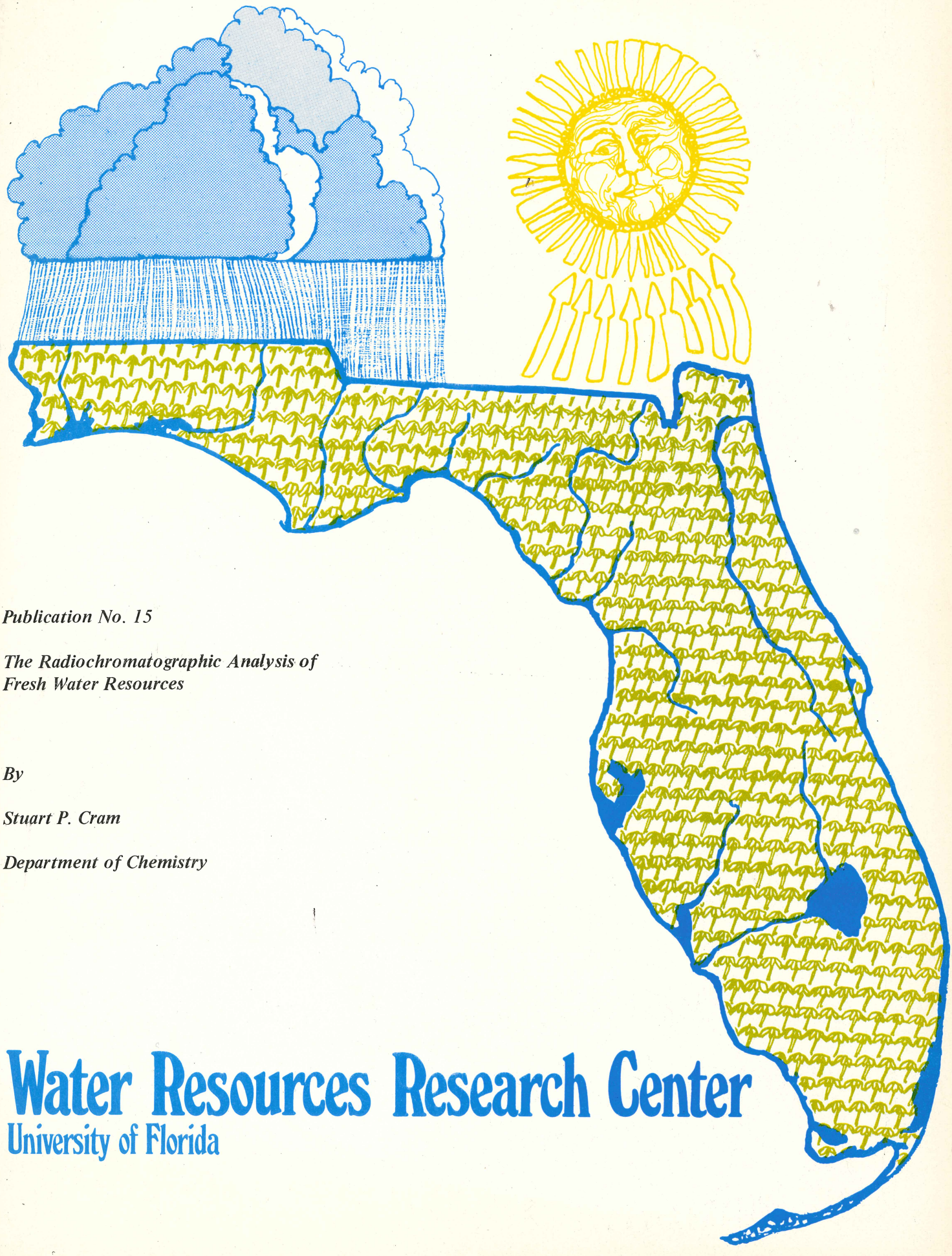

Publication No. 15

The Radiochromatographic Analysis of Fresh Water Resources

By

Stuart P. Cram

Department of Chemistry

Water Resources Research Center
University of Florida

THE RADIOCHROMATOGRAPHIC ANALYSIS OF FRESH WATER RESOURCES

by

STUART P. CRAM
(Principal Investigator)

PUBLICATION NO. 15

FLORIDA WATER RESOURCES RESEARCH CENTER

RESEARCH PROJECT TECHNICAL COMPLETION REPORT

OWRR Project Number A-012-FLA

Annual Allotment Agreement Numbers

14-01-0001-1628 (1969)
14-31-0001-3009 (1970)
14-31-0001-3209 (1971)

Report Submitted: October 28, 1971

The work upon which this report is based was supported in part by funds provided by the United States Department of the Interior, Office of Water Resources Research as Authorized under the Water Resources Research Act of 1964.

TABLE OF CONTENTS

ABSTRACT

The study of radiochromatographic separations for the neutron activation analysis of trace level metals in fresh water sources is reported. Chromatographic separations of metal beta-diketonates were developed for post-irradiation separations. When the trace metals were complexed before irradiation, radiation degradation was found to be a function of the solution concentration, presence of excess ligand, irradiation time, and the neutron flux spectrum. Trifluoroacetylacetone and heptafluorodimethyloctanedione complexes of chromium were quantitatively recovered after irradiation.

Quantitative elution from the chromatographic column of the beta-diketonate complexes of Cr, Mn, Fe, Be, Lu, Gd, and Cu were studied and found to yield recoveries between 52 and 98%. Extensive studies are reported which describe the optimum conditions for separation and account for decomposition and adsorption losses in the system. The development of sampling systems, counting geometries, and sample transfer lines are reported which must be carefully considered when analyzing multicomponent metal chelate mixtures.

Cram, Stuart P.
THE RADIOCHROMATOGRAPHIC ANALYSIS OF FRESH WATER RESOURCES
Completion Report to the Office of Water Resources Research, Department of the Interior, October, 1971, Washington, D.C. 20240
KEYWORDS: neutron activation*/ gas chromatography*/ activation-chromatography coupling*/ fresh water/ trace analysis.

PROJECT PUBLICATIONS

1. Cram, S. P., and Varcoe, F. T., "Gas Chromatographic Separations in Neutron Activation Analysis," Proc. Int'l. Symp. on Modern Trends in Act. Anal., Gaithersburg, Maryland.

2. Wade, R. L., and Cram, S. P., "Quantitative Interpretation of Semilogarithmic Gas Chromatographic Data," Anal. Chem., 41, 893 (1969).

3. Glenn, T. H., and Cram, S. P., "A Digital Logic System for the Evaluation of Instrumental Contributions to Chromatographic Band Broadening, J. Chromatog. Sci., 8, 46 (1970).

4. Juvet, R. S., and Cram, S. P., "Gas Chromatography," Anal. Chem., 42, 1R (1970).

5. Booher, T. R., and Cram, S. P., "Characterization of the Irradiation Stability of Some Chromium Beta-Diketonates for Gas Chromatographic Separations in Neutron Activation Analysis," J. Radioanal. Chem., submitted for publication.

6. McCoy, R. W., and Cram, S. P., "Extention of the Time Normalization Theory of Gas Chromatography for the Minimization of Analysis Time," Anal. Chem., submitted for publication.

7. McCoy, R. W., and Cram, S. P., "High Speed Gas Chromatographic Separations of Volatile Metal Beta-Diketonates," Anal. Chem., submitted for publication.

8. Cottrell, D. B., and Cram, S. P., "A High Precision Digital Data Acquisition System for Neutron Activation Analysis," in preparation.

9. Boerner, B. R., and Cram, S. P., "Absolute Neutron Activation Analysis," in preparation.

INTRODUCTION

Research in the field of water resources and water quality is highly dependent upon the development of new analytical techniques which are specific, sensitive, reproducible, rapid, and suitable for automation. Because of the shortage of analytical chemists in this country, and particularly analytical chemists working in water quality research, new analytical methods of analysis which incorporate the above criteria have not been designed and developed to solve many of the existing problems in this field. The work discussed in this report is directed toward the development of two such analytical techniques, i.e., neutron activation analysis and gas-liquid chromatography, and the coupling of the two complimentary techniques for ultra-trace metal analysis in aqueous systems.

Numerous instrumental methods for elemental analyses in water samples have been reported (1-5), although the number of methods applicable to trace analysis (defined here as being less than 1 μgr of any given material) is considerably more restrictive. The methods of elemental analyses reported to date have generally been very limited in scope, and the breadth of these techniques at the trace concentration level in water analysis has been limited by a number of considerations. First, the wide diversity of matrix materials represents a limitation on the sensitivity of any chemical analysis, as the relationship between the chemical and physical interactions are affected by the environment of the element to be determined. Further, most techniques are subject to interferences by the presence of other chemicals. The sensitivity of these methods is therefore dependent upon the chemical nature of the sample and varies from one sample to the next. This effect is particularly pronounced at trace concentrations.

Neutron activation has likewise been investigated as an analytical tool for the element analysis of aqueous samples (6-8). These investigations have been summarized in Table 1 to illustrate the general applicability of the technique at the trace level. The sensitivities reported do not represent optimum experimental conditions, and indicate the sensitivities only for irradiation times of one hour at a thermal neutron flux of 4.3×10^{12} neutrons/ cm^2 - sec.

TABLE 1

SENSITIVITY AND APPLICABILITY OF THERMAL NEUTRON ACTIVATION FOR ELEMENTAL ANALYSES

Minimum Detection Limit Ranges, μgr	
10^{-5} - 10^{-4}	Mn, In, I, Au, Eu, Dy
10^{-4} - 10^{-3}	Ar, Sc, V, Br, Cs, Hf, Ir, Sm, Ho, Er
10^{-3} - 10^{-2}	Na, Al, Co, Cu, As, Se, Sr, Ga, Rh, Ag, Cd, Sn, Sb, Ba, W, La, Nd, Yb, Lu
10^{-2} - 10^{-1}	Cl, K, Ti, Zn, Ge, Mo, Pd, Ta, Pt, Hg, Ce, Ru, Rb, Zr, Te, Pr, Tb
10^{-1} - 10^{0}	F, Mg, Cr, Ni, Nb, Pb, Y, Tm
10^{0} - 10^{1}	Ca, Os
10^{1} - 10^{2}	Si, S
10^{2} - 10^{3}	O, Fe

Thus it can be seen that neutron activation offers the advantages of dynamic applicability and high sensitivity. Further, the sensitivity of the method is invariant with the nature, size and concentration of the sample. The sensitivity is determined by the nuclear parameters of the element, such as the half-life, cross-section, neutron flux, etc., and are constant regardless of the chemical system being investigated.

The inherent sensitivity and precision of neutron activation analysis at the submicrogram concentration level is dependent upon the accuracy with which the activated, gamma emitting radionuclides can be identified and measured. Many elements have sensitivities that do not differ by more than a factor of 100, and consequently, the bulk of the photoelectric peaks are easily masked when multiple activities are induced by activation (9). This interference is especially serious when the major elemental constituents with large thermal neutron cross-sections are activated.

Partial resolution of gamma-ray spectra can be obtained by variation of the experimental conditions, such as the irradiation and decay times. This approach is not practical when a sample contains even trace amounts of Na, Al, V, Mn, Br, I, Au, etc., because these elements have large activation cross-sections and reach very large specific activities during neutron irradiation, subsequently masking the activities of the other radionuclides in the pulse height spectrum. Although Ge(Li) scintillation detectors considerably enhance the resolution of gamma ray spectra, their depletion depths presently limit their physical size and thereby their counting efficiency. Numerous proposals (10-12) have been reported wherein the instrumental resolution and interpretation of a gamma ray spectrum have been simplified by post-irradiation chemical separations.

The importance of post-irradiation separations in neutron activation analysis has been reviewed (9) and clearly substantiated in the literature (13-16). Currently, solvent extraction (17, 18), extraction with hydrated antimony pentoxide (HAP) (19), and adsorption on MnO_2 (20, 21) are the most common non-chromatographic separation techniques. Paper chromatography (22), thin layer chromatography (23, 24), ion exchange (25) and ion exchange membranes (26), and isotopic exchange (27) have been successfully combined with gamma ray spectrometry in order to give significant improvements in the analyses.

An automatic group separation system for the determination of 40 elements was reported by Samsahl, et al. (28), which is based on ion exchange chromatography and solvent extraction. Recoveries of ≥90% for 29 elements in biological samples in about 2 hours were reported with a mean error of 3% in the analyses. A number of automatic or semiautomatic group separation systems for different kinds of materials have been reported (28-31). Perhaps the most extensive and analytically useful scheme has been reported by Morrison, et al. (32,33). They have developed a group separation scheme which enabled them to measure 41 trace level elements in the Apollo 11 lunar samples by NAA. Their method combines solvent extraction, separation with HAP, and ion exchange to give six groups which can be counted without serious interferences for trace amounts.

Gas and liquid chromatographic separations can be expected to become of increasing importance in neutron activation analysis (NAA) for the separation of radionuclide interferences in complex gamma ray scintillation spectra. Chromatographic separations are rapid, highly efficient, and can be developed without the use of carriers. Further, these separations can be optimized with respect to time, resolution, or sample size as required so that the separation of short-lived isotopes, multicomponent mixtures, or trace constituents, respectively, may be effected. These separations are very important in trace analysis as they effectively give an infinite resolution of the pulse height spectra and enable the theoretical lower limits of detection to be realized. The popularity of the Ge(Li) detector is attributed to its high resolution and the minimum amount of "wet" chemical separations required. Gas chromatography with large volume NaI(Tl) detectors, however, can be automated, and even operated remotely, and therefore possesses all of the advantages of Ge(Li) detectors and has the additional advantage of having a much higher counting efficiency.

Gas chromatography provides a quantitative post-irradiation separation and effectively enchances the sensitivity of activation analysis by:

1. Removing matrix activities
2. Resolving overlapping photopeaks
3. Reducing the dead time of the analyzer
4. Isolating single radionuclide species in order to increase the quantitative precision of pulse height analysis and reduce the amount of interpretation of pulse height spectra and data reduction.

Only a few papers have sought to develop gas and/or liquid partition chromatography for the separation step in NAA. From a recent review of radiochromatographic separations and analyses, it is clear that radiochromatographic separations have been used extensively in radiation chemistry, hot atom chemistry, and biochemistry but not for the separation of photon emitting radionuclides (34). Cram and Brownlee (35-37) first reported the use of gas-liquid chromatography for the clean-up of pulse height spectra in the functional group analyses of the halogens by (n,γ) reactions. The advantages and workability of gas chromatography for high speed post-irradiation separations was demonstrated by eliminating the interferences Na^{24}, Al^{28}, Br^{80}, and I^{128} from the F^{20} spectrum. Further, this previous work resolved the 1.63 Mev photopeak of F^{20} from the 1.64 Mev peak of Cl^{38} in less than 5 seconds so that the analysis for fluorine with the 10.7 second half-life could be used directly. For the activation analysis of fluorine with an (n,γ) reaction, high speed and high efficiency separations are imperative if meaningful analytical results are to be obtained. Even though the higher atomic weight members of the halogen series (i.e., Br and I) have considerably longer half-lives and larger activation cross-sections, they too must be chromatographically separated for analysis at trace concentrations.

