

SYNTHESIS OF Fe⁵⁵- LABELLED FERROCENE

For Use In The Measurements Of The M/L Orbital Electron
Capture Ratio In The Radioactive Decay Of Fe⁵⁵

and

An Attempted Fe⁵⁵ Isotopic Exchange Reaction Between
The Ferricenium And Ferric Ions In Aqueous Acid Medium

A final report submitted to Professor R.W. Fink
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by

Ronald P. Colle

School of Chemistry
Nuclear Research Center
Georgia Institute of Technology
Atlanta, Georgia 30332

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Table of Contents

1.0	Synthesis of Fe ⁵⁵ - Labelled Ferrocene.....	1.
1.1	Introduction and Summary.....	1.
1.2	Evaluation of Prior Syntheses.....	3.
1.3	Preparation of Anhydrous Fe ⁵⁵ -Labelled Ferrous Chloride.....	7.
1.4	Preparation of Sodium Cyclopentadienide.....	8.
1.5	Preparation of Ferrocene.....	10.
1.6	Detailed Procedure for the Synthesis.....	10.
1.7	Evaluation of the Synthesis.....	13.
2.0	Attempted Fe ⁵⁵ Isotopic Exchange Reaction Between the Ferricinium and Ferric Ions in Aqueous Acid Medium.....	18.
3.0	Appendices.....	20.
3.1	A Brief Discussion on the Possibility of the Exchange Reaction Occurring.....	21.
3.2	Abstract of Paper presented at the American Chemical Society 1969 Southeastern Sectional Conference of Undergraduate Student Chemists..	21.
4.0	References.....	23.
5.0	Acknowledgements.....	26.

1.0 SYNTHESIS OF Fe⁵⁵-LABELLED FERROCENE

1.1 Introduction and Summary

The measurement of the M/L orbital electron capture ratio in the radioactive decay of Fe⁵⁵ is of major interest for testing the theories of electron capture for allowed decay. Recent advances in experimental techniques for measuring orbital electron capture ratios have now made it possible to make critical comparisons with theoretical calculations. Fink (1) has recently reviewed these improvements in the experimental aspects and discussed the importance of the Fe⁵⁵ experiment in progress at the Georgia Institute of Technology (2). A summary of all prior precision M/L capture ratios and their comparison with theory has been made by Renier, et.al. (3) in 1968 and by Fink (4) in 1969.

For these precision measurements of the M/L orbital electron capture ratios, single and multiwire proportional counters are used with internal radioactive sources. To be useful, an internal source must fulfill a number of requisites. Briefly, these are:

- a) The source must be a gas or sufficiently volatile at the normal operating conditions of the proportional counter.
- b) The source must be non-electron attaching (i.e. must not contain any electronegative elements, e.g. oxygen, nitrogen or the halogens).
- c) The source must not "quench" the operation of the counter.
- d) The source must be chemically stable to the experimental conditions.
- e) The source must be readily prepared in a fashion insuring a high purity and hopefully good yield.

In 1959 (only 7 years after the discovery of ferrocene) Scobie, Moler, and Fink (5) reported the measurement of the L/K capture ratio in Fe⁵⁵ decay using Fe⁵⁵-labelled ferrocene as an internal source. This was not only the first precision measurement of the L/K capture ratio in Fe⁵⁵ decay, but also the first successful application of internal source spectroscopy utilizing a source other than the elemental gases, e.g. Ar³⁷ (6) and Kr⁷⁹ (7), or in a few cases the hydrides, e.g. Ge⁷¹ (8). This initial use of ferrocene resulted in subsequent measurements using other metallocenes, e.g.

manganocene and cobaltocene for Mn⁵⁴, Co⁵⁷ and Co⁵⁸ decays (9). The metallocenes are ideal internal sources for they satisfy all of the requirements. They are sufficiently volatile, having vapor pressures of approximately 0.2 mm Hg at room temperature (24° C) (10, 11, 12, 13), are non-electron attaching, chemically stable in inert atmospheres, and are fairly easily prepared in high purity.

The method used by Moler (14), to synthesize the Fe⁵⁵-labelled ferrocene and other labelled metallocenes, was found to have several serious difficulties which resulted in a search for a more satisfactory procedure. A discussion and description of these difficulties with an evaluation of Moler's procedure and other prior syntheses is provided in Section 1.2. A number of improvements in the synthesis have been made and are described in detail in Sections 1.3 through 1.6. An evaluation of the synthesis is then given in Section 1.7. A brief summary of the synthesis is provided in Appendix 3.2 as an abstract of a paper presented at the American Chemical Society - 1969 Southeastern Sectional Conference of Undergraduate Student Chemists.

In Section 2.0, an unsuccessful attempt to observe an Fe⁵⁵ isotopic exchange reaction between the ferricenium and ferric ions in aqueous acid medium is described. Its investigation stemmed from the search for a simple and direct method for preparing the Fe⁵⁵-labelled ferrocene. A brief discussion on the possibility of the exchange reaction occurring is provided in Appendix 3.1.

No measurements of the orbital electron capture ratios using the Fe⁵⁵-ferrocene samples have been made at this time. In light of this no further mention on the use of the samples is made beside the brief description of the method of filling the counter which follows. In prior measurements (5, 9, 14) conducted at the University of Arkansas, using metallocenes for orbital electron capture ratios, the samples were contained within glass U-tubes and connected directly to the proportional counter's vacuum-filling system.* Due to the possibility of leakage with glass vacuum stopcocks over long periods of time, it was decided to contain the Fe⁵⁵-labelled ferrocene samples within completely sealed glass ampules. These sealed ampules are then placed in metal cyclinders whose inside diameter is just that of the outside diameter of the ampule. The metal cylinder, which contains a Na-Pb alloy to insure long-time

*Details of this vacuum filling system is summarized in Moler's thesis (14).

freedom from atmospheric contamination, is connected to the counter's vacuum-filling system. To introduce the sample into the counter, the metal cylinder is crushed, breaking the glass ampule inside it, and thus releasing the ferrocene for filling. This method of filling was that used for the Ar³⁷ measurements at the Georgia Institute of Technology (3,15).

In summary, Fe⁵⁵-labelled ferrocene was synthesized for measurements of the M/L orbital electron capture ratio in the radioactive decay of Fe⁵⁵. The method developed for this synthesis is an improvement over an original method used for prior electron capture studies (5,9,14). The method is a well suited radio-chemical preparation where the final use of the sample demands the absence of air and moisture. This synthesis with few modifications, could be used for the preparation of other labelled metallocenes for further measurements of orbital electron capture ratios.

1.2 Evaluation of Prior Syntheses

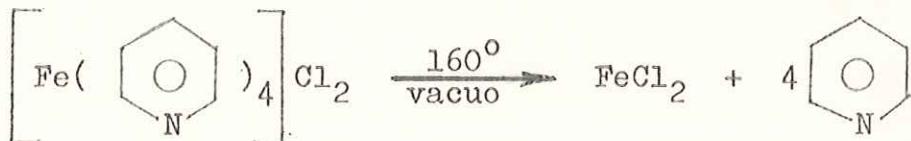
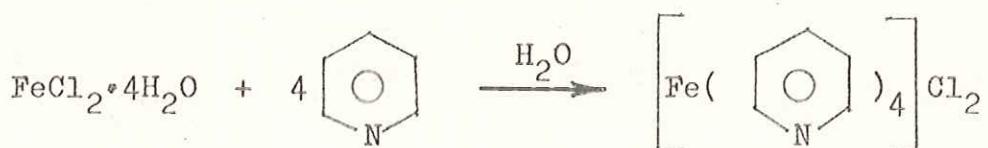
There are many procedures available in the literature for the preparation of ferrocene. An excellent monograph by Rosenblum (12) on the chemistry of the iron group metallocenes provides a summary and review of all these methods. A number of these methods are also provided in detail in R.B. King's book Organometallic Syntheses (16). Perhaps one of the oldest, simplest, and the method upon which this synthesis is essentially based is that developed by Wilkinson and his co-workers (17,18,19,20,21). The method, quite simply, consists of reacting anhydrous ferrous chloride with sodium cyclopentadienide in tetrahydrofuran.

One of the starting reagents, the anhydrous ferrous chloride, is not commercially available due to its great affinity for water. Therefore, the first step in the synthesis, and undoubtedly the most critical and difficult step is obtaining the anhydrous ferrous chloride. This step is critical because water must be excluded from the final source, and therefore of necessity, if possible, from the procedure itself, for two reasons. First, water would destroy the other reagent, i.e., the sodium cyclopentadienide, and secondly because water which contains oxygen is very electronegative and would poison the proportional counter. Its difficulty lies in the fact that iron in the divalent oxida-

valent oxidation state is easily oxidized during its dehydration.

