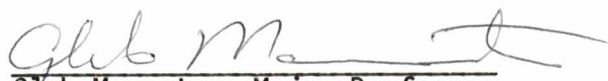
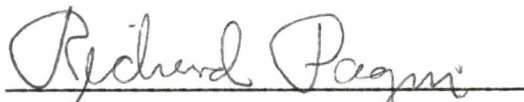


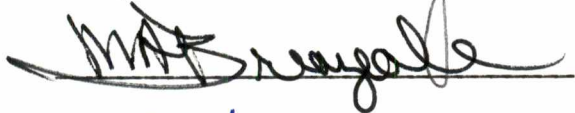
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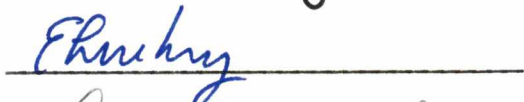
I am submitting herewith a dissertation written by Brisco Lynn Harward entitled "Studies in Molten Chloroaluminates: I. Multipass Spectroelectrochemistry, II. Spectroscopic and Electrochemical Investigations of Iridium Carbonyls." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


Gleb Mamantov, Major Professor

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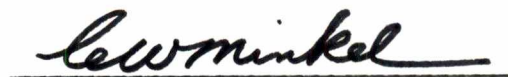

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STUDIES IN MOLTEN CHLOROALUMINATES:
I. MULTIPASS SPECTROELECTROCHEMISTRY
II. SPECTROSCOPIC AND ELECTROCHEMICAL INVESTIGATIONS OF
IRIDIUM CARBONYLS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Brisco Lynn Harward

December 1985

DEDICATION

The author wishes to dedicate this work to his parents in appreciation of their support and encouragement.

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ABSTRACT

The multipass technique is introduced as an optical enhancement method for thin-layer spectroelectrochemistry. In this approach, the light beam is redirected through an optically transparent electrode (OTE) several times by an external mirror assembly. This arrangement is achieved using a low power continuum source which allows simultaneous multiwavelength measurements. The gain in optical sensitivity is directly related to the number of passes through the cell and has a practical limit of three to five. Initial evaluation with an aqueous test system yielded results which agree well with theory. The enhancement is not dependent upon electrode reflectivity and, therefore, the method may be applied to studies in highly corrosive media. Studies of the oxidation of sulfur and the reduction of niobium pentachloride in molten chloroaluminates are presented to demonstrate the utility of this technique for investigations in such media.

Because of interest in Fischer-Tropsch catalysis by $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ in 63/37 $\text{AlCl}_3\text{-NaCl}$, an investigation of both compounds in the melt under CO and CO-H_2 (1:3) was performed. The techniques applied to this study include UV-visible spectroscopy, Raman spectroscopy, infrared spectroscopy, X-ray photoelectron spectroscopy, cyclic voltammetry, and normal pulse voltammetry. These results indicate that the same mononuclear iridium chlorocarbonyl complex is ultimately produced from $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ in the melt under CO. The chloride ligands in this complex are probably coordinated to AlCl_3 as AlCl_4^- , forming a metal carbonyl-Lewis acid adduct.

Studies of $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ in the 63/37 melt under CO-H_2 (1:3) indicate that only a fraction of the original compounds undergoes the same chemistry as under only CO. Infrared spectra suggest the formation of $\text{HIr}(\text{CO})_4$ or similar species under CO-H_2 (1:3) from both original carbonyls. This complex may be responsible for catalytic activity in the melt. There is no evidence for a long-lasting iridium carbonyl cluster in the 63/37 melt under either CO or CO-H_2 (1:3).

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PART I
MULTIPASS SPECTROELECTROCHEMISTRY

CHAPTER I

INTRODUCTION

Molten salts are one of the main classes of nonaqueous solvents. These solvents are usually composed of binary or multicomponent mixtures and exhibit numerous desirable physical and chemical properties, such as high thermal conductivity and stability, high electrical conductivity, and large decomposition voltage. Various aspects of molten salt chemistry have been extensively documented (1-22).

The technological importance of molten salts has been well established. The production of aluminum, alkali metals, magnesium, some refractory metals, and fluorine utilizing molten salt media has demonstrated their usefulness as commercial processes. Accompanying the more current emphasis upon energy-related research, considerable effort has been directed toward the development of rechargeable high energy density molten salt batteries. Most recently, molten salts have been used as interesting solvents for conducting homogeneous catalytic reactions.

The experimental difficulties and problems encountered in molten salt research are frequently quite challenging and are often as unique as the chemistry of the system being studied. Among the analytical techniques which have been successfully applied to investigations in such media are electrochemistry, absorption spectroscopy, and thin-layer spectroelectrochemistry. The research presented in this dissertation has been directed toward the further development and application of these analytical methodologies to the study of important chemical systems in molten chloroaluminates.

A. Molten Chloroaluminates

Chloroaluminates constitute one of the more interesting classes of molten salts. This category includes room temperature systems such as the alkylpyridinium chloride-aluminum chloride melts which usually exist as liquids under ambient conditions. Also included in the chloroaluminate group are the "high-temperature" systems which are produced by fusion of alkali chloride-aluminum chloride mixtures and have liquidus temperatures of 100-400 °C. The chemistry and electrochemistry of haloaluminates, including chloroaluminates, have been reviewed (23-28).

The research presented in this dissertation is concerned primarily with investigations in molten sodium chloroaluminates, mixtures of AlCl_3 and NaCl at 150-200 °C. One of the more interesting characteristics of this and analogous chloroaluminate melts is their adjustable acid-base properties (29). It is convenient to use a modified Lewis acid-base definition to describe these systems. An acid is defined as a chloride ion acceptor, and a base is defined as a chloride ion donor. The following equilibria may be used to describe AlCl_3 - NaCl melts containing 50 to 70 mole % AlCl_3 :



In agreement with the above definition, the species Al_2Cl_7^- and AlCl_4^- are considered an acid and a base, respectively. The values of K_1 , K_2 , and K_3 on the mole fraction scale at 175 °C are 1.06×10^{-7} , 2.86×10^7 ,

and 2.4×10^4 , respectively (30). The acidity of chloroaluminate melts is often expressed in terms of pCl^- , defined as $-\log([Cl^-])$, where $[Cl^-]$ is the molar concentration of chloride ion in the melt. With the appropriate conversion of units from mole fraction to molarity, the following relationship is derived from the expression for K_1 at 175 °C:

$$pCl^- + pAl_2Cl_7^- = 5.1 \quad (4)$$

As the composition of $AlCl_3$ -NaCl melts is varied near the equimolar ratio, the corresponding Cl^- and $Al_2Cl_7^-$ molarities vary by about four orders of magnitude. For the equimolar melt (50-50 mole % $AlCl_3$ -NaCl, hereafter expressed as 50/50 $AlCl_3$ -NaCl), the pCl^- and $pAl_2Cl_7^-$ values are the same (2.55), while for the 52-48 mole % melt, $pCl^- = 5$ and $pAl_2Cl_7^- = 0.1$. For chloroaluminate melts containing more than 52 mole % $AlCl_3$, Equations 2 and 3 must be taken into account to calculate the $pAl_2Cl_7^-$. However, it has been recently shown that pCl^- in chloroaluminates can be related to the activity of NaCl only when the melt composition is not far removed from the equimolar $AlCl_3$ -NaCl value (31). It has been shown that increasing the temperature of chloroaluminate melts results in a decrease in pCl^- of the system (32). Melts containing greater than 50 mole % $AlCl_3$ are considered "acidic", whereas those containing less than 50 mole % $AlCl_3$ are considered "basic" melts. The concentrations of various species of equimolar and 63-37 mole % $AlCl_3$ -NaCl (hereafter expressed as 63/37 $AlCl_3$ -NaCl) melts are listed in Table I.

Table I. Composition^a of Equimolar and 63/37 AlCl₃-NaCl Melts^{b,c}

Species	(50/50)	(63/37)
NaAlCl ₄	1.0 ^d	0.60 ^d
NaAl ₂ Cl ₇	2.5 × 10 ⁻⁴	0.40 ^d
NaCl	2.5 × 10 ⁻⁴	8.0 × 10 ⁻⁸
Al ₂ Cl ₆	3.2 × 10 ⁻⁸	4.5 × 10 ⁻²
AlCl ₃	7.9 × 10 ⁻⁹	5.0 × 10 ⁻⁵

^aExpressed as mole fraction.

^bPlambeck, J. A. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1976; Vol X, Chapter 8.

^cBoxall, L. G.; Jones, H. L.; Osteryoung, R. A. J. Electrochem. Soc. **1973**, 120, 223.

^dApproximate.

B. Spectroelectrochemistry

Spectroelectrochemistry (SEC) is the study of solution redox chemistry by the simultaneous application of both electrochemical and spectroscopic techniques. SEC characteristically involves the optical monitoring of the solution adjacent to a working electrode during the electrochemical oxidation or reduction of an electroactive species. Spectroelectrochemical techniques have been used to acquire spectra and determine redox potentials of electrogenerated species and to study subsequent chemical reactions involving those electrogenerated products. Spectroelectrochemistry often provides additional information about an electrochemical system which cannot be obtained by either electrochemistry or spectroscopy.

The majority of spectroelectrochemical techniques can be divided into two broad categories, absorption and luminescence/scattering spectroscopies. Absorption spectroelectrochemistry includes both transmission and reflectance methods. The second major category is currently composed primarily of Raman spectroelectrochemistry. A more complete discussion of the theory and application of conventional spectroelectrochemical techniques may be found in the literature (33-40).

The most frequently used spectroelectrochemical technique is transmission spectroelectrochemistry. In this method, the radiation beam is directed at normal incidence through an optically transparent electrode (OTE) and the adjacent solution prior to detection.

Numerous types of OTE's have been presented in the literature. The earlier designs were based upon a thin conductive film (tin oxide, platinum, gold, or carbon) deposited on a transparent substrate (41-51).

The major problem with this type of electrode is the inevitable compromise which arises between optical transmission and electrical resistance. The concept of using a solid electrode with small holes to allow passage of the optical beam has also been introduced. The most common OTE of this type is the minigrid electrode, a metal (gold, nickel, silver, or copper) micromesh of 100-2000 lines per inch (52,53). The use of both thin-film and minigrid OTE's with amalgamated surfaces has been reported (54,55). This is desirable due to (a) the extension of the negative potential limit of the electrode resulting from the high hydrogen overvoltage on mercury, and (b) the generally more well-behaved electrochemical reduction of metal ions on mercury than on other solid electrodes (56). High porosity materials which exhibit a large surface area-to-volume ratio have also been employed as OTE's (57,58). Included in this group are reticulated vitreous carbon ("RVC"; Fluorocarbon, Anaheim, CA) and porous metal foam (PMF, "Ampormet"; Astro Met Associates, Cincinnati, OH).

One of the most common arrangements in transmission spectroelectrochemistry is to position the OTE in a conventional transmission cell with a 1-cm pathlength. This method is particularly suited for reaction kinetic studies due to the relatively long electrolysis periods during which semi-infinite diffusion occurs. In the typical chronoamperometric experiment, the potential applied to the OTE is stepped from a region where no significant reaction occurs to a value where the electroactive species undergoes electrolysis at a diffusion controlled rate. For the generation of a single absorbing species R from a nonabsorbing reactant O under semi-infinite diffusion according to:



where n is the number of electrons passed per molecule in the reaction, the resulting absorbance-time ($\mathcal{A}$ - t) response observed at the single surface of a planar OTE is given by (44):

$$\mathcal{A} = 2 \epsilon_R C_0^* (D_0 t / \pi)^{1/2} \quad (6)$$

where ϵ_R is the molar absorptivity of species R at the wavelength of interest, C_0^* and D_0 are the bulk molar concentration and diffusion co-efficient ($\text{cm}^2 \cdot \text{sec}^{-1}$) of species O , respectively, and $\pi = 3.1416$. From an electrochemical standpoint, this response is similar to that given by the integrated Cottrell equation:

$$Q_d = 2nFA C_0^* (D_0 t / \pi)^{1/2} \quad (7)$$

where Q_d is the charge (in coulombs) passed in electrolysis, F is Faraday's constant (9.64846×10^4 coulombs), and A is the electrode area in cm^2 .

The linear relationship between absorbance and $t^{1/2}$ in Equation 6 permits the determination of diffusion coefficients without independent knowledge of the electrode area. If the electrogenerated species undergoes subsequent chemical reaction, a more complicated $\mathcal{A}$ - t behavior is observed. By comparison with the theoretical response for many such mechanistic cases, as predicted by computer digital simulation, the rate constant for the monitored reaction may be estimated (59).