However, organic analyses are rather limited in scope if one is restricted to (n,γ) reactions, and thus it has been necessary to develop gas phase, partition separations for the activation analysis of the metallic elements. (As in the case of the organic functional group analyses, the materials to be separated must have a vapor pressure of at least 1.0 mm Hg at the separation temperature, and must be thermally stable at that temperature.)

Metal analysis by gas chromatography has been shown to be both practical and useful (38). Volatile metal chelates such as the beta-diketonates, have been most often used in these analyses. The use of metal chelates has enabled more than three quarters of the elements in the periodic table to be separated and eluted from a gas chromatograph easily, quickly, and with high resolution. Trace analysis studies (39-41) and the development of new ligands (42) have helped make metal analysis by gas chromatography a powerful tool with a wide range of applicability. It is the inherent speed and selectivity of gas chromatography combined with the chemistry of the metal chelates which makes the technique such an excellent separation method for neutron activation analysis.

The synthesis of the metal chelates using beta-diketone ligands such as 1,1,1-trifluoro-2,4-pentanedione [H(tfa)], 1,1,1,5,5,5-hexafluoro-2,4-pentanedione [H(hfa)], and 1,1,1, 2,2,3,3-heptafluoro-7,7-dimethyl-4, 6-octanedione [H(fod)] is usually simple. The chelates can be made either before or after irradiation of the metal mixture. Post-irradiation synthesis has the advantage of avoiding irradiation of the ligand and chelate. Each radionuclide is chelated quantitatively and is therefore in a form suitable for efficient separation. This advantage is often outweighed by the disadvantage of increased decay time due to additional sample treatment of the radionuclide between irradiation and counting. In order to take full advantage of the speed inherent in the technique, chelation before irradiation is usually necessary.

The irradiation stability of the metal chelates is important and corrections must be made for decomposition in the reactor. The radiolysis of reactor irradiated Cr chelates of [H(tfa)], [H(hfa)], and [H(fod)] has been studied (43). No thermal degradation in the reactor was found, but radiolysis losses of up to 10% were reported when the irradiation time was only 1% of one half-life of chromium. It has been shown that Szilard-Chalmers reactions involving the central metal atom of a metal beta-diketonate yield retentions (percentage of radioactive atoms in the original chemical compound) as low as 4% (44).

Szilard-Chalmers reactions involving solid metal chelates and the use of annealing to increase their retentions have been studied (44-58). The recoil and metal-ligand bond cleavage of chelates after (n,γ) reactions have been used for iostope enrichment (45,46) and the metal is believed to exist as a cation in solution (44). Szilard-Chalmers reactions following (γ,n) reactions have also been discussed (47). Lazzarini (48) has studied the effect of the ligand field on Szilard-Chalmers reactions by studying the retention for 28 complexes of Co(III). Annealing studies have been carried out on Cr tris-acetylacetonate (49-51) and Co tris-acetylacetonate (51-56), which are similar to the chelates used in this work. Repair of reactor irradiation damage can result from heating the chelate (44, 49-58) or exposing it to γ-radiation (51,54). Thus, there is a moderate amount of annealing before a sample leaves the reactor. For the Co tris-acetylacetonate, each type of treatment has about the same effect (54), which is reported to be due to localized heating during γ-irradiation. Preheating of solid samples before neutron irradiation will also increase retention (55), and the presence of an electron donating atmosphere around a solid chelate during annealing has been shown to increase retention (44,57).

Gainer and Ponta (58) have studied thermal annealing of Cr tris-acetylacetonate in methanol solutions. The retention was 32% after 2 hours of irradiation at 2.3×10^{11} neutrons/cm^2-sec, and increased with heating. In the plots of retention versus annealing time at constant temperature, the plateaus had heights which were temperature dependent. At 95° C, 80% retention was obtained, but above 95° C, the retention reached a peak and fell off due to decomposition. Gainer and Ponta also found exchange between $^{51}Cr^{3+}$ in solution and the chromium in the chelate. The work described in this report used both the annealing described by Gainer and Ponta and the technique of adding excess ligand to the solution to be irradiated in an effort to obtain quantitative yields of the irradiated chelate prior to gas chromatographic separation.

PART I

CHARACTERIZATION OF THE IRRADIATION STABILITY OF SOME CHROMIUM BETA-DIKETONATES FOR GAS CHROMATOGRAPHIC SEPARATIONS IN NEUTRON ACTIVATION ANALYSIS

Chromium beta-diketonates were chosen as model compounds for this study because the gas chromatographic separations of these materials have been studied extensively (38,40,59-64) and because of their physiological and toxicological importance at trace concentrations (65-81). Trifluoroacetylacetonate [$Cr(tfa)_3$], hexafluoroacetylacetonate [$Cr(hfa)_3$] and heptafluorodimethyloctanedione [$Cr(fod)_3$] complexes of chromium were studied in order to measure the ligand effect on the stability during and after the irradiation, and the reactivity towards recombination reactions in the presence of excess ligand. The quantitative recovery of the chelates is then reported as a function of the type of ligand, irradiation time, solution concentration, and the effect of the presence of excess ligand.

1. Experimental

The chromium chelates were irradiated as standard benzene (Nanograde, Mallinckrodt Chemical Works) solutions. The $Cr(hfa)_3$ was purchased from Pierce Chemical Company, and the $Cr(tfa)_3$ and $Cr(fod)_3$ were synthesized following published procedures (63,64). The ligands for the syntheses were purchased from Peninsular Chem. Research Corp., and the metals from Fisher Scientific Company.

Quartz (General Electric Company) break seal vials were drawn from 9 mm tubing and used as sample containers. These vials were leached, filled with the solution to be irradiated, and sealed with a torch after the solutions were frozen out. In this manner the vials were sealed air tight and, because of the low sodium concentration, could be handled immediately after irradiation.

The irradiations were performed in the University of Florida Training Reactor (UFTR) and the Georgia Institute of Technology Research Reactor (GTRR). The UFTR is a water cooled, MTR type reactor. At a steady state power level of 60 Kw and a thermal neutron flux of 1×10^{12} neutrons/cm^2-sec, the temperature in the sample position was 60.5° C as measured with an iron-constantan thermocouple.

The GTRR is a heterogeneous, 1 Mw, D_2O moderated and cooled reactor. Since the outlet coolant temperature of the GTRR was only 1° C higher than the UFTR, the irradiation temperatures were assumed to be the same in both reactors. A comparison of the irradiation facilities used is given in Table 2. It should be noted that the irradiation times were adjusted to give the same integrated flux in both reactors.

The gamma ray pulse height spectra were measured with two 3 inch x 3 inch NaI (Tl) crystals (Type 12S12/E-X, Harshaw Chemical Company). Nuclear Chicago Model 10-17 scintillation preamplifiers were used with RC amplifiers (Model 27001, Nuclear Chicago Corp.), superimposed in a mixer amplifier (Model 30-35, Nuclear Chicago Corp.), and counted in a 400 channel pulse height analyzer (Model 34-27, Nuclear Chicago). Data was readout on an ASR Model 33 Teletype and an X-Y plotter (Model 850, Data Equipment Company).

A four column gas chromatograph (Series 4000, Victoreen Instrument Company) with an electron capture detector (Model 4008-3, Victoreen Instrument Company) was used for the separations. The electron capture detector was operated in the DC mode because this model was at least six times more sensitive for $Cr(tfa)_3$ in the DC mode than in a pulsed mode, even though the pulse period was varied from 25 to 125 μsec with a pulse width of 0.5 μsec. Also the background noise in the DC mode was less (ca, 3.5×10^{-12} amps). Peak areas were integrated with a digital integrator (CRS-100, Infortronics Corp.) and a Hewlett Packard Model 7127-A strip chart recorder was connected in series with the digital integrator for an analog display. The chromatograph was modified to bring the Teflon column into the injection port and to run up to the sensitive area of the detector in order to avoid decomposition or adsorption of the metal chelate in the instrument. The chromatographic system is shown in Figure 1.

An extensive study of column materials and conditions showed that the conditions reported in Table 3 gave the most reproducible and quantitative results for the metal chelates and their degradation reaction products.

When the column effluent was to be analyzed by mass spectrometry, the samples were trapped in V-shaped glass melting point tubes in a dry ice-acetone bath. For activation analysis of the effluents, low sodium quartz melting point tubes (General Electric Company) were used for the traps. At all other times a two stage absolute trap was connected to the detector outlet to prevent radioactive or toxic chelates from being vented to the room.

TABLE 2

IRRADIATION FACILITIES

	Georgia Tech Research Reactor	University Florida Training Reactor
Irradiation time	7.0 hrs	4.0 hrs
Thermal flux	5.6×10^{11} neut/cm^2-sec	1×10^{12} neut/cm^2-sec
Power level	1 Mw	60 Kw
Moderator	D_2O and Graphite	Graphite
Irradiation position	Vertical thimble (reflector)	Center vertical port
Cd ratio	2000:1	1:1
Gamma flux	1×10^6 R/hr	2.4×10^6 R/hr

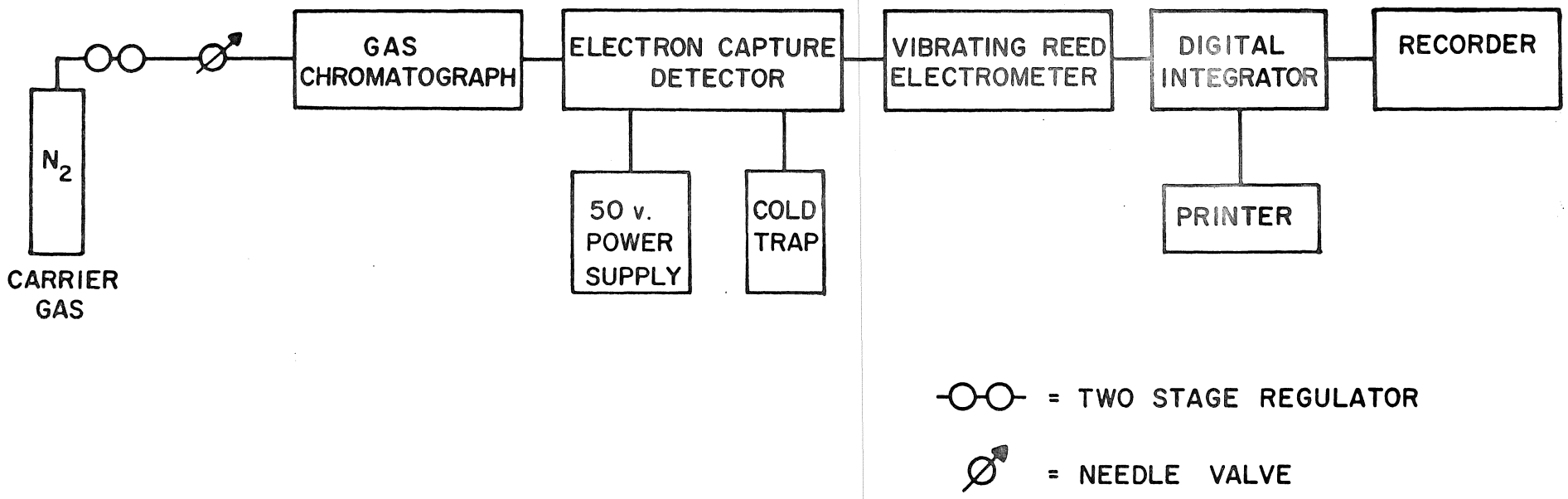

Figure 1. Block diagram of the gas chromatographic separation system

TABLE 3

CHROMATOGRAPHIC CONDITIONS FOR THE SEPARATION OF THE METAL CHELATES

Column = 20 feet of 1/8 inch o.d. Teflon

= 5% QF-1 on 80/100 mesh Chromosorb W, AW (DMCS)

Carrier gas flow rate = 60 ml/min of N_2

Detector polarizing voltage = 30 volts

Temperature	$Cr(hfa)_3$	$Cr(tfa)_3$	$Cr(fod)_3$
Injection port	146° C	200° C	200° C
Column	100° C	160° C	175° C
Detector	150° C	208° C	208° C

Mass spectra were run at 70 ev. on an RMU-6E mass spectrometer (Hitachi Div., Perkin Elmer Corp.). The batch liquid inlet system was heated to 75° C for $Cr(hfa)_3$ and 125° C for the other chelates.

2. Results and Discussion

Since these metal chelates are known to be thermally unstable, standard benzene solutions of each of the chelates were prepared, sealed in the quartz vials, and heated in a laboratory drying oven at 61° C for a period of time equal to the time of irradiation. Chromatographic analysis of the solutions with the electron capture detector showed that there was no measurable thermal degradation at this temperature. Therefore the degradation which is reported for the irradiated samples must be due to radiolysis effects alone.

In order to further isolate the variable parameters which effect chelate degradation, a $Cr(hfa)_3$ solution was sampled periodically from 1 to 168 hours following irradiation in order to follow the Szilard-Chalmers effect due to decay recoil reactions. This study showed that all of the measurable degradation appears to take place in the reactor, within the limits of the measurement error.

The effect of the irradiation time on the radiolysis degradation was also studied. $Cr(hfa)_3$ was chosen for this study because it was the most labile of the beta-diketonates studied. Figure 2 shows that the $Cr(hfa)_3$ is markedly more unstable in a reactor under a thermal neutron flux of $\sim 10^{12}$ neutrons/cm^2-sec. Therefore it is not at all feasible to use the hexafluoroacetylacetone ligand for chromium analyses by GC-NAA as only about 50% of the chromium will be recovered for counting after an irradiation corresponding to $\sim$ 0.03% of the saturation activity for Cr^{51}.

The determination of the concentration dependence of the radiation degradation was of paramount importance in choosing the most stable ligand system and in order to do quantitative analyses. Concentrations from 2.5×10^{-2} mg/ml to 5.3 mg/ml were used. This range was chosen in order to give a signal to noise ratio of $\geq$100:1 at the low concentrations (which corresponds to 1.2×10^{-2} µgr of chelate per 0.5 µl sample injected) and the maximum concentration was limited by the solubility of the chelate in benzene. The samples were chromatographically analyzed before and after irradiation at each concentration and the fraction of metal chelate remaining was calculated at the average of the peak areas for at least five replicate determinations.