In Wilkinson's procedure, (17,18a) the starting reagent is anhydrous ferric chloride and it is reacted with iron powder in tetrahydrofuran under an inert nitrogen atmosphere to obtain the anhydrous ferrous salt. This method presents, however, the difficulty of obtaining anhydrous ferric chloride. There does not appear to be a procedure for obtaining anhydrous ferric chloride which would be suitable for a radiochemical preparation since most of the procedures surveyed (22,23,24,25-p.40) require techniques which are difficult, messy and unquantitative (i.e., require high temperatures and combustion apparatus, distillations, transfer of reagents, etc.).

Moler (5,9,14) in his synthesis of ferrocene for the Fe^{55} electron capture studies obtained the anhydrous salt by a method utilizing pyridine.



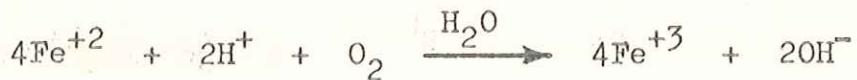
Reagent-grade ferrous chloride tetrahydrate was used as the starting material. This was dissolved in pyridine and the pyridine was evaporated until crystals of the ferrous tetrapyridyl chloride appeared. Crystallization was then completed by cooling. The resultant yellow crystalline mass was then worked-up by filtering, washing with pyridine, drying and powdering. Moler reported that yellow-green anhydrous ferrous chloride was obtained by heating these powdered crystals to 200° under vacuum for several hours.

This method was tirelessly exploited and found to be beset with a number of difficulties. One of the first difficulties was obtaining pure ferrous chloride tetrahydrate. Even a commercially available "reagent-grade" was too contaminated by oxidation to be useful. This was circumvented by preparing the crystals directly from

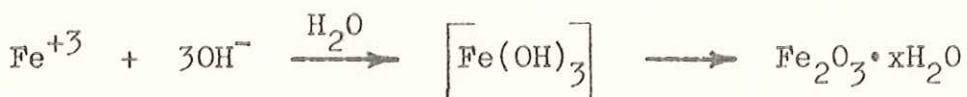
electrolytic iron powder and hydrochloric acid (25-p.12, 26). The second difficulty was that the displacement of the water of hydration by pyridine molecules was not complete even when the pyridine complexes were redissolved and recrystallized up to four times. Lastly, exclusion of oxygen, which is necessary in order to retard the oxidation of the ferrous iron, is nearly impossible because of the many transferring of reagents and handling during the work-up. All of these effects were observed by obtaining as the final product the red-brown iron sesquioxide.

In the labelling process, used by Moler, a volume of the Fe^{55} activity, as FeCl_3 in 0.1 N HCl, was added to the hydrated salt and the normal procedure carried out afterwards. Difficulties are also encountered here. The first is that there would be, of necessity, a loss of activity due to the messy and rather unquantitative crystallization, filtering, washing, drying, and powdering techniques encompassed in this method. The second difficulty is that the Fe^{55} activity present in the trivalent oxidation state would on the subsequent dehydration procedure result in the sesquioxide. There would therefore be two species present, the ferrous chloride and the sesquioxide, competing for reaction with the sodium cyclopentadienide. The reaction would preferentially be with the ferrous iron. The sesquioxide would react with the sodium cyclopentadienide, but as reported in much of the patent literature (27) the reaction appears to require more stringent conditions (i.e. higher temperatures, pressures, and sometimes reducing atmospheres). Since attack of the inactive iron is preferential, the conclusion of course is that a loss of activity could result because of the partial unreactivity of the labelled iron. This neglects of course any exchange of the active iron between the two species which might occur in the short time allowed while in the pyridine solution.

A digression for a moment on the chemistry of these difficulties--which were in fact the difficulties underlying the entire synthesis--may prove useful. It is a well established fact that iron in the divalent oxidation state is stable to oxidation in an acidic medium, however, in the presence of molecular oxygen, oxidation readily occurs by the following reaction:



In aqueous solutions of ferric ions, hydrolysis occurs and results in the formation of hydroxy complexes which really are or at least may be looked at as hydrated iron oxides.



On heating to dehydrate, the sesquioxides are obtained.



This degresion was used for two purposes, first to attempt to show why Moler's method is inadequate, and secondly, to stress the importance of insuring the absence of oxygen from the preparation.

Since good ferrous chloride tetrahydrate crystals were obtained while attempting Moler's pyridine method for dehydrating the salt, it was decided to investigate other procedures starting with this reagent. Since the difficulty in the pyridine procedure appeared to be oxidation during liberation of the pyridine from the ferrous tetrapyridyl chloride complex, reaction of the complex directly with the sodium cyclopentadienide was attempted. Very poor yields of ferrocene, in the range of 30 to 40%, were obtained. No further investigation was made to determine the cause of the poor yields.* A number of other procedures were evaluated with respect to their suitability for a radiochemical preparation and their ability to surmount the difficulties described above. Two of the more satisfactory procedures were a distillation with thionyl chloride (22,23) and treatment with ammonium chloride (29), however the method of choice--which later proved to be a good choice--consisted of dehydrating the salt by heating in vacuo (30, 31, 32). The major advantage of this synthesis over the prior methods is the procedure developed for the formation, labelling, and dehydration of the ferrous chloride, as described in Section 1.3. Other minor improvements mainly in technique were incorporated in the synthesis. These are described throughout

*Grovenstein (28) has indicated that there may be competing reactions, depending on the relative rates since the cyclopentadienyl rings could attack and react with the pyridine in the α -position.

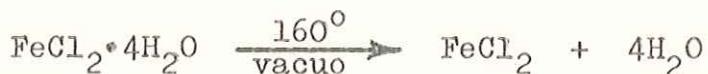
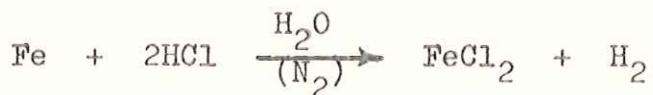
and are summarized in Section 1.7.

Two other methods have been reported for the preparation of radioactive ferrocene. Stranks (33) obtained a mixture of Fe^{55} and Fe^{59} labelled ferrocene by an (n, γ) reaction on inactive ferrocene. On irradiation in a large fast-neutron flux for six days, the relatively high retention of ($\text{Fe}^{55} + \text{Fe}^{59}$) as ferrocene in the ensuing Szilard-Chalmers reaction produced radioactive ferrocene in a $\text{Fe}^{55} : \text{Fe}^{59}$ ratio of 2:1. Since the sample for the orbital electron capture studies must be free of other radioactivity, this method is not applicable.

Mann (30) synthesized Fe^{59} -labelled ferrocene and some derivatives for protein tagging work. The method is a modification of Wilkinson's diethylamine procedure (17) and is beset with the same difficulties described previously. This synthesis does however use a very similar technique for dehydrating the FeCl_2 (cf. Section 1.3).

1.3 Preparation of Anhydrous Fe^{55} -Labelled Ferrous Chloride

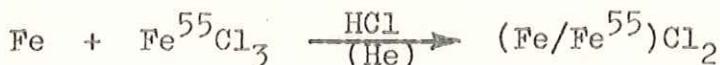
As discussed in Section 1.2, a number of procedures for dehydrating and labelling the ferrous chloride were evaluated. The method chosen consisted of preparing ferrous chloride tetrahydrate by the reaction of iron powder with hydrochloric acid and dehydrating the salt by heating in vacuo (30,31,32). Since the ferrous chloride tetrahydrate is not completely stable to oxidation, it was found to be advantageous to perform the dehydration directly after the preparation of the hydrated salt. The reactions for the formation and subsequent dehydration of the ferrous chloride follow.



Pure electrolytic iron powder (> 99%) was reacted with 6 N HCl under a nitrogen atmosphere to form the ferrous chloride solution. After removal of the water by distillation under reduced pressure, the green hydrated FeCl_2 powder (contaminated slightly with unreacted black Fe powder) was dehydrated by heating to 160°C for 30 min. This entire procedure was effected without having to separate and

transfer reactants since the dehydration was effected in the same reaction flask used to prepare the FeCl_2 . This procedure, aside from successfully preventing oxidation, is also very neat and quantitative and therefore very suitable for labelling the FeCl_2 .