A most useful spectroelectrochemical technique is the optical monitoring of a thin layer of solution confined next to the OTE. Typically, the OTE is sandwiched between two parallel windows with a

resulting pathlength < 0.3 mm. The major advantage of this arrangement is rapid exhaustive electrolysis of the solution adjacent to the electrode. In addition to providing a quick means for acquiring spectra of the oxidized and reduced forms of the electroactive species, thin-layer spectroelectrochemistry can also provide electrochemical information about the redox system (60,61).

In the study of a reversible redox couple using a thin-layer spectroelectrochemical cell, the ratio of the molar concentrations of the oxidized ([O]) and reduced ([R]) forms of the electroactive species may be adjusted by the potential applied to the electrode (E_{applied}) as determined by the Nernst equation:

$$E_{\text{applied}} = E^{0'} + (RT/nF)\ln([O]/[R]) \quad (8)$$

where $E^{0'}$ is the formal reduction potential in volts and T is the absolute temperature ($^{\circ}\text{K}$). Although E_{applied} specifically controls the ratio $[O]/[R]$ at the surface, the corresponding ratio in the adjacent solution layer quickly adjusts to the same value by electrolysis. The redox couple is converted incrementally from one oxidation state to the other by a series of applied potentials. Each potential is maintained until the equilibrium value of $[O]/[R]$ is established according to Equation 8. From the resulting spectrum, the corresponding $[O]/[R]$ ratio may be determined. A Nernstian plot using the values of E_{applied} and spectrally determined $[O]/[R]$ ratios should yield a straight line, allowing the $E^{0'}$ and n -value to be derived from the y -intercept and slope, respectively.

Thin-layer coulometry may also be performed either by direct measurement of the charge passed during a complete electrolysis or by the integration of the recorded chronoamperometric response. The Faradaic charge (Q_F), which is determined from the total charge (Q_T) by subtracting background charge (Q_B) contributions, is related to the number of electrons transferred in the reaction through Faraday's Law:

$$Q_F = Q_T - Q_B = nFVC \quad (9)$$

where Q_F is in coulombs, V is the volume of the thin-layer cell in liters, and C is the molar concentration of the electroactive species. Once the cell volume has been calibrated from the electrolysis of a known electrochemical system, the n -value of an unknown redox couple of known concentration can be similarly determined.

C. Optical Enhancement Methods in Thin-Layer Spectroelectrochemistry

In conventional transmission thin-layer spectroelectrochemistry, the short effective optical pathlength frequently restricts the application of this method to the investigation of strongly absorbing species (62). Considerable effort has been directed toward the development of optical enhancement techniques to extend this methodology to the study of short-lived species and weak chromophores in aqueous solutions. Included in the following discussion are those enhancement methods concerned with the investigation of solution immediately adjacent to the electrode.

Specular reflection at glancing incidence has been introduced as an optical enhancement technique for thin-layer spectroelectrochemistry (62-64). In this method, the light beam is reflected from a solid

electrode at small angles relative to the electrode surface. For various combinations of light sources (helium-neon laser or xenon arc lamp) and electrodes (gold, platinum, or carbon), the sensitivity of this method is reported to be about 100 times that of a comparable experiment using an OTE and thin-layer cell arrangement (64).

Passing the light beam parallel to a solid electrode has been used to monitor the absorbance of electrogenerated species (65-68). Gains in sensitivity greater than 15 have been reported using an electrode length of 0.19 cm (as measured along the optical axis) and argon ion laser (68). This method has permitted optical spatial resolution of the diffusion layer, with concentration vs. distance profiles being obtained for distances down to less than 20 μm from the electrode surface (65,68).

A technique based upon a somewhat similar experimental arrangement is diffractive spectroelectrochemistry (69,70). Instead of monitoring the parallel beam, the light diffracted by the electrode is studied. This method is particularly sensitive to the presence of absorbing species at or near the electrode surface and may have applications in deducing the diffusion layer structure and studying adsorption on electrodes. Experimental optical sensitivities of 120 times that obtained for an OTE under similar conditions have been reported (69). Additional signal-to-noise enhancement by electrochemical modulation of the absorbing species and detection of the resulting ac optical signal has been reported (71).

Spectroelectrochemical monitoring of electrode reactions by multiple specular reflection has been described (72). This method is

based upon a special 4-cm long thin-layer cell with 120- μm spacing between two glass windows, each coated on the inside surface with a reflective gold layer which serves additionally as an electrode. The optical gain of this arrangement results from a very large number of reflections of the light beam between the two electrode surfaces. By altering the angle of incidence of the source, the number of reflections inside the cell may be controlled, allowing the sensitivity of the cell to be varied. Using a helium-neon laser, over 300 reflections between the two electrode surfaces have been achieved, resulting in an optical sensitivity which exceeds that of a conventional OTE thin-layer cell by a factor of several hundred.

Absorption spectroelectrochemistry based upon external reflection from cylindrical microelectrodes has been reported (73,74). Despite the small size (5-280 μm radius) of the electrodes used (gold, platinum, and carbon), the measured absorbances are typically twice the values obtained in OTE experiments for comparable electrolysis times. The very low capacitive charging and Faradaic currents of the microelectrodes result in a cell time constant much shorter than for conventional designs, permitting measurements on the microsecond time scale and operation at a higher duty cycle. Due to the electrode geometry, cylindrical rather than planar diffusion occurs, producing a more rapid flux of reactant to the electrode and subsequent dilution of the electrogenerated products.

Many interesting spectroelectrochemical cells designed to improve optical sensitivity while maintaining short electrolysis periods have been introduced. Several of these strategically position a large

solid electrode out of the light path in a standard 1-cm cuvette, and rely upon the large surface area-to-volume ratio (75,76) and additional mass transport by convection (77-80) to promote rapid electrolysis. More sophisticated designs involve thin-layer cells made from Plexiglass and epoxy (81,82). Recently, a new type of OTE developed by drilling a small diameter hole (500 μm) through a solid conductor material such as glassy carbon or graphite, has been used to fabricate a thin-layer spectroelectrochemical cell with a long optical pathlength (83).

D. Proposed Research

Although various spectroelectrochemical methods have been applied to investigations in molten salt media (84), the development of techniques to improve the optical sensitivity of such measurements is nonexistent. The corrosive nature, moisture sensitivity, and thermal requirements associated with solvents such as molten salts often preclude the use of sophisticated optical systems and fragile cell components.

This part of the dissertation is concerned with the development and application of multipass spectroelectrochemistry as an optical enhancement method for thin-layer spectroelectrochemical investigations in molten salts. Initial evaluation of this technique was performed using an aqueous test system, the reduction of potassium permanganate in 1 molar sodium hydroxide. This methodology was then extended to the study of the oxidation of sulfur and the reduction of niobium pentachloride in molten sodium chloroaluminates to demonstrate the utility of the technique for investigations in such media.

CHAPTER II

EXPERIMENTAL

A. Materials

1. Materials Used and Preparation of Aqueous Solutions

The aqueous solutions used in initial electrochemical evaluation and volume calibration of the thin-layer spectroelectrochemical cells were prepared from certified ACS reagent grade potassium ferricyanide and potassium chloride (Fisher Scientific Co., Fair Lawn, NJ). Distilled water was further treated by passage through a multiple cartridge purification system (Millipore Corp., Bedford, MA). Solutions of potassium permanganate were prepared by dissolving certified ACS reagent grade crystals in a 1 molar (M) sodium hydroxide solution (Fisher Scientific Co.) and were used within several hours after preparation. All aqueous solutions were deaerated with nitrogen immediately prior to use.

2. Materials Used and Preparation of Chloroaluminate Melts

a. Sodium chloride purification. Certified ACS reagent grade NaCl (Fisher Scientific Co.) dried under vacuum at 400 °C for several days usually yielded material of suitable quality. For producing higher purity melts, NaCl was dehydrated in a fritted quartz apparatus by first passing HCl gas over the solid and then over the liquid at 850 °C for 12 hours. The molten NaCl was then purged with prepurified nitrogen for 24 hours, filtered, and then slowly recrystallized. Only clear crystals were selected for use.

b. Aluminum chloride purification. Anhydrous AlCl_3 (puriss. grade, Fluka Chemical Corp., Hauppauge, NY) was further purified by repeated sublimation inside the dry box using the apparatus illustrated in Figure 1. This device was constructed from 3-inch I.D. conical end Pyrex process pipe (O-I Schott Process Systems, Vineland, NJ) with a standard pipe flange assembly and Teflon gasket. Two complete units may be fabricated by halving both a 12-inch length (Part No. 6100-3012) and a 36-inch length (Part No. 6100-3-36) section and utilizing both conical ends from each piece. The 1/2-inch O.D. Pyrex tubing extending from the top section of the sublimator was connected to an additional length of the same tubing by a stainless steel (SS) Cajon Ultra-Torr Union (Part No. SS-8-UT-6, Ridge Valve and Fitting Co., Knoxville, TN). This extension permitted the condensation of any material outside the main sublimator compartment to be monitored. This Pyrex tube was connected to 1/4-inch O.D. Teflon tubing by an Ultra-Torr Reducing Union (Part No. SS-8-UT-6-4) to provide flexibility in both assembly and positioning of the device. Evacuation of the sublimator was controlled by a valve located outside the dry box which leads to a liquid nitrogen cold-trap and vacuum. The lower section of the apparatus was positioned in a furnace and held upright by two support rings. A suitable furnace may be constructed by wrapping a commercial heating tape around a cylindrical wire cage, and insulating the outer surface with aluminum foil to minimize thermal expansion of the dry box environment. A T-type thermocouple (Omega Engineering Inc., Stamford, CT) was used to monitor furnace temperature which is regulated by a variable voltage transformer (Staco Energy Products Co., Dayton, OH) located outside the dry box.

Figure 1. Vacuum sublimation apparatus used to purify aluminum chloride: (A) 3-inch I.D. conical end Pyrex process pipe, (B) flange assembly, (C) Teflon gasket, (D) support ring, (E) 1/4-inch O.D. coiled copper tubing, (F) Tygon tubing, (G) furnace, (H) thermocouple, (I) Ultra-Torr Union, (J) 1/2-inch O.D. Pyrex tubing, (K) 1/4-inch O.D. Teflon tubing, (L) bulkhead connector, (M) regulating and shut-off valves.

