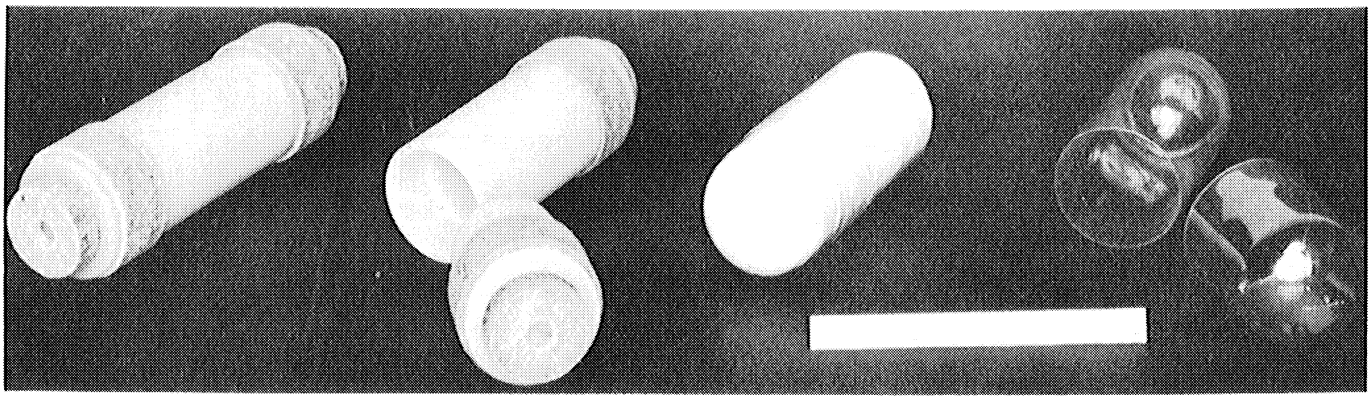


Figure 1. (A) Quick opening nylon rabbit. (B) Nylon and lustroid rabbits

rabbit immediately after return from the reactor core are given in Table I for several irradiation times. The activity seems to consist mostly of 2.3-minute Al^{28} and a longer-lived component of ~ 30 minutes. (Long-lived components observed in the rabbits appear to be 36-hour Br^{82} in the nylon and 15-hour Na^{24} in the felt.) Since it requires only a few seconds to snap open the rabbit by hand, the dose to the hands for short irradiations is minimal. Of course a

large, hot sample in the rabbit could invalidate this premise and require further shielding and remote handling precautions. For most of our current short-lived isotope work, however, it has been possible to open the rabbits by hand. (Finger film tabs are always worn to check the dose received.)

Table I. Dose from Nylon Rabbit Irradiated at 1 mw and Measured 3 Seconds after End of Irradiation.

Irradiation Time	Dose mr/hr
15 sec.	~30
1 min.	~100
2.5 min.	~200
5 min.	~250

A simple lusteroid rabbit 1-1/4" diameter and 3-1/2" long (Fig. 1B), consisting of 2 fitted lusteroid tubes scotch taped together, is also used for some irradiations where quick opening is not required. The weight of a rabbit for this system must be at least 20 grams or else on its return it may not open the exit door sufficiently wide to break the vacuum and will be sucked back into the system.

1. Thermal Neutron Flux and Cadmium Ratios in the Pneumatic Tubes

The pneumatic tubes are positioned near the reflector along the west face of the reactor as pictured in Fig. 2.

Figure 2. Reactor core at 100 kw; taken by its own light. Pneumatic tubes are at left of core.

The fuel elements look white in this picture taken at 100 kw while the graphite reflector rods appear gray. The relative positions of the four pneumatic tubes are shown diagramatically in Fig. 3.

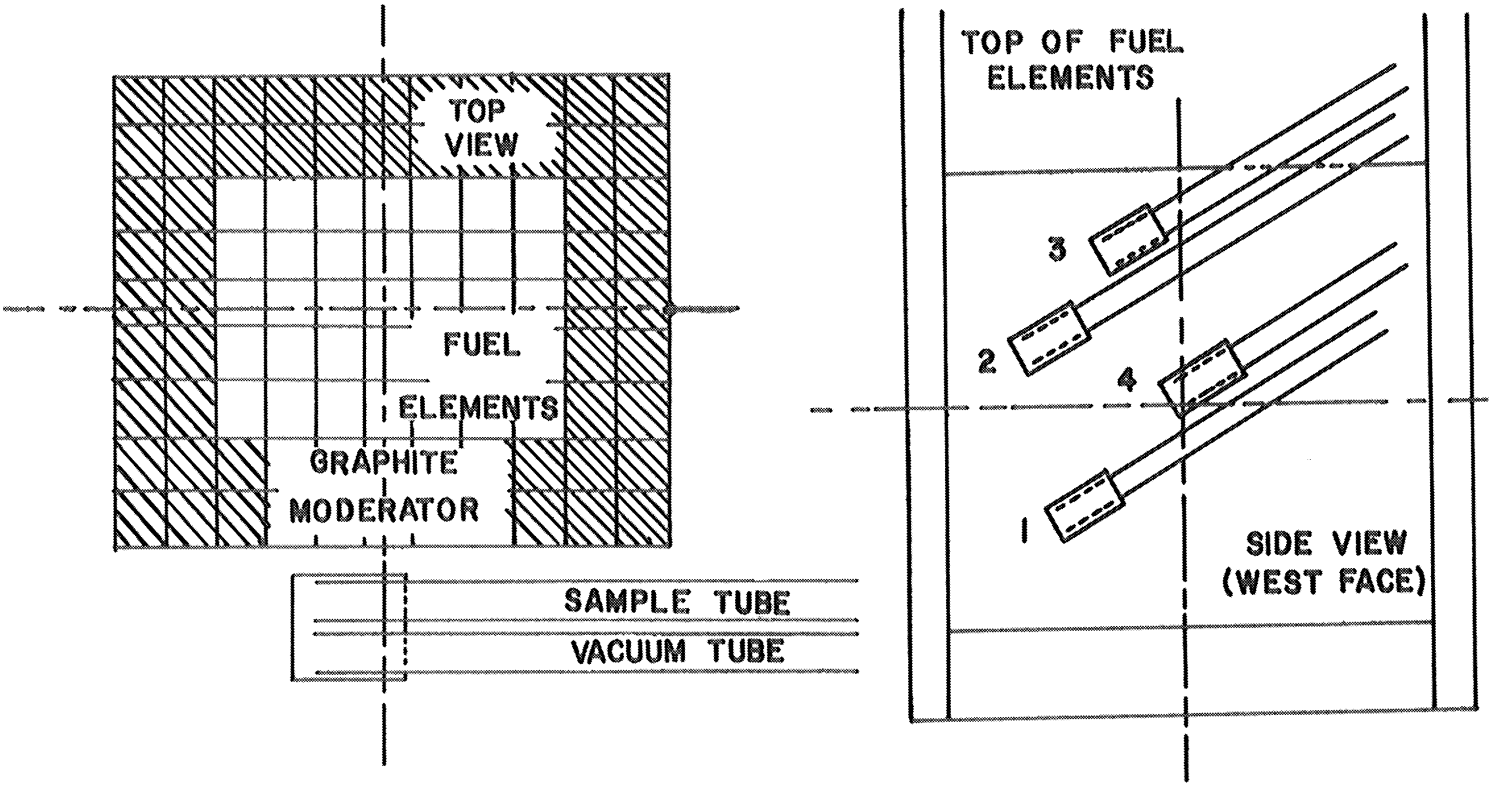


Figure 3. Sketch of pneumatic tube position relative to core; top view and side view.

Relative thermal neutron activities induced in gold foils in each of the four pneumatic tubes were determined at a power level of 100 kw. In addition an absolute activity measurement was made for tube No. 2.

For this measurement dilute solutions of gold and manganese approximately equivalent to 20 $\mu g/cm^2$ foil were irradiated in small square polyethylene envelopes. Duplicate 50 λ samples were taken for 4π counting. The gold samples were also counted absolutely using the 3" x 3" NaI (Tl) crystal and 100-channel analyzer, and in another set-up using a 1-1/2" x 1-1/2" NaI (Tl) crystal with a single channel analyzer. The data for activity of the "bare" and 20-mil-cadmium-covered samples were also used to calculate cadmium ratios for the four pneumatic tubes. The results are summarized in Table II. (M. Wahlgren)

Table II. Pneumatic Tube Data at 100 kw.

Tube	Relative Thermal Neutron Activity	Thermal Neutron Flux*; n $cm^{-2}sec^{-1}$	Cd Ratio (1 mil Au foil)	Cd ratio ($20\ \mu g/cm^2$ Au sol'n)
No. 1	0.91	1.8×10^{11}	15	10
2	0.73	1.40×10^{11} (Au)* 1.47×10^{11} (Mn)**	15	10
3	0.48	9.5×10^{10}	15	10
4	1.00	2.0×10^{11}	15	10

* based on σ_{th} of 98 for gold

** based on σ_{th} of 13.2 for manganese

2. Flux Inhomogeneity in Pneumatic Tube

A variation of flux of ~8% along the length of the rabbit and of ~30% from side to side was observed. Experiments conducted both at 5 watts and 100 kilowatts gave similar results. Four rows of three small gold foils were taped at 90° intervals on the outside of the rabbit and their specific activities compared. Self shielding contribution of sample and rabbit are negligible. The results are not inconsistent with the geometry of the pneumatic tube position and the attenuation of the neutron flux in the water moderator. The data obtained indicate that care must be exercised in the positioning of samples and monitor foils inside the rabbit to insure reproducibility from run to run. (M. Wahlgren)

3. Fast Neutron Measurements in the Pneumatic Tubes

Values for the fast flux in the pneumatic tubes have been determined as a basis for estimation of possible (n,p) interference in activation analysis and for the possible production of carrier-free isotopes. Consideration of the standard threshold reaction (2), the decay schemes involved, and the limited time available for the measurements, indicated that absolute gamma spectrometry without chemical separation would afford useful values with the minimum expenditure of time. The $Al^{27}(n,p)Mg^{27}$, $Mg^{24}(n,p)Na^{24}$, and $Al^{27}(n,\alpha)Na^{24}$ reactions, were used for these measurements. Experiments and calculation showed that the (n,γ) contribution from impurities in the high-purity foils was below a detectable level.

Magnesium and aluminum foils were enclosed in a 10-mil

cadmium envelope and irradiated. After a 30-minute decay (to eliminate 2.3 minute Al^{28}), the 9.5 minute Mg^{27} was measured absolutely using the 3" x 3" NaI (Tl) crystal and 100 channel analyzer. The 15.0 hour Na^{24} was counted, after a decay period of several hours, in a calibrated gamma well counter.

The 840 kev γ-ray of Mg^{27} was used to determine the disintegration rate by the application of the method and efficiency curves of R. L. Heath (3). The disintegration rates of Mg^{27} and Na^{24} measured on the 3" x 3" crystal were within 5% of the values obtained by preparing aliquots of the activities and counting on a 4π counter. Since the reported branching ratios of Mg^{27} were in poor agreement a measurement was made in this laboratory and an abundance value of 68% obtained for the 840 kev γ-ray, confirming the results of Lyon and Lazar (4).

The ratios of Mg^{27} activity produced in the pneumatic tubes were measured and found close to the ratios obtained for the thermal flux. These ratios combined with the absolute flux values measured in tube 2 are the basis for the values listed in Table III below.

Table III. Fast Flux Data for Pneumatic Tubes at 100 kw.

Tube	Ratio	$Al^{27}(n,p)Mg^{27}$	$Mg^{24}(n,p)Na^{24}$	$Al^{27}(n,\alpha)Na^{24}$
		>5.3 Mev neutrons	>6.3 Mev neutrons	>8.6 Mev neutrons
1	0.84	6.9×10^8	4.0×10^8	8.0×10^7
2	0.74	$6.1 \pm 0.1^* \times 10^8$	3.5×10^8	7.1×10^7
3	0.50	4.1×10^8	2.4×10^8	4.8×10^7
4	1.00	8.3×10^8	4.7×10^8	9.6×10^7

* Error is "standard deviation" for 7 samples.

At the high neutron energies involved here, the shape of the fission spectrum is approximated even in the presence of considerable moderator. Thus the three values given for each tube fall on the fission spectrum in every case.

This same technique was also applied (in collaboration with Mr. J B. Bullock of the reactor staff) to a number of fast flux measurements in the core lattice and in the region of the fission plate. It was observed in the lattice measurements that the flux based on the $Al^{27}(n,\alpha)Na^{24}$ reaction was consistently higher by about 10% than would be expected on the basis of the other two reactions. (M. Wahlgren)

B. Michigan Phoenix Memorial Laboratory

Full utilization of the hot chemistry laboratory facilities of this building has continued throughout the year. In addition the "baby cave" located in the room adjoining hot chemistry is finally fully assembled and ready for use. The 2-3/8" lead shield and lead glass window for the box were received in late summer and have been installed, permitting work with several curies of gamma emitters at close range.

Much time and effort have been expended to complete the 12' x 15' room designed to house the 100-channel pulse analyzer. Many problems were encountered in attempting to air condition this room but by June complete temperature and humidity control equipment had been installed.

The 100-channel pulse analyzer was finally delivered the end of March and was set up in a temporary location until the air

conditioning was completed. During April, May and early June a "cave" (40" cube) was built into the outside wall of the room to house the detector for the analyzer. This cave was designed to reduce background as well as to minimize backscattering effects. Construction details of this cave will be given in the next section. The opening of the cave was originally closed by a lead brick wall. During September, however, a 4" steel door was hung over the opening.

Fig. 4 shows the analyzer with the steel door over the cave opening. The center access port of the door can be closed by lead bricks if necessary. Left of the cave is the hollow scintillation detector and behind it the x-ray proportional counter and associated electronics. The three racks compose the 100-channel analyzer with the x-ray plotter on the table. Behind the plotter is the well counter which can be used either with the analyzer or with the scaler at far left. Fig. 5 pictures the east end of the room with the steel door open and the 3" x 3" crystal and photomultiplier housing in place in the center of the cave. A beta proportional counter, a Geiger counter and an electronics bench complete the equipment available in this room.

Most room alterations in the Phoenix Building for our program have been completed. There is a possibility that a pneumatic tube station will be brought directly into the analyzer room or alternatively that a separate system will be devised to rapidly send a sample the 90 feet between the hot chemistry laboratory and the analyzer room - to replace the present 10-15 second run down the hall for short-lived isotopes. No definite plan has yet been made for this extension since the program so far has not demanded it. A temporary detector for the analyzer has been set up on occassion

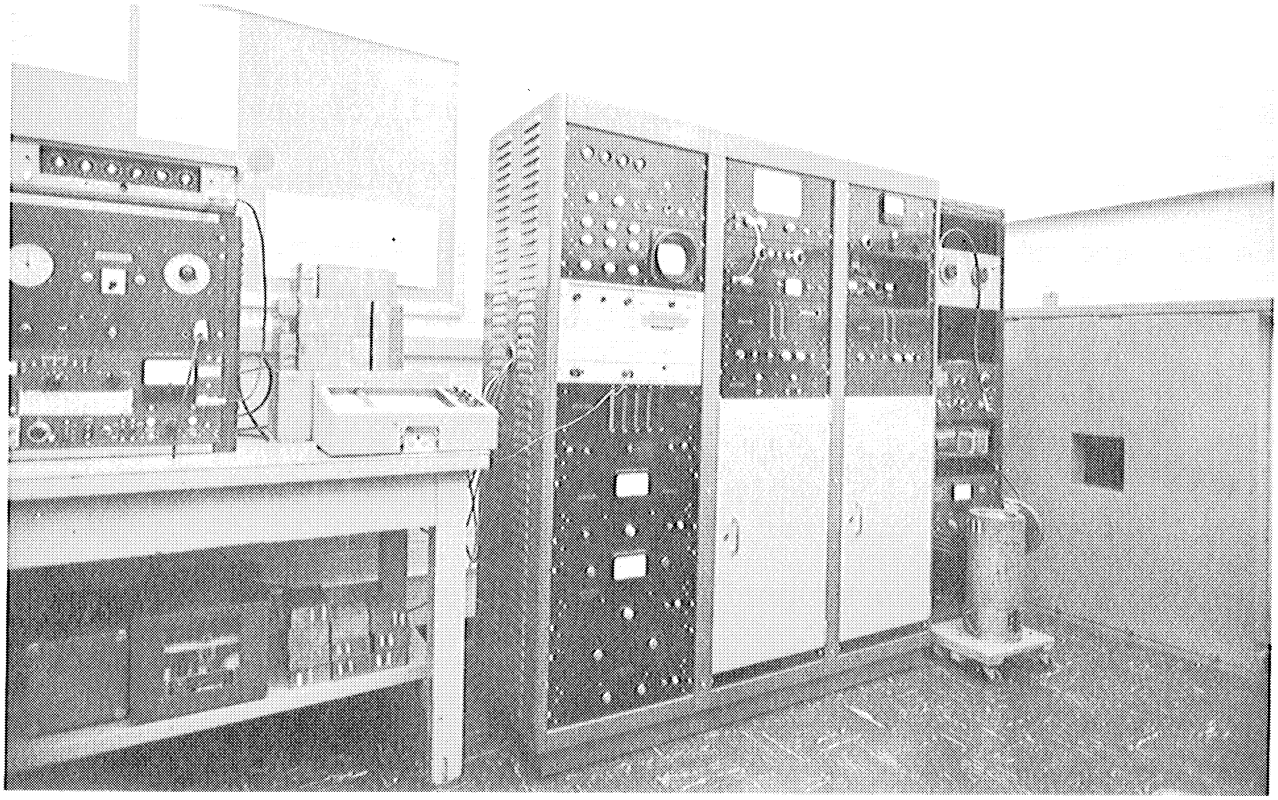


Figure 4. 100-channel analyzer room, north wall.

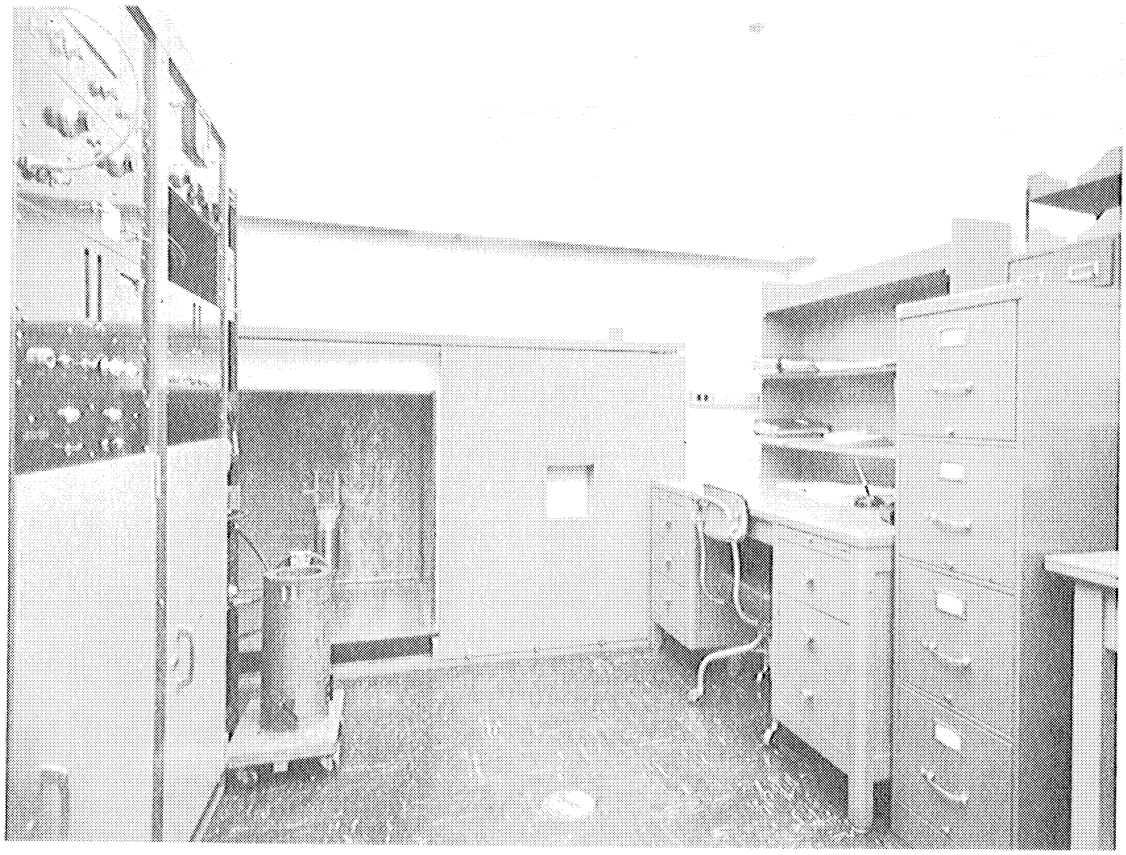


Figure 5. 100-channel analyzer room, east wall.

in the hot lab to facilitate measurement of half-lives of the order of seconds. Permanent connecting lines for this detector will be installed between the two rooms in the near future.

C. Chemistry Building

Although the order for air conditioning room 3023 of the Chemistry Building was placed over a year ago (1) it took more than 8 months to complete the job. All of our specialized and general counting equipment (except that in the Phoenix Building) has been integrated into this one 15' x 30' room which now has temperature and humidity control. In addition the room was recently repainted and asphalt tile was laid on the floor. Routine counting equipment is arranged at the south end of the room as shown in Fig. 6 left to right with their associated electronics: Geiger counter, end window proportional flow counter, "Q" gas flow counter, side window proportional flow counter, 4π counter and scintillation well counter. Fig. 7 shows the other end of room with gamma spectrometer and coincidence equipment, evaporator, beta ray spectrometer and general electronic work area.