In labelling the salt, the Fe^{55} activity, as FeCl_3 in 0.1 N HCl, was added to the Fe powder and both the zero valent iron and the Fe^{55} trivalent ferric ions were converted to the divalent ferrous ion simultaneously as indicated by the favorable oxidation potentials for the system.*

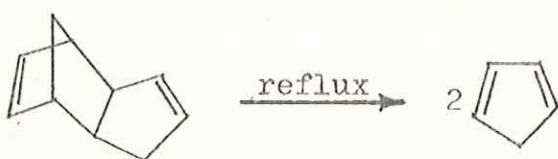


On the subsequent dehydration only one species, the anhydrous FeCl_2 , is obtained and available for reaction with the sodium cyclopentadienide, unlike the pyridine procedure where the unreactive iron sesquioxide is also obtained. As discussed previously this entire procedure was effected without having to separate and transfer reactants and was thus very quantitative. All of the difficulties present in the procedures discussed in Sect. 1.2 are avoided using this method.

1.4 Preparation of Sodium Cyclopentadienide

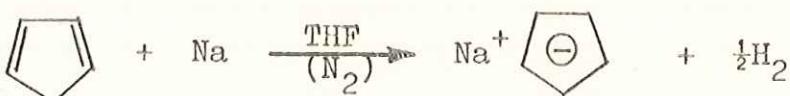
Obtaining the other major reagent, the sodium cyclopentadienide did not pose any serious difficulties. An 18% solution in tetrahydrofuran is available from the Eastman Kodak Company which worked quite adequately. It can be prepared quite readily however in a much greater purity by the reaction of cyclopentadiene and sodium metal in tetrahydrofuran.

The procedure used was essentially that prescribed by Wilkinson, et.al. (17) and the same as used by Moler (9,14). First, bicyclopentadiene is depolymerized by reflux cracking. The monomer obtained is reacted with a sodium dispersion in tetrahydrofuran to form the sodium cyclopentadienide.



*As taken from Latimer (34):





A detailed procedure for these reactions follows.

Cyclopentadiene was obtained by reflux cracking of a technical grade (85-90%) of bicyclopentadiene available from Eastman Kodak Co. This depolymerization was effected using a round bottom flask fitted with a 24 inch Vigreux (Bubble type) column held in a vertical position. Connected to the outlet of the Vigreux column was a simple distilling head fitted with a thermometer and attached to its side arm was a water cooled West-type condenser. The lower end of the West-type condenser was fitted with a two-neck flask which held a calcium chloride drying tube. The receiver was maintained at dry ice temperatures. The bicyclopentadiene contained in the flask was heated to 170°C with an electric heating mantle. Upon refluxing, the monomer distilled over at a temperature of 42°C. Only the fraction distilling within one degree of 42°C was collected to insure purity. The yield of cyclopentadiene was at best 75%. Since the cyclopentadiene dimerizes rapidly at room temperature it must be used immediately or stored at dry ice temperatures. It is possible to keep it for long periods of time at dry ice temperatures: One sample was kept for 26 days with less than 10% polymerization.

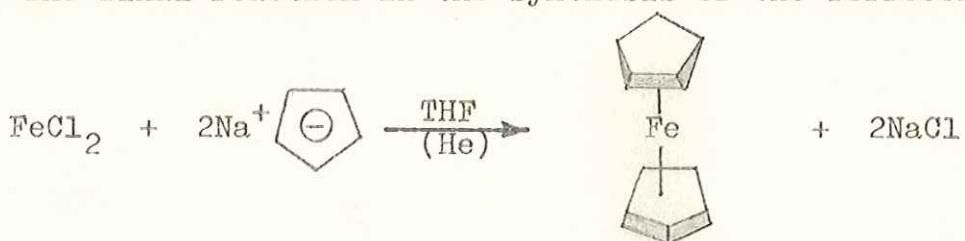
An improvement in this procedure was made however by preparing the sodium dispersion first and distilling the cyclopentadiene directly into the dispersion and thus forming the sodium cyclopentadienide solution in simultaneous steps. The resulting solution was then stored under an inert atmosphere in a closed container fitted with a rubber septum with which aliquots were removed with a hypodermic syringe.

Air and water decomposes sodium cyclopentadienide solutions forming unidentified red-brown decomposition products. The solutions prepared by this method were pale yellow to pink as compared to the partially decomposed blood-red to brown solutions obtained commercially.*

*King (16-p.65) gives a discussion of the ease of oxidation of sodium cyclopentadiene and the difficulty of obtaining colorless solutions. However, "yields...appear to be essentially the same whether the solution is pink, dark red-violet, or any intermediate shades of red. A solution that has been oxidized too extensively to give reliable results will be dark brown."

1.5 Preparation of Ferrocene

The final reaction in the synthesis of the ferrocene follows.



The labelled anhydrous ferrous chloride and the sodium cyclopentadienide was reacted in tetrahydrofuran under an inert atmosphere to form the ferrocene. The reaction if conducted at room temperature is complete within two hours. Helium is used here instead of nitrogen since the final product must not contain electronegative elements like nitrogen.

Wilkinson's procedure (17) suggests it, and Moler found that it was necessary to further purify the solvent to remove water, alcohols, and similar impurities.* In this synthesis, a high quality "Reagent Grade" of tetrahydrofuran, available from Fisher Scientific Co., was found to be adequate after drying over sodium metal. Further purification may be necessary in the synthesis of metallocene which are pyrophoric.

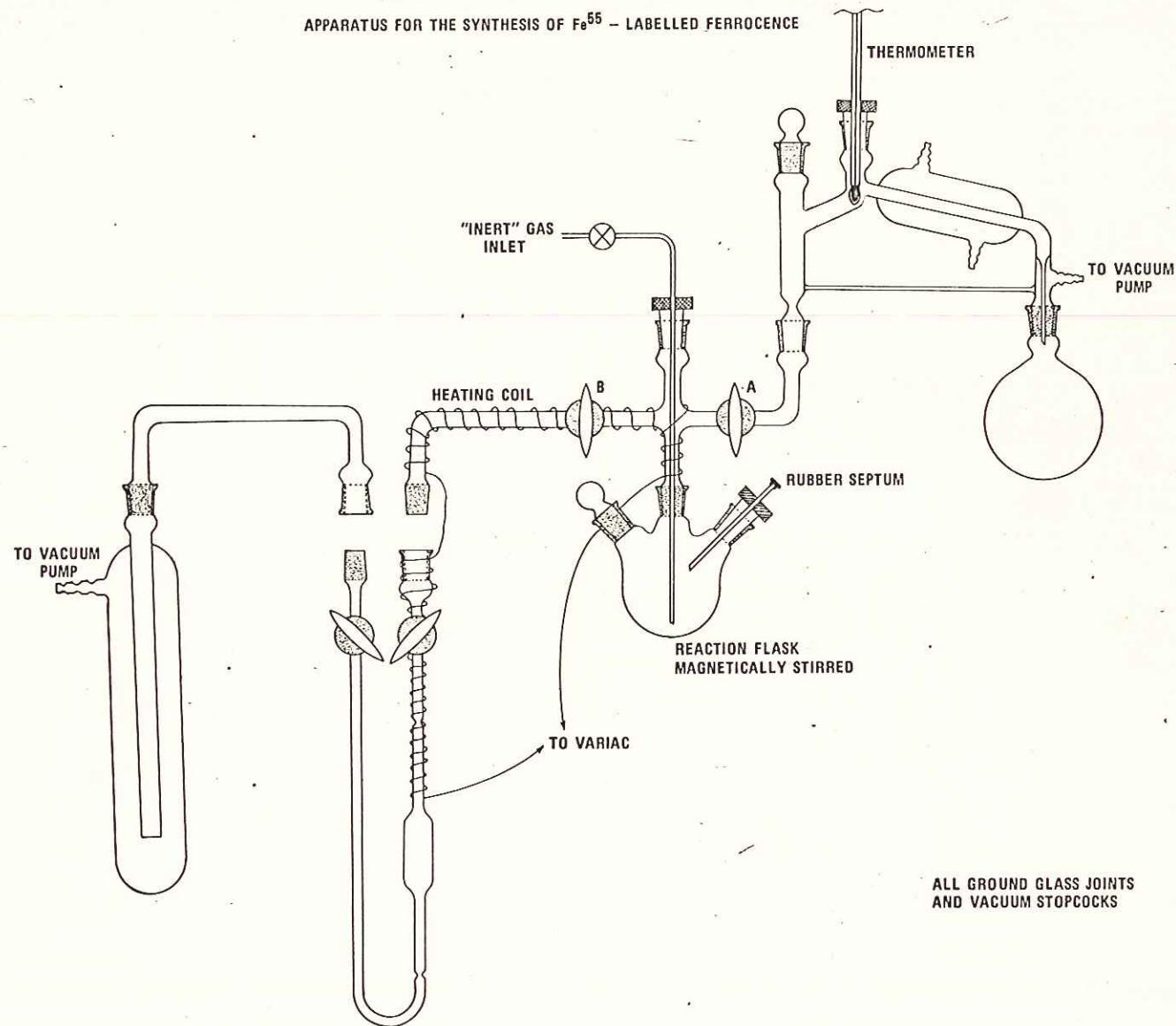
In this synthesis, anhydrous ferrous chloride is used as the limiting reagent, and the sodium cyclopentadienide is used in excess to insure that all of the iron is used in reaction. It was found however that when this reagent is used in excess of 4 or 5 to one equivalent of ferrous chloride, there is a marked decrease in the yield of ferrocene. This appears to be due to trapping and occlusion of the ferrocene in the decomposition products of the unreacted sodium cyclopentadienide caked on the walls of the reaction flask.