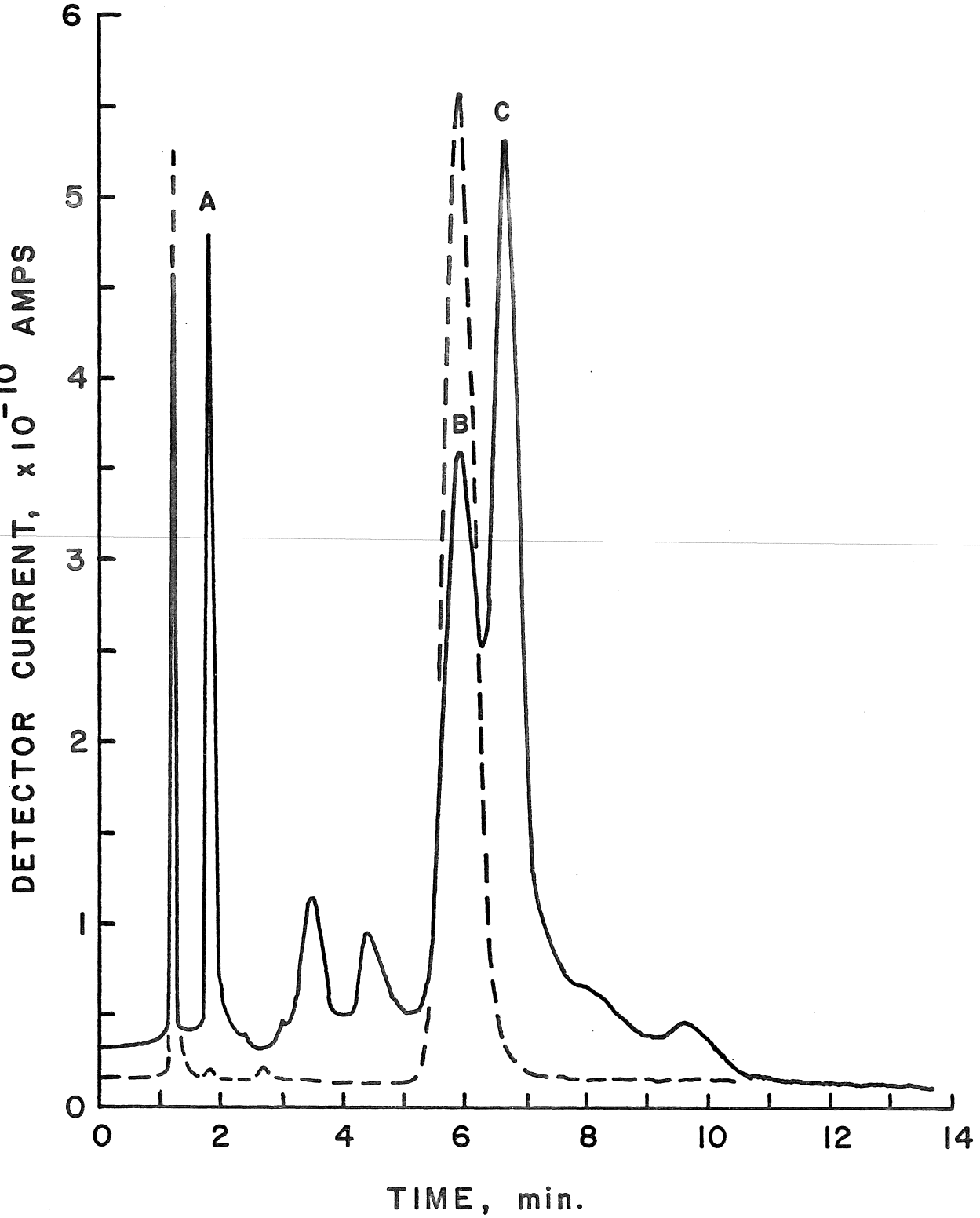

Figure 2. Chromatogram of a 0.1 mg/ml solution of $Cr(hfa)_3$ in benzene before (dashed line) and after irradiation (solid curve) in an integrated thermal neutron flux of 1.4×10^{16} neutrons/cm^2-sec

Typical chromatograms of $Cr(hfa)_3$ before and after irradiation are shown in Figures 2 and 3. After irradiation of the low concentration solutions of $Cr(hfa)_3$, three major peaks were found in the chromatogram. Peak A was identified as hfa by a comparison of retention times. Peaks B and C were trapped for analysis by mass spectrometry and gamma ray spectrometry. The former was identified as $Cr(hfa)_3$ but peak C was not positively identified. The mass spectra showed a parent peak at a mass to charge ratio of 644 but no chromium photopeak was found in the pulse height spectra after extended counting periods.

The ratio of the peak heights of peaks B and C was found to be a function of concentration as the ratio of B to C increased with increasing concentration. This is the expected result and consistent with the Szilard-Chalmers theory if the major degradation products resulted from cleavage of the metal-ligand bond. Such an equilibrium should be affected by the presence of an excess of ligand in favor of the recombination reaction and give larger recoveries of the metal chelate.

The results of the $Cr(hfa)_3$ study are shown in Figure 4. The percent of metal chelate recovered from a benzene solution ranges from 81 to 96% and the recovery is seen to be significantly less in the presence of excess hfa (from 40.5 to 90.0% recovery). These results are seen to be consistent at all concentrations but cannot be explained for this system.

A series of $Cr(tfa)_3$ solutions were also studied in order to determine the ligand effect. These solutions were similarly analyzed chromatographically before and after irradiation. The chromatogram of the $Cr(tfa)_3$ and Nanogram benzene showed only the solvent and chelate peaks and no other peaks were discernable above the baseline noise (3.5×10^{-12} amps). Figure 5 shows the results of this series of experiments. The chelate recoveries ranged from 90 to 98% with increasing metal chelate concentration which is in marked comparison with the less stable hfa chelate. The aliquots containing excess ligand were not analyzed because the tails of the excess ligand peaks obscured the remaining chromatogram due to detector poisoning. Savory et al. (81) used sodium hydroxide to hydrolyze the excess ligand before analyzing by electron capture. However, he reported recovering only 80 - 85% of the chelate. Since at least 90% of the irradiated chelate could be recovered without excess ligand and because of the uncertainty of the hydrolysis effect, the effect of the excess ligand was not measured.

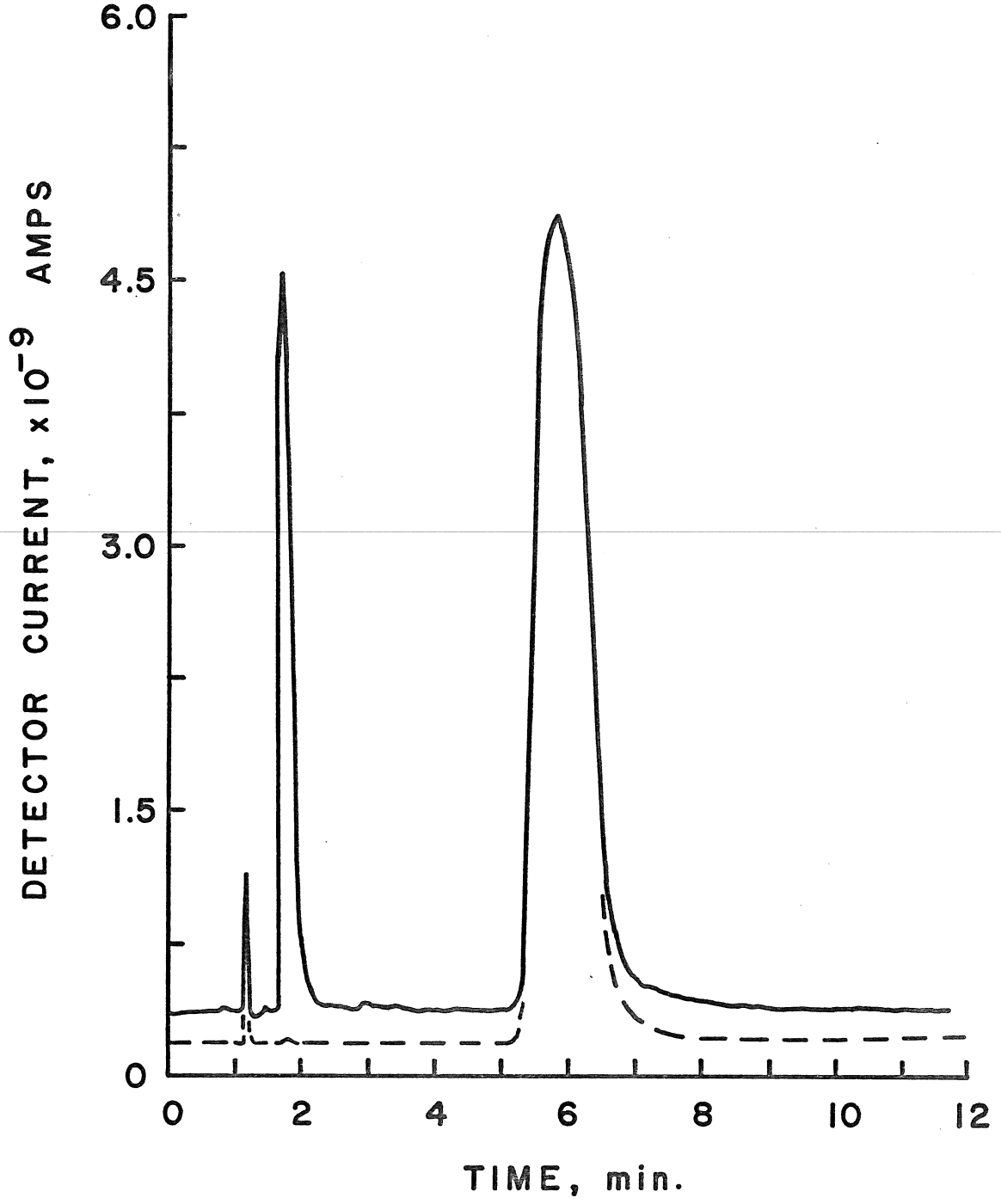

Figure 3. Chromatogram of a saturated solution of $Cr(hfa)_3$ in benzene before (dashed line) and after irradiation (solid line) in an integrated thermal neutron flux of 1.4×10^{16} neutrons/cm^2-sec

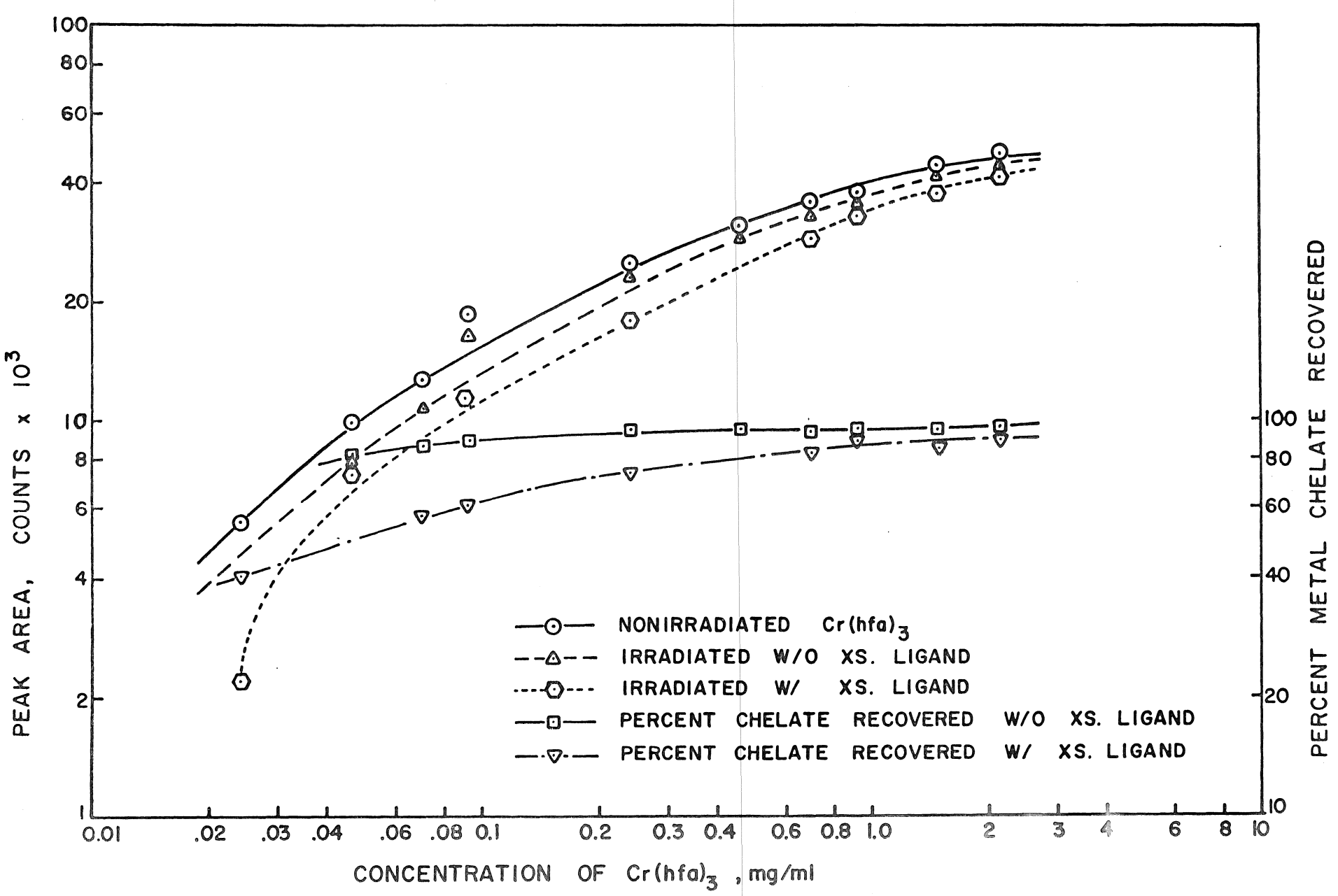

Figure 4. Experimental data for the recovery of $Cr(hfa)_3$ following thermal neutron irradiation