The teaching laboratory used for the Nuclear Chemical Techniques course one semester a year and for research the rest of the year is being remodeled at present. The furniture in this laboratory was very old and it was hard to teach proper respect for and handling of radioisotopes with it. The room will now have all new furniture, the hoods will be refinished, filters and an alarm system will be installed, a false ceiling will cover up pipes on the ceiling and several areas of pipes along the wall will be closed in. The remodeling should be completed by November to give an optimum facility for handling subcurie levels of radioisotopes.

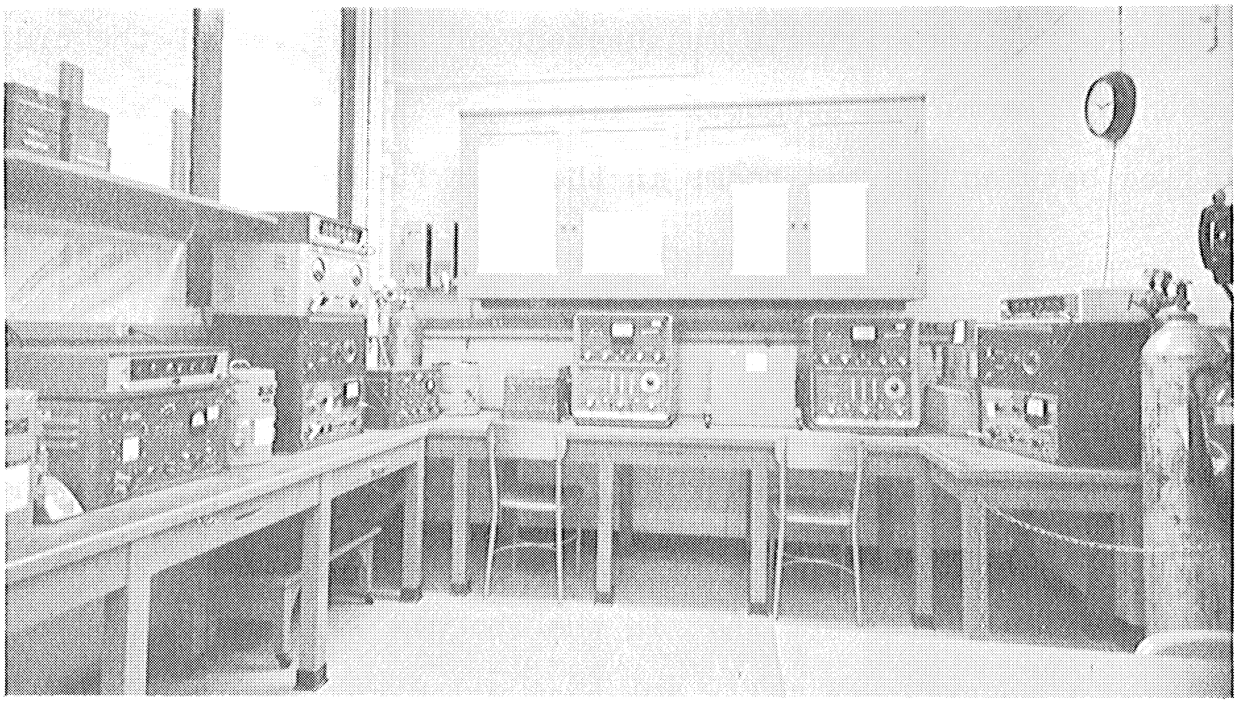


Figure 6. Chemistry counting room, south end.

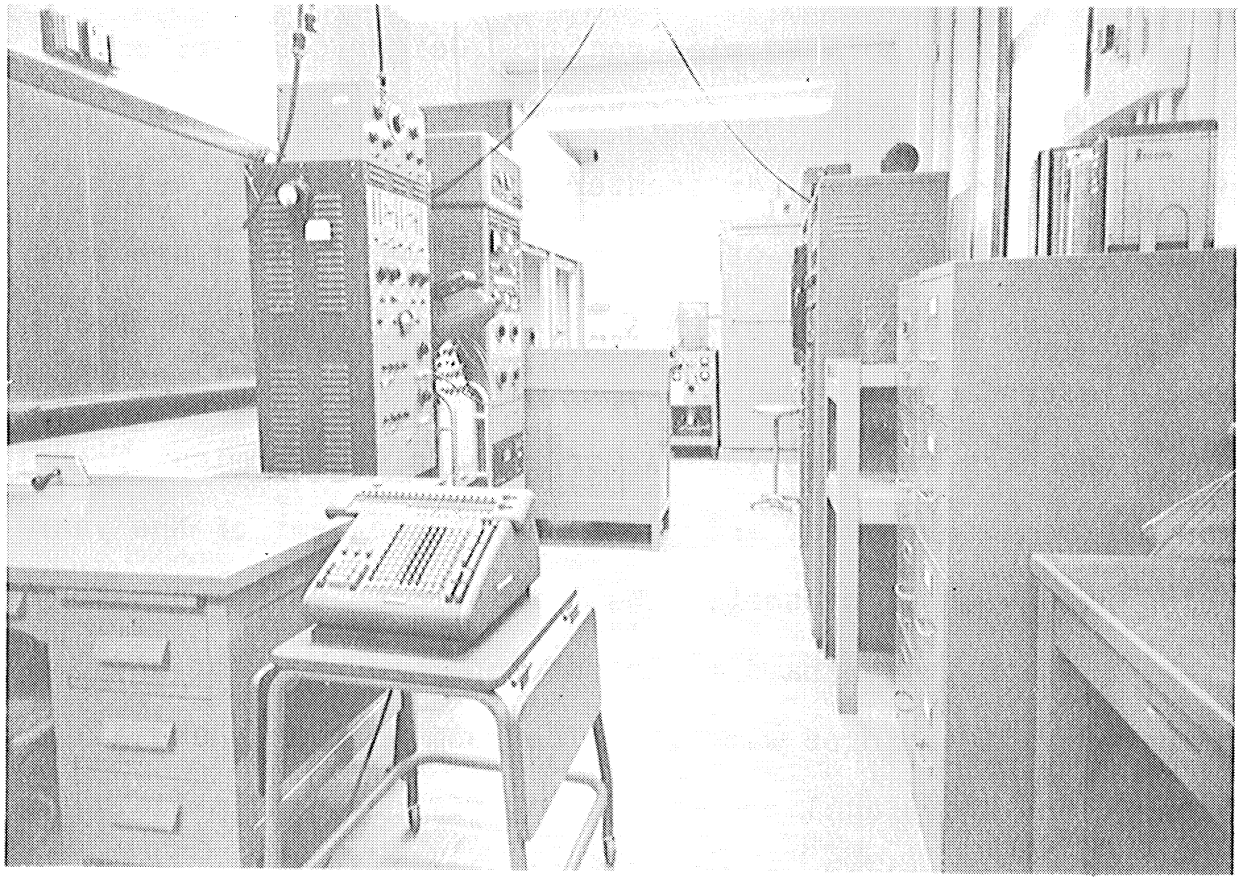


Figure 7. Chemistry counting room, north end.

II INSTRUMENTATION

During the past year as the Michigan reactor began routine operation the counting equipment used in the nuclear chemistry group was assembled into one room. As indicated in an earlier section the outfitting of this specialized room is now complete and few changes in arrangement or equipment are contemplated.

A. 100-Channel Pulse Height Analyzer

The entire measurement program of the group is built around the RIDL dual memory 100-channel pulse height analyzer, Fig. 8, which was finally delivered on March 21, 1958.

The analyzer consists of a triple section 6 foot rack. From top to bottom, and left to right in Fig. 8 they are: timer, scope, tape print out, print out and autograph control, and power supplies; amplifier, converter, "A" memory control, and "A" memory; detector high voltage supply, detector patch panel, "B" memory control, and "B" memory. The block diagram of Fig. 9 will help in identification of these units.

The main advantage of this analyzer is that consecutive spectra can be recorded for short-lived radioisotopes without losing data through the 1 second per channel dead time associated with the printing cycle of the ordinary 100-channel analyzer. The "A unit" is the controlling unit and "B" the slave. The unit may be used as a single 100-channel analyzer but is more frequently used as an automatic dual 100-channel analyzer.

In automatic operation, while "A unit" stores spectral

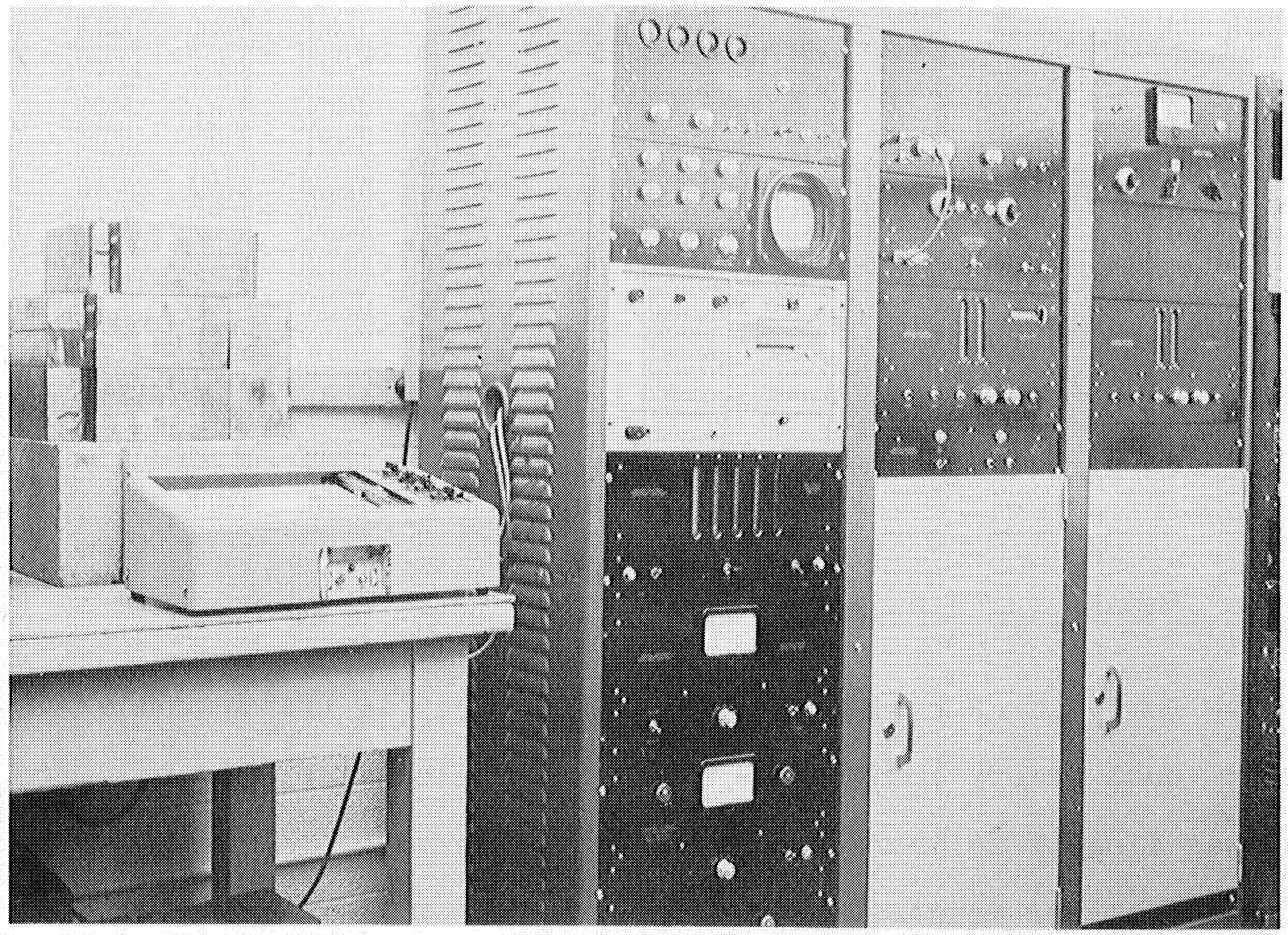


Figure 8. Dual 100-channel pulse height analyzer.

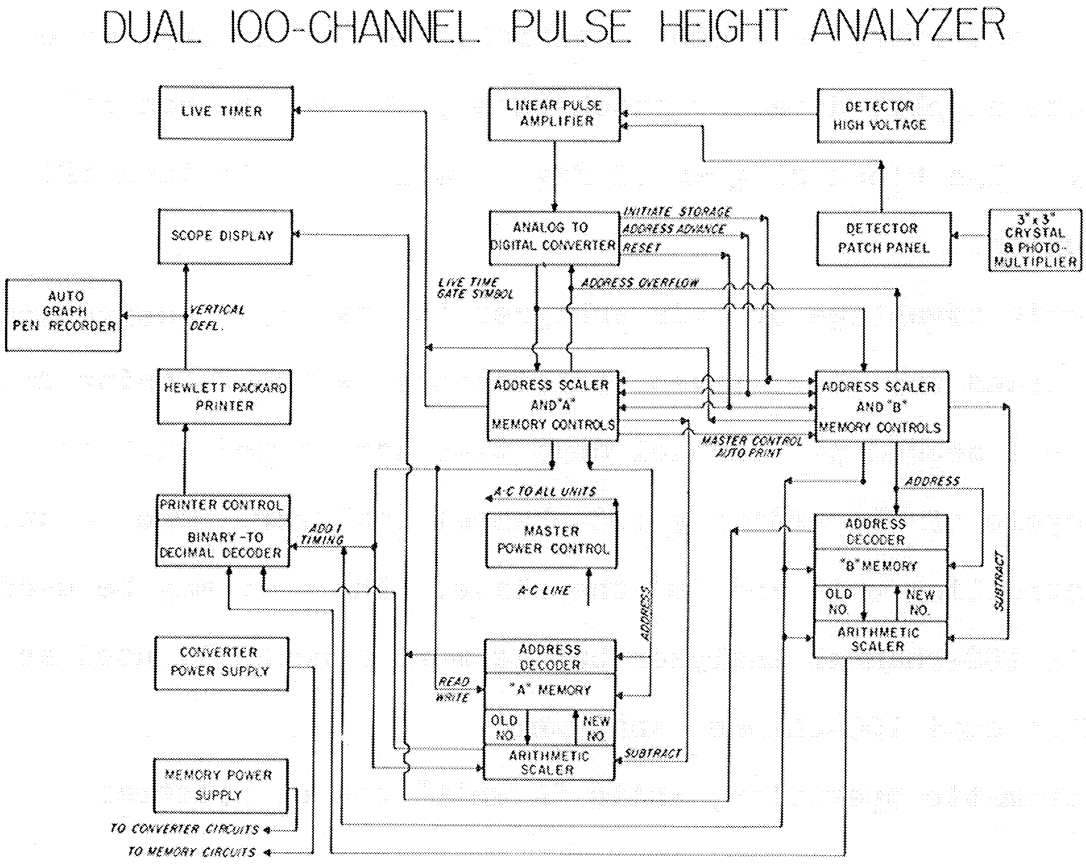


Figure 9. Block diagram of dual 100-channel pulse height analyzer.

information, "B unit" remains in a static condition. At the end of the "A unit" store cycle, the "A unit" prints and plots out its stored information while the "B unit" stores; then the function is reversed and "B" prints out while "A" stores. Since a special fast printer is used a complete print-out cycle of 100-channels can be made in 0.4 minutes. However by adjusting limit controls it is possible to bracket a 20-channel area and print it out completely in 0.1 minutes. This permits measurement of radioisotopes with half-lives of the order of six seconds with ease; the 7.4-second Au^{197m} isomer is readily observable. The only limit is the time necessary to transfer the sample from the hot laboratory to the counting room (or to a detector in the hot lab).

Assembly and testing of the special switching circuitry required to permit this continuous recording held up delivery of the pulse analyzer for over six months but the engineers of the Radiation Instrument Development Laboratory of Chicago staff, headed by J. Wolf finally designed suitable circuitry to meet our requirements. When our machine had finally been completed and checked out, RIDL began incorporating some of this same switching circuitry into their standard analyzer models to permit greater flexibility with short half-lived materials.

Numerous minor electronic difficulties have been experienced in the 6 months since delivery but RIDL has been most helpful in working with our electronics men to iron out these problems. As a result electronic failures have seldom interferred with experimental work. (R. Shideler, H. Nass, W. W. Meinke)

B. Three-inch Scintillation Crystal Detector and Housing

The 3" x 3" crystal, described previously (1), is housed in a cave, 40" x 40" x 40", extended out the side of the Phoenix Building below grade as shown in the sketch of Fig. 10. The cave is lined with 1/2" lead shielding, covered with 0.032" cadmium sheet which in turn is covered with 0.005" copper sheeting.

The experience of Heath et. al. (3) seemed to indicate that a cave of this size would best reduce backscattering peaks. The different linings reduce unwanted X-ray peaks; when lead is struck by energetic gamma rays a lead X-ray is produced; cadmium absorbs the lead X-ray but in turn emits a cadmium X-ray, which is absorbed by the copper. The canned 3" crystal with phototube and temporary sample holder arrangement is shown in Fig. 11 inside the cave. A more permanent mount is under construction.

Figure 12 shows a one hour spectrum of the background on the four Mev range for this detector with the steel door closed but the access hole in the door open. Maximum background occurs in channel four and is 116 c/m but this falls rapidly to 45 c/m in channel 25 and 5 c/m in channel 62. Backgrounds of this order do not hinder our work. Other spectra produced by the analyzer will be shown in later sections of this report. (R. Shideler, H. Nass)

C. Other Detectors

A switching arrangement has been installed on the 100-channel analyzer such that the hollow beta scintillator and the X-ray proportional counter described previously (1, 5, 6) could be used as detectors. A 1-7/8" x 2-1/4" well counter has also been used

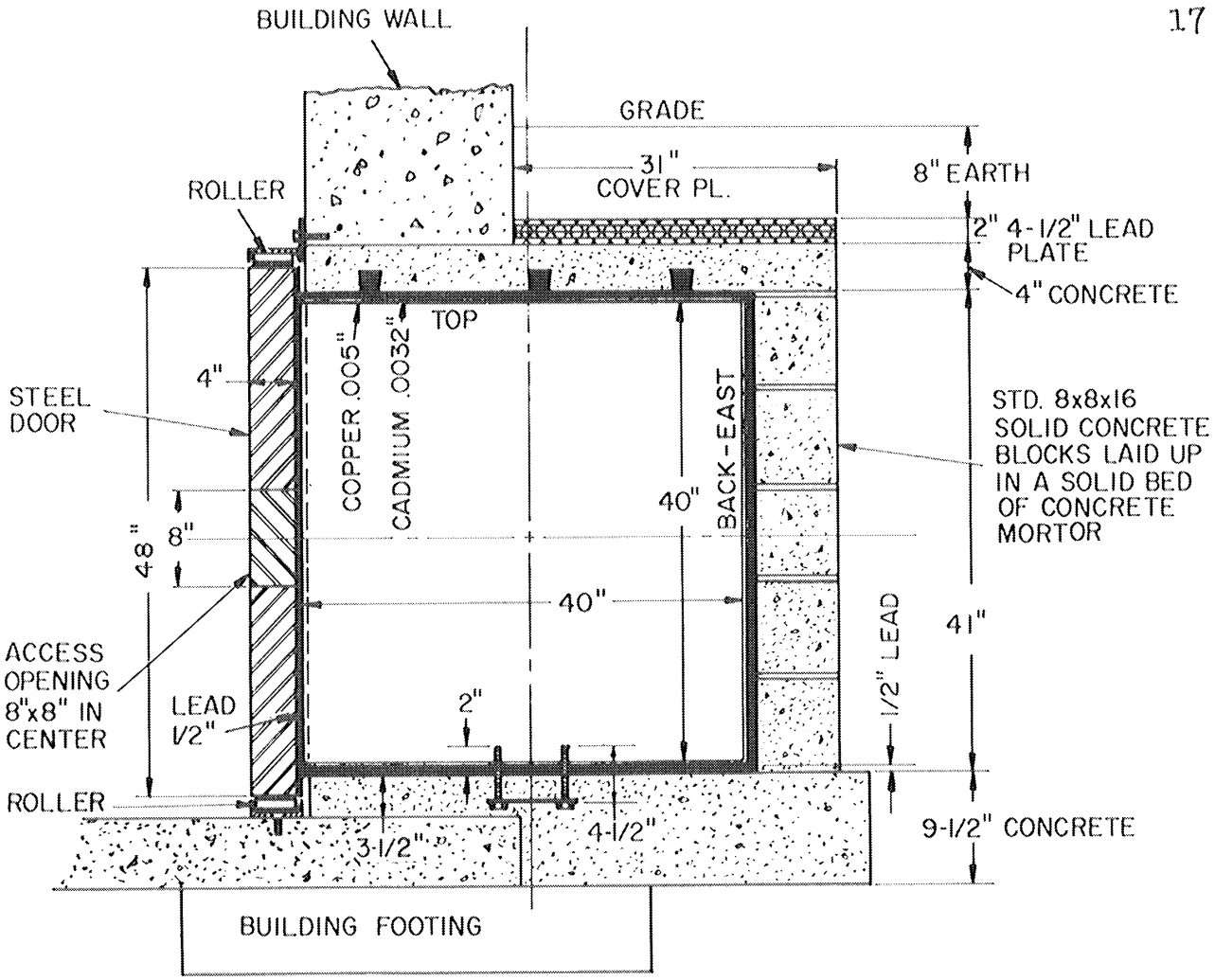


Figure 10. Cave for scintillation detector.