1.6 Detailed Procedure for the Synthesis

To bring together all of the reactions discussed in prior Sections, a detailed procedure for the entire synthesis follows.

The apparatus, as shown in Figure 1, employed only standard taper ground glass joints and vacuum stopcocks to prevent atmospheric contamination by leakage into the system. The vacuum lines were double trapped with vacuum condensers cooled in dry ice/ace-

*The tetrahydrofuran may be purified by passing the solvent through a column of 1/16 inch "molecular sieves" (available from Linde Air Products Co.) or by distillation over lithium aluminum hydride.

FIGURE 1

tone baths. The apparatus after assembly is flamed and vacuum pumped to remove any absorbed moisture from the glass.

First, the iron and Fe^{55} activity is added to the 3-neck flask and the system is purged with an "inert gas" (e.g. nitrogen or helium) to remove the air. Hydrochloric acid purged with nitrogen is then added through the rubber septum. At this time, stopcock A is open to provide an outlet for the hydrogen liberated in the reaction and for the helium which is bubbled through the liquid. Stopcock B is closed. At this point, the side arm on the extreme right could be attached to a vacuum pump, water aspirator, or even a water bubbler intercepted by a calcium chloride drying tube. They all worked with equal success. The reaction is allowed to proceed for several hours with magnetic stirring. When the reaction is complete, as evidenced by termination of effervescence of hydrogen, the gas inlet is closed and the solvent is removed by gentle heating and vacuum pumping. Stirring is continued to minimize spattering. The water after evaporation is condensed and collected in the flask on the extreme right which is cooled to dry ice temperatures. After the water is removed, the green hydrated crystals are further dried by vacuum pumping for several hours at room temperatures. Following this an oil bath heated to 160°C is brought up around the reaction flask and held there to drive off the water of hydration. Vacuum pumping is continued and the dehydration is usually effected within 15 minutes. Stopcock A is then closed; the flask and condenser are then cleaned, reassembled, flamed, and vacuum pumped to remove residual water and air. Stopcock A is again opened and helium admitted to the system. Tetrahydrofuran, which is liberated of dissolved oxygen by purging with helium, is then added through the rubber septum using a hypodermic syringe. Similarly sodium cyclopentadienide, previously prepared and stored under an inert atmosphere, (see Section 1.4) is added through the rubber septum. With magnetic stirring and helium bubbling thru the reaction mixture, the reaction is allowed to proceed for two hours. On completion of the reaction, the tetrahydrofuran is removed from the mixture by vacuum pumping and collected in the flask cooled in a dry ice acetone bath. When the solvent is thoroughly removed, stopcock A is closed, and B is opened and vacuum pumping to the left is commenced. With helium passing into the system, the

flask is heated with an electric heating mantle to sublime the ferrocene. To prevent condensation of the ferrocene onto the walls of the delivery tube, nichrome wire connected to a Variac for heating it, is wound around the glass tubing. The glass U-tube and following cold-trap is cooled to dry ice temperatures. The ampule portion of the U-tube is packed with glass wool to provide a more effective surface area for the condensation of the ferrocene.

After all the ferrocene is contained within the ampule portion of the U-tube, the U-tube is disconnected from the apparatus and the ampule is sealed on both ends. In sealing the ampule, the U-tube is submerged in a cold bath and the tube is sealed one at a time at the two constrictions. After each glass sealing it is necessary to anneal the glass around the seal with a luminous flame to avoid cracking of the glass tubing.

The ferrocene sample is thus contained in a completely sealed glass ampule under an inert atmosphere.

1.7 Evaluation of the Synthesis

The main advantage of this synthesis over prior methods is that, as described in Section 1.6, the entire synthesis is effected without having to separate and transfer reactants. The formation, labelling, and dehydration of the ferrous chloride and its subsequent reaction with the sodium cyclopentadienide is carried out in the same reaction flask. This, therefore, avoids the oxidation of the FeCl_2 and the loss of activity present in prior synthesis (cf. Section 1.2). After the initial addition of the iron powder and $\text{Fe}^{55}\text{Cl}_3/\text{HCl}$, the system is closed and the entire synthesis is conducted in a water- and air-free atmosphere. Using the sealed glass ampule in a metal cylinder technique, the sample was contained in a completely inert atmosphere from its initial synthesis to final filling of the counter.

To test the procedure, in terms of its effectiveness in trapping the ferrocene within the sensitive volume of the U-tube, a simple qualitative spot test was used to detect for the presence of ferrocene. This test was used because of its simplicity and apparent applicability in this limited use. It should in no way be construed as a reliable analytical test for the presence of ferrocene. Reliable analytical methods for quantitative

determination (35,36) and qualitative detection (37,38,39) are available. Concentrated nitric acid will oxidize ferrocene to the deep blue colored ferricenium ion. This blue color can be detected with less than a milligram of ferrocene. On testing the procedure with this spot test, the ferrocene was found to be almost completely contained within the U-tube. Only traces of ferrocene were found on the walls of the condenser. This occurred during the vacuum pumping to remove the tetrahydrofuran and could not be prevented since complete removal of the solvent had to be insured.

The synthesis was found to be very reproducible with yields of ferrocene, with respect to iron, of 75-80%. One "fluke" trial, the best, had a yield of 92%. A typical sample contained within a sealed ampule consisted of 250-300 mg of ferrocene with an activity of 5.3×10^4 cpm per mg as determined using a Ge(li) detector.*

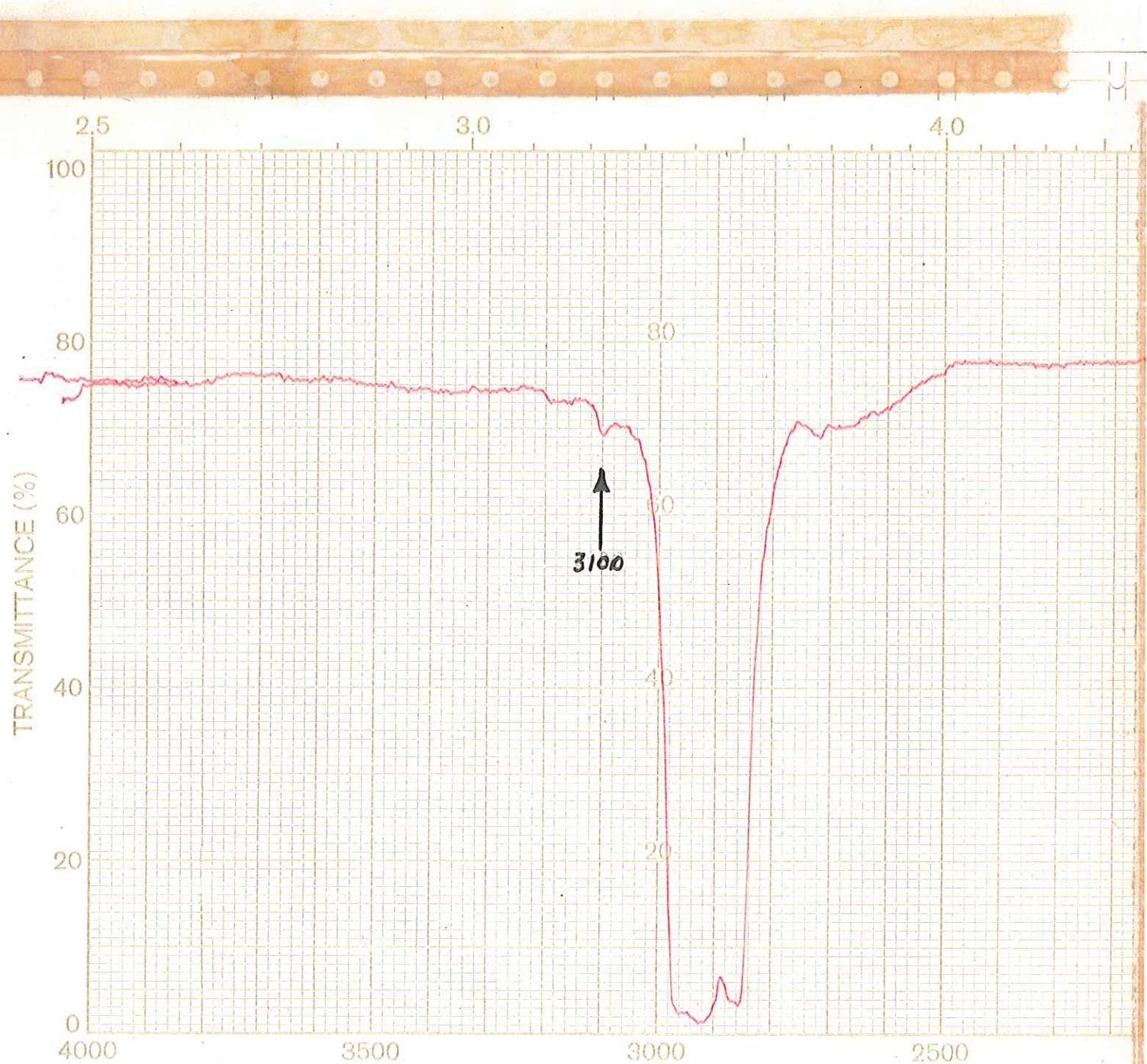
Purity of the ferrocene (and positive identification) was checked by melting point determinations and infrared and nuclear magnetic resonance spectroscopy. Melting points of ferrocene removed directly from the U-tube and ferrocene further purified by two sublimations were found to be identical at 173.5°C . Infrared spectra of ferrocene as a nujol film were measured in the region 2.5 to 40 microns (4000 to 250 cm^{-1}) using NaCl optics. The spectrum for ferrocene in nujol and a nujol blank are provided in Figure 2 and 3 respectively. On comparison with those of prior investigators (Lippincott and Nelson (40), Wilkinson, Pauson and Cotton (11), Kaplan, Kester and Katz (10)) they were found to agree conclusively as shown in Table 1. A proton NMR spectrum of a 5% solution of ferrocene in carbon tetrachloride had a singlet at 5.95τ ** compared to the value of 5.958τ obtained by Tiers (41). This solution was obtained by dissolving the entire contents of the U-tube in CCl_4 and extracting an aliquot for the NMR. This was done to determine if any other impurities were carried over into the U-tube. No other peaks were detected