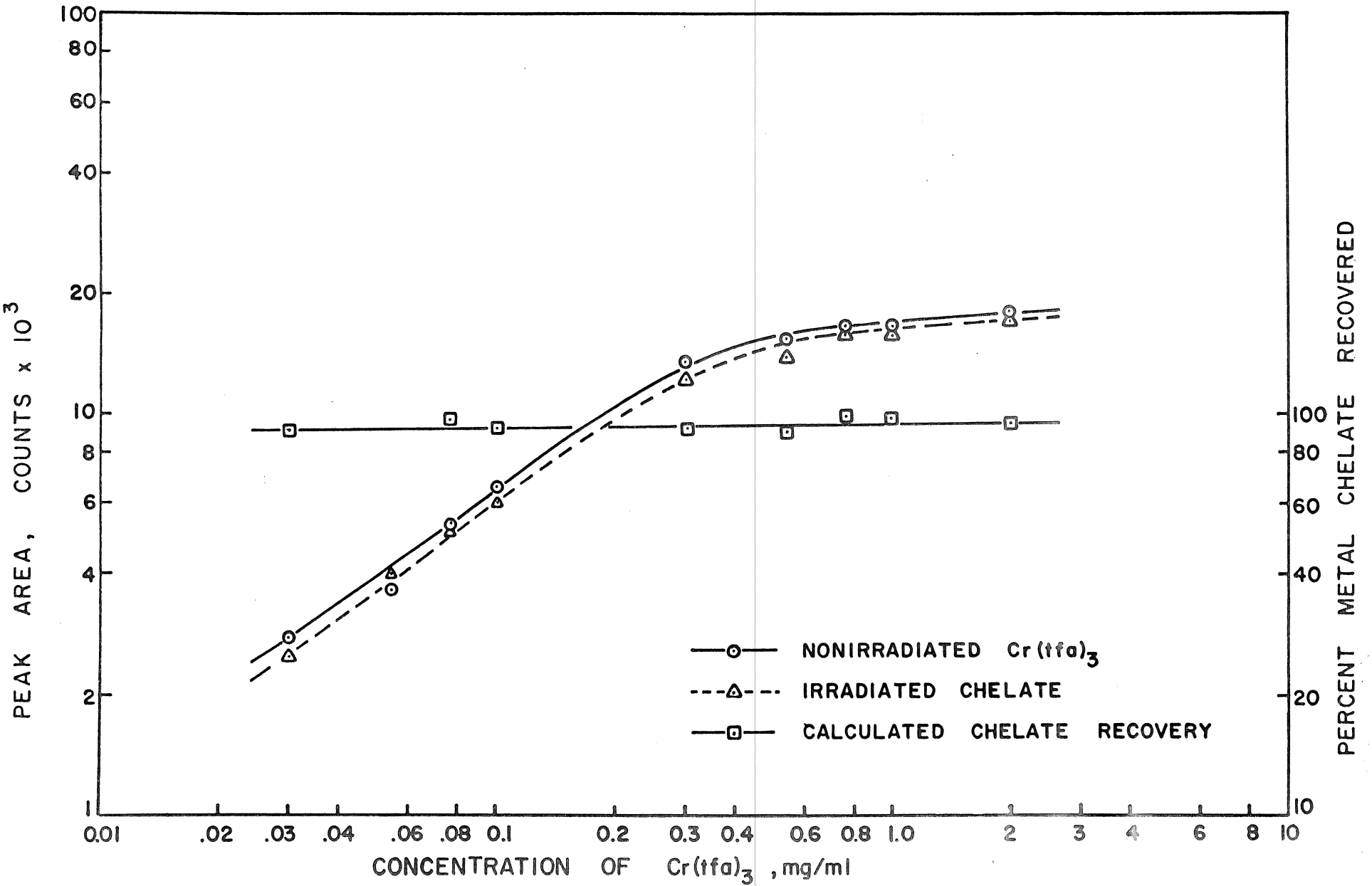

Figure 5. Experimental data for the recovery of $Cr(tfa)_3$ following thermal neutron irradiation

Chromium heptafluorodimethyloctanedione solutions were run under similar conditions and analyzed as before. These solutions were also found to be clean before irradiation within the limits of detection. The recoveries shown in Figure 6, are seen to increase with concentration from 90.0 to 100.0%. The results of the $Cr(tfa)_3$ and $Cr(fod)_3$ studies were particularly pleasing as they indicate that these chelates are stable to irradiation times up to 7 hours and are analytically useful for chromatographic post-irradiation separations in neutron activation analysis.

The relative irradiation stabilities of the three chromium beta-diketonates was found to be $Cr(fod)_3 \simeq Cr(tfa)_3 > Cr(hfa)_3$. The amount of $Cr(hfa)_3$ recovered is more a function of concentration than are the metal chelates of the other ligands. The presence of excess ligand appears to be detrimental to the quantitative recovery of the $Cr(hfa)_3$. The chromatograms showed no radiolysis peaks to obscure the chromatogram with either $Cr(tfa)_3$ or $Cr(fod)_3$ and this study has clearly shown these to be the chelates of choice for chromium analyses.

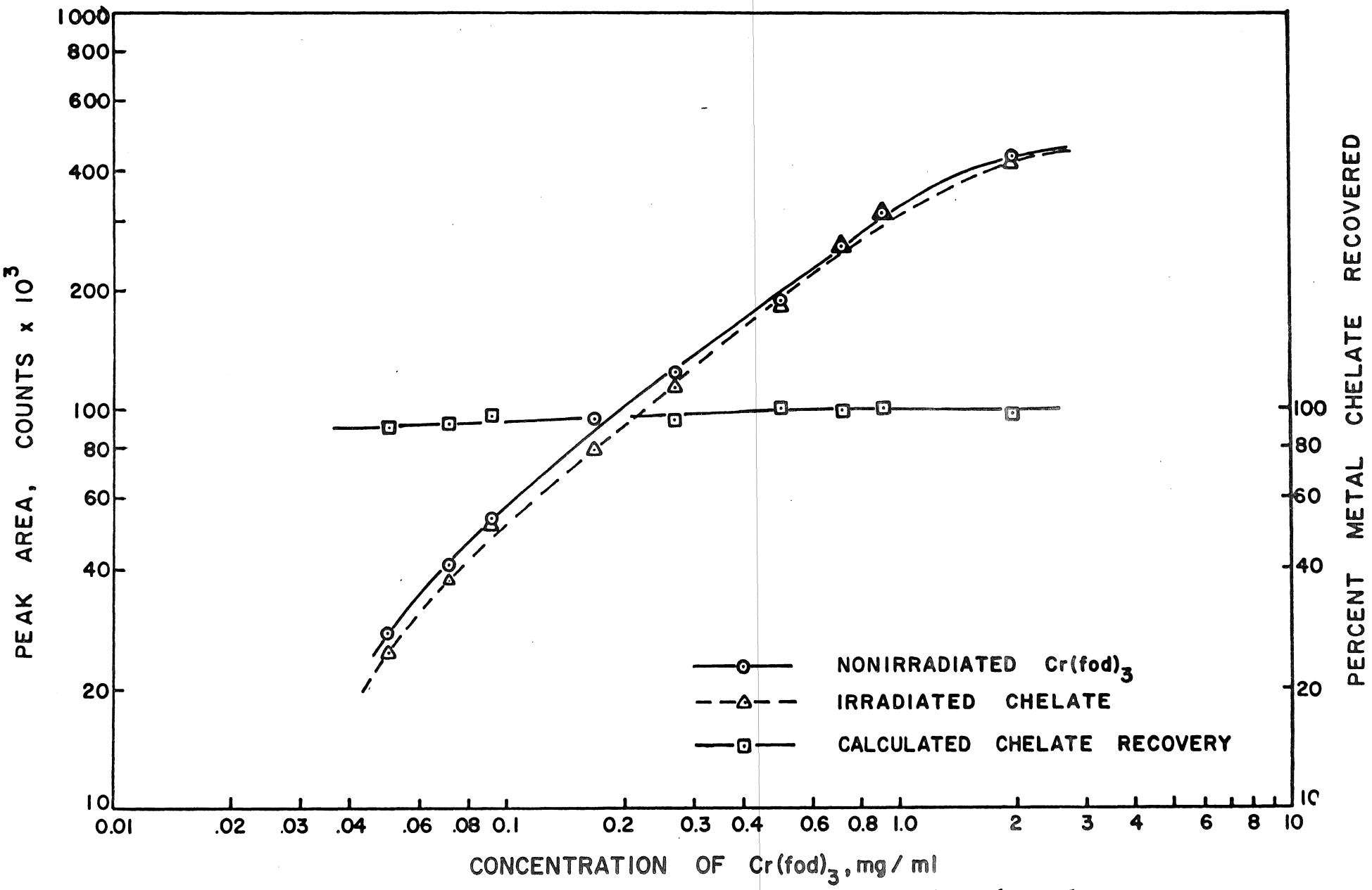

Figure 6. Experimental data for the recovery of $Cr(fod)_3$ following thermal neutron irradiation

PART II

THE QUANTITATIVE GAS CHROMATOGRAPHIC SEPARATION AND ANALYSIS OF RADIOACTIVE, VOLATILE METAL BETA-DIKETONATES

It has been shown that in order to obtain reproducible chromatographic peak areas with the metal chelates, several injections of the chelate solution must be made to "condition" the coulmn before quantitative measurements are made (38). This suggests that the first few injections leave chelate in the instrument, and only after these chelate adsorption sites are filled can a sample be eluted quantitatively. Gainer and Ponta (58) have shown that radioactive chromium ions in solution will exchange with chelated chromium. Exchange reactions might also take place between the chelate in the vapor phase and the chelate held on active sites in the chromatographic column. Under these conditions, the mass of chelate may be quantitatively recovered, but there is no assurance that the activity eluted is representative of the original sample.

In order to keep these reactions to a minimum, glass and Teflon systems have been used. It has been further shown that metal chelates will react with metal columns, and it is suspected that metal injection ports will aid and even catalyze the decomposition. Treatment of the chromatographic system with silanizing agents has also been used in practice to decrease on-column adsorption.

Radiotracer techniques have been known for a long time and applied to metal chelate synthesis and extraction studies (39). However, there has been no application of the technique to the determination of metal chelate residues in gas chromatography. This determination of metal chelate residues is a necessary step in the activation analysis-gas chromatographic technique.

1. Experimental

The gas chromatograph used in these studies was a Varian Model 1200-1 equipped with a 1/4 inch injection port, a hydrogen flame ionization detector and a linear temperature programmer. The columns were 1/8 inch Teflon (Alpha type, TFT-250/11), 0.095 inch I.D. and 0.016 inch in wall thickness. The seals at each end of the column were made by forcing the

column inside a constriction in a Pyrex tube. The injection port linear was a 3 mm O.D. Pyrex tube tapered to fit inside the Teflon column. All of the columns and their operating conditions are given in Table 4.

Liquid samples were injected with a Hamilton 10 µl syringe and a solid sampler was used to inject the sealed ampules (64). Samples to be injected using solid sampler were sealed in quartz tubes 2 cm x 2 mm. Both ends were sealed with a methane-oxygen torch. After filling, the tube was placed inside a 1/8 inch copper tube which was placed in a dry-ice-acetone bath. This prevented decomposition of the chelate by the heat from the torch.

Solid sample injection has many advantages. There is no solvent to interfere with trapping the effluent or obscure the chelate peaks when using a standard gas chromatographic detector. The maximum amount of chelate which can be placed in the solid sampler without overloading the column would require too much solvent for a satisfactory injection. In addition, the sealed quartz tube which contains the sample during irradiation can be placed directly in the solid sampling device without any of the handling or open vessels required for the more conventional liquid injection. Several sampling techniques have been developed for gas chromatography. The type which uses a plunger to break a quartz tube containing the sample is a logical choice for the gas chromatography of irradiated metal chelates.

In order to study the effect of sample size, a series of injections from 1 - 10 µl of a benzene solution of 32 mg/ml of $Cr(tfa)_3$ were run on column 6. The H_2 flow rate on the flame ionization detector was 46 ml/min and the O_2 flow rate was 135 ml/min.

All peak areas were measured with a digital integration Model CRS-100 (Infortronics, Inc.).

2. Quantitative Column Elution

To evaluate the effectiveness of silanization of the gas chromatographic system, a series of 1 µl injections of a solution with 29 mg/ml of $Cr(tfa)_3$ in benzene were injected into column 5. The study was repeated with a $Cr(fod)_3$ solution of the same concentration on column 7. After 4 to 6 chelate injections, 10 µl of DMCS was injected to silanize the system.

TABLE 4

CHROMATOGRAPHIC COLUMNS AND CONDITIONS

Column No.	Literat. Ref.	Length ft	Liquid Phase	Solid Support	He Flow Rate, ml/min	Temperature, °C IP.	Col.	Det.	Chelates
1	39	4	5% SE-52	60/80 mesh Gas Chrom. Z	50	170	80	---	$Be(tfa)_2$
2	--	2	20% High vacuum grease	100/120 mesh AW, DMCS Chrom. P	75	170	150	---	$Cr(hfa)_3$
3	--	4	5% QF-1	80/100 mesh Chrom. W	60	120	100	150	$Cr(hfa)_3$
4	--	4	5% QF-1	80/100 mesh Chrom. W	30	150	100	150	$Cr(hfa)_3$
5	--	4	5% QF-1	80/100 mesh Chrom. W	60	160	135	160	$Cr(tfa)_3$
6	--	4	5% QF-1	80/100 mesh Chrom. W	30	170	150	170	$Cr(tfa)_3$
7	--	4	5% QF-1	80/100 mesh Chrom. W	60	170	150	170	$Cr(fod)_3$
8	--	4	5% QF-1	80/100 mesh Chrom. W	30	200	175	---	$Cr(fod)_3$
9	--	3	15% QF-1	80/100 mesh AW, DMCS Chrom. W	20	165	100	165	$Mn(hfa)_2$

TABLE 4 - CONTINUED

Column No.	Literat. Ref.	Length ft	Liquid Phase	Solid Support	He Flow Rate ml/min	Temperature, °C IP.	Col.	Det.	Chelates
10	64	7.5	10% SE-30	60/80 mesh Gas Chrom. Z	30	205	170	---	$Fe(fod)_3$
11	--	2	20% High vacuum grease	100/120 mesh AW, DMCS Chrom. P	75	170	150	---	$Cu(hfa)_2$
12	83	2	5% SE-30	100/200 mesh Chrom. W	60	170	130	---	$Cu(tfa)_2$
13	--	1.5	20% SE-30	100/120 mesh AW, DMCS Chrom. P	30	150	150	---	$Cu(hfa)_2$
14	82	6	10% SE-30	80/100 mesh Chrom. W	30	230	170	---	$Gd(fod)_3$
15	82	6	10% SE-30	80/100 mesh Chrom. W	30	230	170	---	$Lu(fod)_3$

In order to evaluate the elution of irradiated chelates, solid samples of $Cr(hfa)_3$ and $Cu(hfa)_2$ were irradiated for 4 hours in the UFTR at $\sim/.5 \times 10^{12}$ neutrons/cm^2-sec and injected into columns 2 and 11, respectively. One mg solid samples of $Mn(hfa)_2$ were irradiated 15 min at the same flux and run on column 9. After the chelates eluted, the solid sampler, charcoal trap, and column inlet, column, and outlet system were counted. The quartz fragments in the injection port were counted, the injection port rinsed with acetone, and the solution counted. Similar system counting was done after irradiated solutions had been injected: $Cr(hfa)_3$ in column 4, $Cr(tfa)_3$ in column 6 and $Cr(fod)_3$ in column 8.