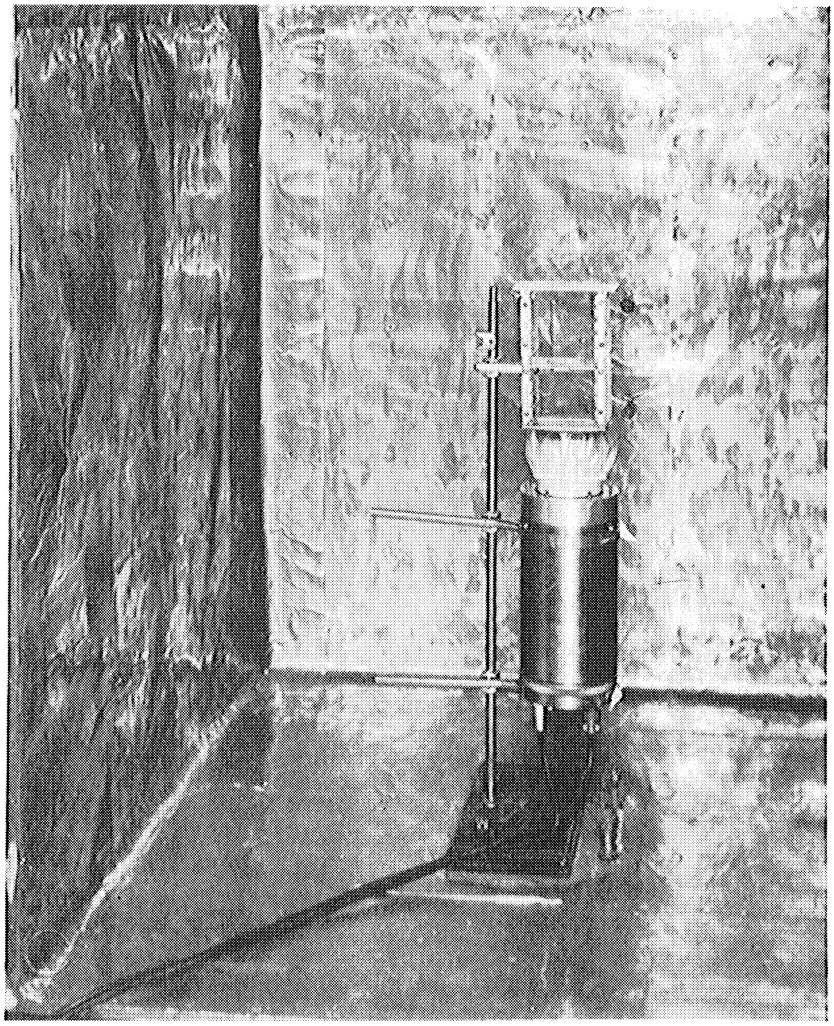


Figure 11. 3" x 3" scintillation crystal housing in cave.

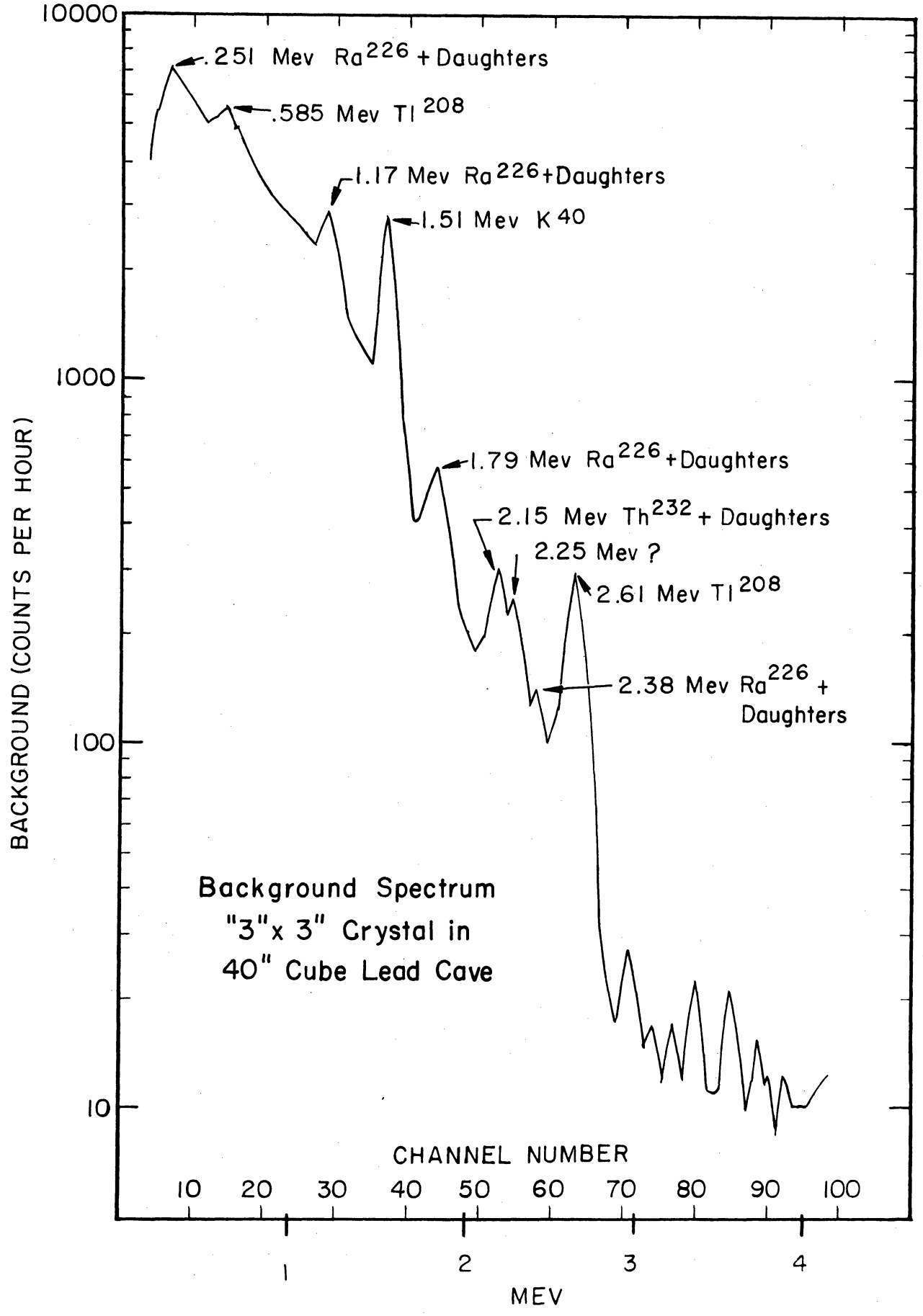


Figure 12. Background spectrum of 100-channel analyzer. (1 hour)

with the analyzer. Future plans include permanent installation of a 1-1/2" x 2" crystal in the hot laboratory with remote control of the analyzer for studying short lived isotopes. (R. Shideler, H. Nass)

D. Resolution Obtained with the 3" x 3" NaI (Tl) Crystal

The resolution of the 3" x 3" NaI (Tl) crystal has been determined as a function of gamma energy. These values are summarized in Table IV.

Table IV. Resolution of 3" x 3" Crystal.

Isotope	Gamma (Mev)	Resolution (%)
Cr^{51}	0.325	11.5
Au^{198}	0.411	10.3
Cs^{137}	0.662	8.75
Mn^{54}	0.840	8.10
Zn^{65}	1.12	7.45
V^{51}	1.44	6.80
Al^{28}	1.78	6.30
Na^{24}	2.75	5.65
S^{35}	3.10	5 55
Na^{24}	4.1 (sum peak)	5.35

The data have proved useful for rapid calculation of peak areas in activation analysis, and in determining the presence of multiple gamma peaks. (M. Wahlgren)

III NUCLEAR CHEMISTRY

Only one cyclotron bombardment was obtained during the past year, and this was for the production of vanadium tracer. Instead since April the emphasis has been on the reactor as a source of radioactivity. This has meant that less emphasis has been placed on nuclear problems than previously.

In one area, however, the facilities at Michigan are ideal for nuclear determinations - the field of short half-lived isotopes. It is anticipated that a number of radioisotopes with half-lives of a few seconds to a few minutes will be reinvestigated with our pneumatic tube-pulse analyzer system.

A. Absolute (d,alpha) Reaction Cross-Sections and Excitation Functions

No further experimental results have been obtained in this area during the past year. The early work of Hall (6) has been accepted for publication in the Journal of Inorganic and Nuclear Chemistry, however, and the later work of Anders (1) is being assembled into manuscript form for submission to the Physical Review. (K. L. Hall, O. U. Anders)

B. Nuclear Data Analysis: Application of Digital Computers

Exploration of a system based on Fourier transforms for obtaining half-life and intercept values with appropriate statistical errors from multi-component decay curves has been continued by D. G. and J. C. Gardner although they are now in Pittsburg. Reports on parts

of this work were presented at the 133rd American Chemical Society meeting at San Fransicso, April, 1958 and at the 13th meeting of the Association for Computing Machinery at the University of Illinois, Urbana, Illinois, June 1958. A paper on the early phases of this work done at Michigan is being prepared and will be submitted for publication in the near future. (D. G. Gardner, J. C. Gardner, W. W. Meinke)

C. New Platinum Activity

Short-lived activities induced in pure samples of a number of different elements are being explored with the pneumatic tube - pulse analyzer system. When high-purity platinum was irradiated for one minute several unreported radiations were observed. A 0.074 Mev γ-ray and a 2.5 Mev β-ray decayed with a 31 $\pm$ 1 second half-life while a 0.395 Mev γ-ray decayed with 16.1 $\pm$ 0.5 second half-life.

These activities do not appear to arise from impurities in the platinum foil and are reduced considerably by cadmium foil indicating that they do not come from $(n,n'\gamma)$ or (γ,γ') reactions.

Several nuclear considerations indicate that the 16-second activity may belong to an isomeric state of Pt^{199}. Some enriched Pt^{198} is being procured to verify this assumption. Other experiments with enriched isotopes will be conducted to assign the 31-second activity. (M. Wahlgren, W. W. Meinke)

IV RADIOCHEMICAL SEPARATIONS

Much emphasis was placed on the program early in the year when personnel were on hand to use the reactor but the reactor was not available. DeVoe has continued his systematic development of optimum radiochemical separations. Several others, however, also report on problems that were studied until the reactor became available.

A. Indium Separations

Following publication of the earlier evaluation work on barium, strontium, calcium and silver separations, and hydroxide scavenges in the November, 1957 issue of ANALYTICAL CHEMISTRY, (7), the indium data mentioned previously (1, 5) were assembled into manuscript form. This paper was presented at the American Chemical Society meeting at San Francisco in April 1958 and has recently been accepted for publication in the January 1959 issue of ANALYTICAL CHEMISTRY. (D. N Sunderman, I. Ackermann, W. W. Meinke)

B. The Development and Evaluation of Radiochemical Separation Procedures for Cadmium

The study of the radiochemical separations of cadmium has been completed. More work has been done on the precipitation methods described in the last progress report (1), and in addition a dithizone extraction and an anion exchange method have been studied.

1. Literature Survey

Although very few radiochemical separations for cadmium have used solvent extraction techniques, there are a large number of quantitative analytical methods in the literature which separate cadmium by this method, with subsequent colorimetric or gravimetric determination of the element. Dithizone (diphenylthiocarbazone) gave sufficient purity of cadmium for spectroscopic use (8) and is discussed in detail (9) for the analysis of rocks.

While the extraction of the iodides of cadmium into diethyl ether seems to be of some interest for radiochemistry is was not studied at this time.

Kraus and Nelson (10) showed that cadmium can be separated from many elements by the use of anion exchange.

2. Discussion and Results

Four procedures have been studied by measuring their yields and decontamination from a large number of tracer impurities. These values are summarized in Table V.

a) 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. Therefore the procedure utilized extraction of the cadmium dithizonate from a 20% tartrate solution at pH 13.5 into chloroform and then back extraction into 0.1 M HCl. The procedure took 10 minutes.

Of the twenty-three elements listed in Table V only Ag, Cu, Tl, and Zn contaminate the separation. The use of ammonium

Table V. Percent Contamination of Cadmium Separations.(a)

Tracer	Extraction (no carrier added)	Ion Exchange (no carrier added)	Precipitation	
			Reinecke (carrier added)	2-(ohydroxyphenyl)-benzoxazole (carrier added)
Cd (b)	77 ± 5	80 ± 5	78 ± 5	80 ± 5
Ag	2	89	99	4
Au	0.4	-	-	-
Ba-La	0.1	0.03	0.06	-
Bi	0.01	-	-	-
Ce-Pr	0.02	0.01	0.03	5
Co	0.03	0.007	0.05	80
Cr	0.1	0.02	0.2	4
Cs	0.08	0.007	0.8	11
Cu	13	-	-	-
Hg	0.1	36	46	-
I	0.06	0.1	0.7	10
In	0.5	0.3	0.1	-
Ir	0.1	0.015	0.08	9
Ni	0.09	-	-	-
Pd	0.1	-	-	-
Ru	0.03	0.12	0.28	80
Sb	0.2	4.6	3	11
Se	0.01	0.01	93	6
Sn	0.3	0.3	0.83	5
Ta	0.6	0.005	0.06	10
Tl	91	0.007	99	4
Zn	64	81	0.6	8
Zr-Nb	0.1	0.03	0.04	-

(a) duplicate runs

(b) based on 5 runs

hydroxide (1M) satisfactorily complexes the silver to prevent contamination, but the dithizonates of Cu, Tl, and Zn remain. When the basicity is raised to 0.5 M NaOH, the copper contamination is reduced to about 0.1%. Unfortunately the yield of cadmium is also reduced to about 50%.

The contamination of thallium can be conveniently removed by utilizing a displacement reaction (8). 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 distilled water is agitated with a chloroform solution of the cadmium and thallium 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 back extraction into 0.1 M HCl results in a removal of cadmium but very little inactive cobalt. The decontamination obtained from thallium by this method is 0.85% with a yield of Cd of 65%. This displacement did not occur with zinc.

In many cases the radiochemist is interested only in a 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.

b) Ion Exchange

Cadmium forms very slightly dissociated chloride complexes which are strongly held on a Dowex II column. Thus the sample was passed through the column in 3 M HCl and contaminating ions were washed off with more 3 M HCl. The cadmium was then eluted

with 0.1 M NH_4OH. The procedure took 15 minutes. The high acid concentration was used to prevent hydrolysis of many 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 assure that all is present in the +1 state. This is done by heating the solution with 0.1 M sodium bisulfite. Since the TlCl was carrier-free, it did not precipitate.

Ion exchange can be used to separate Zn, Hg, and Ag from cadmium by replacing the ammonium hydroxide eluant by 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. Cadmium is observed to have two peaks in the elution curve, a fact which indicates the presence of more than one complex chloride anionic species. The yield of cadmium was found to be about 55%, with a contamination of 1.0, 0.5, and 0.3% for Zn, Hg, and Ag, respectively.

c) Precipitation

Procedures for precipitation with the Reinecke salt and with 2-(o-hydroxyphenyl) benzoxazole were summarized in the last progress report (1).

3. General Applicability

The data of Table V are plotted in graphic form in Figs. 13 and 14. 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.

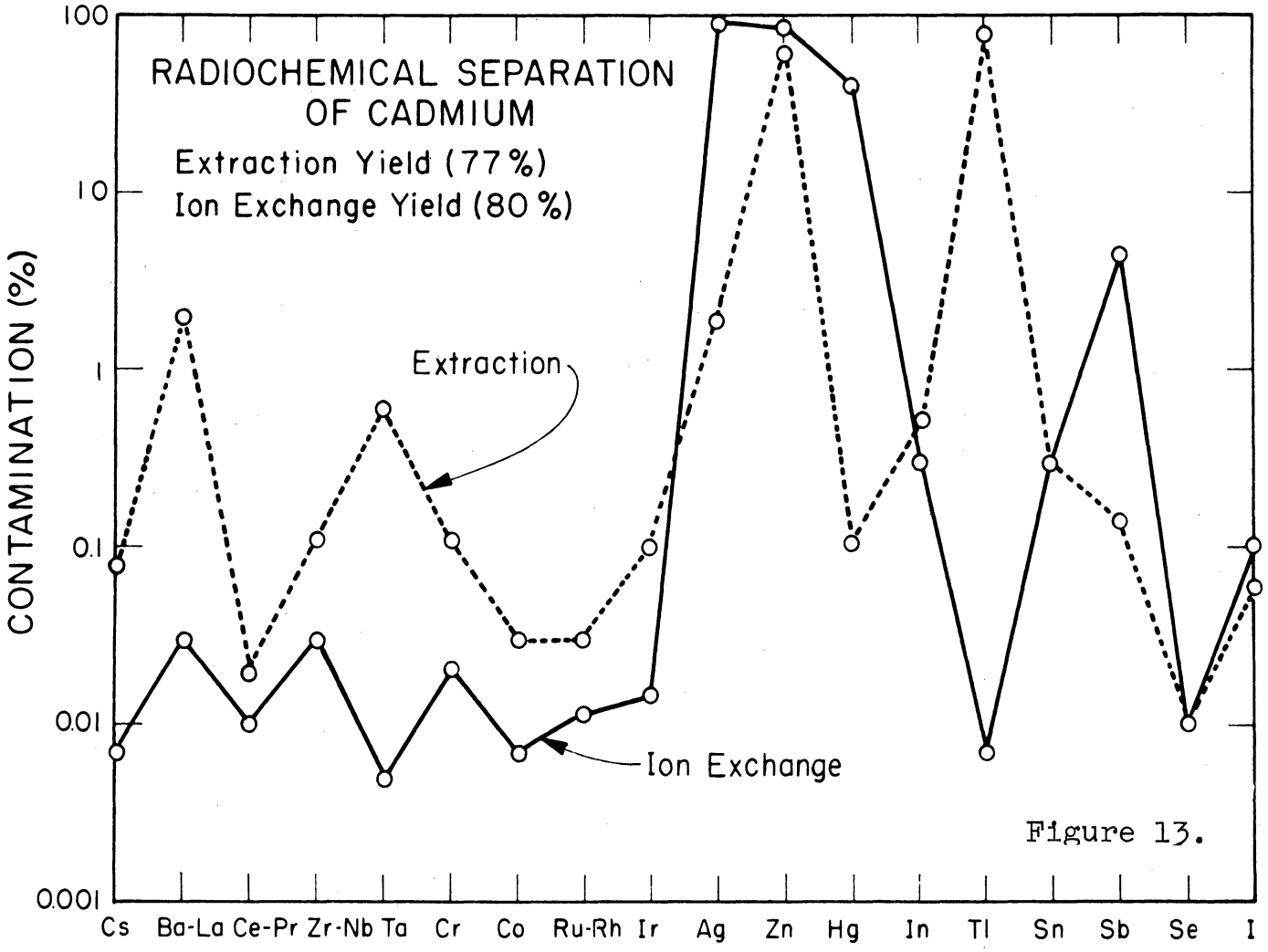


Figure 13.

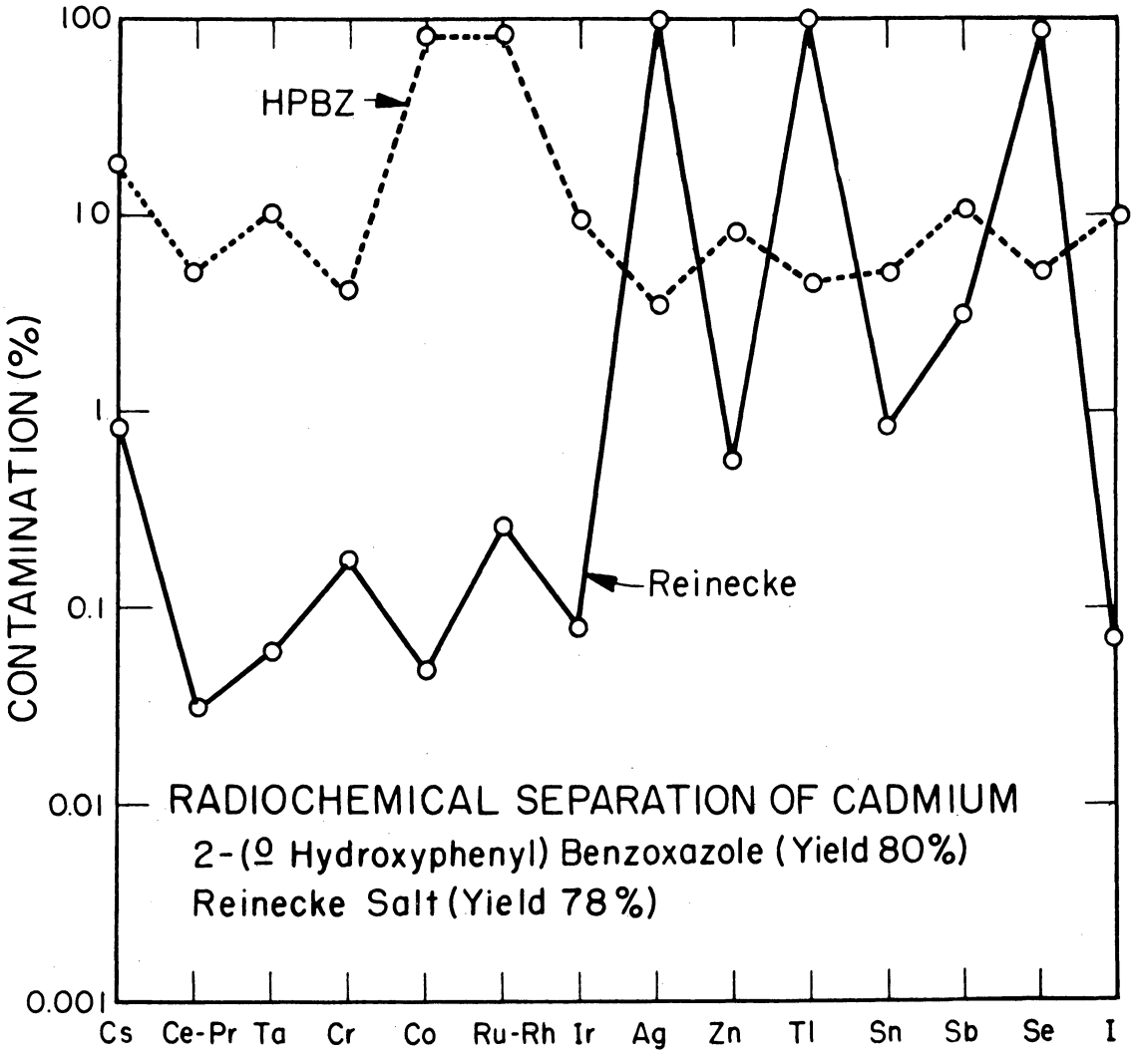


Figure 14.