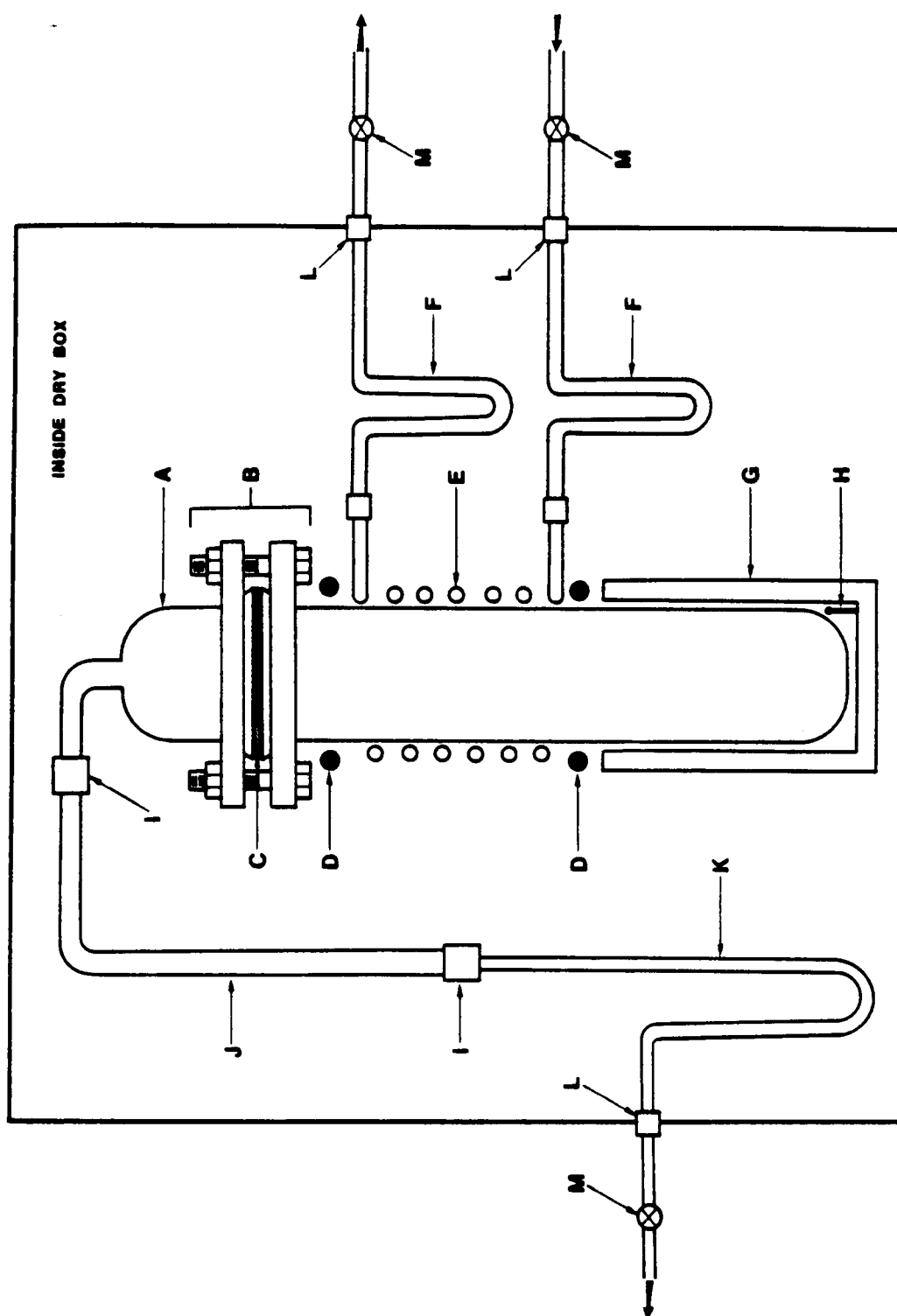


Figure 1.

A cooling coil constructed from 1/4-inch O.D. copper tubing is used to promote sublimation in the region immediately above the furnace. A coolant system based upon air flowing at $0.3\text{--}0.5\text{ L}\cdot\text{min}^{-1}$ initially through a similar coil outside the dry box immersed in an ethanol-ice bath ($-10\text{ }^{\circ}\text{C}$) is sufficient for this purpose. For flexibility, Tygon tubing was used to connect the sublimator coil to the external coolant system. External valves regulated air flow through the coil and permit isolation of the dry box when not in use.

Typically, $0.6\text{--}0.8\text{ kg}$ of AlCl_3 and $20\text{--}30\text{ g}$ NaCl were loaded into the lower section of the sublimator prior to assembly. The unit was evacuated for 15 minutes to remove any adsorbed volatile impurities. The vacuum valve was then closed, and the transformer set to produce a furnace temperature of $215\text{ }^{\circ}\text{C}$. Simultaneously, air flow through the cooling system was started.

During sublimation, the more dense AlCl_3 -saturated- NaCl layer extracts impurities from the Al_2Cl_6 layer above (85). When only a small amount of solid AlCl_3 remained, the operation was terminated. After cooling to room temperature, the unit was disassembled and the sublimed AlCl_3 collected. The material was carefully dislodged from the glass walls of the lower unit by using a long-stem chisel fabricated from 1/4-inch stainless steel rod. Large pieces of AlCl_3 were then crushed with a large mortar and pestle and readied for further purification or melt preparation. The entire operation required only 6-8 hours, thereby allowing a large quantity of material to be purified in a relatively short time. Three sublimations were usually sufficient to yield material of acceptable purity.

The purity of aluminum chloride prepared in this manner was often examined by obtaining a Raman spectrum of the molten AlCl_3 (Al_2Cl_6) at 200 °C (86). The absence of a fluorescence background is correlated with a material of low organic contamination. Figure 2 illustrates typical Raman spectra for AlCl_3 samples at 200 °C taken before and after purification. Details of the instrumentation used to acquire Raman spectra are presented in Part II.

c. Chloroaluminate melt preparation. The chloroaluminate melts were prepared by weighing the appropriate amounts of purified AlCl_3 and NaCl inside the dry box and loading them into a Pyrex ampoule, frequently with several small pieces of aluminum metal (m5N grade, Alfa Inorganics, Danvers, MA). The ampoule was temporarily closed with Tygon tubing compressed with a thumbscrew clamp, and then transferred outside the dry box to a vacuum manifold constructed from greaseless fittings and Teflon stopcocks. A liquid nitrogen cold-trap was used to isolate the manifold from the vacuum pump, and the absolute pressure of the system was monitored with a Veeco Model TG-70 TC vacuum gauge and Type DV-1M vacuum probe. The ampoule was evacuated for 1/2 hour at an absolute pressure of 1-5 mTorr and then sealed under vacuum with a natural gas-oxygen torch. The mixture was then fused and digested over aluminum for several hours in a rocking furnace at 175 °C. The aluminum reduces any metallic impurities more noble than aluminum. Additional manual agitation of the ampoule during the initial stages of heating the mixture was required to prevent aluminum dendrite formation.

Following digestion, the water-like clear melt was poured away from the aluminum and frozen at room temperature. When needed, the

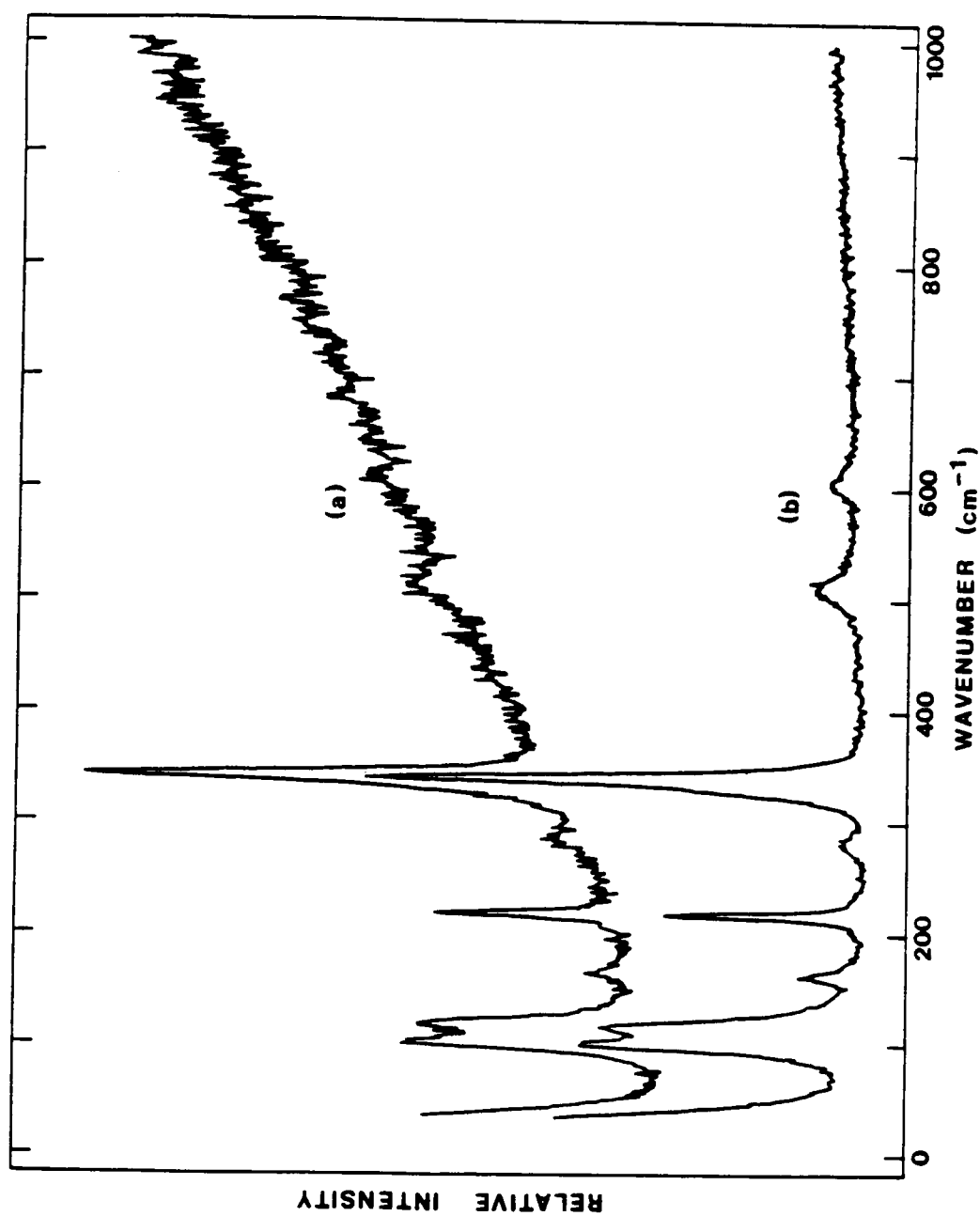


Figure 2. Raman spectra of aluminum chloride at 200 °C: (a) before and (b) after purification.

ampoule was returned to the dry box, cracked open, and the solid core of chloroaluminate removed. This solid was then pulverized to a fine powder to permit further processing.

Frequently, the electrochemical purity of chloroaluminate melts was evaluated from the background cyclic voltammogram at a platinum microelectrode. A small sample (10-15 g) cell suitable for this purpose is shown in Figure 3. After the cell was loaded with crushed $\text{AlCl}_3\text{-NaCl}$ through the threaded glass connector, the vacuum stopcock was secured with the Teflon bushing assembly and closed. The cell was then taken outside the dry box, evacuated, and placed in a preheated furnace.

A typical cyclic voltammogram (CV) of a "clean" 63/37 $\text{AlCl}_3\text{-NaCl}$ melt at 175 °C taken with a scan rate of 100 $\text{mV}\cdot\text{sec}^{-1}$ is presented in Figure 4 and is similar to results previously observed (87). Current densities $\gg 1 \text{ mA}\cdot\text{cm}^{-2}$ at 100 $\text{mV}\cdot\text{sec}^{-1}$ are usually indicative of the need for further purification. The instrumentation used to perform cyclic voltammetry is described in the "Electrochemical Measurements" section of this chapter.

Recently, a method for the electrochemical determination of oxide contamination in $\text{AlCl}_3\text{-NaCl}_{\text{satd}}$ melts has been reported (88).

d. Solutes and chloroaluminate solution preparation. Elemental sulfur (t5N5 grade, Alfa Products, Danvers, MA) was used without further purification. Niobium pentachloride (puriss. grade, Alfa Products) was purified by sublimation at 100 °C in a Pyrex tube sealed under vacuum. Typically, three sublimations permitted NbCl_5 to be separated from the corresponding white oxychloride, NbOCl_3 (89).

Solutions of sulfur and niobium pentachloride were prepared in the dry box by weighing a desired amount of crushed $\text{AlCl}_3\text{-NaCl}$ solid

Figure 3. Small sample (10-15 g) cell used to determine background cyclic voltammograms of chloroaluminate melts: (A) 90° vacuum stopcock with Teflon plug and Viton O-Rings; (B) threaded glass connection with (a) Teflon bushing, (b) aluminum washer, (c) Viton O-Ring, (d) Teflon sleeve, and (e) #7 Ace-Thred; (C) thermocouple well; (D) tungsten wire lead; (E) platinum foil counter electrode; (F) platinum wire working and quasi-reference electrodes.