In order to separate the effects of adsorption and on-column reaction from the radiolysis decomposition of the metal chelates, pure radioactive chelate solutions were prepared. These were injected into their respective columns (see Table 4) in a series of 5 µl injections, 1 min apart. The series of injections totaled 50 µl and 100 µl. After the carrier gas had been allowed to flow after the last injection for 3 times the retention time of the chelate, the system was dismantled and the components counted. The packing was counted in a 60 x 15 mm Pyrex petri dish.

3. Counting System

All radioactivity measurements were made using two 3 x 3 inch NaI(Tl) detectors connected to the multichannel pulse height analyzer system previously described. A block diagram of the counting system is shown in Figure 7. The three different counting geometries shown in Figure 8 were studied and they are described in detail elsewhere (34). The exponential dilution flask exhibited sever adsorption properties and was difficult to heat uniformly, and consequently, will not be considered here.

The spiral coil flow-through geometry consisted of a 57 inch piece of 1/8 inch O.D. #316 stainless steel tubing with a 0.005 inch wall (Superior Tube Company). It was wound in a spiral 2 7/8 inch O.D. x 1 1/8 inch I.D. The inlet and outlet arms each consisted of 6 1/2 inches of tubing. The charcoal traps were made from 5 inch pieces of tubing packed with 1 inch of 40-50 mesh charcoal. The packing began at the center and extended toward the outlet. Some of the charcoal traps were made from the same stock as the spiral. Others were 1/8 inch O.D. Teflon lined aluminum tubing or 3 mm O.D. Pyrex.

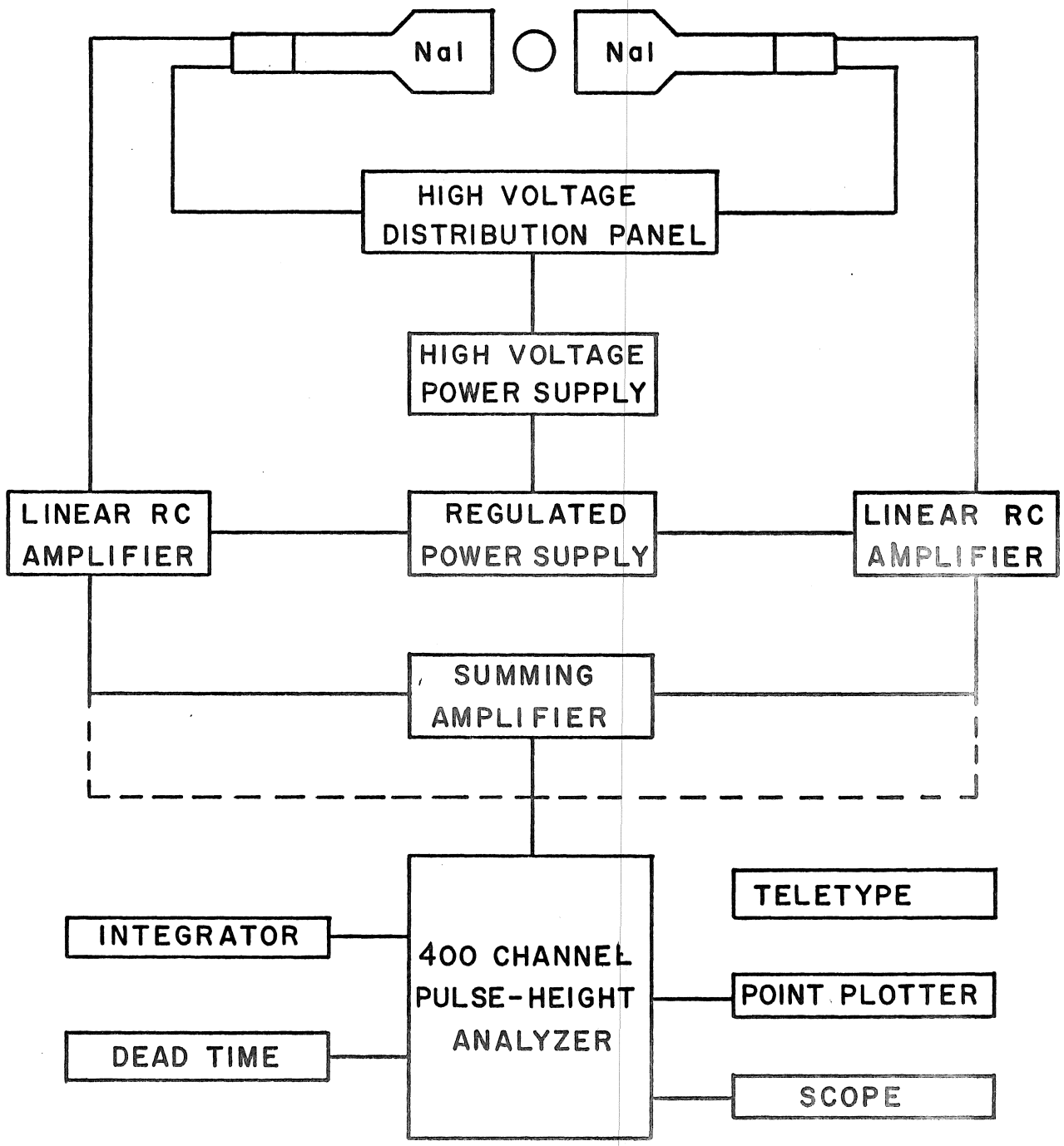

Figure 7. Block diagram of the NaI(Tl) detector and counting system used for radiochromatography

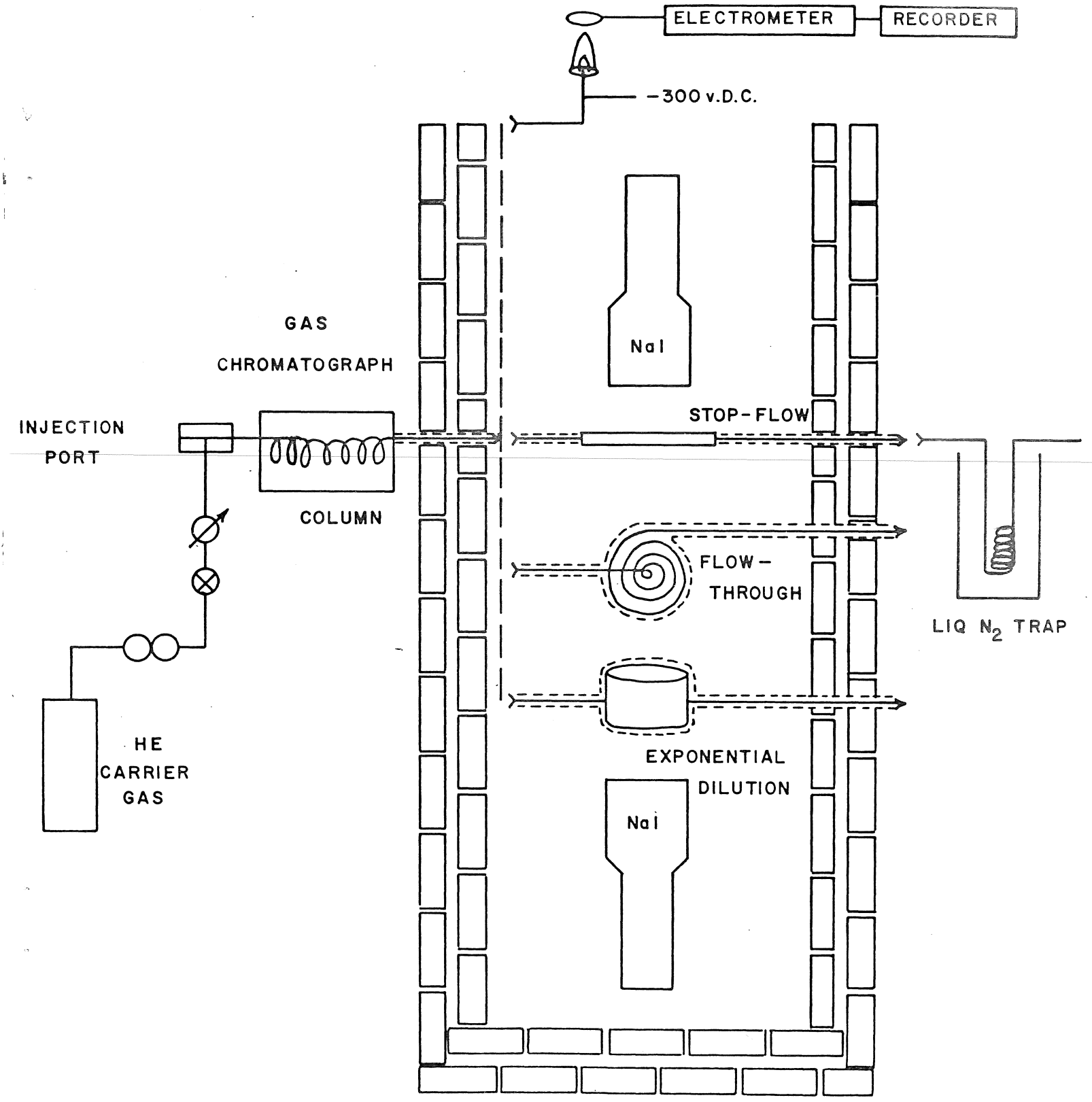

Figure 8. Counting geometries studies for measuring the radiochromatographic effluent activity

The reversible counting geometry consisted of a 6 inch piece of Teflon tubing packed with 2.5 inches of 20% SE-30 on Chromosorb P, (AW DMCS). This tube was enclosed in a larger aluminum tube wrapped with heating wire. Cool air could be passed around the Teflon tube inside the aluminum tube to cool the geometry. A He purge line was connected upstream to help flush the counting geometry.

The sample counting in geometries connected to the system was done in a cave beside the gas chromatograph. A heated Teflon tube passed through the oven wall into the cave. The cave had 8 inches of lead between the detectors and the gas chromatograph, 4 inches of lead on the side, top, and back, and no lead on the bottom and front. The inside dimensions were 24 x 20 x 8 inches.

Sample counting, where the traps were removed from the gas chromatograph system, was done in a lead cave 40 x 22 x 12 inches with 4 inches of lead on 5 sides and 2 inches on the bottom.

The response of the NaI(Tl) detector as a function of position was obtained by passing a 0.2 inch long by 0.061 inch diameter piece of molecular sieve containing Cs^{137} across the surface of the can containing the detector. Two perpendicular passes were made. The time sequence store mode of the analyzer was used to obtain a plot of relative response versus position.

Three different modes of counting radioactive metal chelates were used. Where two or more radionuclides were present, a pulse height spectrum was taken and the areas under the photopeaks integrated using a PDP-8/L laboratory computer (Digital Equipment Corp.). When only one radionuclide was present, a single channel analyzer was used and the entire spectrum above a few kev was measured. When radiochromatograms were made, the time sequence store mode of the analyzer was used.

The flow through spiral counting geometry was used at 170° C with a continuous He carrier gas flow of 30 ml/min to obtain radiochromatograms of $Cu(hfa)_2$ - $Cr(hfa)_3$ mixtures using column 2. The time sequence store mode of the analyzer was used with a dwell time of 0.02 min/channel.

The stop-flow counting geometry was operated in a flow-through mode at a constant temperature of 115° C with a sorbent identical to column 13 inside. The geometry was held at 60° C to trap effluents, such as the $Cu(hfa)_2$, and then heated to 150° C to desorb the complex. The procedure for repetitive use of the reversible stop-flow counting system was:

1. Start carrier gas, apply cool air to geometry
2. Inject sample
3. Wait 2.5 - 3.0 min, stop carrier gas flow
4. Count sample 10 min
5. Heat geometry and allow purge gas to flow for 15 min
6. Cool geometry, stop purge gas, and make a 10 min background count
7. Restart carrier gas and trap the next component.

Irreversible charcoal traps were used to obtain integral radiochromatograms. The metallic traps were cooled with dry ice, but the 3 mm Pyrex traps required no cooling. The integral chromatograms were obtained by stopping the carrier gas flow and counting the accumulated activity in the trap. $Cu(hfa)_2$ - $Cr(hfa)_3$ mixtures were injected as solids and counted using this technique.

4. Chelation Studies

The H(tfa), H(hfa), and H(fod) ligands (Peninsular Chem. Research) were all redistilled prior to use. For H(tfa), the 107° C fraction was collected. The $Cu(hfa)_2$ and $Cr(hfa)_3$ were used as purchased (Pierce Chemical Company). The Mallinckrodt Nanograde benzene was dried over a 13X molecular sieve. The Vitreoseal quartz for the ampules was obtained from the Thermal American Fused Quartz Company.

$Cr^{51}Cl_3$ in 1 N HCl, 0.02 mg/ml, 3.7 mCi/ml (Union Carbide), $Fe^{59}Cl_3$ in 1 N HCl, 2 mCi in 0.83 ml (New England Nuclear Corp.) and $Be^{7}Cl_2$ in 0.5 N HCl, 2 mCi in 0.5 ml (New England Nuclear) were used as tracers in these experiments.

The atmospheric sublimation apparatus consisted of an 8 cm x 6 mm O.D. Pyrex tube bent into a "U" shape with a connecting tube on each end. The apparatus was heated in the gas chromatographic oven. The He flow through the tube and the heat applied by the oven were sufficient to sublime the chelates and move them from the bottom of the "U" through a short piece of Teflon tubing to a 3 mm O.D. Pyrex trap outside the oven. This trap was maintained at room temperature.

The vacuum sublimation apparatus was a standard design with a 15 mm O.D. Pyrex pot and an 8 mm O.D. cold finger. It was connected to a mechanical forepump.