Table VI. Radiochemical Determination of Cadmium.

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

	Contamination Factor
Extraction (dithizone) cadmium is separated into 10 ml. of 0.1 N HCl	10 Zn,Tl 10^2 Ag 10^3 Cr,Hg,In,Ir,Sn Ta,Zr-Nb,Ba-La 10^4 Ce,Co,Cs,I,Ru,Se YIELD 77%
not separated Zn,Tl	
Ion Exchange (anion exchange in HCl) Add sufficient HCl to the above solution to give 3 M conc. Pass through the column and use standard procedure	10 Zn 10^2 Ag 10^4 Hg,Sb 10^5 In,Sn,Tl 10^7 Cr,I,Ir,Ru,Ta, Zr-Nb,Ba-La 10^8 Se,Cs,Co,Ce YIELD 80%
not separated Zn	
Precipitation (Reinecke salt) Add necessary carriers to the eluant of ion exchange and use standard procedure	10^2 Ag 10^3 Zn 10^4 Hg 10^5 Tl, Sb 10^7 Sn 10^8 Se,In 10^9 Ru,I 10^{11} Ta,Zr-Nb,Ir,Cs, Cr,Co,Ce,Ba-La YIELD 78%

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

OVERALL YIELD 48%

As can be seen, the least separation is that from silver. Extraction is the only one of the three procedures which gains any separation from silver, so that repetition of this separation step will give a decontamination factor of 10^4. The same applies to the Reinecke salt separation from zinc. With the exception of silver and zinc an overall decontamination factor of at least 10^4 is obtained from the 20 elements listed.

These results have been described in detail and discussed in a paper presented at the 134th American Chemical Society meeting in Chicago, September, 1958 and are being submitted for publication in ANALYTICAL CHEMISTRY. (J. DeVoe)

C. Tin Separations

This problem is an extension of the study of the development and evaluation of radiochemical separations to another element in the valley of the fission product distribution curve.

Analytical chemistry indeed suffers from the lack of a good clean, rapid separation for tin. Many of the procedures which give moderately satisfactory results in quantitative procedures are entirely unsuited as a radiochemical separation step mainly because the procedure becomes too time consuming when a desired decontamination is required. In view of this an effort was made to carefully search the literature to find a method which would satisfy the requirements of a radiochemical separation.

1. Literature Survey

a) Distillation

Tin may be distilled as the halide (Br^-, Cl^-, or I^-) from

acid solution. Lundell and Hoffman (11), have made a thorough study of the bromide distillation in six different media. In general, Ge, Rh, Mo, Sb, As, Hg, and Se would be expected to give significant amounts of contamination. Ordinarily the method requires a long time. An attempt will be made in this laboratory to devise a procedure which will allow separation within the imposed time limit of thirty minutes. One distinct advantage to this method is that the separation should be able to be done on a carrier-free basis.

b) Coprecipitation

When manganese dioxide is precipitated it has been found (12, 13) that tin coprecipitates with it to the exclusion of many other ions. Investigation of this procedure has begun in this laboratory.

c) Precipitation

As a general class of radiochemical separations the use of a solid reducing agent such as granulated aluminum to reduce carrier-free (or even with carrier) quantities of tin on its surface, is being considered for study. This type of separation may conveniently fit in with the study of the distillation separation of metals which is under way.

d) Miscellaneous Methods

The following is a list of radiochemical or quantitative separations which are considered to be of minor use as a separation step.

Methods	Comments as a radioactive procedure
1. Electrodeposition:	elaborate apparatus needed to give carefully controlled potential for selectivity; time consuming
2. Precipitation:	
a. dithiol	not selective (*)
b. silicotungstic acid	not selective
c. di-2ethyl hexyl phosphoric acid	5 cations interfere
d. diethyldithio-carbamate	not selective
e. cupferron	not selective (*)
f. benzenearsonic acid	not selective
g. dithizone	probably a satisfactory method with careful pH control
h. dioxide of thiourea	not selective
i. ammonium benzoate	not selective
j. 8 hydroxyquinoline	probably a good method with proper pH control
k. tannin	information concerning this is lacking in the literature
l. sulfide	many scavenges needed - time consuming
3. Ion Exchange:	cation exchange proves difficult; anion exchange can give separation, but it will require careful elution techniques which will be time consuming

(*) Most organic precipitants give precipitates which are gelatinous and must be aged for long periods of time.

2. Preliminary Study of Coprecipitation of Tin on Manganese Dioxide

The effect of the coprecipitating ability of MnO_2 for Sn was studied as a function of the acid strength of the medium (HNO_3). The coprecipitation was found to increase with decreasing hydrogen ion concentration. This indicated that hydrolysis of the tin may have an effect on its ability to be carried by MnO_2, and that the system does not involve coprecipitation in the sense of a mixed crystal formation. Several other ions which hydrolyzed behaved in a similar manner.

Cesium was found to contaminate the precipitate, thus indicating another process for contamination. Freshly prepared MnO_2 was stirred with 1 N HNO_3 and separated. The precipitate was washed with distilled water thoroughly until there was no change in the pH (4.2) of the wash. Ten milliliters of 1 M NaCl solution were added to the MnO_2 and stirred for 2 minutes. The pH of the NaCl solution dropped to 2.5. Radioactive Cs^{137} on the MnO_2 could also be displaced by a 1 M NaCl solution, indicating that the MnO_2 acts as a cation exchanger. Whether the effect is one of surface adsorption or of integral combination within the crystal has not been determined.

In any case the procedure for utilizing the MnO_2 in tin separations has had to be modified to one using tin carrier as a hold-back while essentially scavenging the contaminating activities from the solution. (J. DeVoe)

D. Radiochemical Separations by Vacuum Distillation

The use of distillation procedures for the separation of

substances has been known for centuries. Only in the last 40 years, however, has any satisfactory separation by this means been made for metals and inorganic compounds, and even then the number of separations has been limited. This study was instituted to determine if distillation could be used to separate many radioactive nuclides of the elements.

A wide variety of procedures could be used. One could utilize differences in the vapor pressures of the metal. This procedure seems particularly promising because it may be adaptable to a carrier-free type of separation, and also because a wide variety of selective reagents are available for prior reduction of a given element to the metal from a mixture of compounds. A few preliminary results are given below. Another procedure involving distillation of the chlorides of the elements may also be investigated later.

1. Apparatus

If the amount of metal distilled is to be measured, the system should localize the distillate and the activity should be easily removed from the apparatus. To realize this a narrow beam of distillate will have to be collected on a removable plate. To maintain a uniform beam the possibility of atomic and molecular collision must be removed by distilling in a vacuum. The apparatus sketched in Fig. 15 and pictured in Fig. 16 was designed to accomplish this.

For this system the vacuum must be sufficient (e.g. 10^{-3} mm Hg) to insure a mean free path approximately equal to the 30-40 mm distance between the furnace and the collector. The collector is a metal foil or plastic material wrapped around the cold finger and held in place by a copper wire.

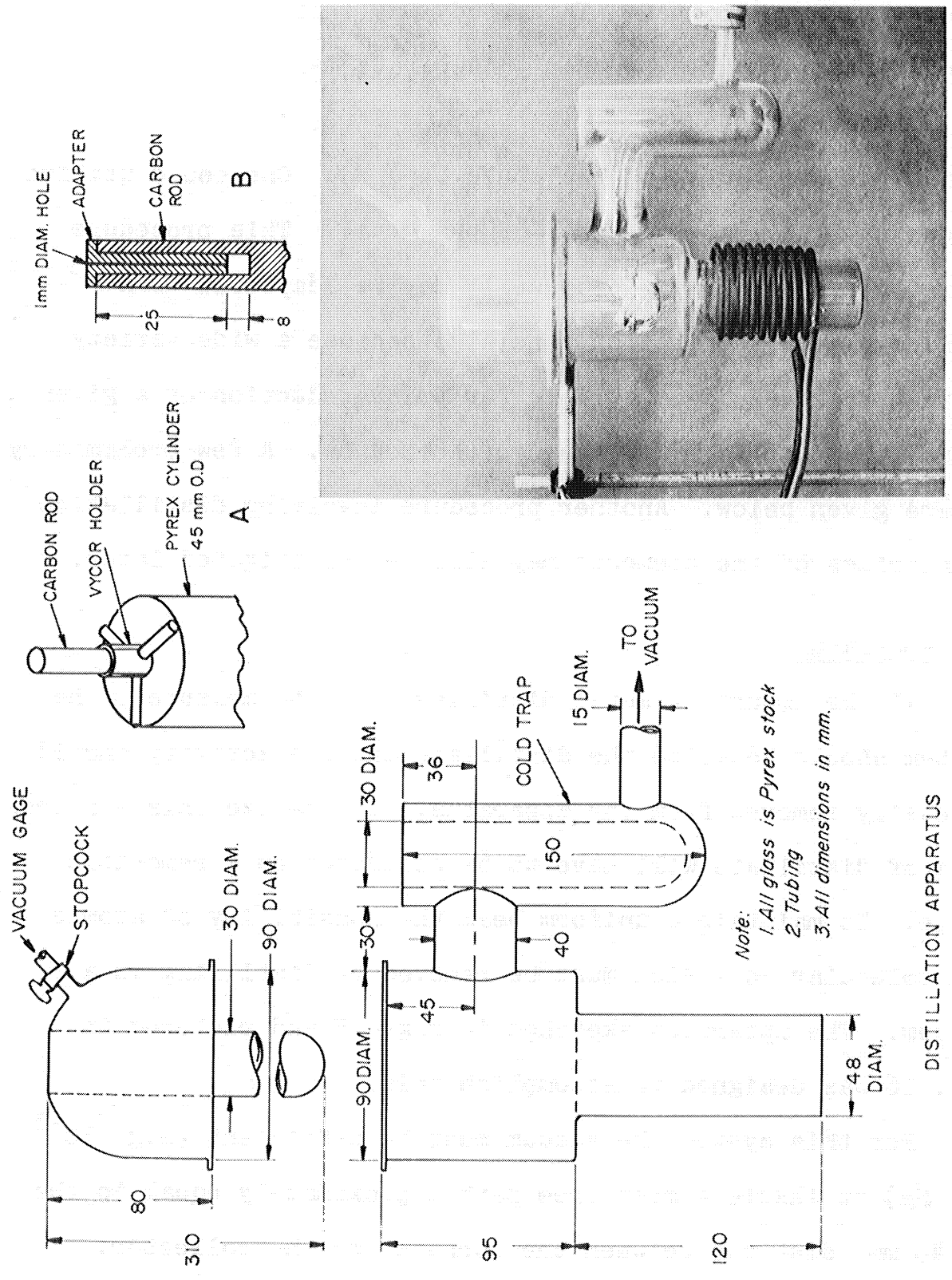


Figure 15. Distillation apparatus for radiochemical separations.

Figure 16. Assembled apparatus for radiochemical separations.

The furnace consists of a 6 mm diameter carbon rod, 50 mm long with a hole 4 mm diameter and 33 mm deep. It is held in an upright position by a special Vycor holder (Insert A, Fig. 15) which rests on a glass cylinder inside the apparatus.

Adjustment of the collector to furnace distance is made by using glass cylinders of different heights. An induction coil supplies the necessary heat. An adapter made of carbon (Insert B, Fig. 15) was used to further collimate the beam. Fig. 17 shows the apparatus with induction heaters in operation in a hood.

2. Operating Procedure

The metal (less than 5 mg.) is placed in the bottom of the hole of the carbon rod. The adapter is then placed in the carbon rod furnace, and this is put in the holder. The system is sealed and evacuated. Liquid nitrogen is placed first in the cold trap next to the pump and then in the cold trap above the collector. The temperature is raised to about 100 degrees for 10 minutes to outgas the carbon rod furnace.

The distillation is then allowed to continue at higher temperatures and the material collected is removed and weighed. By weighing the furnace and collector before and after distillation one can estimate the efficiency of both the collection and evaporation operations. The operating vacuum has been estimated with a thermocouple gage to be better than 10^{-3} mm of Hg.

3. Results with Inactive Elements

Table VII gives experimental percentage values obtained

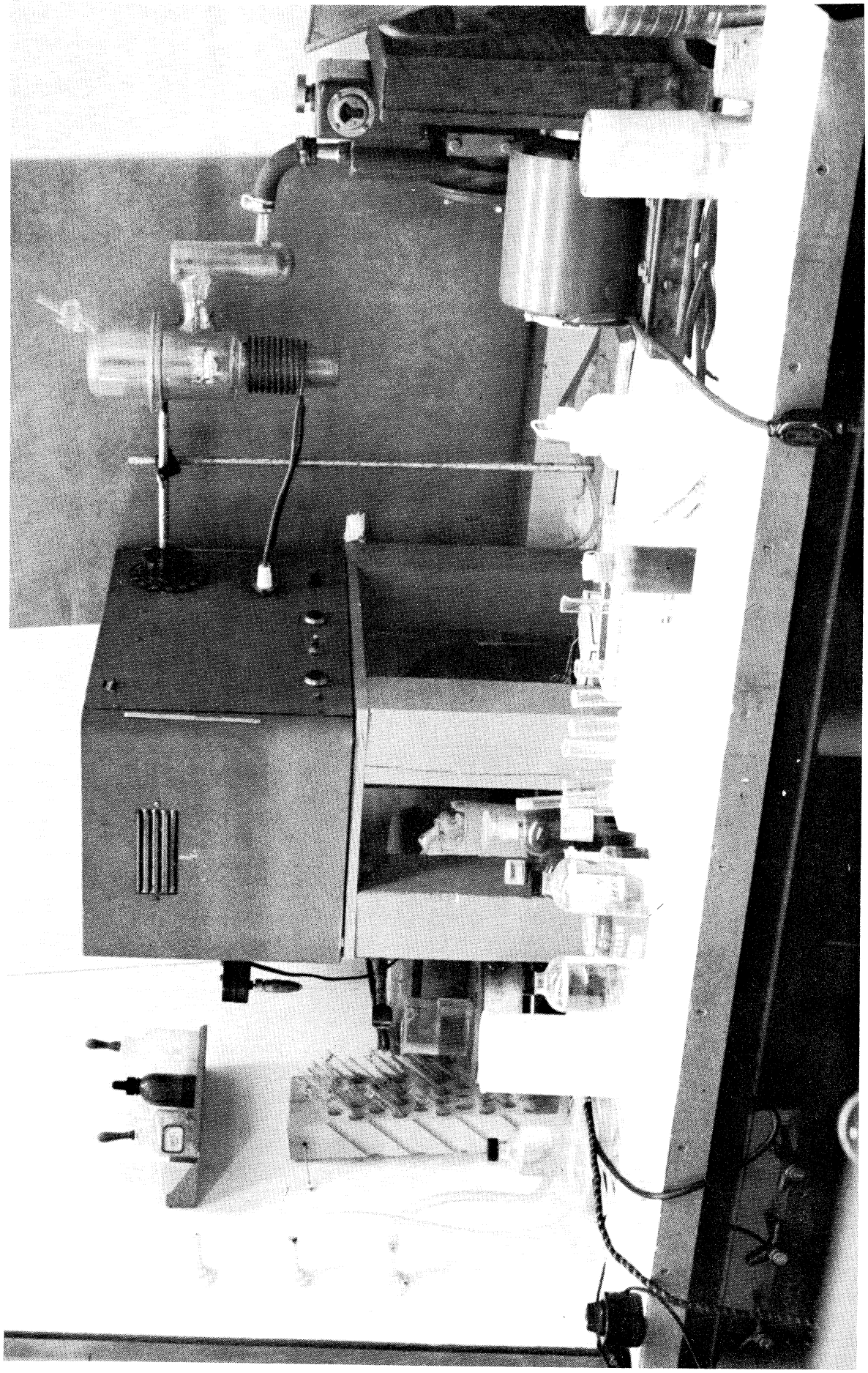


Figure 17. Complete set-up for distillation studies.

for the distillation efficiency using 3 mg amounts of the metal in the apparatus described above.

Table VII. Experimental Distillation Efficiency for Three Milligram Samples.

Element	Boiling Point at 760 mm Hg (Literature value)	% Collected	% Evaporated
Hg	375	100	100
As	615	100	100
Se	688	40	100
Cd	767	100	100
Zn	907	100	100
Sb	1380	30	100
Tl	1457	60	--
Pb	1620	100	100
Bi	1560	65	100
Ag	1950	100	100

Except for a few isolated cases, the data of Table VII show that the distillation process is an efficient one for milligram quantities.

4. Future Experiments

A very useful adaptation of the method would be the distillation (in most cases sublimation at 10^{-3} mm of Hg) of carrier-free amounts of radioactivity. The procedure would utilize a solid phase reducing agent such that the carrier-free amounts of activity will reduce at the solid surface, and

then collect on the solid phase. Only a few samples have been attempted experimentally to date.

Aluminum will reduce Ag, Pb, Hg, Sn, Tl, Te, Se, Cu, Cd, Co, Ni, Au, and Pt. If granulated aluminum metal is agitated with dilute tracer solutions of Hg, Sn, and Se (as obtained from Oak Ridge National Laboratories), in the presence of a small amount of HCl, it was found that some of the activity (30%-70%) remains on the aluminum after prolonged washing with distilled water. However, the efficiency of evaporation from these metal mixtures was very poor.

It was found that activity of silver tracer was retained (50% of the total) by the aluminum at temperatures well above that required for evaporation of milligram quantities of silver. This may be due to an intermetallic compound formation or the presence over the droplet of an oxide film which is not reduced by the carbon furnace.

Tin would be an ideal melting medium and reducing agent if the reduction could be carried out in HCl only. Presence of appreciable amounts of HNO_3, however, would result in stannic acid formation.

Another approach would be removal of the more volatile solid phase of the reducing agent by distillation leaving the carrier-free residue behind. Metallic mercury will reduce Ag, Au, and Pt. If silver tracer is agitated with a small droplet (30-50 mg) of mercury, the silver activity will enter the mercury. By transferring to the furnace and very carefully distilling the mercury (at the lowest heat possible), all of the activity is left behind as a carrier-free residue ($\sim$20 μgm Ag).

Appreciable amounts of the other noble metals, Pt, Au, etc. should be the only interferences in the residue. The silver would then be evaporated by raising the temperature.

At present the main problem with this separation is the collection of the silver activity, which at present has not been above 25% although evaporation from the furnace has been quantitative. Experimental investigation of decontaminations by this method has not yet begun, but calculation of the vapor pressures of the contaminants indicates that a good separation (decontamination factor of 10^2-10^4) should be possible.

5. Further Applications

The advantage of a flux or melt such as tin, to afford even heat transfer has not as yet been demonstrated for carrier-free quantities. This will be investigated. Zinc may be applied in a case similar to mercury above. Investigation of the distillation of the chloride compounds will be made.

6. Summary, Present Status

An apparatus has been designed and set up to investigate the possibility of radiochemical separations, both with and without carrier, by vacuum distillation. Preliminary experimental data seem to indicate the feasibility of multiple separations by this technique. Many more experiments are planned to define the limits of applicability of the method. (J. DeVoe)

E. Liquid Anion Exchangers: The Extraction of Zn and Ag from Chloride Solutions by Dioctylamine Salts

Partly esterfied polybasic acids in inert organic solvents, such as dihexylphosphate HP in mineral oil, extract cations from aqueous electrolyte solutions by a process that can be considered as cation exchange:

$$2HP + M^{2+} = MP_2 + 2H^+ \qquad (1)$$

Correspondingly substituted amines such as dioctylamine R in trichloroethylene show extractability for anionic metal complexes very analogous to anion exchange:

$$2RH^+Cl^- + ZnCl_4^{=} = (RH^+)_2ZnCl_4 + 2Cl^- \qquad (2)$$

The name "liquid anion exchanger" is applied to this process.

Extensive study has been made of the physico-chemical variables involved in the extraction of tracer Zn and Ag from HCl solutions, to compare the results with the conventional resin anion exchangers (14-17) such as Dowex 1, polystyrene methylene (trimethyl) ammonium chloride. What follows is a summary of an invited paper (18) for Zeitschrift Für Physikalische Chemie; figures are taken from the manuscript, with German concentration conventions. Part of this work was done at MIT (19), the rest at the University of Michigan.

The liquid anion exchangers extract metal amion complexes from aqueous solutions with high selectivity anionic complexes. The extraction curves (distribution coefficient D versus activity $a = (Cl^-)\gamma \pm$ of complex-forming agent) have the same general form and the same type of charge with different cations as is observed

with solid anion exchangers. In Fig. 18 the extraction of tracer Zn from solutions of CaCl, HCl, and LiCl by a solution of 10% methyldioctylamine in trichloroethylene is shown in a log-log plot. This is to be compared with Fig. 19 which gives similar curves for the absorption of tracer Zn by a solid anion exchanger (Dowex 1, 4% cross linked) from chloride solution.