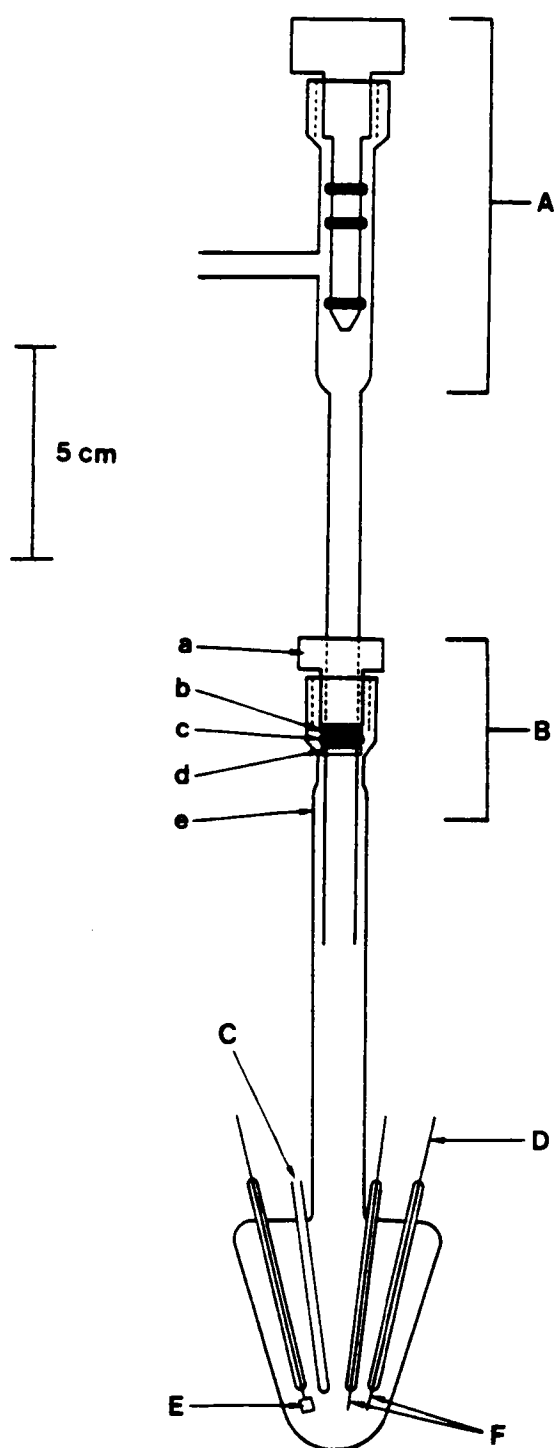


Figure 3.

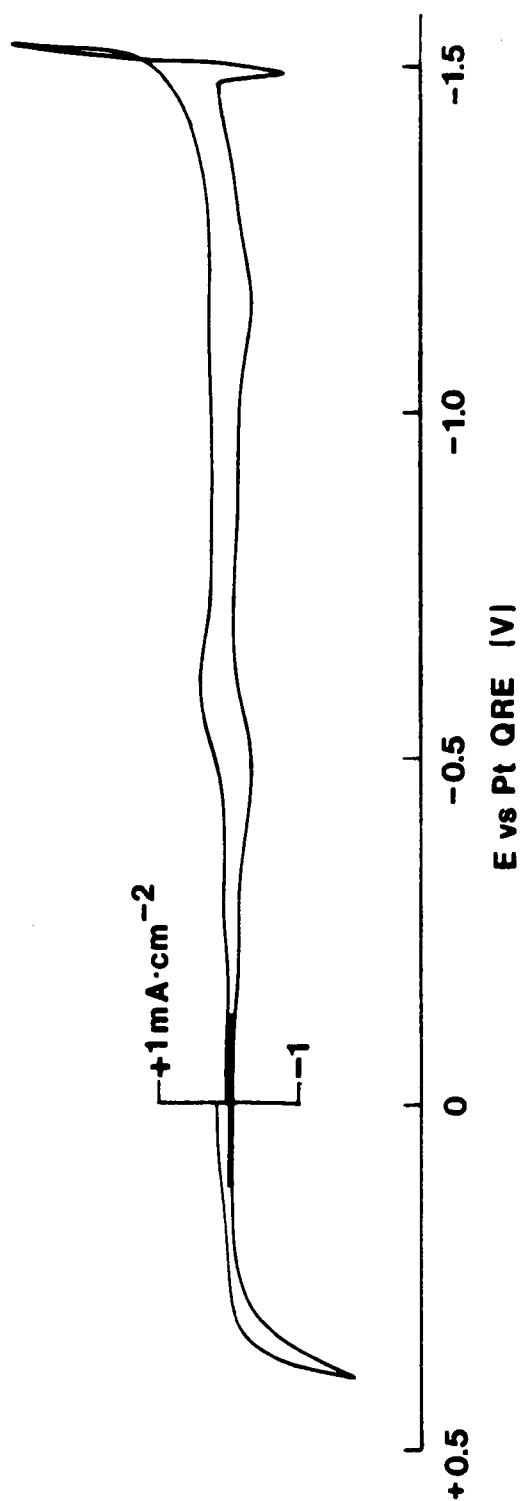


Figure 4. Background cyclic voltammogram of 63/37 $\text{AlCl}_3\text{-NaCl}$ at 175°C acquired using platinum working, counter, and quasi-reference (QRE) electrodes: initial potential = $0.00 \text{ V vs. Pt QRE}$; initial scan direction negative; scan rate = 100 mV/sec .

into a Pyrex ampoule and adding the appropriate weight of solute. The ampoule was then evacuated and sealed as before and digested at 175 °C until a homogeneous solution was obtained. The solution was then frozen at room temperature, returned to the dry box, and processed as described previously. For calculating molar concentrations, melt volumes were estimated from published density data (90).

B. Apparatus

1. Apparatus Used in Aqueous Multipass Spectroelectrochemistry

a. Thin-layer spectroelectrochemical cell. Early attempts to achieve the multipass effect in aqueous media involved the use of a traditional thin-layer cell with an open solution reservoir (which houses the counter and reference electrodes) located at the cell base (61). Besides restricting the placement of mirrors near the cell windows, this arrangement permitted condensation of solution vapor on the mirror surfaces, resulting in a significant noise problem.

The aqueous spectroelectrochemical cell used in initial evaluation of the multipass technique corrects for both of these problems and is illustrated in Figure 5. Four Teflon spacers (0.0135-inch thick) were used to center a platinum screen (80-mesh, 7 X 22 mm) OTE between two quartz microscope slides (1 X 1 inch, 1-mm thick), resulting in an optical pathlength of 0.084 cm. The platinum screen was obtained at ORNL and had been fabricated from 0.003-inch diameter platinum wire, resulting in a 0.0095-inch spacing between adjacent strands. Electrical contact was made by an additional platinum wire (0.020-inch diameter) spot-welded to the screen. A 5-mm O.D. Pyrex tube, which terminated

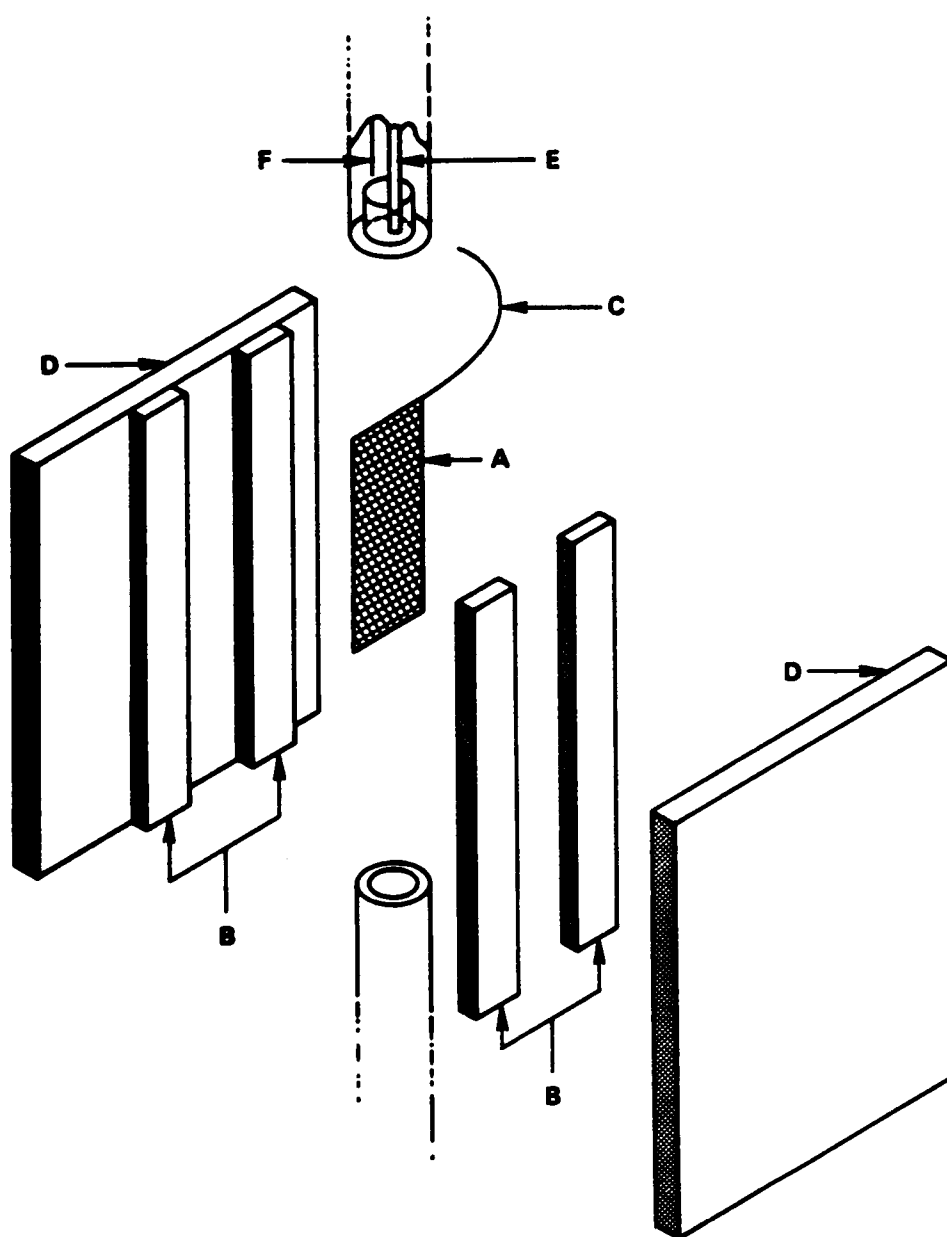


Figure 5. Aqueous thin-layer spectroelectrochemical cell: (A) 80-mesh platinum screen, 7 X 22 mm; (B) 0.0135-inch Teflon spacers; (C) platinum wire lead; (D) quartz window; (E) SCE; (F) platinum wire counter electrode; pathlength = 0.084 cm.

with a standard taper joint, was glued to the top of the cell. This tube contained the solution reservoir into which a saturated calomel reference electrode (SCE) and platinum wire counter electrode were inserted. A commercial SCE (Altex Beckman No. 531287, VWR Scientific Inc., San Francisco, CA) was modified by replacing its junction with an asbestos frit inserted in a 9-inch disposable pipet filled with saturated KCl solution. A Teflon sleeve was placed around the fritted area to minimize diffusion of electroactive species from the reservoir to the OTE. A 3-mm O.D. Pyrex tube with a Teflon stopcock was glued to the bottom of the cell. Epoxy adhesive ("Torr Seal"; Varian Associates Vacuum Division, Palo Alto, CA) placed outside the thin-layer region and around the unit secured the assembly together.

b. Optical components. Two thermometer clamps attached the aqueous cell to a support rod centered on a rotary stage (Model 470, Newport Research Corp., Fountain Valley, CA), which facilitated cell alignment with respect to the optical beam. Two 1/4-m aluminum triangular optical benches (Part No. 22-6837, Ealing Corp., South Natick, MA) and XZ translational stages (Part No. 22-4899, Ealing Corp.) were used to position quarter-wave front surface mirrors attached to adjustable mounts (Model 240, J. A. Noll Co., Cumberland, MD) on both sides of the cell to achieve the three-pass optical arrangement described in Chapter III.

2. Apparatus Used in Molten Salt Multipass Spectroelectrochemistry

a. Thin-layer spectroelectrochemical cell. The spectroelectrochemical cell used for molten salt studies is illustrated in Figure 6. This device is a hybrid design incorporating desirable characteristics

Figure 6. Molten salt thin-layer spectroelectrochemical cell: (A) 80-mesh mesh platinum screen OTE, 10 X 40 mm; (B) platinum foil counter electrode; (C) thermocouple well; (D) Al/Al(III) reference electrode in fritted compartment with fill hole; (E) #7 and (F) #11 threaded glass connectors with: (a) Teflon bushing, (b) aluminum washer, (c) Viton O-ring, and (d) Teflon sleeve; (G) tungsten wire lead; additional platinum wire microelectrode not shown for clarity; pathlength = 0.10 cm.