Mixtures of 2 mg of solid $Cr(hfa)_3$ and 1 mg of solid $Cu(hfa)_2$ were sealed in 2 mm x 2 cm quartz tubes and irradiated for 4 hours at 10^{12} neutrons/cm^2-sec in the University of Florida Training Reactor (UFTR). Solid 1 mg samples of $Mn(hfa)_2$ were sealed and irradiated under the same conditions for 15 min. The $Cr(hfa)_3$ and $Cu(hfa)_2$ mixture was injected into columns 2 and 11 (see Table 4), and the $Mn(hfa)_2$ was injected into column 9. No annealing treatment was used on either sample. The chromatographic column was then dismantled and each component counted.

$Cr(tfa)_3$, $Cr(fod)_3$, and $Cr(hfa)_3$ were dissolved in Nanograde benzene, irradiated for 14 hours at 6.5×10^{11} neutrons/cm^2-sec in the Georgia Technology Research Reactor (GTRR), and injected without further treatment into columns 5, 7, and 3, respectively. Each of these columns, charcoal traps, and injection port liners were similarly counted.

Thermal annealing of irradiation damage in $Cr(tfa)_3$ was studied by irradiating two benzene solutions: one containing 30.2 mg $Cr(tfa)_3$ and 2.7 mg H(tfa) (10% excess) in 1 ml of benzene, and the other contained 30.4 mg $Cr(tfa)_3$ and 27 mg H(tfa) (100% excess) in 1 ml of benzene for 14 hours at 6.20×10^{11} neutrons/cm^2-sec in the GTRR. Part of the sample with 10% excess ligand was injected into column 5 without treatment. The rest was annealed (heated) 9 hours at 100° C and then injected. The sample with 100% excess ligand was annealed 9 hours at 100° C in its sealed irradiation vial and injected. All three columns were dismantled and counted.

Hot $Cr(tfa)_3$ was prepared by synthesizing the chelate using Cr spiked with Cr^{51} as the starting material. Forty mg $CrCl_3 \cdot 6 H_2O$ was spiked and dissolved in 1.5 ml H_2O in a 5 ml round bottom flask. Three hundred mg of urea and 86 mg (10% excess) of H(tfa) were added, and the mixture refluxed at 100 - 115° C for 7 hours. The insoluble product was filtered, washed with H_2O, and air dried. The product was dissolved in ether and placed in the atmospheric sublimation apparatus. After the ether had evaporated, the temperature was raised to 150° C for 15 min. Forty-seven mg of purple product was recovered from the trap under a flow rate of 10 ml/min.

Radioactive $Cr(fod)_3$ was also prepared by synthesizing the chelate using chromium spiked with Cr^{51} as the starting material. Fifty-two and one-half mg $Cr(NO_3)_3 \cdot 9 H_2O$ was spiked and dissolved in 0.5 ml absolute ethanol in a 10 ml round bottom flask. One hundred thirty-four and two tenths mg (10% excess) H(fod) dissolved in 1 ml absolute ethanol

was added. After heating for 1 hour at 80° C, the mixture was transferred to the atmospheric sublimation apparatus. Heating for 1 hour at 140° C with 10 ml/min He flow transferred 6.5 mg chelate to the trap.

A solution containing 43.5 mg $Lu(fod)_3$ and 42.1 mg H(fod) in 1.5 ml benzene was prepared. One ml of this was irradiated for 14 hours at 5 x 10^{11} neutrons/cm^2-sec in the GTRR. It was annealed 10 hours at 100° C. The sample was vacuum sublimed at 115° C for 15 min. Thirty-three and one-half mg pale yellow chelate was obtained.

The same procedure was applied to $Gd(fod)_3$, except that the sublimation was for 45 min at 150° C.

Radioactive $Fe(fod)_3$ was synthesized from $FeCl_3$ spiked with Fe^{59} dissolved in ethanol. H(fod) was added and immediately after mixing, the deep red chelate was formed. It was extracted into 2.5 ml hexane and sublimed at atmospheric pressure at 140° C. Six mg of deep red chelate was obtained. The pale red crystals were discarded.

Radioactive $Be(tfa)_2$ was synthesized from $BeSO_4 \cdot 4\ H_2O$ spiked with Be^7. Forty-one mg $BeSO_4 \cdot 4\ H_2O$ and 90.0 mg NaAc were dissolved in 1.5 ml H_2O. One hundred mg (50% excess) H(tfa) dissolved in absolute ethanol was added. The white product was extracted into benzene and vacuum sublimed at 65° for 15 min. Thirty-four and a half mg chelate was obtained.

The $Cu(tfa)_2$ was synthesized according to the method of Berg and Truemper (84). A saturated benzene solution with excess solid chelate, 65.5 mg total weight, was irradiated for 7.5 hours at 10^{12} neutrons/cm^2-sec in the UFTR. The sample was annealed at 115° C for 7 hours and vacuum sublimed at 115° C.

5. Results and Discussion

Both solid and liquid samples were evaluated in this study. The solid sampler's large sample size (1-2 mg) was ideal from the standpoint of counting, especially when using the flow-through type geometries. However, the activity measurements made on the solid sampler and quartz fragments in the injection port showed large amounts of radioactive residue, most of which was due to Szilard-Chalmers decomposition. There were visible chelate residues in the sampler barrel and among the quartz fragments, indicating either that the injection port was not hot enough, or that the solid sampling technique needed to be improved. This contributed to the injection port activity to a small extent.

The length of the sealed sample tubes which were broken by the solid sampler was found to be critical. If the tubes were too long, large amounts of glass (or quartz) fragments prevented all the sample from leaving the sampler barrel. If the sample tubes were too short, they were not broken at all, and were forced upward, breaking the injection port liner which surrounded the solid sampler barrel. For 0.060 inch O.D. melting point capillaries, the best lengths were found to be between 0.406 inches and 0.469 inches. For liquid injections of 5 µl or less, the total sample activity was so low that long counting times were required. When a total of 100 µl of $Cu(tfa)_2$, injected 5 µl at a time (in order not to overload the column) 7×10^6 cpm were measured in the trap. If all factors affecting recovery are linear, a 1 µl injection should have at least 7×10^4 cpm activity which is roughly 70 times background.

The results of the injected sample size study are shown in Figure 9. The benzene $Cr(tfa)_3$ chromatograms gave one peak for benzene and two chelate peaks. The second chelate peak area was only 10% of the first and it was necessary to integrate both chelate peaks together. From these results it is seen that the 10 µl sample deviates significantly from linearity and is therefore considered as the upper limit of liquid sample injections.

In terms of eluting the chelates quantitatively, the silanization did not produce any measurable improvement. Even after 70 µl of DMCS has been injected, the chelate peak areas were the same as those observed before any DMCS had been injected.

For all of the solid injections the elution efficiency was poor. Eighty - ninty% of the activity was found in the injection port, the solid sampler, and the column inlet. Both the quartz fragments and the acetone rinse were radioactive. Most of the activity was removed from the injection port by this procedure. The only time any radioactive chelate was measured was when the sample activity was so high that the 5% which was eluted was hot enough to be counted.

The color and appearance of the solid $Cr(hfa)_3$, $Cu(hfa)_2$, and $Mn(hfa)_2$ did not change during irradiation. Since only 2 atoms in 10^9 of the chelate undergo the (n,γ) reaction during a 15 hour irradiation at 10^{12} neutrons/cm^2-sec, only a small fraction of the sample is effected by the Szilard-Chalmers reaction. Thus, even though these solids may have been essentially unaffected by irradiation, the chelation of the radioactive atoms was by no means quantitative. This was shown by the results of the gas chromatograph residue measurements. When solid $Cr(hfa)_3$ and $Cu(hfa)_2$ were

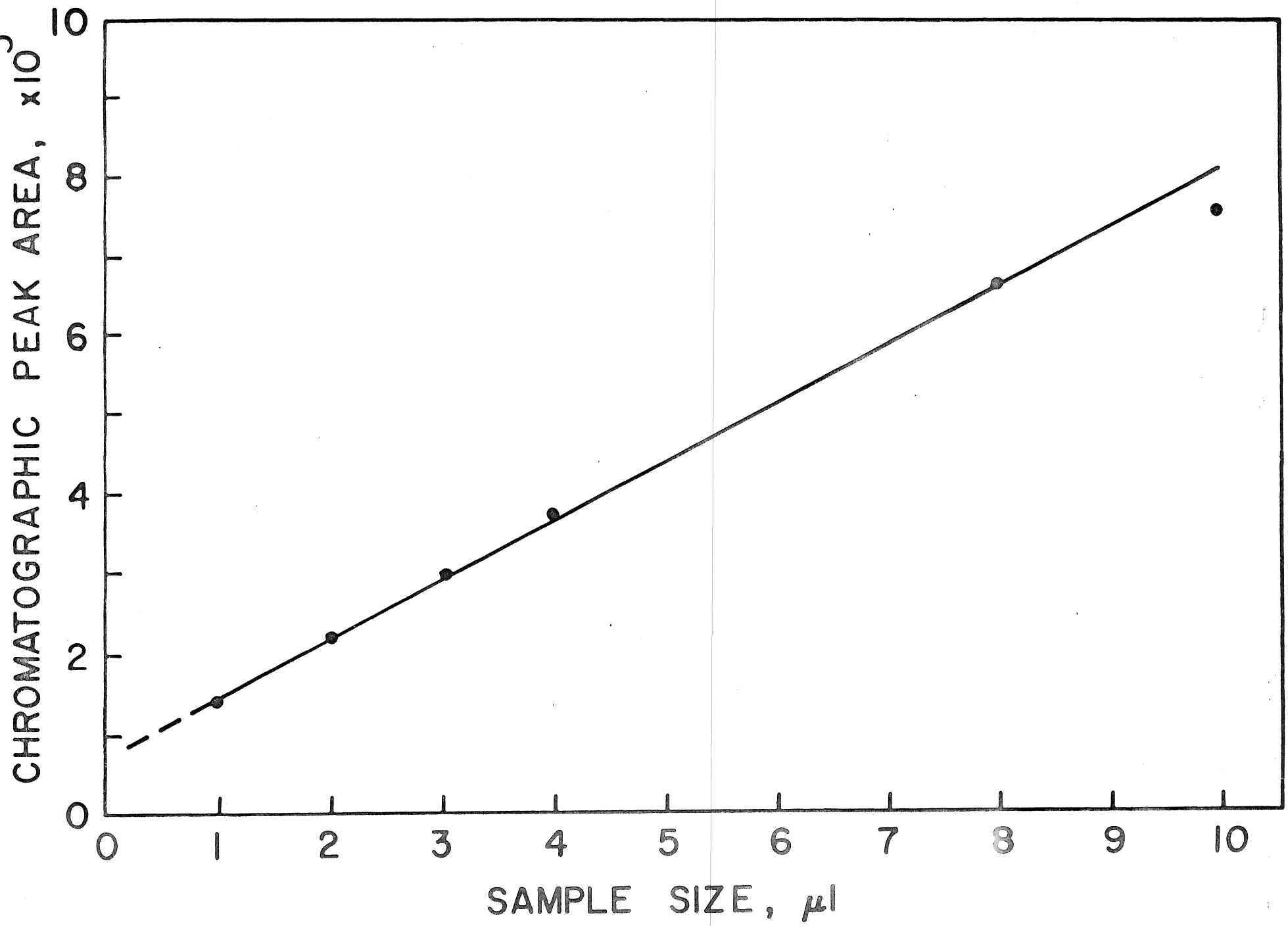

Figure 9. Effect of sample size on the quantitative elution of $Cr(tfa)_3$ on Column 6

injected into columns 2 and 11, respectively, large amounts of activity were found in the solid sampler, the injection port, and the head of the column. Smaller amounts of activity were found at the middle of the column and at the outlet. When a charcoal counting trap was used for the above experiment, approximately 50% of the radioactive sample was found in the charcoal trap. Undoubtedly, there was some annealing in the reactor and/or the injection port. After the irradiated solid $Mn(hfa)_2$ was injected, no trace of Mn^{56} was found beyond the injection port. There was apparently insufficient annealing to rechelate any Mn^{56}.

The $Cr(tfa)_3$, $Cr(fod)_3$, and $Cr(hfa)_3$ solutions behaved the same way as the solids. Very small amounts of activity were found in the counting geometry and large amounts stayed in the injection port.

The use of a Teflon injection port liner showed no improvement over quartz. The injection port retention was not due to the liner material, since hot chelate passed through the rest of the Teflon tube satisfactorily.

The results of the $Cr(tfa)_3$ annealing experiment are shown in Table 5. The residue study was used to evaluate the purity of the radioactive chelate. The figures from an untreated sample similar to this one are included for comparison. It can be seen that heating at 100° C for 9 hours in conjunction with irradiation with a 100% excess amount of ligand is quite effective in minimizing the amount of unchelated radioactive metal. When only 10% excess ligand was used the results were much better than when no treatment was used. Still, the results were poor. Heating caused some improvement, but only with 100% excess ligand were the results optimum.

The solutions which were irradiated and not annealed were equally unsatisfactory. Here, there was no significant solid residue in the injection port as most of the metal chelate was eluted through the column. Only the small number of radioactive nucleii apparently underwent radiolysis and were consequently not in a form suitable for chromatographic elution. Only after annealing can irradiated chelate solutions be used for gas chromatography (see Table 5).

The solution of $Cr(tfa)_3$ which was irradiated with 100% excess ligand and then annealed gave excellent chromatographic results. The sublimation step used in the residue study for purifying the irradiated mixture is apparently not necessary for efficient elution. Table 6 lists the results of the residue studies of the chelates.

TABLE 5

EFFECT OF POST-IRRADIATION ANNEALING
OF $Cr(tfa)_3$ IN BENZENE

	Activity Recovered, % of Total			
Annealing Excess Ligand	None 0%	None 10%	9 hrs, 100°C 10%	9 hrs, 100°C 100%
Injection port liner	89.7	11.0	2.80	0.88
Column packing	3.8	35.8	3.0	1.43
Column tubing		0.25	0.7	0.38
Charcoal trap	7.0	52.9	93.5	97.30

NOTE: Chromatographic analysis run on Column 5 (Table 4).

TABLE 6

PERCENT RECOVERY OF METAL CHELATES
IN CHROMATOGRAPHIC SYSTEM

Chelate	Column No.	Residual Activity, % of Total			
		Injection Port Liner	Column Packing	Teflon Tubing	Trap
$Cr(tfa)_3$	5	0.35	1.36	0.38	98.16
$Cr(tfa)_3$[a]	5	11.06	35.81	0.25	52.87
$Cr(tfa)_3$[b]	5	2.80	2.97	0.70	93.50
$Cr(tfa)_3$[c]	5	0.88	1.43	0.38	97.30
$Cr(fod)_3$	7	0.35	15.7	0.75	83.0
$Be(tfa)_2$	1	0.07	2.7	3.0	94.2
$Fe(fod)_3$	10	0.30	23.0	2.48	74.3
$Cu(tfa)_2$	12	1.30	23.0	3.5	72.2
$Gd(fod)_3$	14	1.0	35	1.3	63
$Lu(fod)_3$	15	0.51	7.0	0.43	92.1

[a]Irradiated with 10% excess ligand

[b]Irradiated with 10% excess ligand and annealed

[c]Irradiated with 100% excess ligand and annealed

The $Cr(tfa)_3$ results were quite good. The poorer $Cr(fod)_3$ results may have been due to a higher column temperature which would have contributed to decomposition on the column packing, since a large portion of the activity was found there.