*The counted sample consisted of an "invisible" film (50.3 g) mounted on a planchet and covered with Mylar film (1.8 mg/mm^2). The detector was an ORTEC 8013-08 Ge(Li) detector and was counted at a 8.0 mm source to window distance.

** Peak positions are given in ppm relative to tetramethylsilane which is assigned to a value of 10τ .

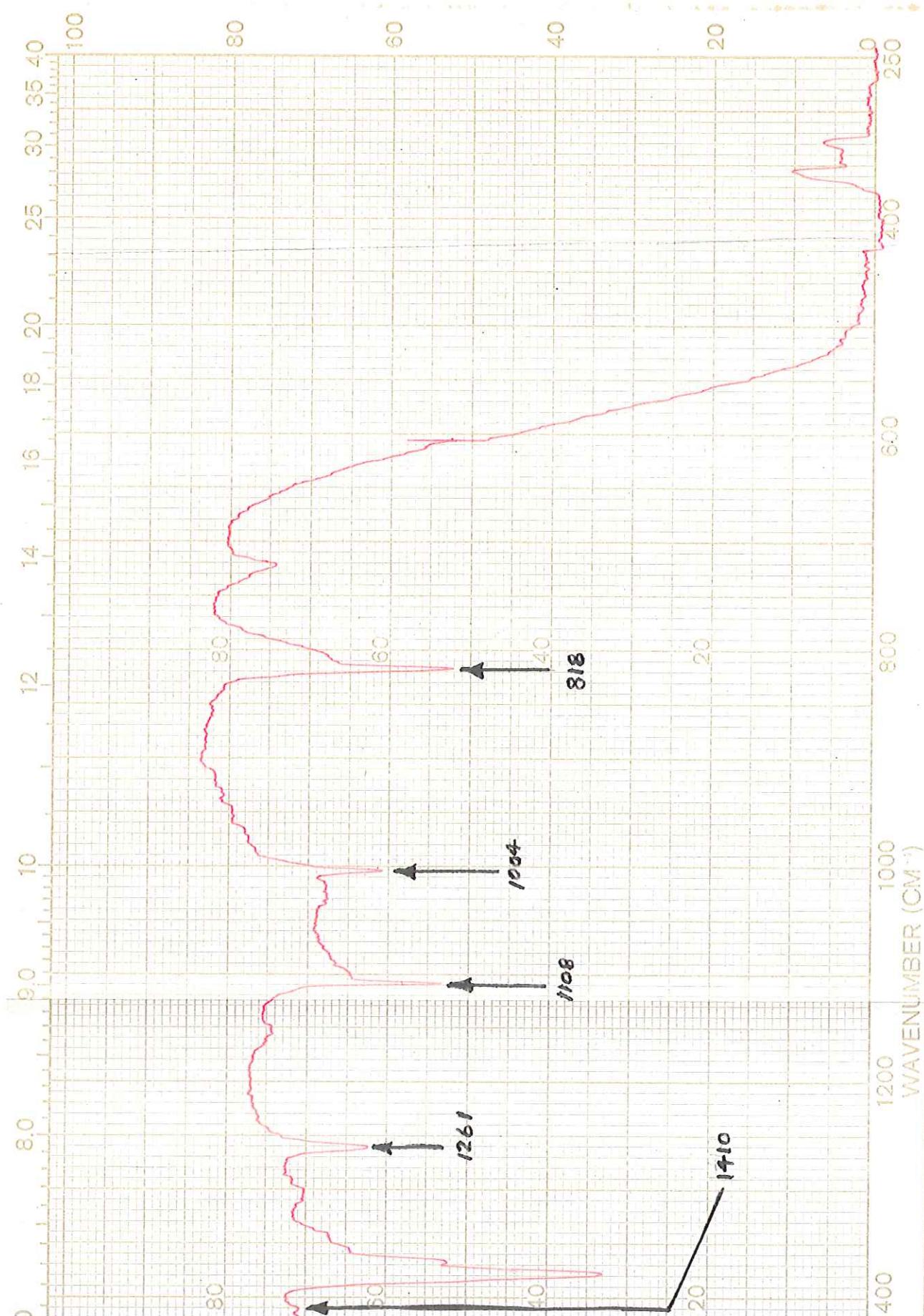
FIGURE 2

Infrared Spectrum of Ferrocene in Nujol



SAMPLE	FERROCENE, $\text{Fe}(\text{C}_5\text{H}_5)_2$
ORIGIN	Prep. III - F110868

SOLVENT	Nujol
CONCENTRATION	-
CELL PATH	liquid
REFERENCE	air



ERIKIN-ELMER 457 Grating Infrared tometer	SCAN SPEED SLIT N	OPERATOR Cole
internally at 2000 & 600 cm ⁻¹	PURKIN-EELMER	DATE THU 14.6.8
	PART NO. 457-5001	REF. NO.