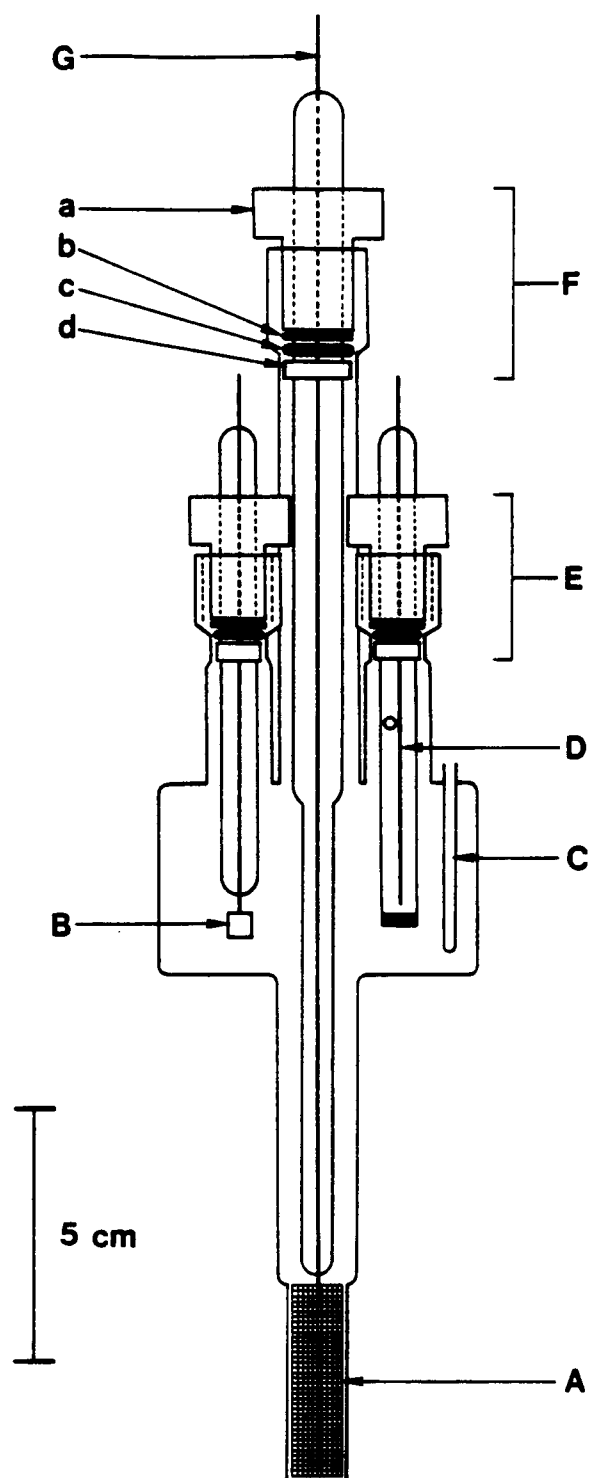
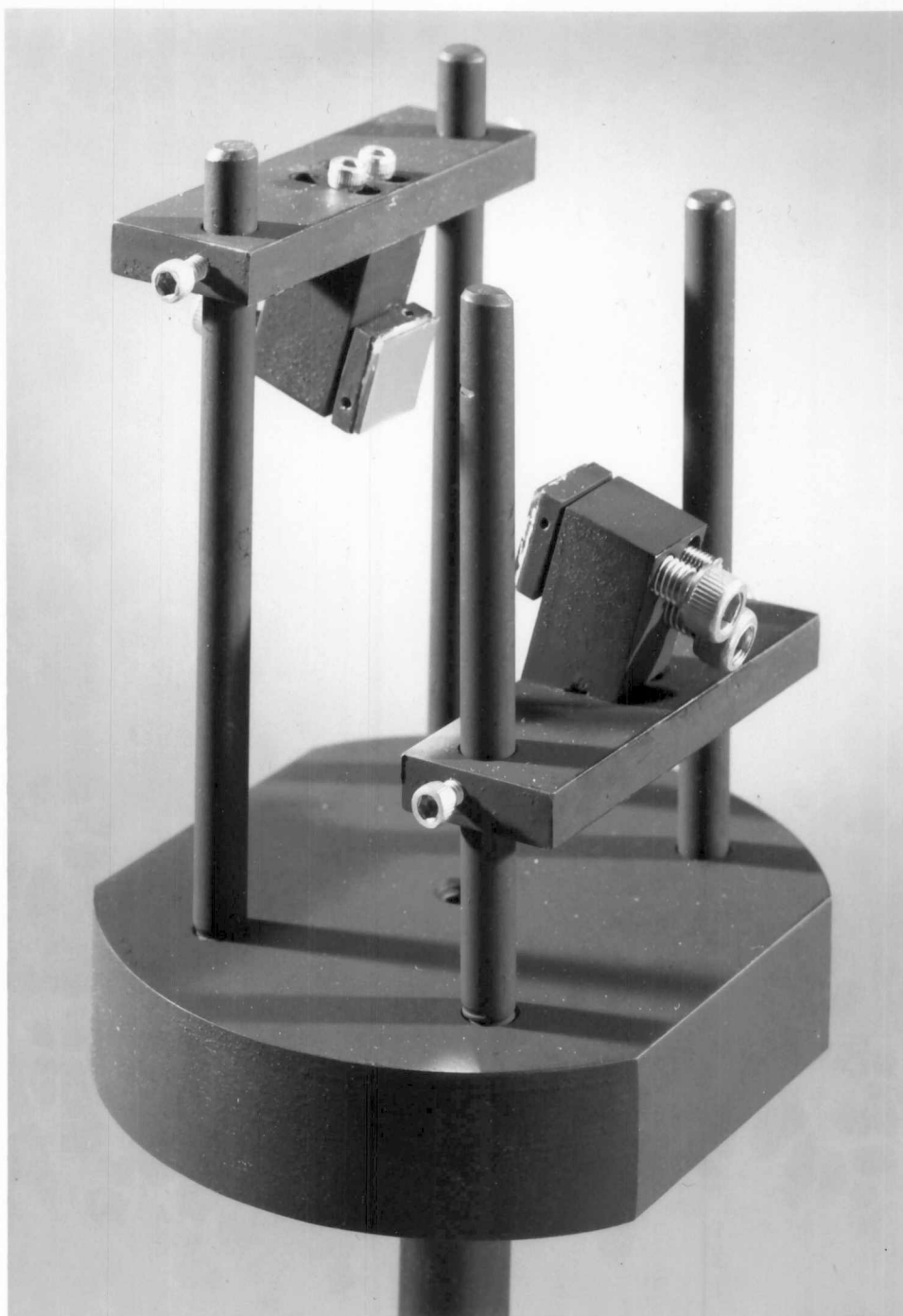


Figure 6.

from previously reported "high-temperature" (91) and "low-temperature" (92) molten salt cells. Large ratio rectangular Pyrex tubing (1 X 10 mm I.D., Vitro Dynamics, Rockaway, NJ) was used to form the thin-layer optical region. A platinum screen (80-mesh, 10 X 40 mm) served as the OTE. An aluminum wire reference electrode, isolated from the main cell compartment by a glass frit (4-8 micron porosity, Ace Glass Inc., Vineland, NJ), a cylindrical platinum foil counter electrode (3.14 cm²), and a platinum wire microelectrode (0.10 cm², not shown for clarity) were also inserted into the cell. All electrodes were secured by threaded glass connectors equipped with Viton O-rings and Teflon bushings (Ace Glass Inc.). Due to problems with leakage, resulting from thermal deformation of the Teflon bushing, an aluminum washer of appropriate dimensions was inserted between the bushing and O-ring to provide mechanical support and thus maintain an adequate seal at elevated temperatures. A Teflon sleeve cut from shrinkable Teflon tubing ("Korvex"; Berghof America Inc., Raymond, NH) was positioned immediately below the O-ring to prevent dusting of the seal by AlCl₃-NaCl powder during cell loading. This was observed to enhance O-ring longevity. Two K-type thermocouples (Omega Engineering Inc.), one inserted in a permanent thermocouple well in the main cell compartment and the other attached to the outer edge of the optical region, permitted accurate monitoring of the temperature of the cell's contents. An external opaque mask was attached to the thin-layer region to prevent light not passing through the OTE from reaching the detector.

b. Optical components. The mirror assembly used to produce the multipass effect inside the optical furnace is shown in Figure 7. The

Figure 7. Multipass mirror assembly.



support assembly was constructed from aluminum and stainless steel and was coated with an opaque high-temperature resistant paint to minimize stray reflections. A 1/4-20 threaded hole in the center of the base permitted a rod to be attached and removed, thereby allowing insertion and removal of the mirror assembly from the furnace while operating at elevated temperatures. Two 12 X 12-mm front surface mirrors (Part No. 31005, Edmund Scientific, Barrington, NJ) were attached to adjustable mirror mounts, each centered on a rectangular support plate. Displacement in the vertical direction was achieved by sliding the plate between parallel support rods. Two fine resolution socket-head screws allowed adjustment of the mirror angles.

c. Optical furnace. The optical furnace consisted of a Pyrex tube (10-cm O.D., 45-cm length), oriented vertically, wrapped with nichrome heating ribbon ($0.93 \text{ ohm}\cdot\text{ft}^{-1}$). A second glass tube of slightly larger diameter, encased in a 1-inch thick Kaowool blanket (Babcock & Wilcox Co., Augusta, GA) and Teflon cover, fit over the heating tube to provide electrical and thermal insulation. Two optical ports with 62-mm diameter quartz windows (Part No. 7895, Ace Glass Inc.), each fabricated from a threaded glass connector (Part No. 7644-25, Ace Glass Inc.) and Teflon window holder assembly (Part No. 7896-30, Ace Glass Inc.), were located 8 cm from the bottom of the furnace at a 180° alignment. The furnace rested on an insulated aluminum plate attached to a flat carrier base (Part No. 22-4170, Ealing Corp.), which facilitated alignment with other external components on a 1-m aluminum triangular optical bench (Part No. 22-6894, Ealing Corp.). Furnace temperature was controlled by a variable voltage transformer

(Model W5MT3, GenRad, Concord, MA) and monitored by K-type thermocouples (Omega Engineering Inc.) at selected locations.

The cell was positioned in the furnace by two aluminum support rings, lined with Teflon, which clamp the main cell body. These metallic rings were connected to three 3/16-inch diameter threaded steel rods which suspended the cell from an aluminum disc serving as the furnace top. Electrical contact to each electrode was made with an alligator clip attached to a Teflon-insulated wire inserted through the furnace lid.

d. Dry box. All manipulations of solid $\text{AlCl}_3\text{-NaCl}$ were performed in a Vacuum Atmospheres Model HE-43-2 DRI-LAB dry box with a Model HE-493 DRI-TRAIN purification system and Model HE-63-P PEDATROL automatic pressure controller. The inert gas used in this system was prepurified nitrogen (99.998 %, MG Scientific Gases, Knoxville, TN). The moisture level in the box (typically <2 ppm) was monitored constantly with a Panametrics Model 700 Hygrometer. Periodically, the oxygen level in the dry box was empirically determined by observing the lifetime of the exposed tungsten filament of a 130-Volt AC, 6-watt light bulb (Sylvania No. 16938, GTE Products Corp., Salem, MA). A duration of several (3-5) days was considered to be indicative of an acceptably "low" O_2 level. All weighings inside the dry box were performed using an Arbor Model 206A electronic balance with 0.1 mg accuracy. Prior to use in the dry box, all glassware and stainless steel utensils were cleaned with a laboratory detergent ("Micro"; International Products Corp., Trenton, NJ), rinsed with distilled water, and dried at 120 °C for 24 hours.

C. Instrumentation

1. Optical Measurements

The light source used for multiwavelength analysis was a 20-watt quartz halogen lamp (Bulb No. 1974, General Electric, Cleveland, OH) powered by a 6-volt A.C. transformer (Stancor Essex, Logansport, IN) operated in series with a constant voltage transformer (Sola Electric Co., Chicago, IL). To insure operation at thermal equilibrium, the bulb was positioned in an aluminum housing cooled with a subminiature fan. The spectral output of the lamp was modified with a Corning No. 4039 glass filter to optimize the source with respect to detector response in the 400-800 nm region. Multiwavelength optical measurements were performed with a computer-controlled rapid scanning spectrometer (RSS) system located in the Analytical Chemistry Division at ORNL. A block diagram of the system is shown in Figure 8. The Tektronix Model J20 Spectrometer and Model 7J20 Spectrometer Plug-In are interfaced to the PDP-8/I minicomputer through an ORNL RSS-Computer Interface which was designed by L. N. Klatt of the Analytical Chemistry Division, ORNL. The spectrometer is a silicon-based vidicon system which permits operation in the 200-1100 nm spectral region. A simplified diagram of the operation of the RSS is shown in Figure 9.