The $Be(tfa)_2$ results were similar to those of the $Cr(tfa)_3$. The third column, however, appeared to hold a large portion of the activity. There was no explanation for this. It is not a problem with sample purity because the injection port did not contain any more activity than it did in the other two runs.

The $Gd(fod)_3$ data was less accurate than the other experiments because the sample had decayed through 3 half-lives considerably before it was counted. This meant that a mixture of daughters and other Gd isotopes were present, the half-life of which was unknown, and therefore no decay correction could be made. The results are accurate to the extent that they show nearly 1/3 of the total activity on the column packing. This is different from the $Lu(fod)_3$ result, even though they are both rare earths and both experiments used identical columns. This is similar to the $Cr(tfa)_3$ - $Cr(fod)_3$ results.

The $Fe(fod)_3$ also left a large residue on the packing material. Some was also present on the column tubing, which would indicate that the chelate and liquid phase did interact and that accurate quantitative results will be difficult to realize. The $Cu(tfa)_2$ behaved similarly. The larger amounts of residue in the column is due to the low operating temperature for that particular experiment.

In summary, the $Cr(tfa)_3$, $Be(tfa)_2$, and $Lu(fod)_3$ with the columns which were used with them seem to be good choices for gas chromatography of radioactive metals. The rest of the chelates seem to be restricted by the nature of the column packing. A better choice of chromatographic conditions, then, will probably make activation analysis work with these chelates feasible also. Further, it is seen that reaction irradiation of the metal chelates requires post-irradiation annealing of both solid and liquid samples.

The relative response of the Na(Tl) crystal as a function of sample position is an important consideration in the design of counting geometries. Consecutive samples need to be held in regions of the same response if reproducible results are to be obtained. Figure 10 shows the plot of response versus position for the 3 x 3 inch NaI detectors used in this study. The region where the response decreased by no more than 10% from the maximum was found

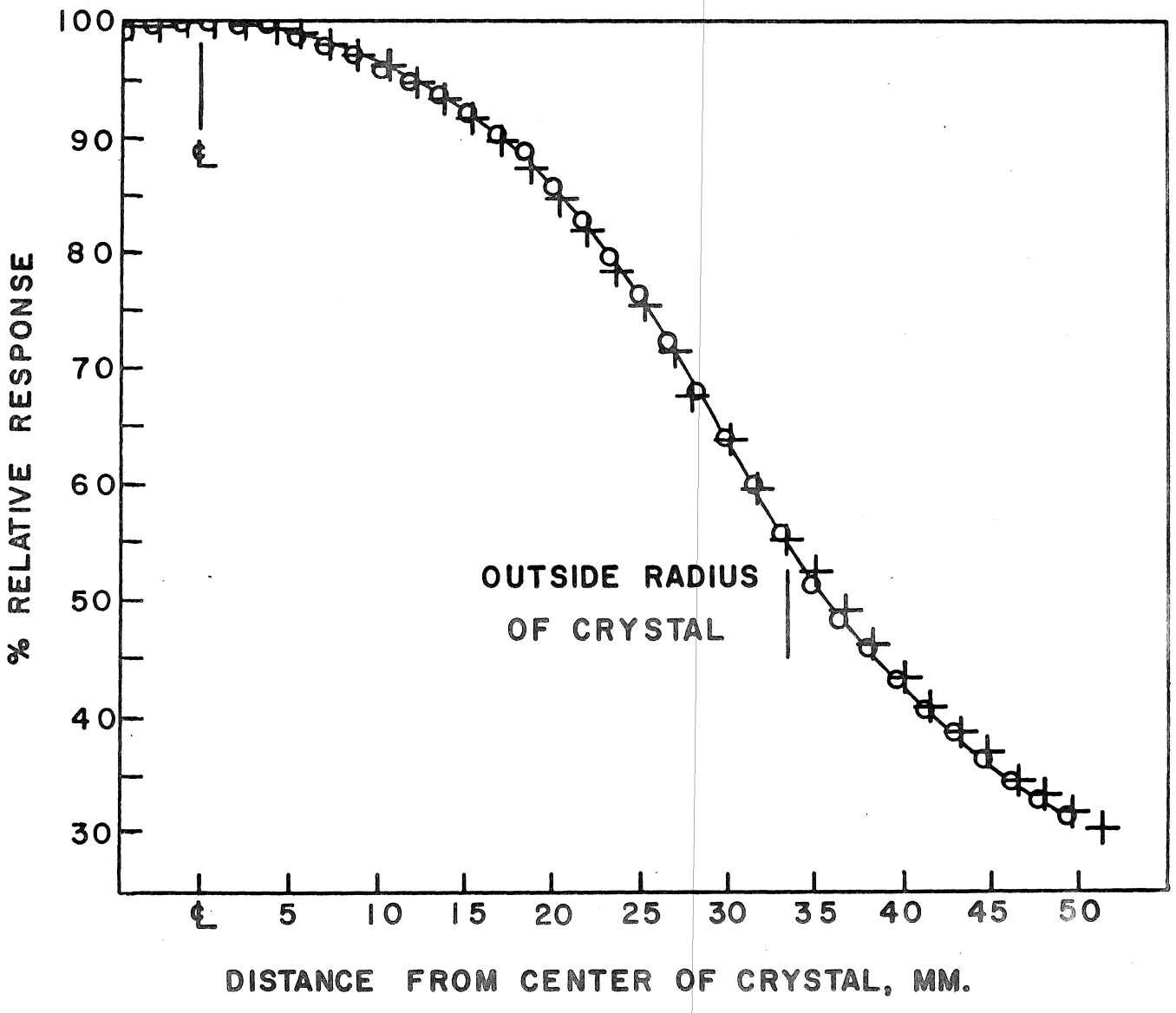

Figure 10. Response of the NaI(Tl) detector as a function of position on the crystal face. Points denoted by circles represent the response of the facing side of the detector face

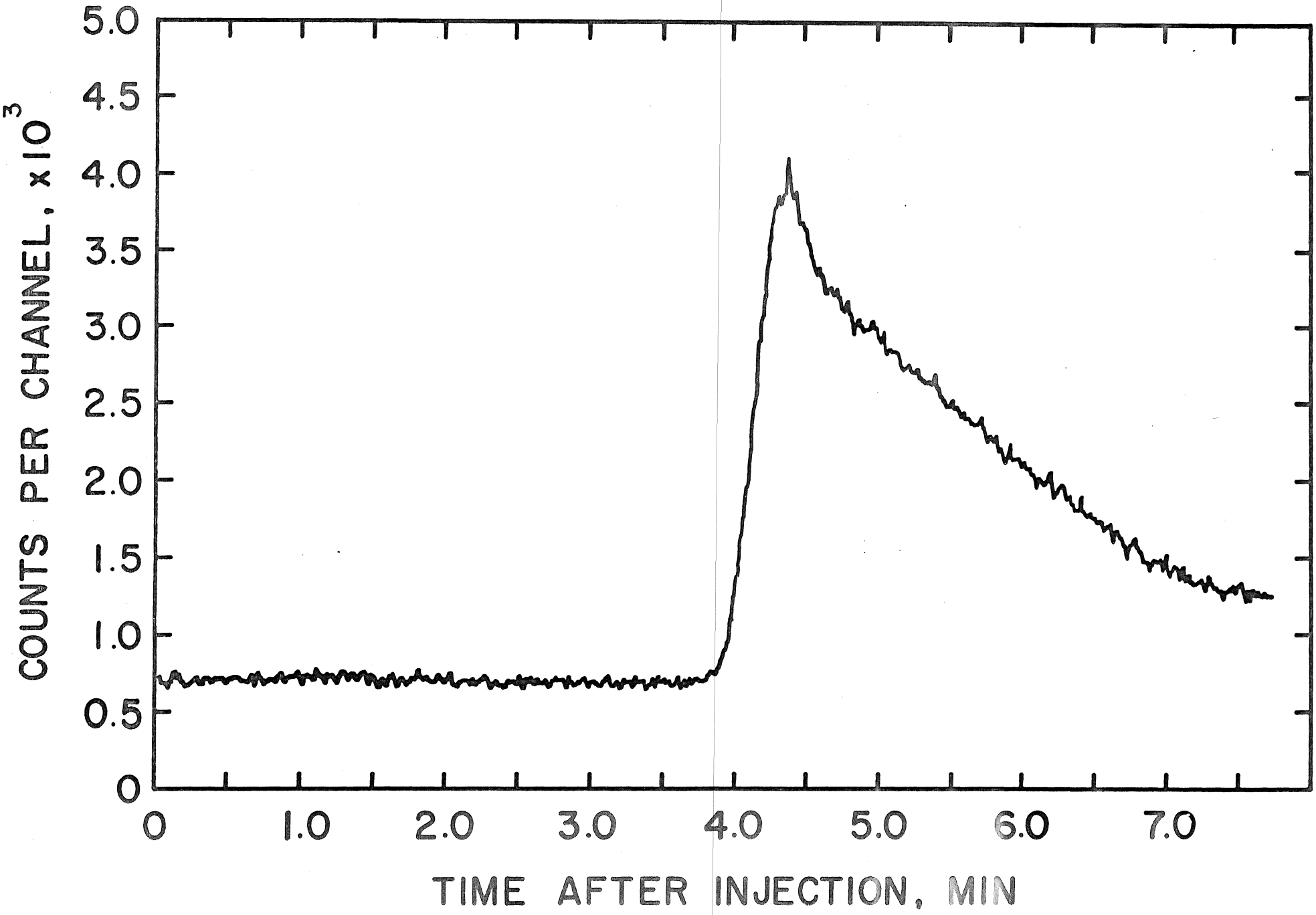

Figure 11. $Cu(hfa)_2$ activity counted in a stainless steel flow-through counting geometry, after separation from a $Cu(hfa)_2$-$Cr(hfa)_3$ mixture

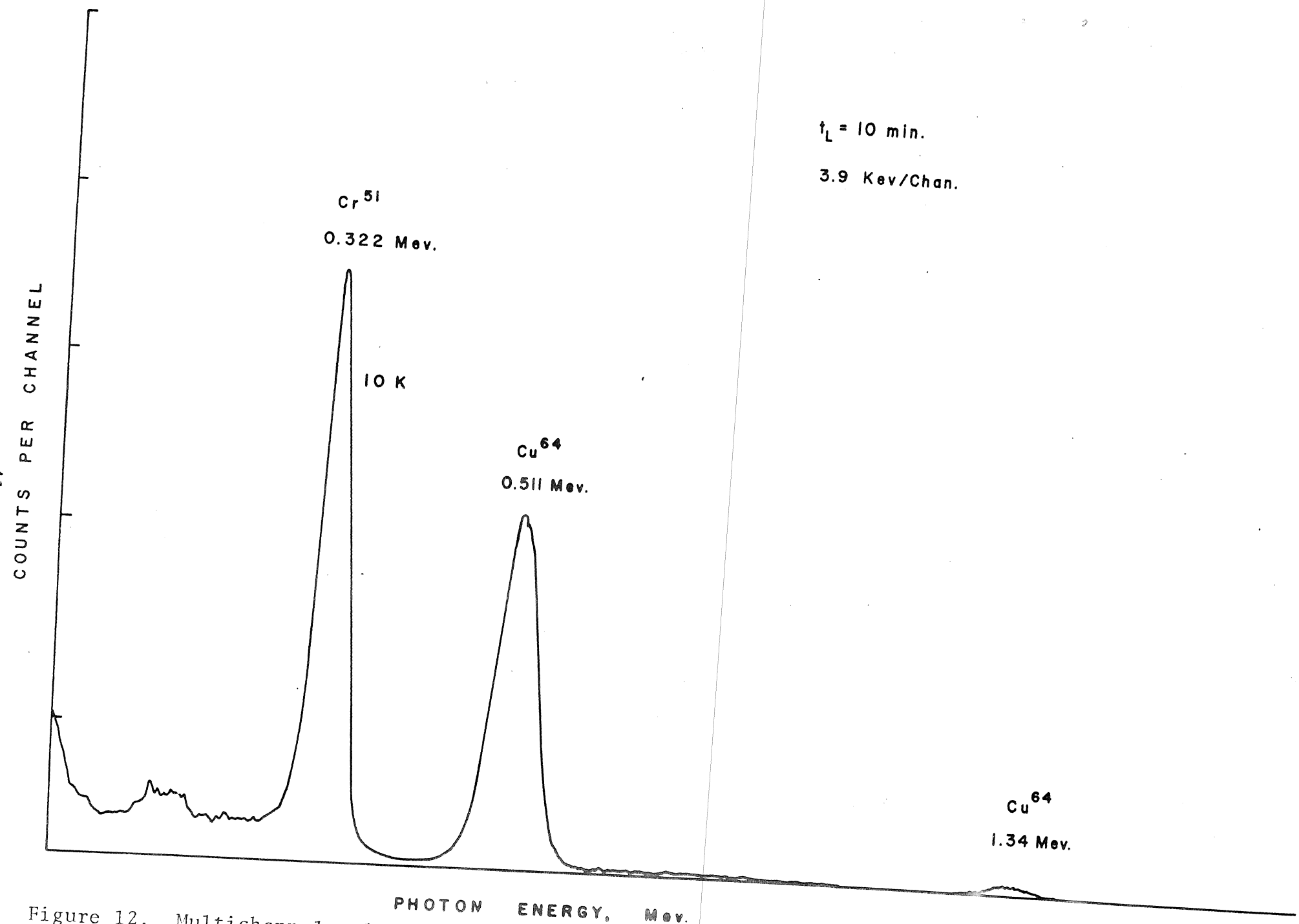

Figure 12. Multichannel pulse-height spectrum taken after the gas chromatographic separation of Cr^{51} followed by the elution of Cu^{64}

purge gas are applied to flush the geometry. After it is cool again it is ready for the next component of the sample to be eluted and trapped. Here is complete flexibility, indefinite counting time, freedom from critical stop flow timing, and complete reversibility.