It is difficult to study the effect of the concentration of the active groups of the ion exchanger on the absorption of ions from aqueous solutions. This can however by very easily done with the liquid ion exchangers, because by simple dilution of the organic phase their concentration can be varied over a wide range. Fig. 20 represents the dependence of the extraction coefficient of Zn on the concentration of the amine in the organic phase. It is obvious that in the double log scale all the curves are parallel and have a slope of 2, indicating that D increases as the square of the amine concentration. This proves that for the absorption of one Zn atom two amino groups are necessary and the absorbed complex probably has the form $(RH)_2ZnCl_4$ (RH^+ stands for the substituted ammonium ion). This curve also shows that the cation effect is independent of the concentrations in the organic phase and must have its cause in the aqueous solution. The slope of 2 at low Cl^- activity in Figs. 18 and 19 suggests that the step leading to the absorption or extraction of Zn can be described (14) by:

$$Zn^{++} + 2Cl \longrightarrow ZnCl_2 \qquad (3)$$

$$ZnCl_2 + 2RHCl \longrightarrow (RH)_2ZnCl_4 \qquad (4)$$

The desorption which occurs at higher Cl^- concentrations is given by:

$$(RH)_2ZnCl_4 + 2Cl^- \longrightarrow 2RHCl + ZnCl_4^= \qquad (5)$$

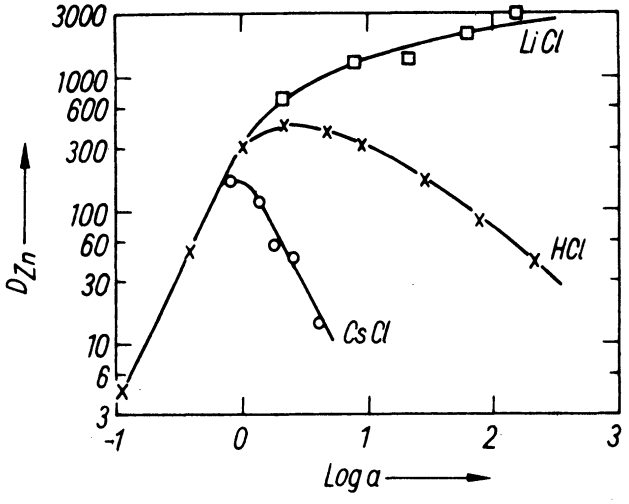


Figure 18

Extraction of tracer Zn from solutions of CsCl, HCl, and LiCl by a liquid anion exchanger (10% methyldioctylamine in trichloroethylene).

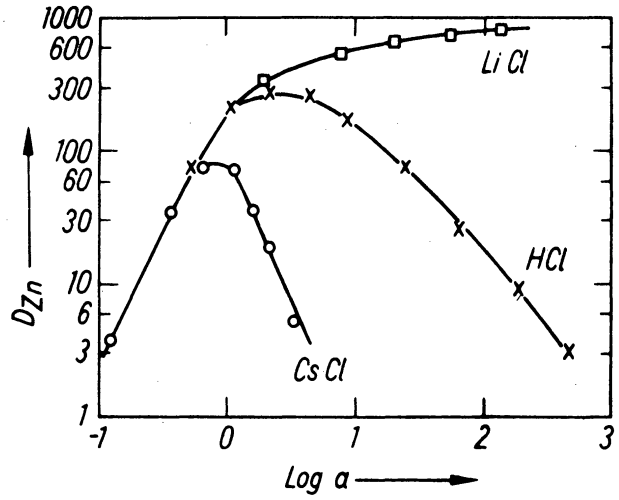


Figure 19

Absorption of tracer Zn from solutions of CsCl, HCl, and LiCl by a solid anion exchanger (Dowex 1, 4% cross-linked).

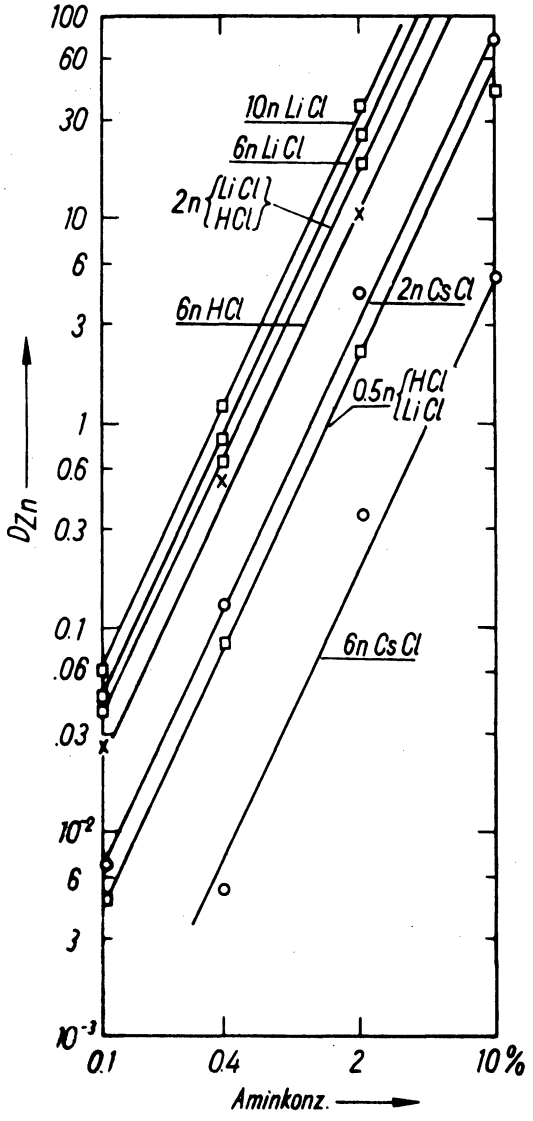


Figure 20

Liquid anion exchange: dependence of the extraction coefficient of Zn upon the concentration of the active group (amine) in the organic phase.

Therefore at higher Cl^- concentrations the curve should have the slope -2. This is seen in Fig. 19 with CsCl as supporting electrolyte only, large deviations being obvious with HCl and LiCl.

Fig. 21 shows the extraction of Ag from chloride solutions as a function of the Cl^- activity; Fig. 22 gives the dependence of the distribution coefficient on the amine concentration. The analysis of the slopes suggests that the complex absorbed is R_2AgCl_3 and that the desorption is given by:

$$(RH)_2AgCl_3 + 3Cl^- \rightleftharpoons 2RHCl + AgCl_4^{\equiv} \qquad (6)$$

The absorption or extraction of Br^- by the anion exchanger can occur only by the formation of the ammonium bromide in the exchange phase RBr and its exchange by Cl^- ions must be described by:

$$RHBr + Cl^- \rightleftharpoons RHCl + Br^- \qquad (7)$$

Therefore slopes of -1 and +1 have to be expected for the curves log D versus log Cl and log D versus log amine concentration, as is seen in Fig. 24 for CsCl, HCl, and LiCl, and as in Fig. 23 for HCl. Again the LiCl and HCl curves show considerable deviations from the expected slope. Obviously only CsCl can be considered as an ideal supporting electrolyte. Further details and more complete analysis of the data are given elsewhere (18). (U. Schindewolf)

F. Extractions with Aniline

Preliminary investigations of the possibility of using aniline as an extractant have been completed. Aniline $C_6H_5NH_2$ dissolves in water to the extent of 3 gm/100 ml of water at 18°C and acts as

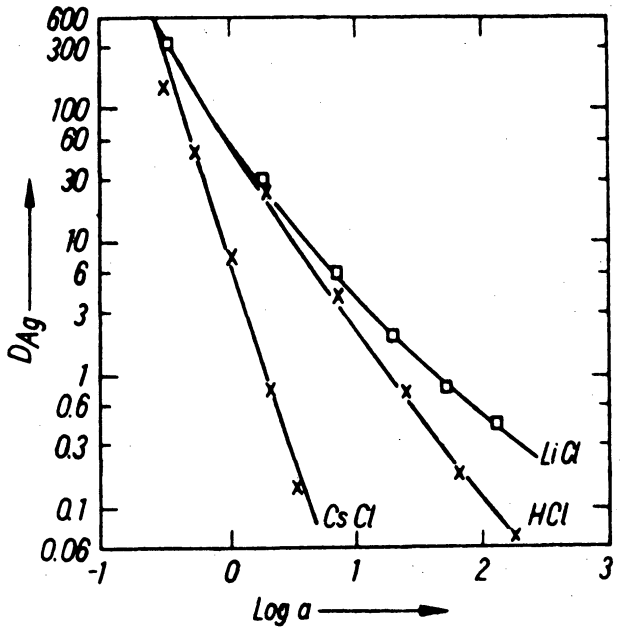


Figure 21

Liquid anion exchange: extraction of Ag from chloride solutions as a function of the chloride ion activity.

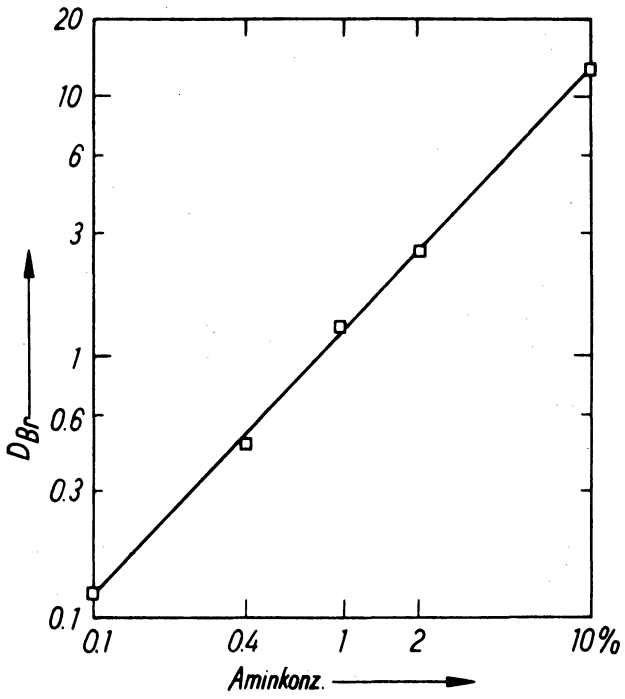


Figure 23

Liquid anion exchange: extraction of bromide ion from chloride solutions as a function of the chloride ion activity.

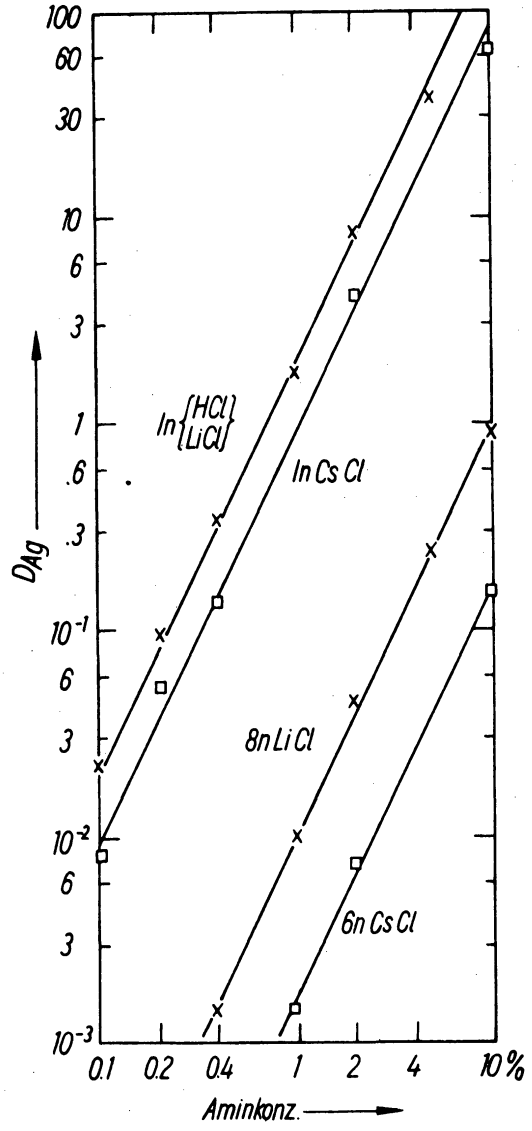


Figure 22

Liquid anion exchange: extraction of Ag from chloride solutions as a function of the active group (amine) concentration.

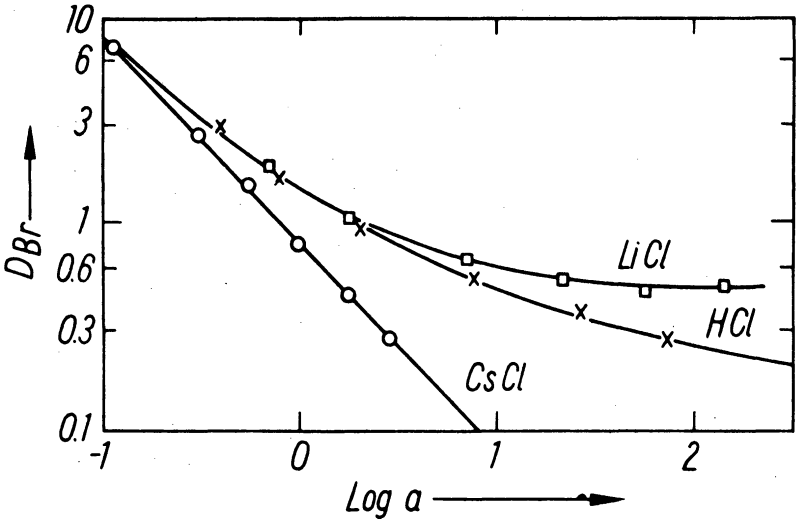


Figure 24

Liquid anion exchange: extraction of bromide ion from chloride solutions as a function of the active group (amine) concentration.

a very weak base in this solvent ($K_b = 3.8 \times 10^{-10}$). The aniline can coordinate elements like Ag^+ to form a neutral complex which is more soluble in the aniline layer than in the aqueous.

1. Experimental

All reagents used were of analytical grade. The tracer solutions used to measure the distribution coefficients were Ag^{110}, Hg^{203}, Ru^{106} and Pd^{109}. The procedure for the determination of the distribution coefficient ($D = \frac{\text{Activity/ml organic phase}}{\text{Activity/ml aqueous phase}}$) is as follows.

Known volumes of ammonium acetate-acetic acid buffer of the desired pH, of the tracer solutions, and of the organic layer were tightly sealed in a screw cap lusteroid vial. The tube is then shaken in a mechanical agitator for 45 minutes. The volumes of each layer are aliquoted and counted with either a GM counter or a proportional counter.

The following data have been obtained for various conditions of the extraction with silver.

a) Extraction of Ag at Different Aniline Molarities

Bis-(2 chloroethyl) ether has been used as a diluent; equal volumes organic and aqueous; pH = 6.84.

Molar conc. of aniline	11	10	5	2.5	1	0.5
D	136	129	52	1.07	1.07	0.25

b) Extraction with Different Ag Concentrations

Aniline undiluted; equal volumes organic and aqueous; pH = 5.5.

M $AgNO_3$	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
D	61	153	125	197	304

c) Extraction of Ag at High Ionic Strength

Aniline undiluted; equal volumes organic and aqueous; pH = 6.83.

In addition 1 M $NaNO_3$ D = 550

In addition 6 M $NaNO_3$ D = 680

d) Extraction of Hg at Different Aniline Molarities

bis-(2 chloroethyl) ether used as diluent; equal volumes organic and aqueous; pH = 6.48.

Molar conc. of aniline	11	10	5	2.5	1	0.5
D	92	57	45	30	22	19

e) Extraction of Ru at Different Aniline Molarities

Conditions and diluent same as (a).

Molar conc. of aniline	10	5	1	0.5
D	94	3.5	3.6	2.7

f) Extraction of Pd at Different Aniline Molarities

Conditions and diluent same as (a) except aniline

Molar conc. of aniline	11	10	5	2.5	1	0.5
D	14	12	5.7	4.4	1.7	4.3

2. Discussion

The distribution coefficient can be expressed approximately as $D = K b_o^n$ where b_o is the molar concentration of aniline in the organic phase, n = number of molecules coordinated with one atom of the element.

Assumptions made are that the pH is constant, that hydrolysis of the cation does not occur, that there is no anion complex formed, and that the concentration of intermediate coordination

compounds is very small. If these are true a plot of log D vs log b_o should give a straight line with slope equal to n. Figure 25 shows such a plot and from the slope of the curves one finds that Ag, Ru and Pd coordinate with 2, 5 and 1 molecules of aniline respectively. The slope of mercury (0.03) is not understood.

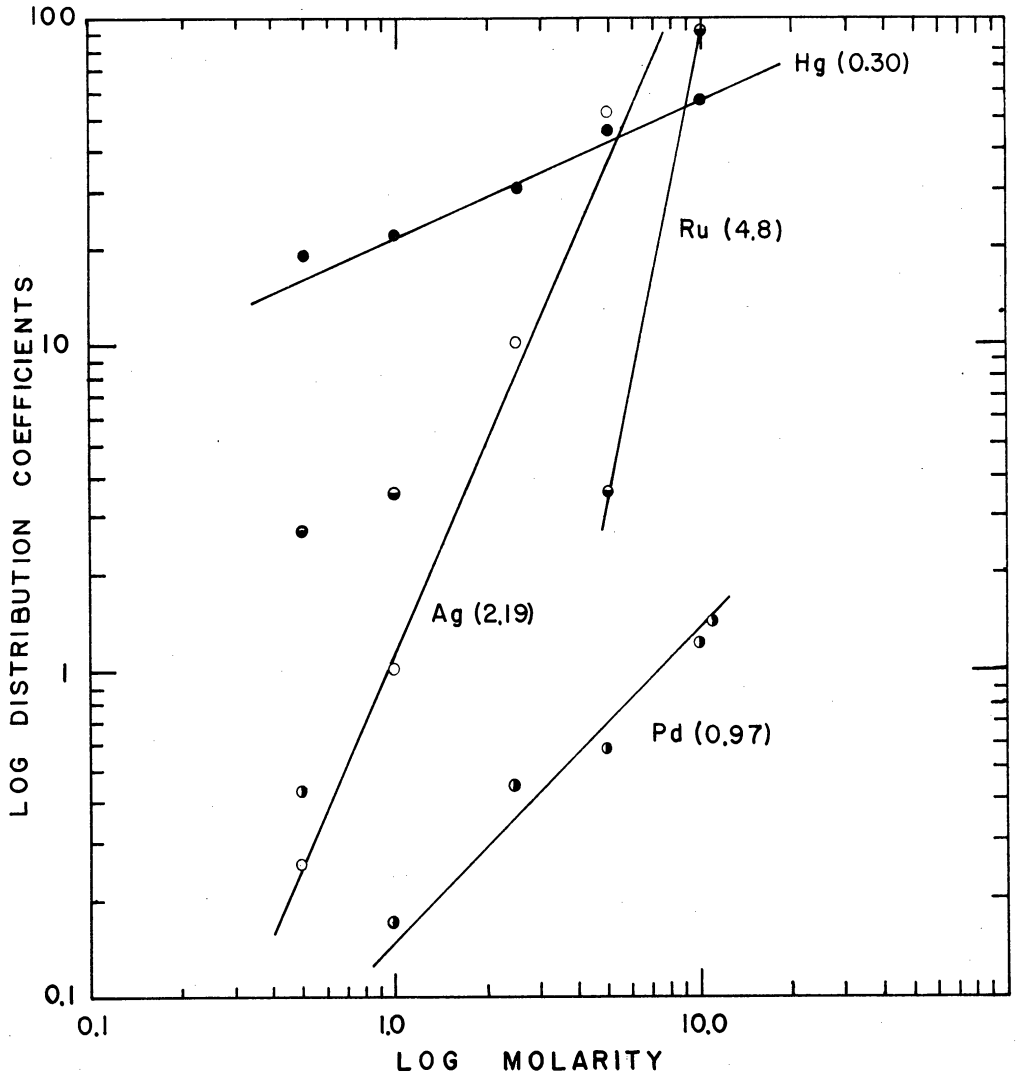


Figure 25. Distribution coefficient at different molarities for Hg, Ag, Ru and Pd.

Using the conditions described above, it was found that the time to equilibrate the system in an extraction was long, at least 1 hour. This may be due to the formation of aniline acetate from the buffer.

At present the procedure has not been perfected, but a distribution coefficient of 100-300 would permit interesting applications. (E. Bruninx)

G. A New "Milking" Method for Carrier-Free Fr^{223}

In earlier studies for the separation of "carrier-free" Cs^{137} (Rf = 0.5) by cellulose chromatography with phenol (liquified by equilibration with 2 N HCl) advantage was taken of the fact that only a few cations are able to migrate out of a nitric acid solution of irradiated uranium containing all the fission products. It was pointed out, however, that the orgin of the chromatogram has to be treated with H_2O_2 in order to suppress Zr^{96} interference.

Since an 8 cm. long cellulose column is sufficient to provide an excellent Cs-Rb separation (20) with Cs first eluted, it was thought that a similar technique could be applied for repeated separations (milking) of Fr^{223} from its parent Ac^{227} (1.2% α branching) and from most of the other decay products of the family.

The short half-life of Fr^{223} (21-22 min.) and the low alpha branching would make such a procedure useful particularly if it could avoid repeated manipulation of the bulk of the actinium parent.

Other processes so far reported for the carrier-free separation of Fr^{223} (Perey 21, 22) (Hyde 23) requires the treatment of the whole sample of actinium.