To obtain a transmission spectrum, polychromatic light is passed through the sample and into a polychromator where it is dispersed by a grating. A 400-nm wide segment of the spectrum (200 nm in the UV region) is directed across the face of the vidicon detector where it is read as light intensity vs. wavelength by an electron beam. The sweep frequency of this beam can be adjusted so that spectra may be acquired

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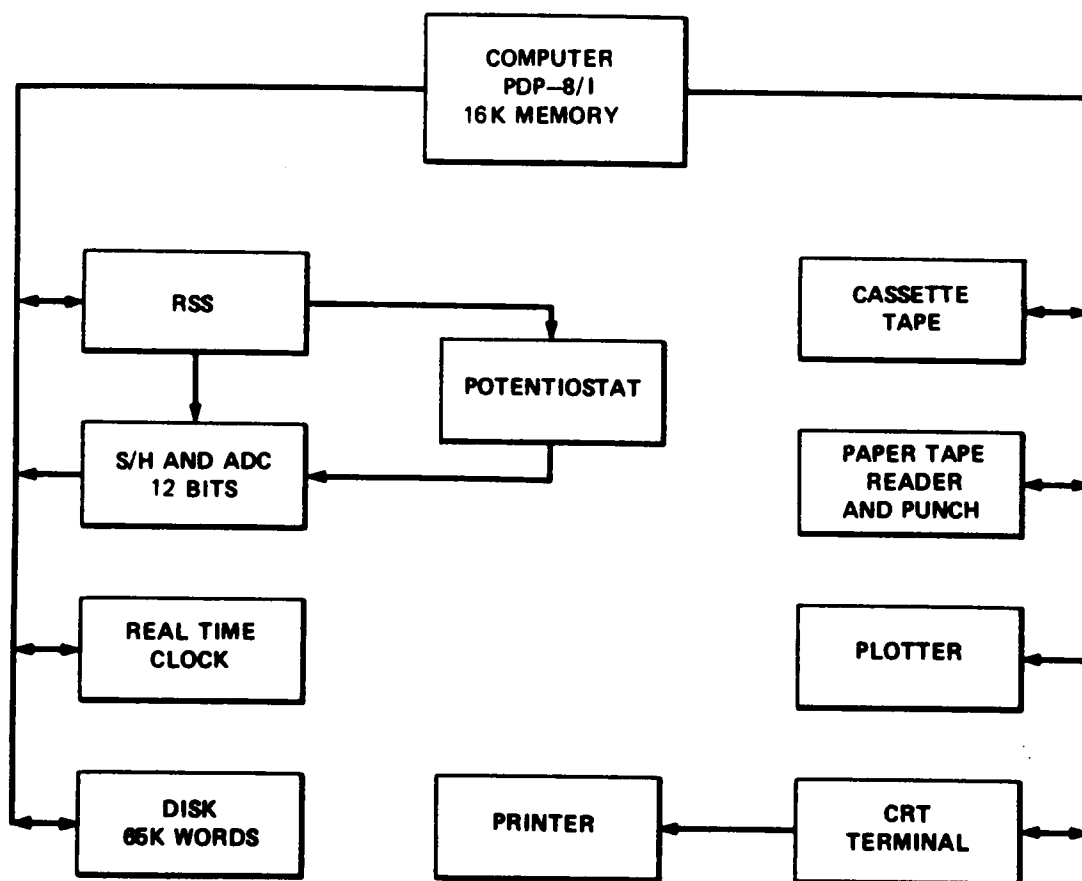


Figure 8. Block diagram of the computer/spectrometer system.

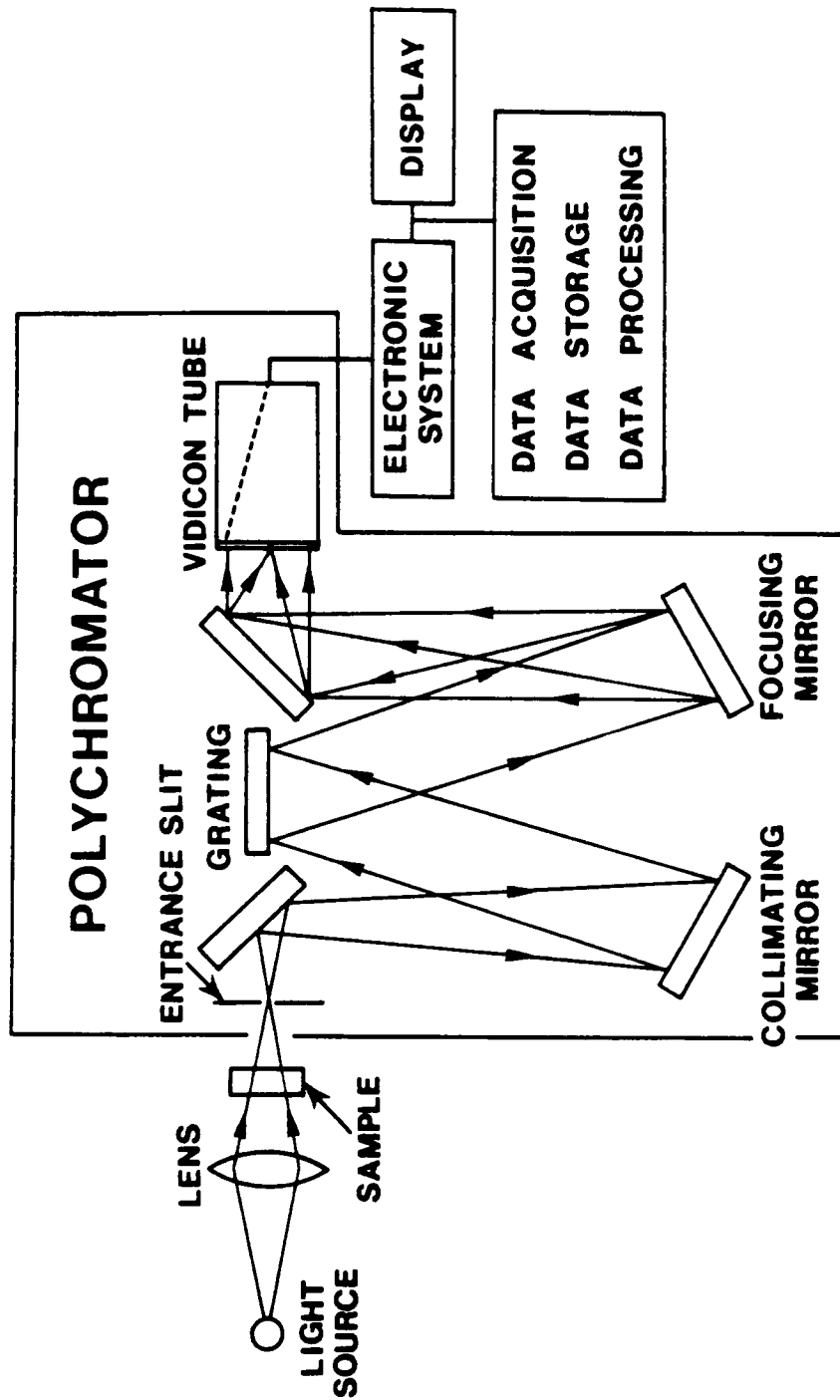


Figure 9. Diagram of RSS operation.

at time intervals varying from 50 msec to 5 sec. Since the spectrometer operates in a single-beam mode, a 100 % transmission spectrum (with no sample in the beam) must also be acquired, and the corresponding absorbance value is calculated using the computer. The noise level of these measurements was typically $<5 \times 10^{-3}$ absorbance units. An ORNL Model Q-2943B Potentiostat is also interfaced to the system; this allows synchronization of the start of spectral data acquisition with the potential step applied to the OTE, as well as simultaneous acquisition of both spectral and electrochemical data. A more detailed description of the computer-spectrometer interface system is available in the literature (93). Further information on the computer/spectrometer and its operation may be found elsewhere (94). The computer programs used are presented in the Appendix.

The PDP-8/I computer is exclusively dedicated to control of the RSS system and processing of data. The computer contains 16K of core memory and is equipped with the following peripherals: a 12-bit Digital Equipment Corporation (DEC) analog-to-digital converter (ADC) with a 32-channel multiplexer; two DEC Model DF-32 discs, each with a capacity of 32K words; a Sykes Compu/corder 100 cassette tape drive; a Digitronics paper tape reader and a Data Specialties, Inc. Model M-75C paper tape punch; and a Data General Dasher Model TP1 terminal/printer. Spectra or other data can be plotted either with a Linseis Model LY1800 X-Y recorder or a Tektronix Model 603 Storage Monitor.

For selected experiments involving attempts to achieve a large number of passes, a 4-mWatt helium-neon laser (Model 145-02, Spectra-Physics Inc., Mountain View, CA) was used as the source and a photodiode

(Model PIN-10D, United Detector Technology Inc., Santa Monica, CA) as the detector. Photodiode response, resulting from operation in the photoconductive mode, was amplified and then sampled by the ADC of the computer.

2. Electrochemical Measurements

Initial electrochemical testing of the spectroelectrochemical cells by cyclic voltammetry of potassium ferricyanide solutions was performed with a Princeton Applied Research (PAR) Model 174A Polarographic Analyzer and PAR Model 175 Universal Programmer. The resulting potential vs. current curves were recorded either with a Hewlett-Packard Model 7045A or Houston Omnigraphic Model 2000 X-Y recorder.

Thin-layer coulometry of aqueous solutions was performed with the computer-interfaced ORNL Model Q-2943B potentiostat. During exhaustive electrolysis, the current was periodically sampled and stored by the computer. The resulting charge vs. time curve was calculated by computer integration of the chronoamperometric response using the trapezoidal rule approximation (95). A background coulogram (of the solvent only) obtained in the same manner could be subtracted from this curve to provide a more accurate Faradaic response.

To check the purity of molten salt solutions immediately prior to spectroelectrochemical analysis, cyclic voltammograms obtained using the computer-interfaced potentiostat and Linseis X-Y recorder were compared with published results.

D. Procedure

1. Procedure Used in Aqueous Multipass Spectroelectrochemistry

Prior to filling with test solutions, the aqueous spectroelectrochemical cell was cleaned with concentrated HCl, rinsed with distilled water and ethanol, and dried under vacuum. The cell was filled with solvent only and used to optically align the system.

For multipass experiments using the continuum source, the light beam was first collimated with a 50-mm focal length (FL) quartz lens and directed through the Corning No. 4039 glass filter. A second quartz lens (FL = 150 mm) was used to focus the light through the thin-layer cell and mirror assembly to produce the 3-pass arrangement described in Chapter III. The first and third pass were oriented at normal incidence to the OTE; for the second pass, $\alpha = 64^\circ$. Another quartz lens (FL = 150 mm) was placed on the opposite side of the cell to recollimate the beam and direct it toward the detector. An additional quartz lens (FL = 50 mm) was then used to focus the beam onto the polychromator slit of the RSS. Light intensity (and beam diameter) could be regulated by adjustment of an iris diaphragm attached to the lamp housing.

For multipass experiments using the laser source, the beam was directed through the thin-layer cell five times with $\alpha = 75^\circ$ for each pass. The only additional optical component used was an iris diaphragm placed immediately in front of the photodiode (30 cm from cell) to discriminate the primary analytical beam from stray reflections.

Conventional single pass experiments ($\alpha = 90^\circ$), using either source, were performed with the analogous optical arrangement omitting the mirror assembly.

After optical alignment, a 100 % transmission (% T) spectrum was recorded and stored for subsequent absorbance calculations. If desired, the reference and counter electrodes were temporarily inserted, and a background coulogram was obtained. The reference solution was then removed, the cell filled with test solution, and the reference and counter electrodes reinserted. The initial potential was applied to the OTE and a corresponding transmission spectrum ($t = 0$) acquired. Initiation of the potential step and all data acquisition and storage were controlled by the computer.