Figure 13 shows a 400 channel radiochromatogram which illustrates the reversibility of the geometry. A solid $Cu(hfa)_2$ sample was injected into column 13. The activity suddenly rises as the radioactive plug enters the geometry. Since flow is not stopped the tail of the chromatographic peak accumulates and the count rate slowly increases. At channel 364, heat was applied to the 60° geometry and the trapped chelate started to move. First it moved to a more sensitive counting position, as indicated by the steep rise in count rate. Then the rate drops to the background level as the radioactive material is flushed from the geometry.

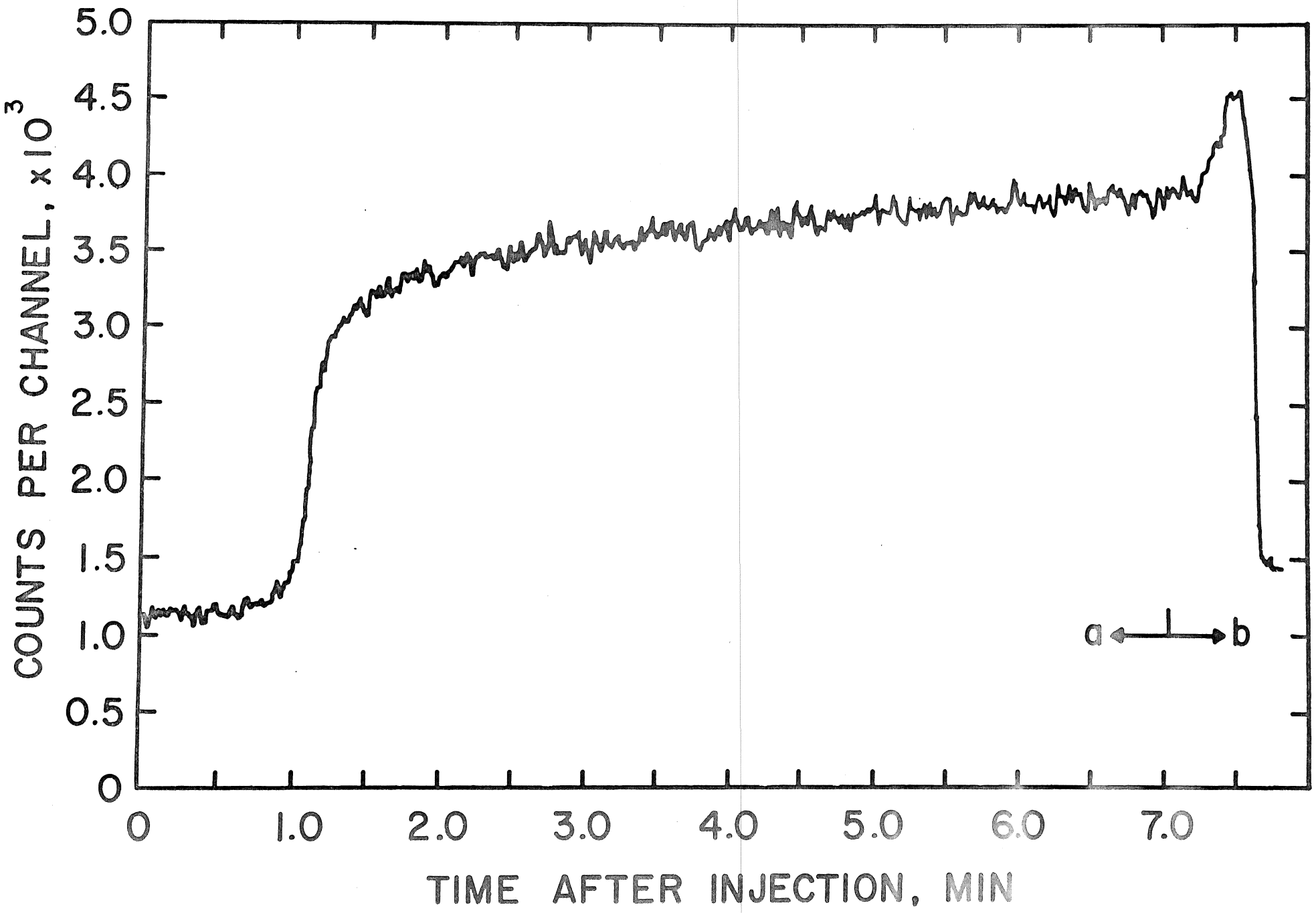

Figure 13. Radiochromatogram illustrating the counting of $Cu(hfa)_2$ in the reversible counting geometry

ACKNOWLEDGEMENTS

The diligence and dedication of the members of this research group during the period of this grant has made this work possible. They are the ones who are responsible for the productivity of this project. Particularly, the efforts of Dr. R. W. McCoy, Mr. F. T. Varcoe, Mr. T. R. Booher and Miss J. Durham should be recognized. The collaborative efforts and stimulating discussions of the entire group are sincerely appreciated.

LITERATURE CITED

1. Fishman, M. J., Robinson, B. P., and Midgett, M. R., Anal. Chem., 39, 261R (1967).

2. Okun, D. A., et al., J. Water Pollution Control Federation, 37, 587 (1965).

3. Christman, R. F., et al., J. Water Pollution Control Federation, 38, 685 (1966).

4. Kitano, Y., and Nasu, Y., Bunsek, Kagaku, Shinpo Sosetsu, 1964, 140R, C.A., 63, 12873c (1965).

5. Monnier, D., Arch. Sci. (Geneva), 18, 273 (1965). C.A., 64, 4253b (1966).

6. Landstrom, O., and Wenner, C. G., Aktiebolaget Atomenergi, Stockholm AE-204 (1965). C.A., 12361g (1966).

7. Yule, H. P., Anal. Chem., 38, 818 (1966).

8. Leddicotte, G. W., and Moeller, D. W., U.S. At. Energy Comm., CF-61-5-118 (1961).

9. Ross, W. J., Anal. Chem., 36, 1114 (1964).

10. Albert, P., Pure Appl. Chem., 1, 111 (1960).

11. Brownlee, J. L., U.S. AEC Rept. TID-6311 (1960).

12. Kusaka, Y., and Meinke, W. W., Natl. Acad. Sci., Natl. Res. Council, Nucl. Sci. Ser. NAS-NS-3104 (1961).

13. Ruch, R. R., Tera, F., and Morrison, G. H., Anal. Chem., 37, 1565 (1965).

14. Brune, D.,and Landstroem, O., Radiochim. Acta, 5, 228 (1966).

15. Smales, A. A., Mapper, D., and Fouche, K. F., Geochim. Cosmochim. Acta, 31, 673 (1967).

16. Thompson, B. A., and LaFleur, P. D., Anal. Chem., 41, 852 (1969).

17. Hahn, K. J., Tuma, D. J., and Quaife, M. A., Anal. Chem., 39, 1169 (1967).

18. Hahn, K. J., Tuma, D. J., and Sullivan, J. L., Anal. Chem., 40, 974 (1968).

19. Girardi, F., and Sabbioni, E., J. Radioanal. Chem., 1, 169 (1968).

20. Shipman, W. H., Anal. Chem., 38, 1175 (1966).

21. Bigliocca, C., Girardi, F., Pauly, J., Sabbioni, E., Meloni, S., and Provasoli, A., Anal. Chem., 39, 1634 (1967).

22. Patek, P., and Sorantin, H., Anal. Chem., 39, 1458 (1967).

23. Houtmann, J. P. W., Proc. Intern. Conf. on Activation Techniques in the Life Sciences, IAEA, Vienna, p. 171 (1967).

24. Bark, L. S., Duncan, G., and Graham, R. J. T., Analyst, 92, 347 (1967).

25. Tera, F., and Morrison, G. H., Anal. Chem., 38, 959 (1966).

26. Eisner, U., Rottschafer, J. M., Berlandi, F. J., and Mark, H. B., Anal. Chem., 39, 1466 (1967).

27. Tang, C. W., and Maletskos, C. J., Science, 167, 52 (1970).

28. Samsahl, K., Wester, P. O., and Landstrom, O., Anal. Chem., 40, 181 (1968).

29. Aubouin, G., Diebolt, J., Junod, E., and Laverlochere, J., Proc. Intern. Conf. Modern Trends in Activation Analysis, College Station, Texas, 1965.

30. Girardi, F., Merlini, M., Pauly, J., and Pietra, R., Proc. Symp. Radiochemical Methods of Analysis, Vol. 2, Salzburg, 1964, p. 3.

31. Moiseev, V. V., Kusnetsov, R. A., and Kalinin, A. J., Proc. Intern. Conf. Modern Trends in Activation Analysis, College Station, Texas, 1965.

32. Morrison, G. H., Gerard, J. T., Travesi, A., Aurie, R. L., Peterson, S. F., and Potter, N. M., Anal. Chem., 41, 1633 (1969).

33. Morrison, G. H., Gerard, J. T., Kashuba, A. T., Gangadharm, E. V., Rothenberg, A. M., Potter, N. M., and Miller, G. B., Science, 167, 505 (1970).

34. Cram, S. P., Advances in Chromatography, Vol. 9, J.C. Giddings and R.A. Keller, eds., Marcel Dekker, New York, 1970, p. 243.

35. Cram, S. P., and Brownlee, J. L., J. Gas Chromatog., 5, 353 (1967).

36. Cram, S. P., and Brownlee, J. L., J. Gas Chromatog., 6, 305 (1968).

37. Cram, S. P., and Brownlee, J. L., J. Gas Chromatog., 6, 313 (1968).

38. Sievers, R. E., and Moshier, R. W., Gas Chromatography of Metal Chelates, Pergamon Press, New York, 1965.

39. Ross, W. D., and Sievers, R. E., Talanta, 15, 87 (1968).

40. Ross, W. D., Sievers, R. E., and Wheeler, G., Anal. Chem., 37, 598 (1965).

41. Ross, W. D., and Sievers, R. E., Anal. Chem. 41, 1109 (1969).

42. Scribner, W. G., Smith, B. H., Moshier, R. W., and Sievers, R. E., J. Org. Chem., 35, 1696 (1970).

43. Booher, T. R., M.S. Thesis, University of Florida, Gainesville, Florida, 1969.

44. Shankar, J., India At. Energy Comm., BARC-348, Bhabha At. Resch. Centre, 1968.

45. Lin, T. K., and Yeh, S. J., J. Nucl. Sci. Technol. (Tokyo), 3, 289 (1966).

46. Torko, J., Energ. Atomtech, 20, 200 (1967).

47. Nath, A., and Nesmeyanov, Radiokhimiya, 5, 125 (1963).

48. Lazzarini, E., J. Inorg. Nucl. Chem., 29, 7 (1967).

49. Gainer, I., and Ponta, A., Rev. Roum. Phys., 13, 645 (1968).

50. Gainer, I., and Ponta, A., Rev. Roum. Phys., 13, 887 (1968).

51. Machado, J., Machado, R. M., Vargas, J., Chem. Effects of Nucl. Transformations, Proc. Symp., Vienna, 1964, 2, 195 (1965).

52. Thomas, V. G., Nath, A., and Shankar, J., USAEC Tech. Rept., NP-12330, p. 415 (1962).

53. Thomas, V. G., Nath, A., and Shankar, J., USAEC Tech. Rept., NP-12330, p. 407 (1962).

54. Shankar, J. Venkateswarlu, K. S., and Lol, M., J. Inorg. Nucl. Chem., 28,11 (1966).

55. Shankar, J., Nath, A., and Thomas, V. G., J. Inorg. Nucl. Chem., 30, 1361 (1968).

56. Thomas, V. G., Indian J. Chem., 1, 247 (1969).

57. Rao, K. A., and Nath, A., Radiochimica Acta, 5, 162 (1966).

58. Gainer, I., and Ponta, A., Rev. Roum. Chim., 13, 401 (1968).

59. Sievers, R. E., Moshier, R. W., and Morris, M. L., Inorg. Chem., 1, 966 (1962).

60. Sievers, R. E., Ponder, B. W., Moshier, R. W., and Morris, M. L., Inorg. Chem., 2, 693 (1963).

61. Ross, W. D., Anal. Chem. 35, 1596 (1963).

62. Ross, W. D., and Wheeler, G., Anal. Chem., 36, 266 (1964).

63. Hill, R. D., and Gesser, H., J. Gas Chromatog., 1, 10 (1963).

64. Sievers, R. E., Connolly, J. W., and Ross, W. D., J. Gas Chromatog., 5, 241 (1967).

65. Baetzer, A. M., Damron, C., and Budaez, V., A.M.A. Arch. Indust. Health, 20, 136 (1959).

66. Brieger, H., Ztschr. F. Exper. Path. V. Therap., 21, 393 (1920).

67. Goldman, M., and Karotkin, R. H., Am. J.M.Sc., 189, 400 (1935).

68. Major, R. H., Bull. John Hopkins Hosp., 33, 56 (1922).

69. Mancuso, T. F., Industrial Med. and Surgery, 20, 393 (1951).

70. Morris, G. E., A.M.A. Archivis of Dermatology, 78, 612 (1958).

71. Pascale, L. R., Waldstein, S. S., Engbring, G., Dubin, A., and Szanto, P. B., J.A.M.A., 149, 1385 (1952).

72. Curran, G. L., J. Biol. Chem., 210, 765 (1954).

73. Mertz, W., Roginski, E. E., and Reba, R. C., Amer. J. Physiol., 209, 489 (1965).

74. Mertz, W., and Schwarz, K., Measurements of Exocrine and Endocrine Functions of the Pancreas, J. B. Lippincott Company, Philadelphia, Penn., pp. 123-237 (1961).

75. Schroeder, H. A., J. Nutr., 88, 439 (1966).

76. Schroeder, H. A., Balassa, J. J., and Tipton, I. H., J. Chron. Dis., 15, 941 (1962).

77. Schwarz, K., and Mertz, W., Arch. Biochem. Biophys., 85, 292 (1959).

78. Glinsmann, W. H., Feldman, G. J., and Mertz, W., Science, 152, 1243 (1966).

79. Glinsmann, W. H., and Mertz, W., Metabolism, 15, 510 (1966).

80. Levine, R. A., Doisy, R. J., and Streeten, D. H. P., Diabetes, 15, 539 (1966).

81. Savory, J., Mushak, P., and Sunderman, F. W., J. Chromatog. Sci., 7, 674 (1969).

82. Springer, C. S., Meek, D. W., and Sievers, R. E. Inorg. Chem., 6, 1105 (1967).

83. Tanaka, N., Shono, T., and Shinra, K., Nippon Kagaku Zasshi, 89, 669 (1968).

84. Berg, E. W., and Truemper, J. T., J. Phys. Chem., 64, 482 (1960).