1. Perey: The francium remains in solution after precipitation of all other isotopes by Na_2CO_3 and $BaCrO_4$ in two successive steps.
2. Perey: The francium is eluted on a strip of paper by a 10% ammonium carbonate solution; Ac^{227} stays at the origin but has to be freed of derivatives before the elution.
3. Hyde: The francium is coprecipitated several times with silicotungstic acid with the addition of concentrated HCl;

the precipitate, redissolved, is passed over a Dowex-50 column adsorbing Fr, which is then eluted with concentrated HCl.

In the laboratory it was found that a column of pure cellulose is unsuitable for repeated milking of somewhat pure Fr^{223} samples because of a small Th^{227} contamination.

It was possible to obtain a sample of francium pure from the point of view of the long half-lifed Th^{227} contamination, using a column filled with a mixture of cellulose (2.5 gm) and finely ground ZrO_2 (0.25 gm) providing the sample contains some H_2O_2. It was also found that addition of Dowex-2 and AgCl to the cellulose has very little effect on a small, rapidly decaying contamination due apparently to Tl^{207}. These latter steps are consequently not needed.

For a sure, routine milking, and when the last traces of the short half-life Tl^{207} are to be removed, an additional decontamination step consisting of a double $BaSO_4$ precipitation or a combined $Fe(OH)_3$-$BaSO_4$ precipitation is required.

The total time needed to obtain the carrier-free francium sample in a 2-5 ml aqueous solution is of the order of one half-life (~20 min), like the other processes in use.

This process compares favorably with the others previously published, since it makes possible a "repeated milking when needed", avoiding frequent manipulations of somewhat strong Ac^{227} sources. Details of this procedure are being prepared for publication.
(J. Fouarge, W. W. Meinke)

H. TTA Extraction Curves

TTA in benzene solution can often be very useful in a selective chelation-extraction of one element from another. Although extraction vs pH curves have been run with TTA for a number of elements most are reported in AEC documents and no general summary of these curves is available.

A compilation of these extraction curves has been made and is presented in an insert labelled Fig. 26 bound at the end of this report. It should prove useful as a general guide to the chelating ability of TTA. A project report consisting of this graph and the many references from which the graph was compiled will be issued in the near future. (E. Sheperd, W. W. Meinke)

V ACTIVATION ANALYSIS

Since April this area has received most of our attention and effort. With the reactor now operating at 1 megawatt it is anticipated that the utilization of short-half-lived radioisotopes in activation analysis will continue to be a major effort of the group.

A. Review Articles and Data Correlation Summaries

1. Sensitivity Charts for Thermal Neutron Activation

Sensitivity values for the elements have been computed based on a thermal neutron flux of 10^{12} n cm^{-2} sec^{-1} and irradiation times of 6 minutes and 600 minutes (10 hours). Counting efficiencies have been estimated (using a Geiger Counter in most cases) but no allowance has been made for time of radiochemical separations.

These values have been included in tabular form in a review article on activation analysis by Schindewolf published in Angewandte Chemie (24). They have also been transposed into graphical form (with the addition of values for 1000 hours) and these three sensitivity graphs have been submitted to ANALYTICAL CHEMISTRY for publication. The graph for the 6-minute irradiation is shown in Fig. 27. (U. Schindewolf, W. W. Meinke)

2. Industrial Applications of Activation Analysis

A review article on activation analysis has been written in French with special emphasis on the applications of the method to industrial analysis. This article has been submitted to a French industrial journal, "l'Industrie Chimique Belge", for publication. (J. Fouarge)

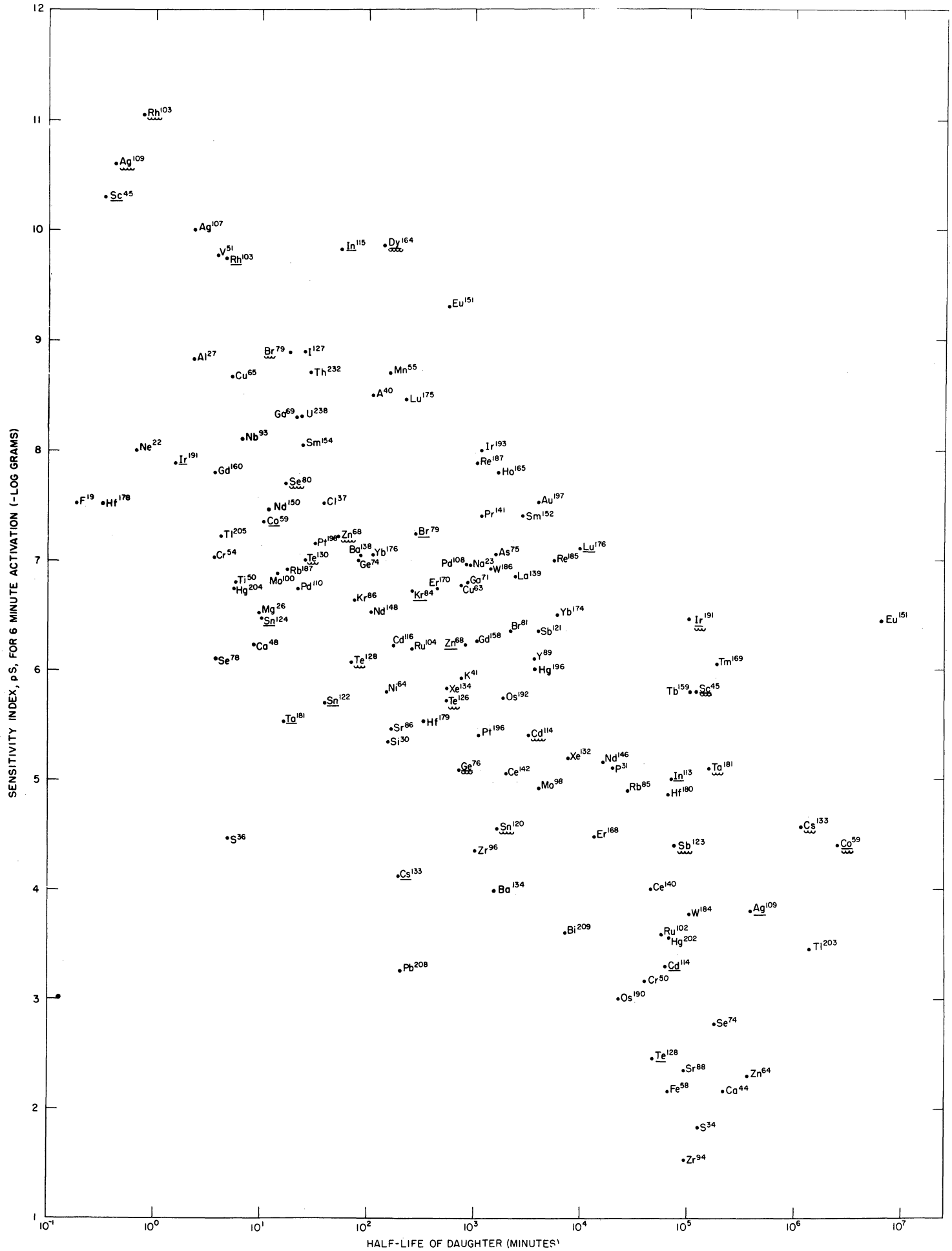


Figure 27. Sensitivity chart for 6-minute irradiation.

3. Comparison of Activation Analysis and Conventional Methods for Analysis of Trace Elements in Marine Organisms

A comprehensive review has been made of the abundance values reported for all trace elements in seaweed, mollusks, crustaceans, fishes and in sea water. The sensitivities of standard spectrophotometric and flame photometric techniques for such analyses have been compared with the sensitivities expected from activation analysis techniques.

A graphical comparison of these sensitivities is given in Fig. 28. The solid straight line indicates the line of equal sensitivity for both methods. A sensitivity index was used in this graph to facilitate comparison of sensitivities and was defined as the negative logarithm of the sensitivity: pS (sensitivity index) = -log S where S designates the sensitivity in grams.

Activation analysis eliminates the problem of contamination by reagents and is particularly useful for the analysis of minute traces. While it is not an "all purpose" method for every element it does show promise of increasing the detection sensitivity for a number of elements by factors of 10, 100 or more as well as making possible the discovery of elements not previously found in marine organisms, such as elements of the ruthenium or platinum groups and indium.

This review has been submitted for publication. (R. Fukai, W. W. Meinke)

4. Review of Fundamental Developments in Nucleonics

A biannual review was completed in November, 1957 covering late 1955 to late 1957 without overlapping the previous review (25).

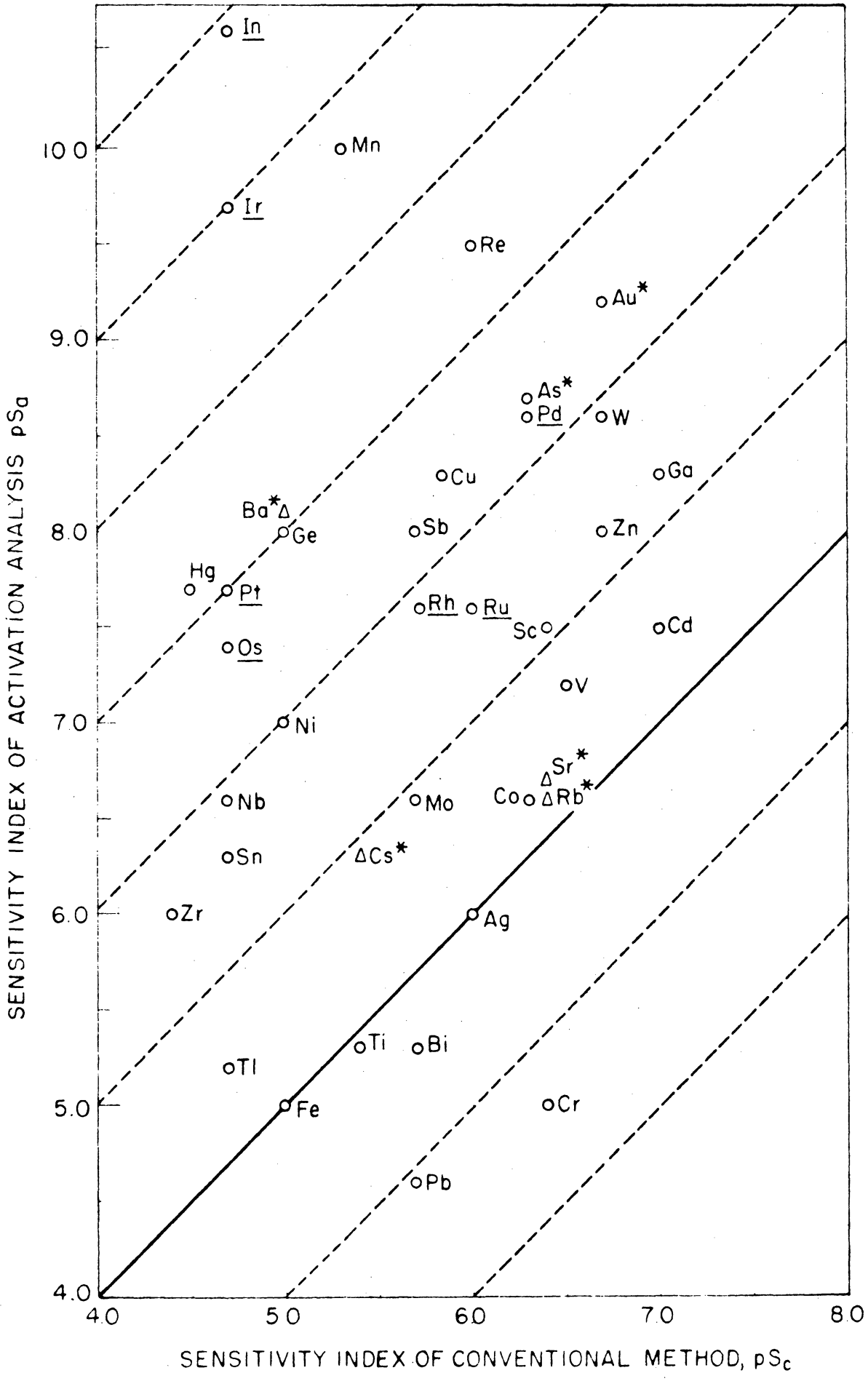


Figure 28. Comparison of sensitivity of activation analysis with that of conventional methods. o spectrophotometric; Δ flame photometric; * activation analysis has already been used.

The new paper published in the April reviews section of ANALYTICAL CHEMISTRY (26) contains 1279 references including references to reports that had been declassified during the previous two years as well as pertinent information presented at the 1955 Geneva, 1956 Lisbon, and 1957 UNESCO conferences. The references were arranged by subject in the text and appeared with complete titles, alphabetically by author in the bibliography of the review. (W. W. Meinke)

B. Activation Analysis with an Antimony-Beryllium Neutron Source

This work, described previously (5), was finally accepted for publication and appeared in the September 1958 issue of ANALYTICAL CHEMISTRY (27). Included in the article is a table giving calculated sensitivities for the elements using a 1.5 curie source for irradiations of 5, 15 and 60 minutes duration. Some experimental sensitivities are also reported for the 60 minute irradiation time. (A. K. De, W. W. Meinke.)

C. The Determination of the Rhodium, Silver, and Indium Content of Chondritic Meteorites

A knowledge of the abundance distribution of nuclear species on a cosmic scale is a prerequisite to the formulation of a theory of the formation of the elements. Suess and Urey (28) in a critical discussion of available abundance data have reported the apparent unreliability of previous analytical data for a number of trace elements. Data have been obtained in this laboratory for three of these elements utilizing 4.4 min Rh^{104}, 2.3 min Ag^{108}, and 54 min In^{116}.

The short half-lives and favorable cross sections for these isotopes permit the use of relatively short irradiations and rapid, simple chemical separations.

A fusion technique was developed to permit rapid dissolution of the sample after irradiation. An electrically driven vibrating agate mortar and ball (29) was used to grind the sample to a uniform fine powder before irradiation. Immediately upon return of the rabbit from the core, the powdered sample was added to molten sodium peroxide in a nickel crucible, fused for one minute, and the crucible rapidly cooled by dipping the bottom into a beaker of water. The solidified melt was then dissolved in a solution containing sufficient HCl to neutralize the sodium peroxide, and in addition containing the reagents required for the first step of the chemical separation. The detailed chemical separation procedures developed for these analyses are given in Section VI.

For the short lived activities it was necessary to run the standard with a gold monitor foil in a separate irradiation. The activity of the monitor foil was then compared to that accompanying the meteorite sample. The flux was reproducible for these runs within the error of the foil weighing and the counting statistics. The "standard" activity and validity of the analyses for each of the isotopes was checked by the addition of an aliquot of standard to a meteorite sample which was then processed through the complete separation. Using these techniques it was possible to begin counting the sample within two half-lives or less for each of the three elements.

The results obtained from duplicate analyses of five meteorites were 0.19 $\pm$ 0.02 ppm for rhodium, from single analyses 0.10 $\pm$ 0.03 ppm

silver, and an upper limit for indium of 10^{-3} ppm. The same value was obtained for indium by irradiating for a longer time at a higher flux at the Argonne National Laboratory and making a chemical separation to measure the 49 day In^{114}. The absence of In^{115} in meteoritic material could be attributed to thermal excitation at some time in its existence to the beta decaying In^{115m}. However, the apparent absence of In^{113} as well, and the reported value for thallium (30) (< 0.01 ppm) seems to indicate that a more reasonable explanation could be based on a fractionation or other chemical effect having occurred at some time. (U. Schindewolf, M. Wahlgren)

D. Activation Analysis for Selenium and Tellurium in Stony Meteorites

This investigation was carried out in cooperation with Argonne National Laboratory before the Michigan reactor was operating at high powers.

Samples of 50-200 mg of powdered meteorite wrapped in aluminum foil were irradiated together with suitable neutron monitors. Sometimes these monitors consisted of meteorite samples to which a known amount of selenium or tellurium had been added (at least 50 times the amount originally present), sometimes of small amounts (5-10 μg) of carrier evaporated on filter paper and wrapped in aluminum foil. Selenium and tellurium contamination from the aluminum foil was negligible.

After irradiation and a suitable cooling time the powdered material was fused with about 20 mg carrier of selenium or tellurium in 1-2 grams of sodium peroxide in a nickel crucible. After cooling, the solid cake was dissolved in 6 N HCl. Elemental selenium and

tellurium were then precipitated from a boiling solution by a fast stream of SO_2 gas and filtered off.

Further purification was achieved by repeated scavenging with iron hydroxide and SO_2 precipitation. The final solution containing selenium and tellurium in 3 N HCl was passed through an anion exchange column 4 cm long and 8 mm diameter, filled with Dowex-1 x8, 100-200 mesh. This column has a high separation factor ($>10^4$) for these elements. Selenium passes through the column within 3-5 column volumes of 2-4 N HCl while tellurium is strongly absorbed (distribution coefficient of 10^3). Rapid elution of tellurium is effected by 0.2-0.5 N HCl.

After another SO_2 precipitation the selenium and tellurium (respectively) were filtered off and mounted for counting. Chemical yields in all experiments were between 50 and 80%. The separation was tested with a variety of trace elements (Ag, Ce, Co, Cs, Hg, Ir, Nb, Ru, Sb, Sc, Ta, Zn, and Zr) for each of which a decontamination factor of $> 10^4$ was found.

The selenium samples were counted with a 256-channel analyzer using a 3" x 3" NaI (Tl) detector (at Argonne National Laboratory) and the characteristic peaks of Se^{75} were used for the final analysis. No contamination in any of the Se samples isolated from the irradiated meteorites could be detected in the gamma spectrum.

The tellurium samples were also checked for impurities with the gamma spectrometer and finally counted with an end window type flow proportional beta counter. In addition to the 9.4-hour Te^{127} from neutron activation of stable Te^{126} there appeared a considerable amount of 77-hour Te^{132} with its 2.3-hour I^{132} daughter from fission of uranium contamination in some samples.

Experimental results have been obtained on samples of seven different meteorites. These results are being interpreted in light of previous data on chemical analysis of meteorites. Conclusions will be published with discussion in the future. (U. Schindewolf)

E. Rhodium Determination in C.P. Ruthenium Metal

Activation analysis without chemical separation, for rhodium contents on the order of a few parts per million in ruthenium metal, has been performed using the pneumatic tube system and the 100-channel gamma spectrometer. 500 mg samples of ruthenium metal were irradiated for 5 seconds at a flux of 1.4×10^{11} n cm^{-2} sec^{-1} and transferred immediately to the pulse analyzer. Although a considerable amount of Ru^{105} activity is also present, the rapidly decaying gamma ray of 42-second Rh^{104} at 550 kev is easily distinguished in the series of gamma spectra obtained at 24 second intervals.

The rhodium content of a C.P. ruthenium metal sample was found to be 31 ± 5 ppm based on seven analyses. The rhodium content after distillation of the sample as ruthenium tetroxide was reduced to a level undetectable by this method. (M. Wahlgren)

F. Determination of Vanadium in Petroleum Process Streams

Typical crude oils contain several metallic elements which when deposited on a cracking catalyst will reduce its activity. The petroleum industry has thus become interested in analyzing for amounts of these elements on the order of 0.1-1 ppm.

Methods in common use for vanadium suffer from one or more of the following disadvantages: large sample volumes are necessary

requiring ashing or concentration procedures which may result in loss of vanadium by volatilization; times required for analysis generally amount to several hours; sensitivity and reproducibility not as great as might be desired; involved chemical separations may be required to separate the desired element from interfering materials.

An activation analysis method for vanadium utilizing the 3.8-minute V^{52} has been developed which requires a sample of 3 cc or less, involves no ashing or concentration procedures or chemical separations, and can be completed in less than 30 minutes.

Short irradiations of the oil sample sealed in polyethylene containers give spectra which show a prominent peak at 1.47 Mev of V^{52} that decayed with a 3.8-minute half-life when consecutive spectra were plotted with the analyzer as shown in Fig. 29. Figure 30 shows a similar type of curve for a Venezuelan crude oil.

The activity found under this vanadium peak (with proper corrections for background, etc.) is related to the amount of vanadium present in the sample as shown in Fig. 31. Typical analyses of samples that had been previously analyzed by chemical methods are given in Table VIII. (These samples were kindly furnished by O. I. Milner of Socomy-Mobil Oil Co.)

It can be seen from the table that vanadium can be determined in petroleum process streams in amounts as low as 0.1 ppm. This work was done at a time when the Michigan reactor was operating at a power level of 100 kilowatts. The reactor is now operating intermittently at its full power of 1 megawatt and it is probable that better reproducibility and sensitivity could be obtained for samples determined at a flux level approaching 10^{13} n cm^{-2} sec^{-1}.