2. Procedure Used in Molten Salt Multipass Spectroelectrochemistry

The molten salt spectroelectrochemical cell and platinum electrodes were cleaned in concentrated HCl, followed by rinsing with distilled water and ethanol, and dried at 120 °C for 24 hours. The aluminum reference electrode was cleaned with a mixture of concentrated $\text{H}_3\text{PO}_4:\text{H}_2\text{SO}_4:\text{HNO}_3$ (in the volumetric ratio 4.2:3.5:1), and then rinsed and dried as described above. The cell and electrodes were transferred to the dry box, where the powdered $\text{AlCl}_3\text{-NaCl}$ mixture containing the analyte was added. The reference electrode and an absorbance cell (for 100 % T measurements) were filled with a mixture of the same composition but with the analyte absent. All electrodes were tightly secured before removing the spectroelectrochemical cell from the dry box. The 100 % T cell was evacuated and sealed according to standard laboratory practice. Both cells were preheated in an auxiliary furnace to experimental temperature.

The optical arrangement was the same as that used in multiwave-length aqueous measurements, except for the addition of the furnace windows between the 150-mm FL quartz lenses. After positioning either cell in the optical furnace, adjustment of the mirror assembly for alignment of the light beam was permitted by briefly removing the furnace windows. A 100 % T spectrum was acquired using the blank solution and stored for future absorbance calculations. The absorbance cell was then removed and the spectroelectrochemical cell positioned in the optical furnace. The remaining procedure and data acquisition were identical to aqueous studies using the RSS/computer system.

CHAPTER III

RESULTS AND DISCUSSION

Multipass spectroelectrochemistry (MPSEC) has been introduced as an optical enhancement technique for thin-layer spectroelectrochemistry in molten salt media (96-100). In this method, the optical beam is redirected through an OTE several times by a mirror assembly positioned outside the thin-layer cell.

A. Theory

For a single pass of an optical beam through the thin-layer cell shown in Figure 10, assuming a single absorbing species R is being produced under semi-infinite diffusion conditions from a nonabsorbing reactant O according to Equation 5 (p. 8), the resulting chronoabsorptometric response is given by:

$$\mathcal{A} = 2k\epsilon_R C_0^* (D_0 t / \pi)^{1/2} \quad (10)$$

where the constant k has been introduced in Equation 6 (p. 8) to account for non-planar electrode geometries and the angle α at which the light beam passes through the OTE. For example, if linear diffusion to both surfaces of a 1000 lines per inch minigrid is monitored by a light beam at normal incidence ($\alpha = 90^\circ$), then $k = 2$. If the optical beam is incident at $\alpha < 90^\circ$ with respect to the same OTE, then $k = 2/\sin \alpha$. For a coarse platinum screen (e.g., 80 mesh), the symmetrical nature of the concentration profile at each individual wire results in an optical response independent of α during periods when semi-infinite diffusion occurs. After exhaustive electrolysis of the thin-layer region, the

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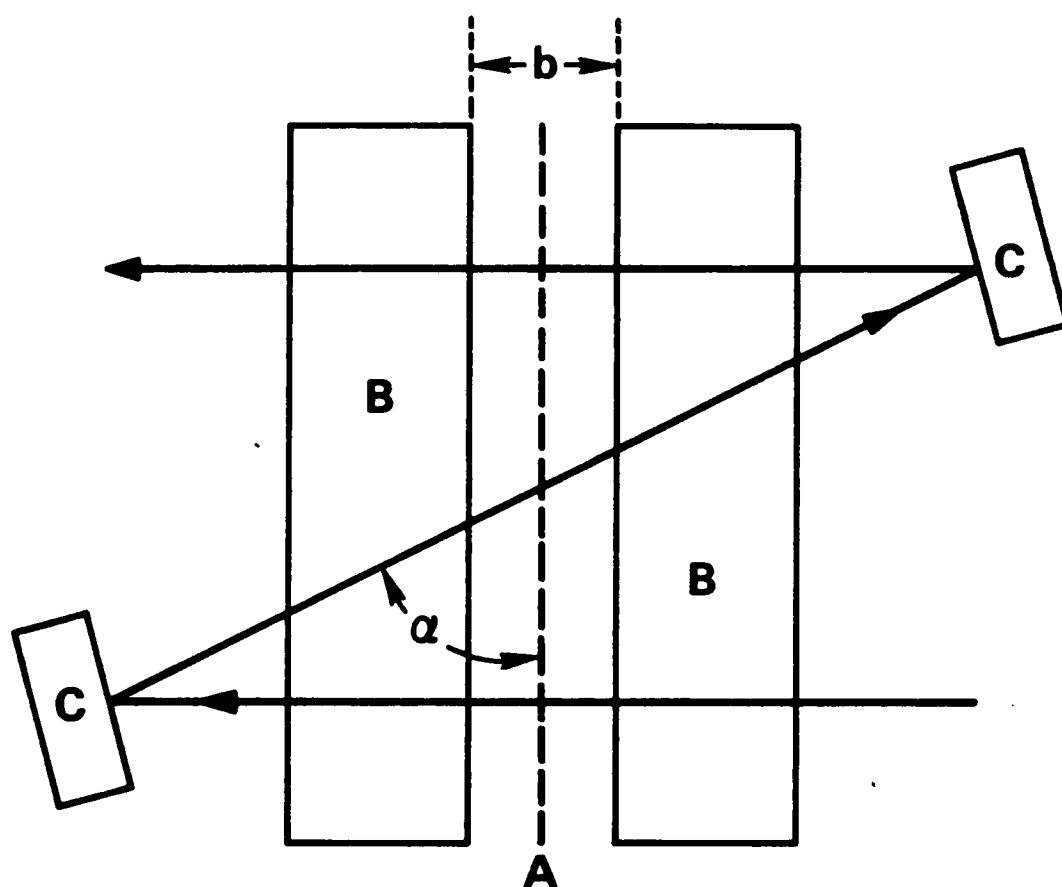


Figure 10. Multipass spectroelectrochemical arrangement with three passes of the optical beam through the thin-layer cell: (A) OTE, (B) cell windows, (C) front-surface mirrors.

steady-state absorbance $\mathcal{A}_{\infty}$ is independent of electrode geometry and is given by:

$$\mathcal{A}_{\infty} = \epsilon_R b C_R / \sin \alpha \quad (11)$$

where b is the distance between cell windows and C_R is the molar concentration of the generated species R after electrolysis.

For the MPSEC technique, multiple passes through the OTE are achieved by reflecting the light beam by two mirrors positioned on opposite sides of the thin-layer cell at an appropriate orientation. Figure 10 illustrates a three-pass arrangement. The first and third pass of the light beam through the OTE are at normal incidence, while the second is at an angle which is substantially less than 90° . The resulting time-dependent absorbance for j passes through the thin-layer cell under semi-infinite diffusion conditions is given by:

$$\mathcal{A} = 2k' \sum_{i=1}^j (1/\sin \alpha_i) \quad (12)$$

where $k' = k \epsilon_R C_0^* (D_0 t / \pi)^{1/2}$. Similarly, after complete electrolysis of the reactant, the steady-state absorbance is given by:

$$\mathcal{A}_{\infty} = \epsilon_R b C_R \sum_{i=1}^j (1/\sin \alpha_i) \quad (13)$$

The gain in optical sensitivity is defined as the ratio of the response for j passes compared to that for a single pass at normal incidence. For periods where semi-infinite diffusion is valid, the

theoretical gain is given by the ratio of Equations 12 to 10, while at steady-state, the expected gain is given by the ratio of Equations 13 to 11.

B. Aqueous Multipass Spectroelectrochemistry

1. Thin-layer Cell Evaluation

Initially, the electrochemical response of the thin-layer cell was evaluated by cyclic voltammetry of the ferricyanide system:



The cyclic voltammograms for $4.0 \times 10^{-3} \text{ M K}_3\text{Fe(CN)}_6$ in 1 M KCl and for 1 M KCl only are shown in Figure 11, and are characteristic for exhaustive electrolysis in a typical thin-layer cell (61). The E°' estimated using the equation (61):

$$E^\circ' = (E_{pc} + E_{pa})/2 \quad (15)$$

where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively, is 0.225 V vs. SCE , in very good agreement with the value obtained using a conventional cell (0.227 V vs. SCE) and that reported in the literature (101,102). The peak potential separation ΔE_p ($E_{pa} - E_{pc}$) of 150 mV at 1 M KCl indicates that a potential gradient across the OTE exists. This iR drop was observed to increase proportionately with a decrease in supporting electrolyte concentration for $[\text{KCl}] = 0.5\text{--}1.0 \text{ M}$. The increase in cathodic current for the background CV near the reverse potential is due to reduction of H^+ on platinum (103) and is not observed for a similar CV of a blank 1 M NaOH solution. The chronocoulometric response for thin-layer controlled

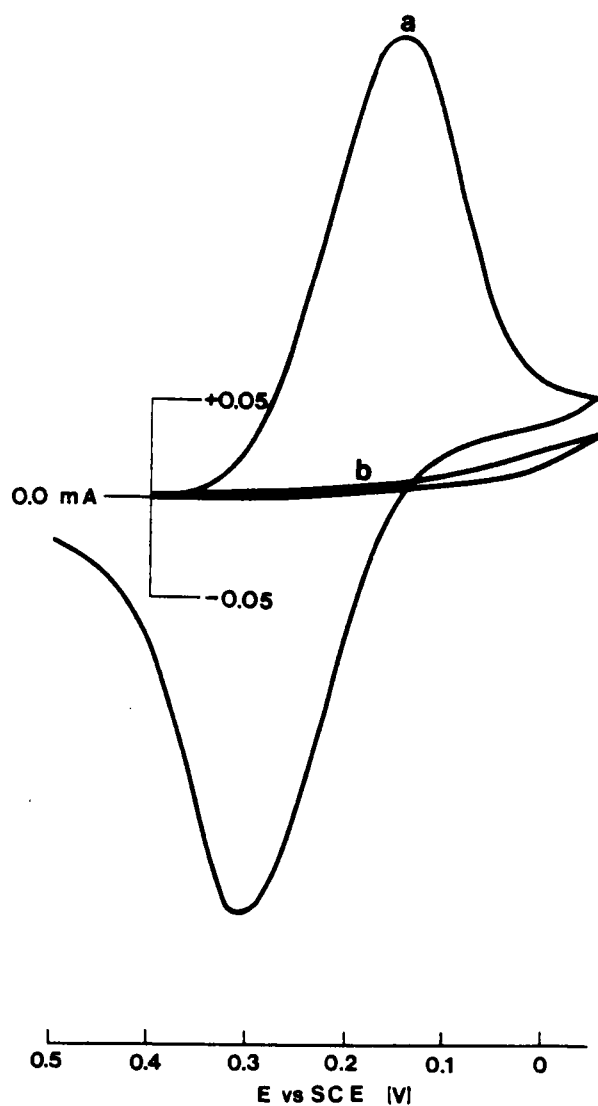


Figure 11. Test cyclic voltammograms using aqueous thin-layer cell: (a) $4.0 \times 10^{-3} \text{ M K}_3\text{Fe(CN)}_6$ in 1 M KCl , (b) 1 M KCl only; initial potential = 0.40 V vs. SCE ; initial scan direction negative; scan rate = $1 \text{ mV} \cdot \text{sec}^{-1}$.

electrolysis of the ferricyanide system is shown in Figure 12. The resulting Faradaic charge vs. time curve indicates very good isolation of the optical region from the bulk reservoir. The cell volume was determined to be 98 μl using Equation 9 (p. 10).