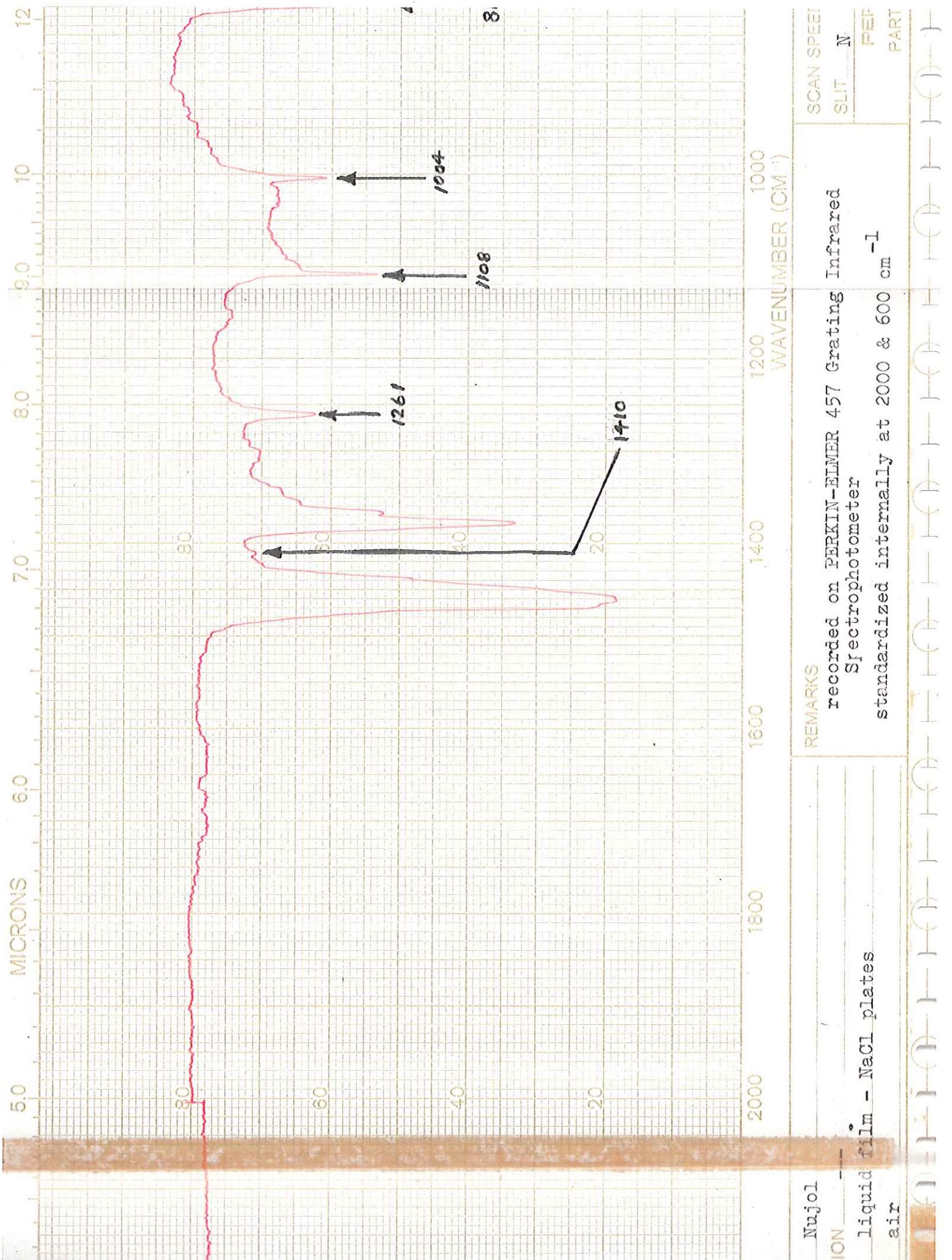
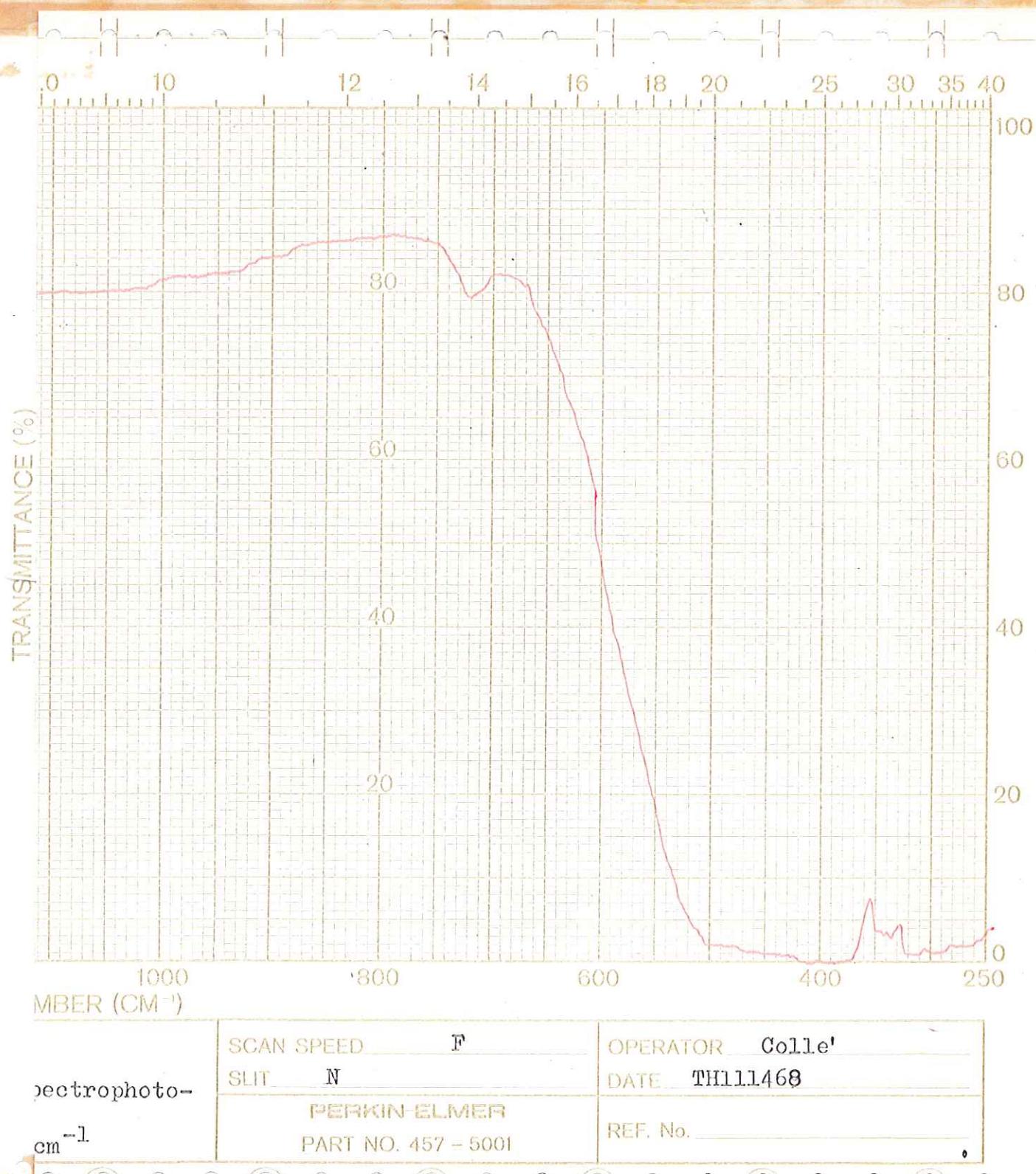
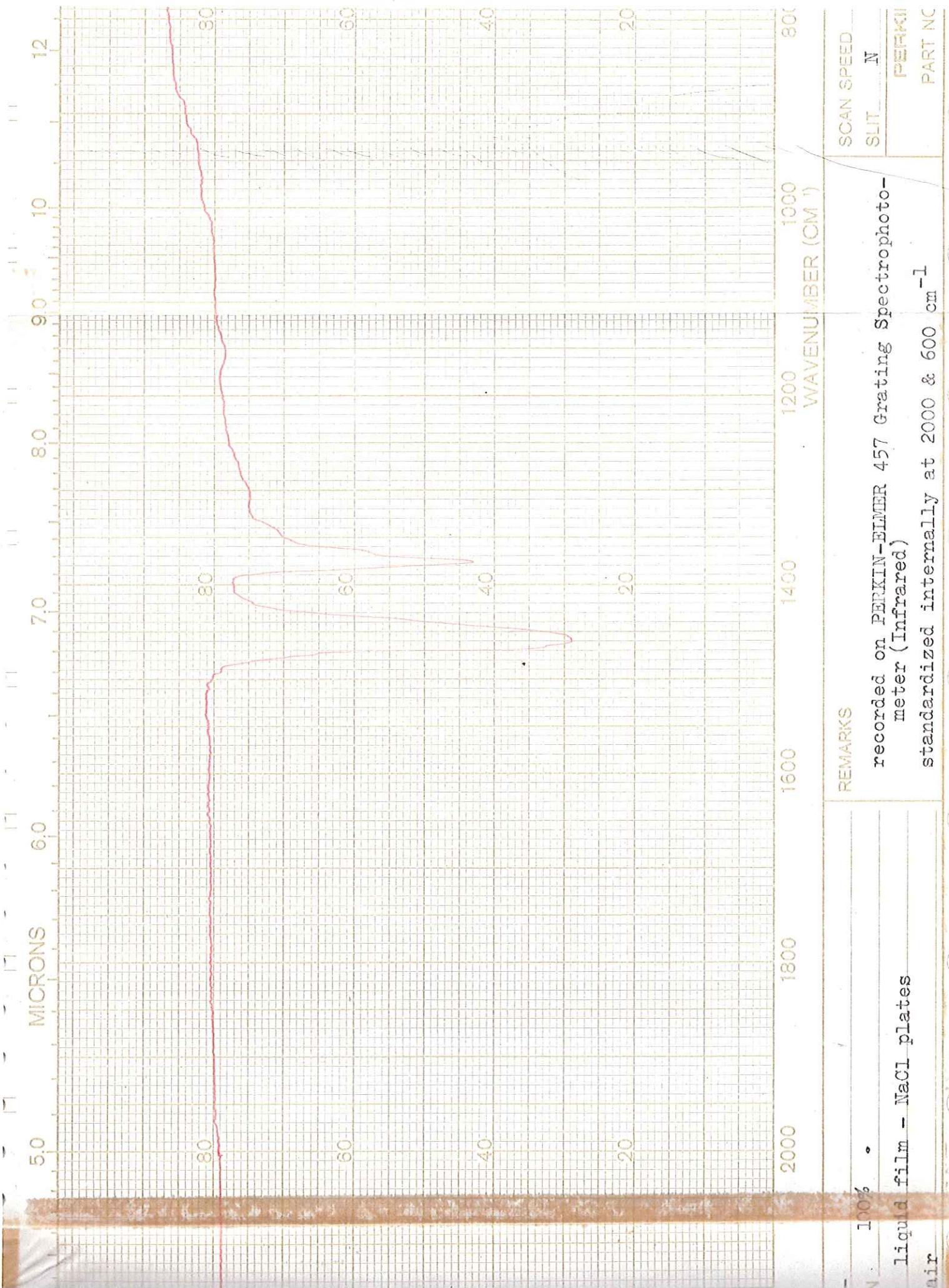
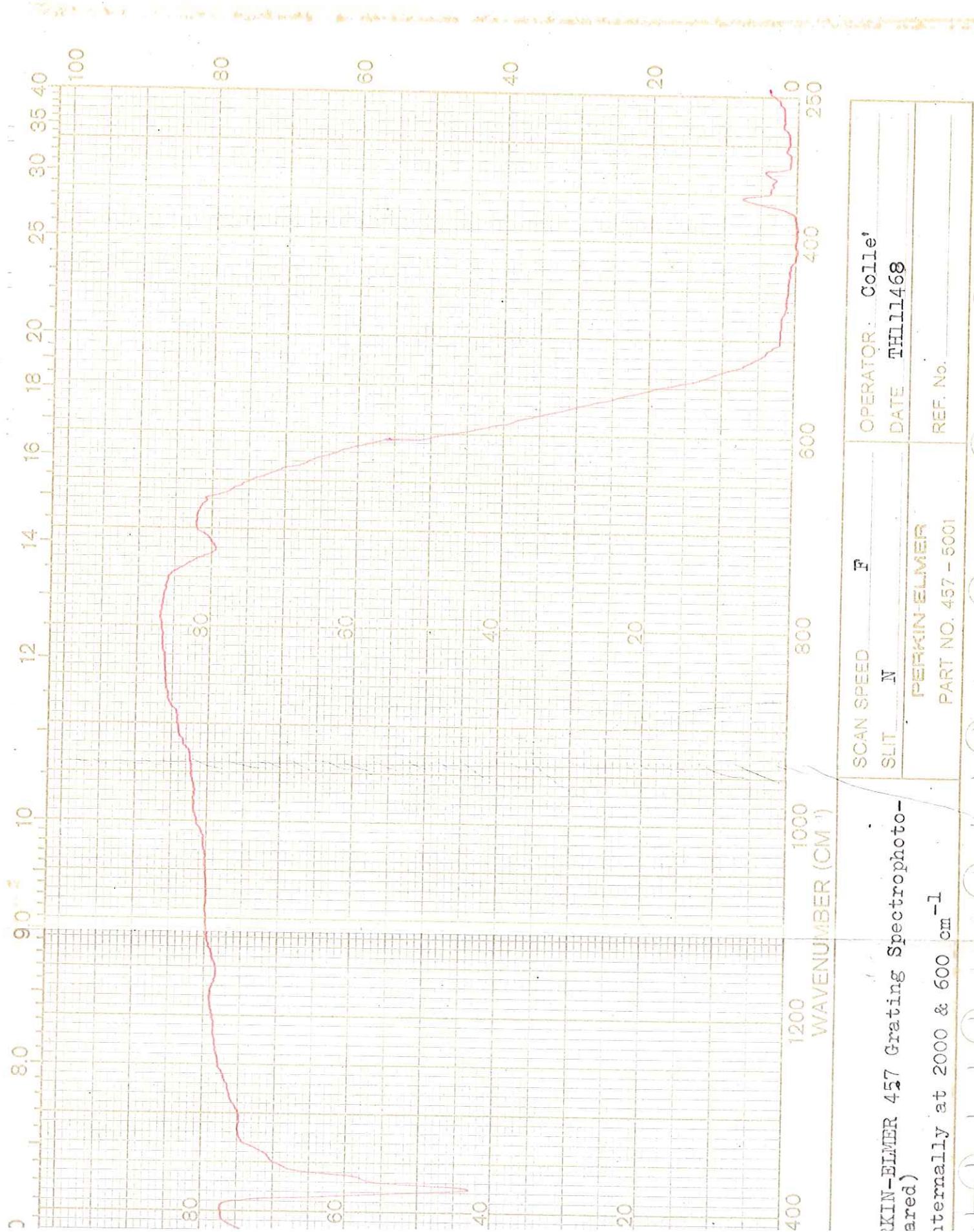