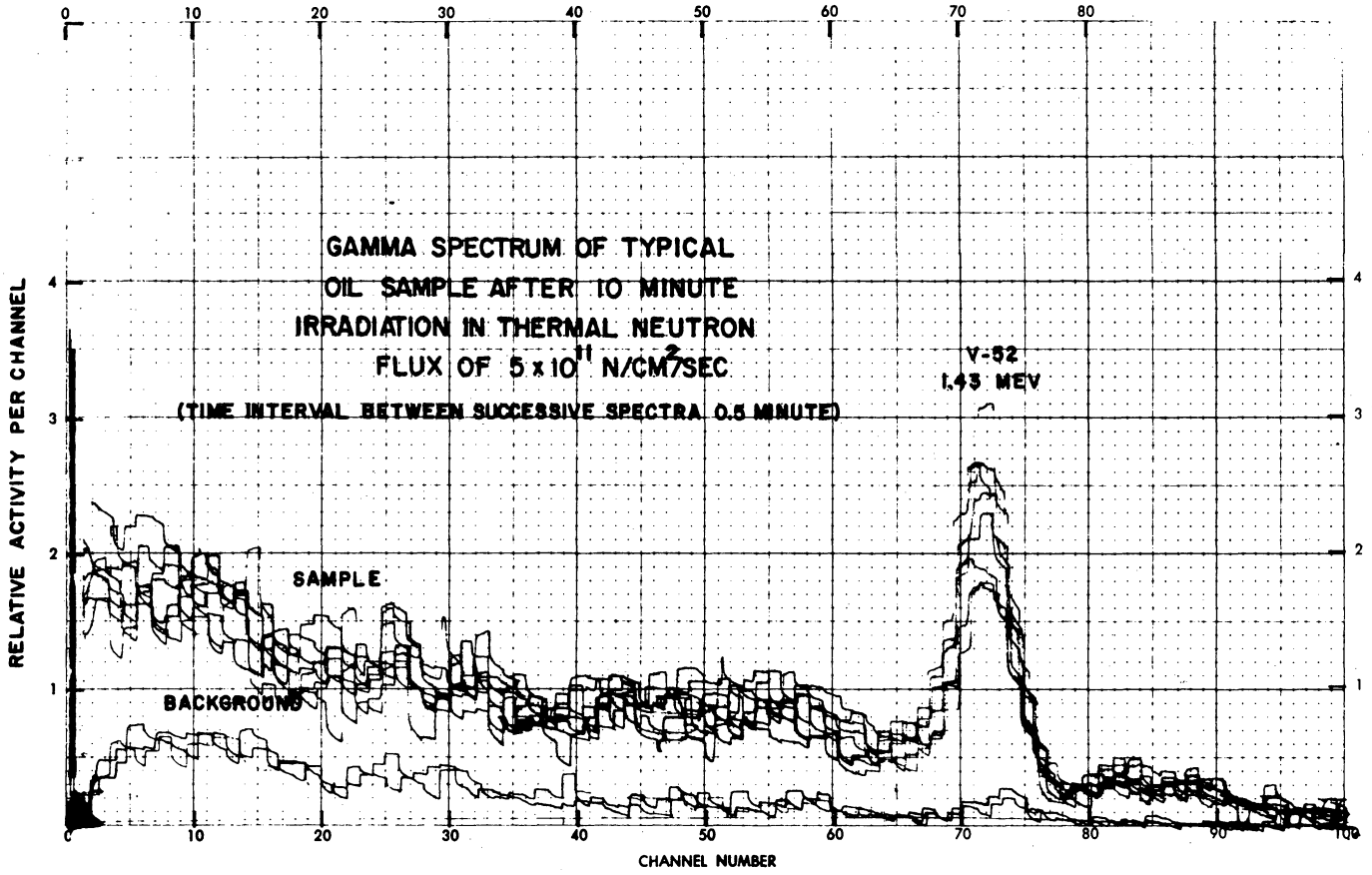


Figure 29. Spectrum of process stream oil.

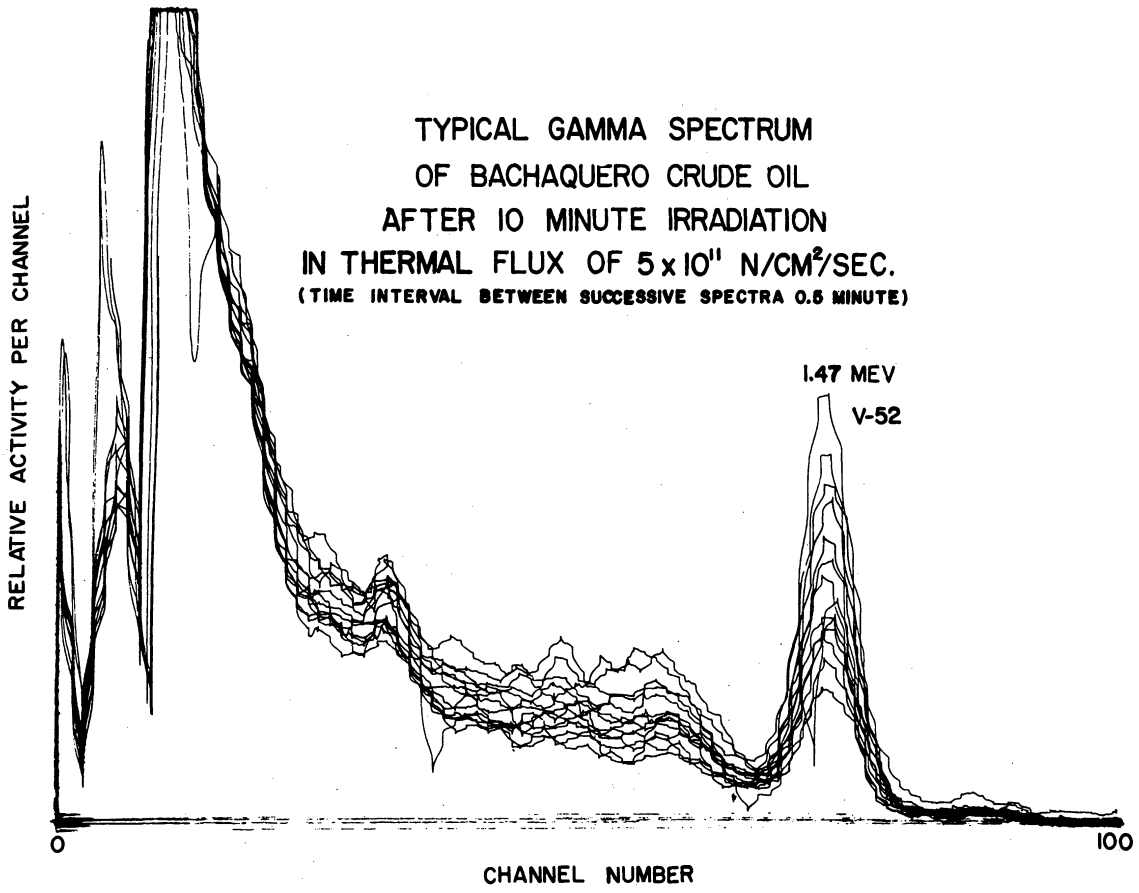


Figure 30. Spectrum of crude oil sample.

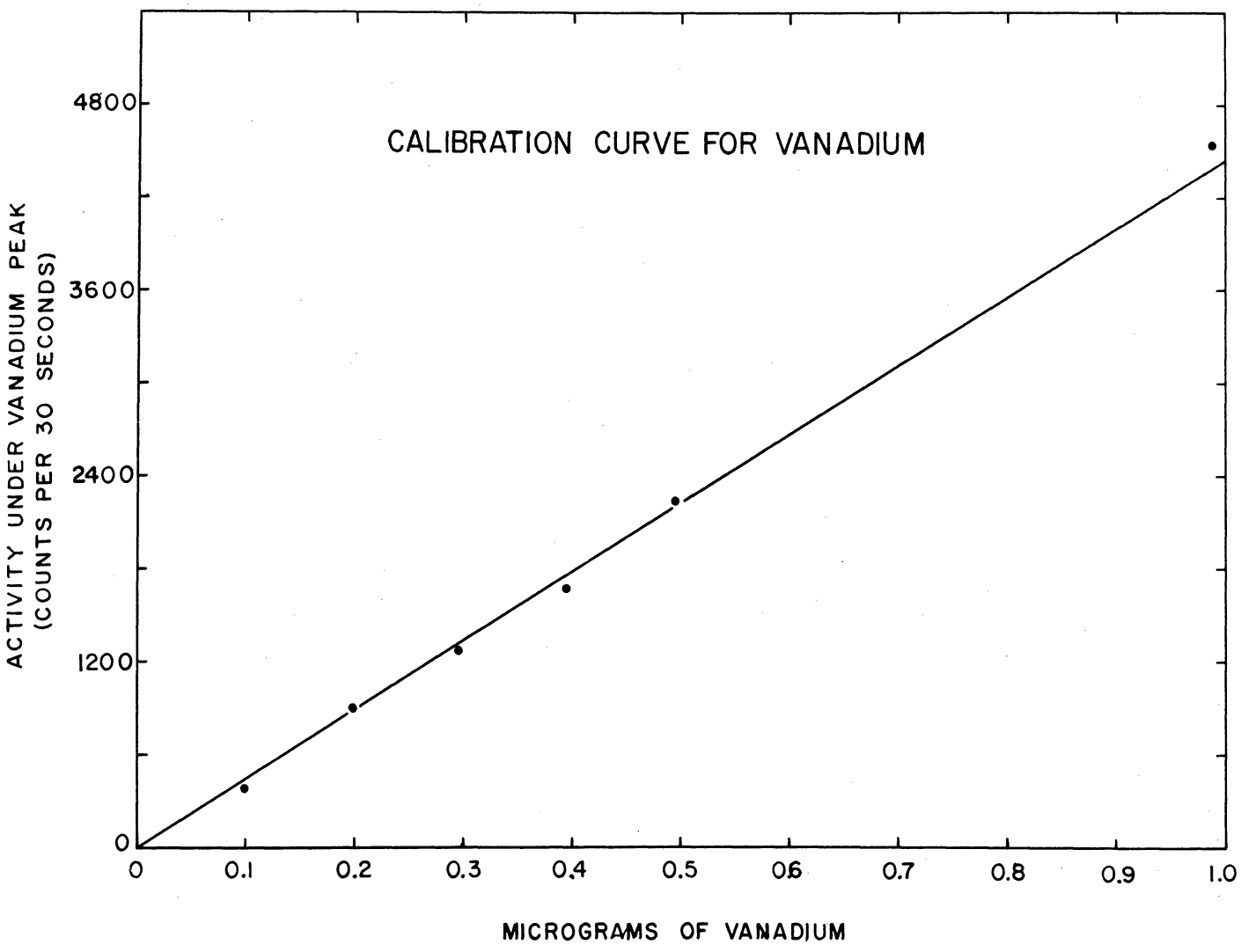


Figure 31. Calibration curve for vanadium (oil analysis).

Table VIII. Typical Analysis of Oil Samples by Chemical Methods.

Sample No.	Number of Determination	Average Value p.p.m.	Error ± ("Standard Deviation")	Reported Value (Chemical p.p.m.)
1	3	0.49	3.7%	0.47
2	3	1.65	0.4%	1.66
3	4	0.987	1.7%	1.00
4	4	0.135	7.4%	0.11
5	6	0.234	10.1%	0.27

Several samples of cracking catalyst containing vanadium were also activated for analysis. It was found, however, that the 1.78 Mev γ-ray peak from Al^{28} was so intense that measurement of the vanadium peak was difficult. Procedures are possible in which a rapid chemical separation is made after a peroxide fusion of the powdered catalyst, but these techniques have not yet been applied to these samples.

This vanadium study is being written up in detail for publication. (J. Brownlee, W. W. Meinke)

G. Activation Analysis of Vanadium in Marine Organisms

In order to know the distribution and variation of trace elements in marine organisms, a series of studies have been conducted using activation analysis. Analysis for vanadium using the 3.8-minute V^{52} was the first method studied.

1. Preliminary Experiments

Prior to the analysis of samples, the extractability of vanadium with TTA (Thenoyltrifluoroacetone)-benzene solutions and with cupferron-chloroform were checked. The results obtained are summarized as follows:

a) Procedure A

Extraction of V^{4+} with TTA-benzene solution.*

Condition: 0.25 M TTA-benzene solution; 1 min. shaking with equal volume of TTA-solution.

Recovery of V^{4+} by TTA-extraction: 65 ± 5% at pH ~ 5 (before extraction), 3.6 ~ 4.1 (after extraction).

Recovery of V^{4+} with 1 M HCl from TTA-extract: 99%.

Recovery of V^{5+} as cupferrate-ppt·from 1 M HCl solution 48 ± 3%.

Recovery through whole procedure: ~ 30%.

Time required: ~ 10 min.

pH dependence of TTA extraction is given in Fig. 32.

* No appreciable extraction of V^{5+}.

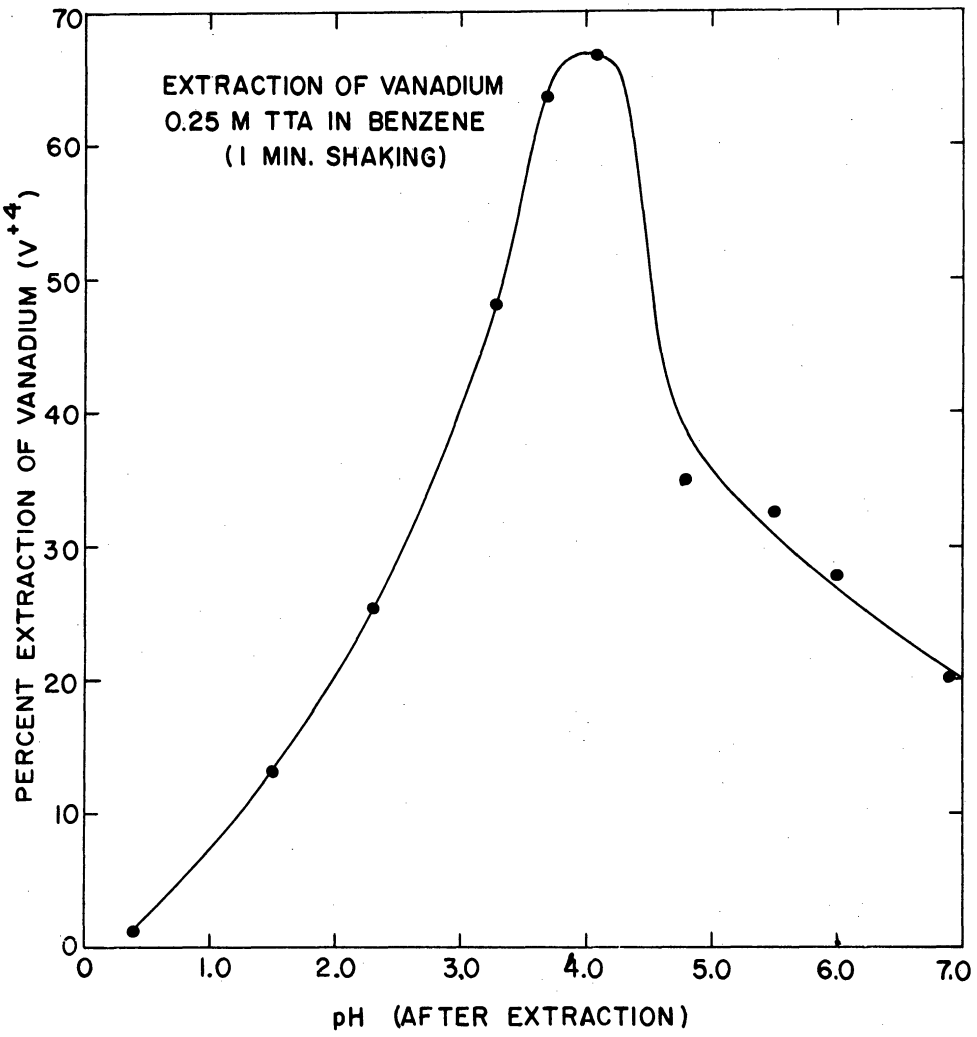


Figure 32. Extraction of vanadium with TTA.

b) Procedure B

Extraction of V^{5+} with cupferron and chloroform.

Condition: 2.5 ml of 6% cupferron aqueous solution and 10 ml of chloroform for V in 1 M HCl solution. 30 sec. shaking.

Recovery of V^{5+} by cupferron-chloroform extraction: 91.5 $\pm$ 1%.

Recovery of V^{5+} with 1 M NaOH from chloroform layer: 20 $\pm$ 5%.

Recovery of V^{5+} as cupferrate-ppt from NaOH-extract: 65 $\pm$ 15%.

Recovery through whole procedure: ~ 15%.

Time required: ~ 9 min.

2. Analytical Procedure

On the basis of the preliminary experiments, schemes for the chemical separations were selected and are recorded in Section VI. However, for the actual analyses the preparation of solid counting samples has been given up. Instead, liquid counting samples prepared by the cupferron-chloroform extraction procedure have been used for counting. The time required for separation has thus been reduced to 3.5 min. by using this procedure.

Fifty to 100 mg of ash were irradiated for 10 min. in the pneumatic tube system at a reactor power level of 100 kw. After the chemical separation (c.f. Section VI) two samples were counted simultaneously by using both the scintillation well counter (1" x 1-1/2" crystal) and the 100-channel γ-spectrometer (3" x 3" crystal). The decay of V^{52} (3.8 min. half-life) was followed for ~20 min. by both of the instruments.

3. Flux Monitor

In each irradiation ~10 mg of gold foil (1 mil) was used as a flux monitor. After irradiation the gold foil was dissolved in 4 ml of aqua regia and diluted to 10 ml. A 100 λ aliquot of this solution was then taken for counting.

For more than 20 irradiations an average flux of 0.89×10^{11} neutrons cm^{-2} sec^{-1} was obtained. The fluctuations in flux from one sample to another (and one day to another) at the nominal 100 kw level did not frequently exceed 10%.

4. Calibration Curve

The calibration curve shown in Fig. 33 was constructed on the basis of data obtained for standard synthetic samples,

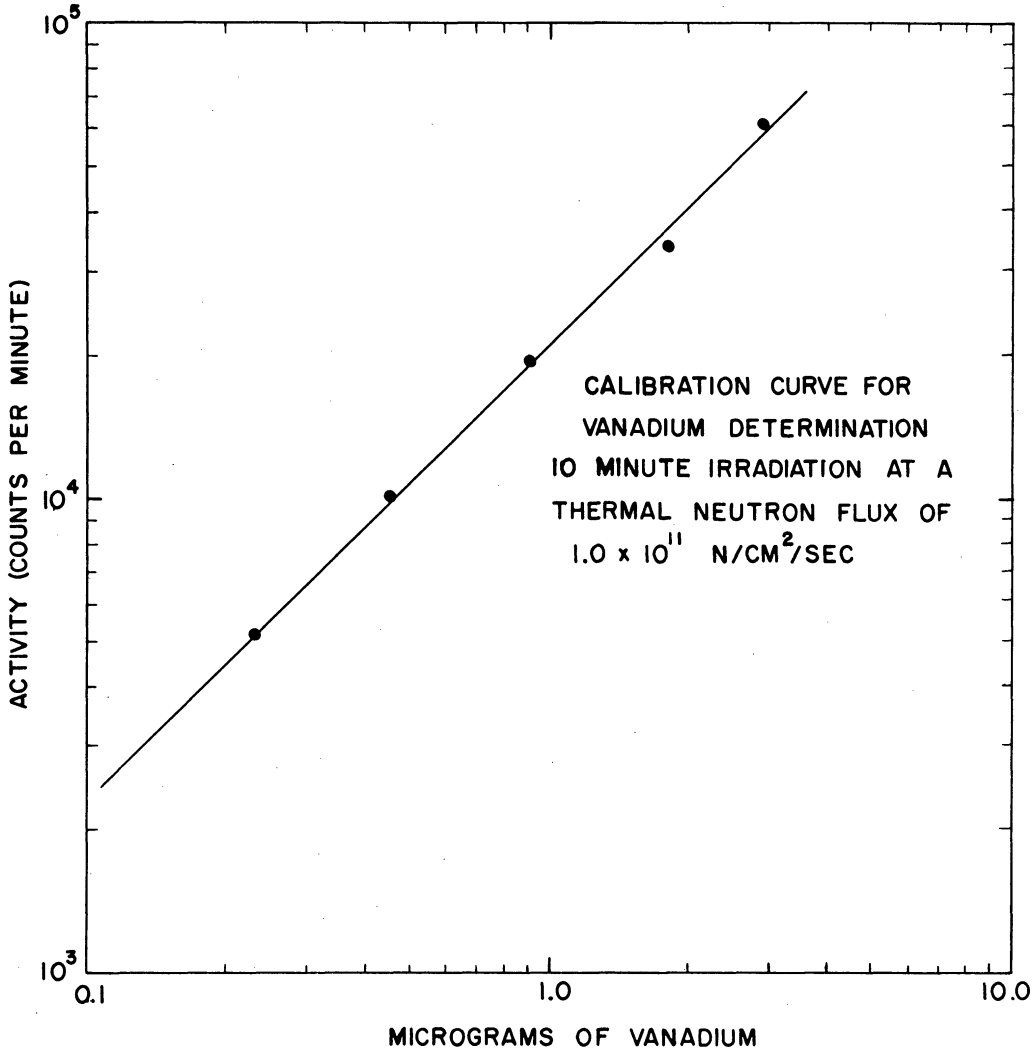


Figure 33. Calibration curve for vanadium (biological ash).

prepared by adding known amounts of vanadium standard solution to pure calcium oxide. Corrections for the fluctuation of neutron flux were included.

5. Results Obtained

Sample	Sample Weight Used (mg)	V ppm in Ash
Ulva sp (seaweed) collected at Urayasu, Tokyo Bay in May, 1956	100.0	105
Porphyra sp (seaweed) collected at Chiba, Tokyo Bay in Dec., 1956	58.5	75
collected at Chiba, Tokyo Bay in Mar., 1957	51.0	484
Mackerel (meat)	93.5	0.81
Clam (meat)	102.0	17.1

6. Notes

In these analyses the data obtained by the 100-channel analyzer were used only to make a positive identification of the vanadium. The lower limit of quantitative determination by the scintillation well counter may be estimated to be as low as 0.02 μg V, while for the 3" crystal-100-channel analyzer it is ~0.1 μg V. Reproducibility was fairly good. The error should not exceed ± 10%.