FIGURE 3

Infrared Spectrum of Nujol







KIN-ELMER 457 Grating Spectrophotometer
internally at 2000 & 600 cm⁻¹

OPERATOR: College
DATE: THU 11468

SCAN SPEED	F	SLIT	N
PEAKIN-ELMER		PART NO. 457 - 5001	
REF. No. _____			

TABLE 1

INFRARED SPECTRA OF FERROCENE

(intense bands only in cm^{-1})

Lippencott & Nelson (40)	Wilkinson, Pauson & Cotton (11) (a)	Kaplan, Kester, & Katz (10)	Present Study (b)
CCl_4 , CS_2 , Nujol Sol'ns	KBr pellet	CCl_4 sol'n	Nujol film
478			(c)
492			(c)
811		811	818
1002	\sim 1010	999	1004
1108	\sim 1110	1108	1108
		1257 (w)	1261
1411	\sim 1430	1410 (w)	(d) 1410 (w)
3085	\sim 3100	3080	(d) 3100 (w)

(a) approximate values only, read from reproduced spectrum

(b) see Figures 2 and 3

(c) masked by Nujol absorption

(d) partially masked, present in shoulder of Nujol absorption

on sweeping the field from 0 to 10τ . Peaks for the most likely impurities would have occurred as a singlet at 9.17τ for H_2O and as a pair of quintets at 6.25τ and 8.15τ for the tetrahydrofuran.(42).

In summary, the method developed for this synthesis of Fe^{55} -labelled ferrocene is a well suited radiochemical preparation of the metallocene where the final use of the sample demands the absence of air and moisture.

2.0 Attempted Fe^{55} Isotopic Exchange Reaction Between
Ferricinium and Ferric Ions in Aqueous
Acid Medium

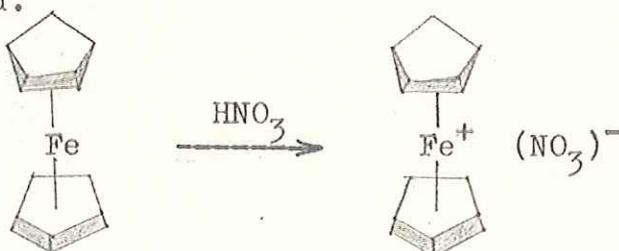
An attempt was made to observe an Fe^{55} isotopic exchange reaction between the ferricinium and ferric ions in an aqueous acid medium. The investigation stemmed from the search for a simple and direct method for preparing Fe^{55} -labelled ferrocene. The exchange, although unsuccessful, would have provided an extremely simple method for labelling ferrocene with Fe^{55} since essentially all that would have been needed is to prepare inactive ferrocene (or for that matter purchase it commercially), oxidize it to the ferricinium ion with nitric acid (43), let it exchange with Fe^{55} -ferric ions, and reduce the labelled ferricinium ions back to ferrocene using stannous chloride (43).

Wilkinson, et.al. (18c) in 1956 reported that in aqueous ethanol over a period of twelve months there is no exchange between iron atoms in ferrocene and ferrous ions. This was later confirmed by Sutin and Dodson (44) in 1958. As justified on purely theoretical grounds on the nature of the bonding in ferrocene this was to be expected (not at the time of course). Similarly, on a theoretical basis, it would be predicted that an iron isotopic exchange reaction between the ferricinium and ferric ions would also not occur.* Prediction and truth do not

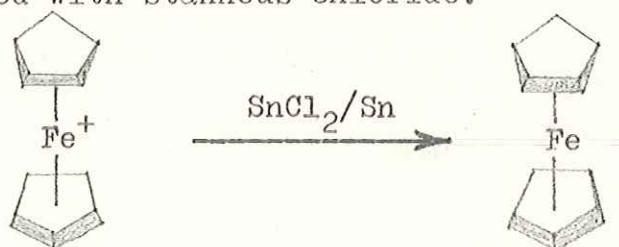
*See Appendix 3.1 for a brief discussion on the possibility of the exchange reaction occurring.

always agree and although the possibility appeared slim this exchange reaction was never studied and it was with this lack of evidence that the study was undertaken.

The exchange experiment in itself was quite simple. The ferricenium ion was prepared by oxidizing ferrocene with 4 N nitric acid.



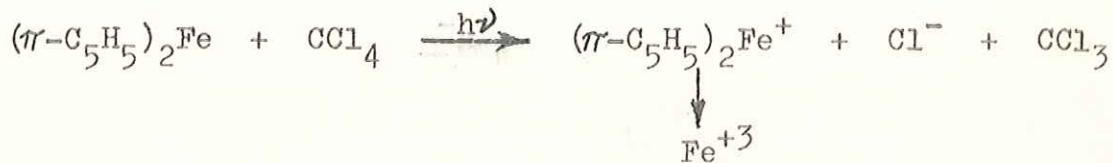
To the resulting deep blue ferricenium nitrate solution,* the Fe^{55} activity, as ferric chloride in 0.1 N hydrochloric acid, was added. The ferricenium and ferric ions were allowed to equilibriate for 24 hours. The ferricenium nitrate solution was then reduced with stannous chloride.



The reduction proceeds very slowly even in the presence of tin metal, and 24 hours was allowed to complete the reduction. The resultant ferrocene which precipitated and suspended in solution was collected on a fritted glass filter and washed with large quantities of distilled water to remove any absorbed activity or stannous chloride. The ferrocene was then removed from the filter with carbon tetrachloride** and collected by evaporation of the solvent. The ferrocene was then further purified by sublimation. These last two steps, removing the solvent and the sublimation, were conducted in essentially the same fashion and using the same apparatus as described in Section 1.6 for the syn-

*The solution exhibits dichromism. Dilute solutions appear blue, while more concentrated solutions are blood red (12-p.49).

**Carbon tetrachloride solutions of ferrocene in the presence of light decompose on standing (12-p.42,45):



thesis. A very thin film of the purified ferrocene was then evaporated onto a glass planchet and counted using a NaI(Tl) detector. No activity above natural background was detected on counting for over 20 minutes.

Using this method, per cent recovery of ferrocene of about 70% could be obtained for a complete oxidation and subsequent reduction cycle. Part of the problem is that, although the ferricenium ion is moderately stable in acid solution, some hydrolysis does occur (45). This hydrolysis which eventually results in decomposition limits the length of time that can be allowed for the exchange to occur.

Although the expected result was that it would not exchange, and this is exactly what was found, the attempt was by no means conclusive since the time allowed for the species to equilibrate may have been many orders of magnitude less than half-time of exchange. Also, the exchange was attempted only in an acidic aqueous medium. Possibly, an exchange might occur in other solvents, and under other conditions.

In summary, it was very conclusive that the exchange under these experimental conditions did not occur, but it is not, however, conclusive that an iron isotopic exchange in ferrocene-like structures can not occur.

3.0 APPENDICES

3.1 A Brief Discussion of the Possibility of the Exchange Reaction Occuring

The theoretical justification, for ferrocene not undergoing exchange, is that the bonding in ferrocene is entirely covalent. According to contemporary molecular orbital treatments (several of these treatments are summarized by Rosenblum (12) and Wilkinson and Cotton (45)) the main iron to ring bond is considered to be a two electron covalent bond between the iron d_{yz} orbital and the π -molecular orbitals of the cyclopentadienyl rings (46). The arguments for an iron exchange in ferricenium are more diverse.

The ferricenium ion contains one less electron and this

loss of an electron could result in a partial localization of the electrons in the bonding orbitals and may then add enough ionic character to the species to allow an isotopic exchange. Two lines of evidence support this. First, Pavlik and Subrt (47) from frequency shifts of fundamental vibrations using infrared spectroscopy found an increasing weakening of iron to ring bonds in the series: ferrocene, ferrocenonium $[(\pi\text{-C}_5\text{H}_5)_2\text{FeH}^+]$, and ferricenium. The cause of the bonding changes is attributed to localization of charges on the iron atom. Evidence from studies of the Mossbauer effect on the oxidation of Fe^{57} -labelled ferrocene also supports this. From these studies, Zahn, et.al(48) contend that the electron involved in the oxidation must be removed from a $3d^5$ metal orbital. If this is the case then the ferricenium ion and manganocene would be isoelectronic. Manganocene is ionic and does exchange with ferrous ions to give qualitative yields of ferrocene (18c). This suggests that it is possible that the ferricenium ion does contain some ionic character. There is strong evidence however, namely the absence of electron spin resonance for the ferricenium ion either in solution or in the solid state (12, p.45) that localization does not occur.

In the above discussion the only criterion considered on justifying whether or not an exchange would occur was purely on bond type (i.e. covalent or ionic). This is not totally true, for as far back as 1942, Ruben, Kamen, et.al. (49) at Berkeley studied iron exchange reactions on a number of organometallic compounds, mainly iron porphyrins, and found that structural factors seemed to be more important than covalent-ionic character in determining the readiness of a metallic ion (in an organometallic compound) to undergo exchange. Their results also seemed to indicate that the rate of exchange depends more on structure than on bond type. Since the ferricenium ion and ferrocene are very similar in structure, this adds more justification to a prediction that the exchange would not occur.

3.2 Abstract of paper presented at American Chemical Society 1969 Southeastern Sectional Conference of Undergraduate Student Chemists, April 18-19, 1969, Tuscaloosa, Alabama.

(following page)

Paper presented at American Chemical Society 1969 Southeastern Sectional Conference of Undergraduate Student Chemists, April 18-19, 1969 Tuscaloosa, Alabama.

SYNTHESIS OF Fe⁵⁵- LABELLED FERROCENE
FOR USE IN
ORBITAL ELECTRON CAPTURE RATIO MEASUREMENTS*

Ronald P. Colle** and R. W. Fink

School of Chemistry, Nuclear Research Center
 Georgia Institute of Technology, Atlanta, Georgia 30332

ABSTRACT

Iron-55 labelled ferrocene (bis-cyclopentadienyiron(II)) was synthesized for measurements of the M/L orbital electron capture ratio in the radioactive decay of Fe⁵⁵. Several previous methods were evaluated with respect to the subsequent use of the sample as a vaporous source in a multiwire proportional counter(cf. Scobie, Moler, and Fink, Phys. Rev. 116, 657 (1959)). The method chosen consisted of using anhydrous labelled FeCl₂ as the limiting reagent and reacting it with sodium cyclopentadienide in tetrahydrofuran. After removal of the solvent by evaporation under reduced pressure, the ferrocene was removed from the reaction mixture and collected by sublimation. The labelled ferrous chloride was obtained by adding Fe⁵⁵ activity (as FeCl₃ in HCl) to electrolytic iron powder and reacting the mixture with HCl. After removal of the water, the salt was dehydrated to anhydrous FeCl₂ by heating in vacuo. This method permitted preparation of ferrocene with specific activites in the range of 2.5 μ C/mg. The entire synthesis was conducted in a water- and air-free atmosphere and was effected without having to seperate and transfer reactants. The sample was contained in a completely inert atmosphere from initial synthesis to final filling of the counter. Prior work on M/L orbital electron capture ratios has been summarized by Renier, et. al. (Phys. Rev. 166, 935(1968)) and by Fink (Phys. Rev. in press (1969)).

* Supported in part by the U. S. Atomic Energy Commission.

** Speaker

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

FRANK H. NEELY
NUCLEAR RESEARCH CENTER

August 5, 1969

Mr. Ronald P. Colle
Mason Lab--R.P.I.
Troy, New York 12181

Dear Ron:

Thanks for your nice letter. We are glad you are well situated at RPI and doing exciting accelerator work. I hope the draft will not take you away from the work there.

The problem of Fe^{55} -ferrocene that you did as a senior research project is most important to us. We will make these runs in the counter very soon. I must say that the way you handled this project was excellent. We have never had such high quality professional work and excellent written report on any piece of undergraduate research before. It is better than most graduate students do, and it shows that you are definitely PhD material.

You are always welcome back in our group.
Good luck.

Sincerely yours,

R.W. Fink
R. W. Fink
Professor