There are many possibilities for improving the procedure to increase the sensitivity. However, since the sensitivity stated above seemed to be sufficient for the present purpose, further improvements were not tried. (R. Fukai)

H. Activation Analysis of Arsenic in Marine Organisms

Although the best method for radiochemical separation of arsenic should be the distillation method, it requires time and some skill for successful operation. By using γ-spectroscopy the problem can be solved in a simple way. In this work a simple chemical separation of arsenic by coprecipitation has been developed and applied to the ashes of marine organisms.

1. Analytical Procedures

Three to six samples of ash were simultaneously irradiated for 5-9 hours in contact with the surface of the reactor-core in the reactor pool. Each sample (~500 mg) was contained either in sealed quartz tubing or polyethylene tubing with 8 mm-diameter. The polyethylene tubing was preferable for the irradiation of several hour duration at the power level of 100 kw.

After irradiation the samples were allowed to stand for 15 hours to eliminate short-lived activities (but unfortunately not the large amount of Na^{24} present) and then chemical separation of arsenic by coprecipitation with phosphomolybdate was made as outlined in Section VI.

The separated arsenic, with a fairly high β-activity of P^{32}, was counted by the 100-channel γ-analyzer with the 3" x 3" crystal. The spectra obtained by the analyzer were analyzed for the 0.56 Mev γ-ray of As^{76}.

2. Flux Monitor

For monitoring the neutron flux 5 mg foils of Al-Co were attached to both sides of each sample container. The cobalt content of this foil was 0.546%. After the induced activity of Al died out, the long lived activity of Co^{60} was counted directly by the 100-channel analyzer.

On the average, a flux of 6.1×10^{11} neutrons cm^{-2} sec^{-1} was obtained for the pool irradiation. However, fluctuations in this flux value were rather large depending on the section of the surface of the core at which the samples were placed.

3. Calibration Curve

The calibration curve given in Fig. 34 was constructed on the basis of the data obtained for the analysis of standard synthetic samples prepared in a manner similar to those for vanadium.

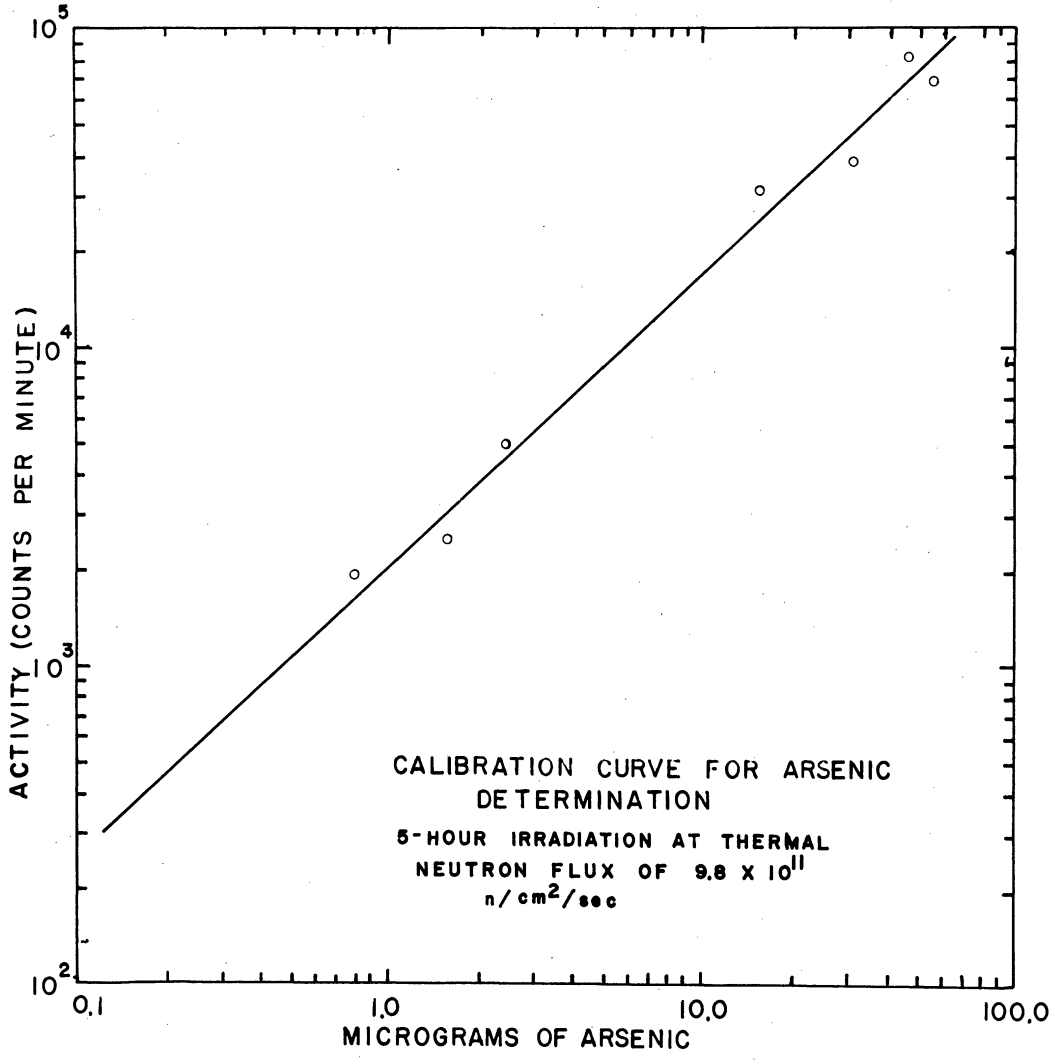


Figure 34. Calibration curve for arsenic (biological ash).

4. Results Obtained

Sample	Sample Weight Used (mg)	As ppm in Ash
Ulva sp. (seaweed) collected at Enoshima, Sagami Bay in May, 1956	498.4	5.6
Mackerel (meat)	497.3	0.34
Clam (meat)	498.8	<0.1
Shrimp (meat)	507.8	1.1

5. Notes

In spite of the considerable bremstrahlen from P^{32}-β-rays, a definite γ-peak of As^{76} was obtained in the analysis of γ-spectra. The lower limit of quantitative determination at the conditions stated above may be around 0.1 μgm As. The error was estimated to be around ± 25%. (R. Fukai)

I. Preliminary Experiments for Activation Analysis of Cobalt

Rapid chemical separation of cobalt by using α-nitroso-β-naphthol as a precipitant has been checked. However, the chemical yield obtained so far has been poor, ranging from 15 to 20%. The time required for separation was 10 minutes.

The lower limit of quantitative determination of cobalt by γ-spectroscopy for Co^{60m} (10.5 min half-life, 0.059 Mev -γ) may be around 0.1 μg (10 min irradiation) at the power level of 100 kw. (R. Fukai)

J. Preliminary Experiments for Activation Analysis of Niobium

Rapid chemical separation of niobium as a Nb_2O_5 precipitate from HNO_3 solution has been checked. The chemical yield was ~50% and the time required for separation was ~10 minutes, the degree of purification was fairly good.

The lower limit of quantitative determination of niobium by γ-spectroscopy for Nb^{94m} (6.6 min half-life, 0.0415 Mev-γ) may be around 2 μg (10 min irradiation) at the power level of 100 kw. For the analysis of niobium in biological materials it seems to be necessary to increase the sensitivity by a factor of at least 100. Other radiochemical separation procedures are being explored for this element. (R. Fukai)

VI SEPARATION PROCEDURES

CHEMICAL SEPARATIONS

Element separated: Vanadium

Procedure by: Fukai

Target material: Biological ash

Time for sep'n: ~10 min.

Type of bbdt: Neutron (in pneumatic tube) 10 min at reactor power level of 100 kw.

Equipment required: standard

Yield: ~30%

Degree of purification: Enough for γ-spectroscopy

Advantages: Rapid separation

Procedure:

(1) Put the irradiated ash into a beaker in which 15 ml of hot 4 M NaOH solution with 10 mg $\overline{V}$-carrier is already contained. Heat 30 sec on a burner to digest the ash.

(2) Add 5-6 ml of conc. HCl to dissolve the ash. Heat for a while if necessary.

(3) Add 3 drops of 10% $SnCl_2$ solution to reduce $\overline{V}^{5+}$ to $\overline{V}^{4+}$ (blue solution should be obtained).

(4) Dilute the solution to ~50 ml with distilled water.

(5) Adjust pH of the solution to around 5 by using 1 M NaOH solution and testing with Hydrion pH-paper. (Faint grey-white precipitate of tin should appear).

(6) Transfer the content of beaker to a separatory funnel. Add ~50 ml of 0.25 M TTA-benzene solution and shake vigorously for 30 sec. (Green color appears in organic layer).

(7) Add 25 ml of 6 M HCl to the separated organic layer and shake 30 sec to recover $\overline{V}^{4+}$ in inorganic layer.

(8) Add 5-10 drops of 1 M $KMnO_4$ solution to oxidize $\overline{V}^{4+}$ to $\overline{V}^{5+}$.

(9) Add 2 ml of 6% cupferron aqueous solution while cooling in dry ice bath. Let stand for ~1 min to allow the precipitate formed to settle.

(10) Filter by using 1" filter paper and filter funnel with chimney. Mount for counting.

CHEMICAL SEPARATIONS

Element separated: Vanadium

Target Material: Biological ash

Type of bbdt: Neutron (in pneumatic tube) 10 min at reactor power level of 100 kw.

Yield: 41.5% ± 1%

Degree of purification: Enough for γ-spectroscopy

Advantages: Rapid separation

Procedure by: Fukai

Time for sep'n: ~4 min.

Equipment required: standard

Procedure:

(1) Irradiated ash is digested for 30 sec in 15 ml of hot 4 M NaOH solution containing 10 mg-$\overline{V}$-carrier.

(2) Add 10 ml of conc. HCl to dissolve the ash. Dilute the solution to 50 ml with water.

(3) Transfer the solution to a separatory funnel in which 10 ml of chloroform is already placed.

(4) Add 2.5 ml of 6% cupferron aqueous solution and shake vigorously for 30 sec.

(5) Let stand for 40-60 sec to separate the layers.

(6) Transfer the organic layer to marked tubes and count. (Notes)

Notes:

In this case both the scintillation well counter (1" x 1-1/2" crystal) and 100-channel γ-spectrometer (3" x 3" crystal) were used for counting. Two 5 ml counting samples were used, one for each counter.

CHEMICAL SEPARATIONS

Element separated: Arsenic

Procedure by: Fukai

Target Material: Biological ash

Time for sep'n: ~ 30 min.

Type of bbdt: Neutron (in pool irrad.) 5-9 hrs at reactor power level of 100 kw.

Equipment required: standard

Yield: 60%

Degree of purification: Good, except for phosphorus activity

Advantages: Simple and rapid. Possibility of parallel operations.

Procedure:

(1) Dissolve the irradiated ash in 5 ml of conc. HNO_3 by heating. Add 10 mg of P-carrier. Dilute to ~50 ml.

(2) Add 1 ml of saturated Br_2-water to oxidize As^{3+} to As^{5+} and expel the excess Br_2 by boiling.

(3) Add 3 gr of NH_4NO_3 crystal to the solution.

(4) Add 10 ml of 10% Ammonium molybdate solution while hot (temperature of the solution should be higher than 70°C) to precipitate phosphomolybdate.

(5) Let stand for 20 min and filter. Mount for counting.

CHEMICAL SEPARATIONS

Element separated: Rhodium

Procedure by: Schindewolf

Target Material: Meteorite

Time for sep'n: 9 min.

Type of bbdt: Neutron, 5 min. 100 kw.

Yield: 50-70%

Equipment required: 60 mm fritted Buchner funnel, 125 mm fritted Buchner funnel, burner and tripod, filter chimney, miscellaneous beakers, beaker tongs, nickel crucible, wash bottles - water, alcohol

Advantages: rapid

Procedure:

(1) Fuse 1 g. irradiated sample with 8 g. sodium peroxide for one minute. (finely ground samples)

(2) Dissolve melt in solution containing 100 ml water, 25 ml HCl, 2 ml rhodium carrier, and 2 ml iron carrier.

CAUTION!! SAFETY WINDOW MUST BE DOWN

(3) Slowly add saturated sodium nitrite solution until ferric hydroxide has precipitated. Heat briefly.

(4) Filter through large Buchner fritted funnel.

(5) Add 5 g. each of potassium nitrite and chloride, swirl.

(6) Filter through 60 mm fritted funnel.

(7) Wash precipitate with water.

(8) Dissolve nitrite complex on filter with hot 0.5 N HCl.

(9) Add metallic zinc, swirl, add to filter chimney.

(10) Wash final sample with hot dilute acid, water, and dry with alcohol.

Chemical yield: weigh as rhodium

CHEMICAL SEPARATIONS

Element separated: Silver

Target Material: Meteorite

Type of bbdt: Neutron, 5 min. 100 kw.

Yield: 80%

Advantages: rapid

Procedure by: Schindewolf-Wahlgren

Time for sep'n: 5 min.

Equipment required: 60 mm fritted Buchner funnel, filter chimney, burner and tripod, filter flasks, aspirator, miscellaneous beakers, beaker tongs, nickel crucible, wash bottles-water, alcohol

Procedure:

(1) Add 2 ml silver carrier to crucible; dry.

(2) Fuse 1 g. irradiated sample with 8 g. sodium peroxide for one minute. (finely ground samples)

(3) Dissolve melt in solution containing 100 ml water, 25 ml HCl.

CAUTION!!!

(4) Filter off silver chloride, wash with water.

(5) Dissolve silver chloride from fritted funnel with hot ammonium hydroxide.

(6) Add metallic zinc, swirl one minute.

(7) Pour through filter chimney.

(8) Wash final sample with hot dilute acid, water; dry with alcohol.

Chemical yield: thiocyanate titration.

CHEMICAL SEPARATIONS

Element separated: Cadmium

Procedure by: DeVoe

Target Material: ——

Time for sep'n: 25 min.

Type of bbdt: ——

Equipment required: all standard equipment

Yield: 62%

Degree of purification: Factor $>10^5$ for In, Sn, Tl, Cr, I, Ir, Ru, Ta, Zr-Nb, Se, Cs, Co, Ce

Advantages: carrier-free separation

Procedure:

(1) Add 1 ml sodium tartrate solution (20%) to a suitable extraction vessel.

(2) Adjust the pH to 13.5 -(0.1 N) with dilute NaOH using Hydrion pH paper. The total volume should be 10 ml.

(3) Add 10 ml of dithizone solution (0.75 mg/ml of $CHCl_3$).

(4) Stir mechanically for 2 minutes.

(5) Draw off the chloroform layer into 10 ml of 0.1 N HCl and stir for 2 minutes.

(6) Add sufficient HCl to the 0.1 N HCl to bring the concentration to 3 M.

(7) Pass this solution through an ion exchange column of Dowex II, 300 mesh which has been equilibrated with 3 M HCl.

(8) Wash the column with 10 ml of 3 M HCl.

(9) Elute with 0.1 N NH_4OH and discard the first 1/2 ml; collect the next 3 ml of eluate.

Notes:

Contaminants not separated are Zn and Ag [4]
Decontamination factor for Hg and Sb = 10^4

CHEMICAL SEPARATIONS

Element separated: Indium

Target Material: Meteorite

Type of bbdt: Neutron, 5 min, 100 kw.

Yield: 50%

Degree of purification: very good

Advantages:

Procedure by: Schindewolf-Wahlgren

Time for sep'n: 30 min.

Equipment required: filter chimney, burner and tripod, miscellaneous beakers, beaker tongs, 250 ml separatory funnel, hydrogen sulfide cylinder, nickel crucible, 7 mm ion exchange column

Procedure:

(1) Fuse 1 g. irradiated sample with 8 g. sodium peroxide for 2 minutes. (finely ground sample)

(2) Dissolve melt in 50 ml water containing 2 ml carrier solution.

CAUTION!!

(3) Add 40 ml 9 N HBr, heat to boiling, cool.

(4) Extract with two 40 ml portions of ether.

(5) Wash combined ether volumes with two 20 ml volumes of 4.5 N HBr.

(6) Strip ether with 30 ml of 6 N HCl solution.

(7) Boil down to about 5 ml; pass over small Dowex-2 anion exchange column.

(8) Scavenge with palladium sulfide, filter.

(9) Buffer with bisulfate, precipitate indium as sulfide.

(10) Pass slowly through filter chimney, air dry.

Chemical yield: weigh as indium sulfide (In_2S_3)

VII PERSONNEL, PUBLICATIONS, TALKS

A. Personnel Listing

Project Director Meinke, W. W.

Post Doctoral Brunix, E.(') (Michigan Memorial Phoenix Project No. 121)

Fouarge, J.(') (Exchange student from Liege, Belgium)

Fukai, R. (Exchange student from Tokyo, Japan)

Kaiser, D. (Michigan Memorial Phoenix Project No. 151)

Schindewolf, U.(')

Graduate Students Brownlee, J.*

DeVoe, J.*

Wahlgren, M.*

Undergraduate Students Sargent, M.**

Sheperd, E.**(')

Staff Assistant Maddock, R. S.

Typing Blackburn, J.**

Schwing, J.**

Electronics Shideler, R. W.**

Nass, H.**

*Half time

**Hourly

(')Terminated

B. Papers and Reports Published

1. Decay Scheme of Co^{62}. Donald G. Gardner and W. Wayne Meinke. Phys. Rev. 107, 1628 (1957). 4 pages, 3 figs.
2. Evaluation of Radiochemical Separation Procedures. Duane N. Sunderman and W. Wayne Meinke. Anal. Chem. 29, 1578 (1957). 12 pages, 3 figs.
3. New Determination of the Phosphorus-32 Half-Life. O. U. Anders and W. Wayne Meinke. Nucleonics 15, No. 12, 68 (1957).
4. Chemische Analyse durch Neutronenreaktionen. U. Schindewolf. Angewandte Chemie 70, 181 (1958). 7 pages, 2 figs.
5. Review of Fundamental Developments in Analysis: Nucleonics. W. Wayne Meinke. Anal. Chem. 30, 686 (1958). 42 pages.
6. Flüssige Anionenaustauscher. U. Schindewolf. Zeitschrift für Electrochemie 62, 335 (1958). 6 pages, 7 figs.
7. Beta-Ray Spectroscopy Using a Hollow Plastic Scintillator. Donald G. Gardner and W. Wayne Meinke. The International Journal of Applied Radiation and Isotopes. (In Press).
8. Activation Analysis with an Antimony-Beryllium Neutron Source. Anil K. De and W. Wayne Meinke. Anal. Chem. 30, 1474 (1958). 9 pages, 9 figs.
9. Activation Analysis; Radiometric Analysis; Assay of Radioisotopes. Encyclopedia of Science and Technology. (In Press). W. Wayne Meinke. McGraw Hill.
10. L'Analyse Chimique Par Activation Aux Neutrons. Jacques Fouarge. l'Industrie Chimique Belge (Submitted).

11. Determination of (d,α) Reaction Cross Sections. K. Lynn Hall and W. Wayne Meinke. J. of Inorganic and Nuclear Chemistry (In Press).

12. Summary of All-Union Conference on the Application of Radioactive and Stable Isotopes in the National Economy and Science of the USSR - 1957. W. Wayne Meinke. AECU-3768

13. Analysis of Trace Elements in Marine Organisms. A Comparison of Activation Analysis and Conventional Methods. Rinnosuke Fukai and W. Wayne Meinke. Linnology and Oceanography. (Submitted).

14. Radiochemical separation of Indium. W. Wayne Meinke, I. B. Ackermann and D. N. Sunderman. Anal. Chem., January 1959. (In Press).

15. Sensitivity Charts for Neutron Activation Analysis. W. Wayne Meinke. Anal. Chem. (Submitted).

C. Talks

1. W. W. Meinke, "Radiochemical Techniques in Analytical Chemistry", Analytical Group, Delaware Section, American Chemical Society, Wilmington, Delaware, January 21, 1958.
2. W. W. Meinke (with D. N. Sunderman and I. Ackermann), "Radiochemical Separation of Indium", Symposium on Radiochemical Analysis, American Chemical Society, San Francisco, April 14, 1958.
3. D. G. Gardner (with W. W. Meinke), "Evaluation of a Hollow Plastic Scintillator as Applied to Beta-Ray Spectroscopy", Symposium on Radiochemical Analysis, American Chemical Society, San Francisco, April 14, 1958.
4. D. G. Gardner (with J. C. Gardner and W. W. Meinke), "A New Mathematical Approach to the Resolution of Multicomponent Radioactive Decay Curves", Symposium on Radiochemical Analysis, American Chemical Society, San Francisco, April 14, 1958.
5. W. W. Meinke, "Introduction of Nuclear Techniques in Undergraduate Courses in Chemistry", Michigan College Chemistry Teachers Association, Ypsilanti, Michigan, May 10, 1958.
6. W. W. Meinke, "Activation Analysis" and "Radiochemical Separation" presented before ASEE-AEC Summer Institute on Reactor Theory and Experiment, Ann Arbor, July 21 and August 6, 1958.
7. J. R. DeVoe (with W. W. Meinke), "Radiochemical Separation of Cadmium" Analytical Review, American Chemical Society, Chicago, September 11, 1958.

8. W. W. Meinke, Panel member for discussion of Nucleonics Section of Second Conference on Analytical Chemistry in Nuclear Reactor Technology", Gatlinburg, Tenn., October 1, 1958.
9. W. W. Meinke, "Radiochemical Techniques in Research", Chemistry Seminar, Flint College of University of Michigan, Flint, Mich., October 8, 1958.
10. W. W. Meinke, "The New Elements", Student Affiliate of American Chemical Society, Ann Arbor, October 22, 1958.

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