2. Permanganate Reduction in 1 Molar Sodium Hydroxide

The test solution selected for initial development and evaluation of the multipass technique is the one electron reduction of permanganate to manganate in 1 M NaOH at 0.20 V vs. SCE:



This redox system has been investigated previously (57,94,104,105). The reduction of 1.0×10^{-3} M KMnO_4 in 1 M NaOH was monitored using the 3-pass arrangement illustrated in Figure 10 (p. 44) and is presented in Figure 13. The permanganate adsorption band at 526 nm disappears while bands at 438 and 603 nm due to manganate appear. Well-defined isosbestic points are observed at 467 and 560 nm. Further information regarding the absorption maxima and molar absorptivities for these species may be found in the literature (106). Plots of absorbance vs. time for 438, 526, and 603 nm bands are shown in Figure 14, indicating completion of the reduction in approximately 2.5 minutes and stability of MnO_4^{2-} in this medium. Thin-layer coulometry confirmed the electron stoichiometry of the reduction ($n = 1.00 \pm 0.03$). Plots of absorbance vs. square-root of time were constructed for 438, 526, and 603 nm, for both single and 3-pass arrangements to confirm that semi-infinite diffusion was occurring. A linear relationship was observed for times less than 12.3 sec ($t^{1/2} < 3.5 \text{ sec}^{1/2}$). This observation is

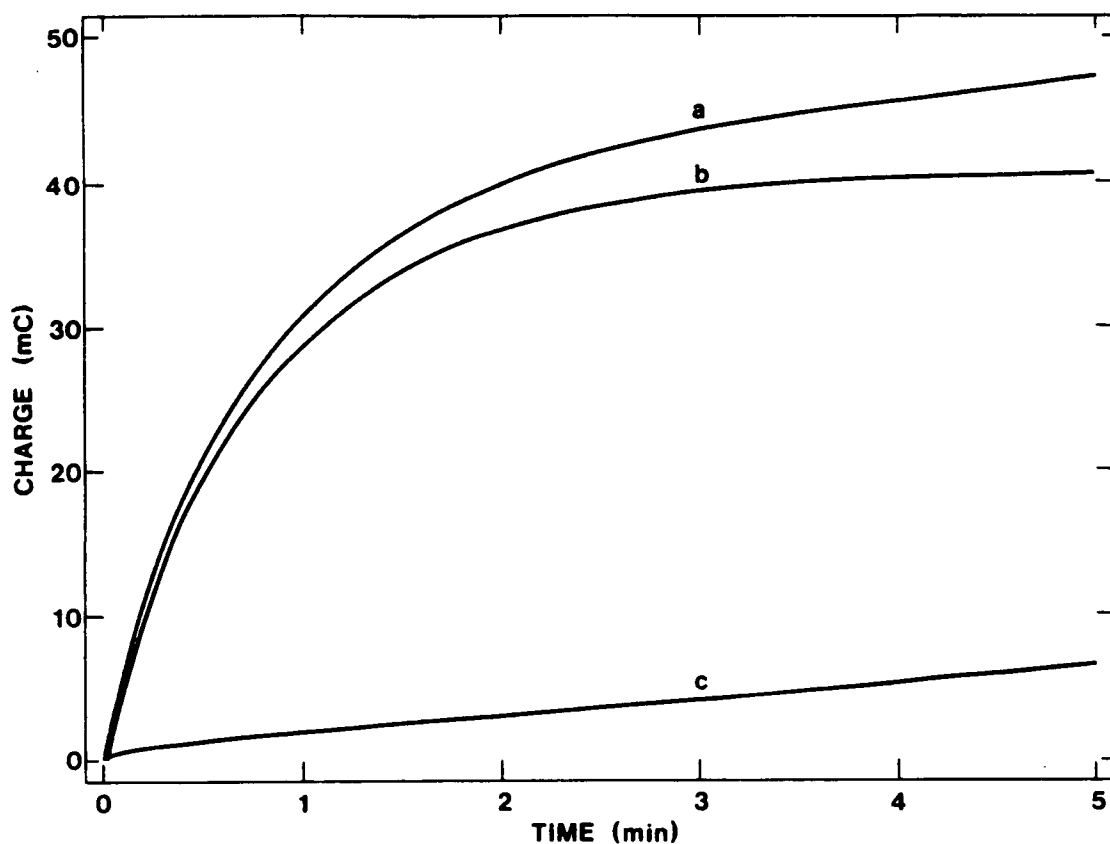


Figure 12. Chronocouloulogram for reduction of ferricyanide using aqueous thin-layer cell: (a) total charge, (b) Faradaic charge, and (c) background charge; potential stepped from 0.40 to 0.00 V vs. SCE; cell volume = 98 μ l; $K_3Fe(CN)_6$ concentration = 4.0×10^{-3} M in 1 M KCl.

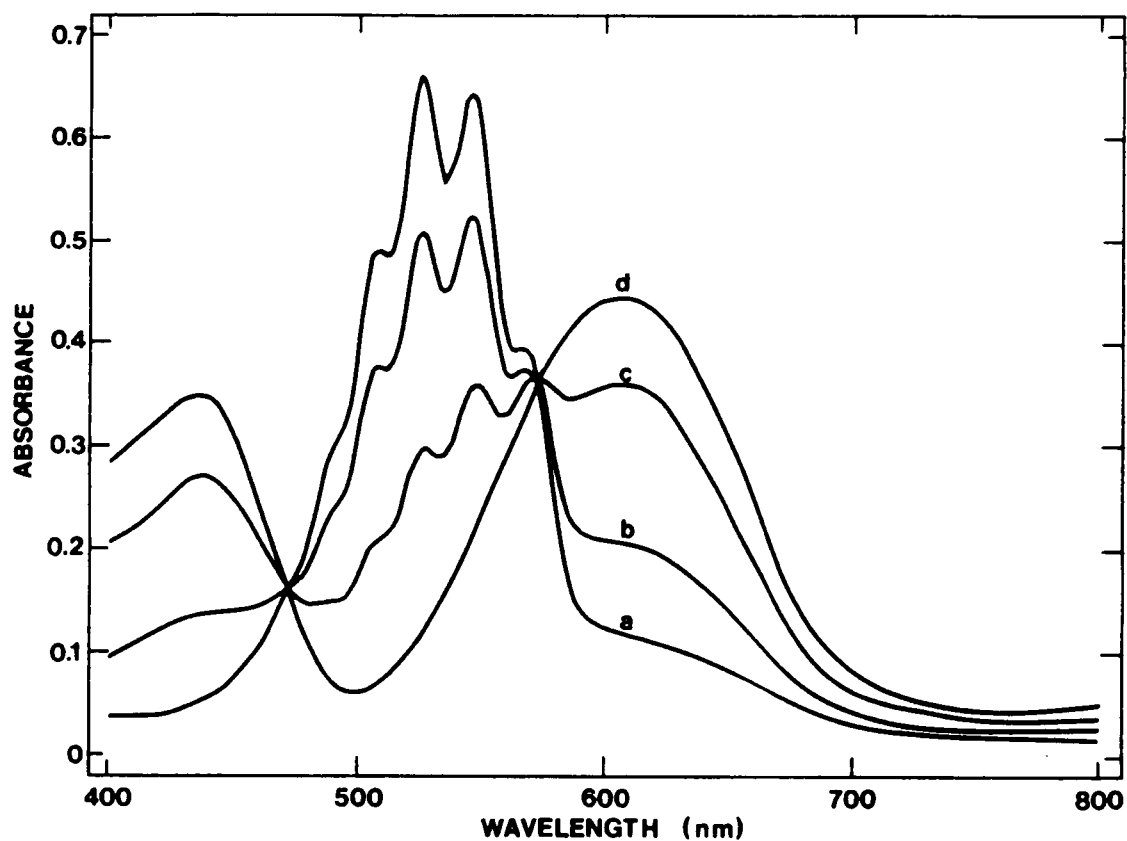


Figure 13. Reduction of permanganate using MPSEC (3-pass) arrangement; time after initiation of the reduction (sec): (a) 0, (b) 5, (c) 24, (d) 240; potential stepped from 0.40 to 0.20 V vs. SCE; KMnO_4 concentration = 1.0×10^{-3} M in 1 M NaOH.

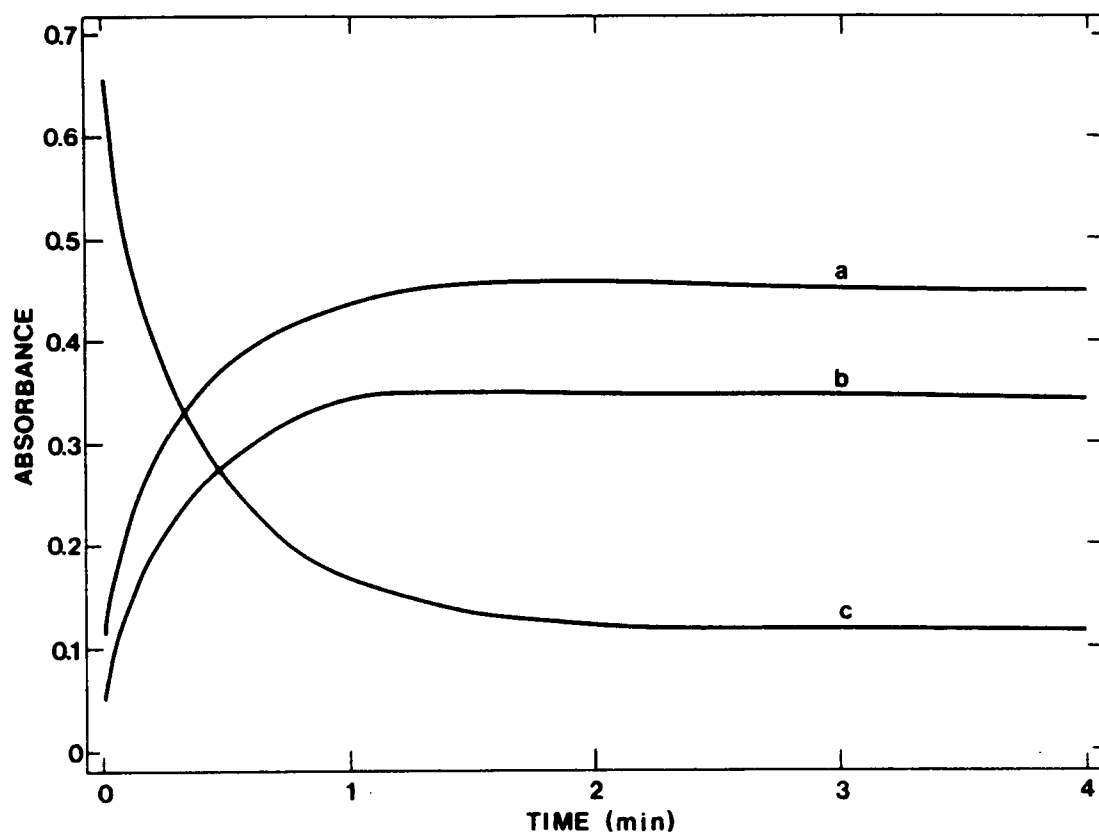


Figure 14. Absorbance vs. time for reduction of permanganate using MPSEC (3-pass) arrangement: (a) 603 nm, (b) 438 nm, (c) 526 nm; potential stepped from 0.40 to 0.20 V vs. SCE; KMnO_4 concentration = 1.0×10^{-3} M in 1 M NaOH.

in agreement with a predicted overlap of the diffusion layer from adjacent strands of the platinum screen as estimated from (53):

$$C(x,t)/C^b = 0.5 = \text{erf}[x/2(Dt)^{1/2}] \quad (17)$$

where erf is the error function (107), $D = 1.0 \times 10^{-5} \text{ cm}^2\cdot\text{sec}^{-1}$, and x = one-half the distance between adjacent strands. The average gain in optical sensitivity for the 3-pass arrangement resulting from analysis of all three wavelengths is 2.99, in excellent agreement with the theoretical value of 3 when semi-infinite diffusion is valid. After complete electrolysis, a comparison of the absorbance for a single and three-pass arrangement was made. Because of difficulties associated with the fabrication of a thin-layer cell with exactly parallel windows, the b term of Equation 13 (p. 45) must be included inside the summation sign. These individual b_i values were determined from Beer's Law plots for each region of the thin-layer cell using a conventional ($\alpha = 90^\circ$) single-pass arrangement. Deviations of $\pm 2.4\%$ from the window spacing calculated using OTE and space dimensions (0.084 cm) were observed. By incorporating the measured b_i values and $\alpha = 64^\circ$ (as estimated using Snell's Law) into Equation 13 (p. 45), the predicted gain is 3.11. The observed gain (3.17) agreed within 2 % of this value.

To determine the practical limit for the number of passes in a MPSEC experiment, the continuum source and array detector were replaced with a helium-neon laser and photodiode. Although five passes were achieved, it became increasingly difficult to discriminate between the analytical beam and stray reflections. Plots of absorbance vs. square-root of time, although linear for $t < 12.3 \text{ sec}$, exhibited gains significantly higher than predicted values. One explanation for this

observation is an alteration in the position of the optical beam resulting from a change in refractive index of the solution due to heating by the laser source (108), which is further compounded by each pass at $\alpha < 90^\circ$. Because of primary interest in multiwavelength analysis, further development of the technique using a highly collimated and monochromatic source was not pursued.

C. Molten Salt Multipass Spectroelectrochemistry

1. Thin-layer Cell Evaluation

After replacement of the Al(III)/Al reference electrode with a SCE, the electrochemical response of the molten salt cell was determined similarly to the aqueous cell. Cyclic voltammograms for $4 \times 10^{-3} \text{ M}$ $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl and for the supporting electrolyte only are shown in Figure 15, and exhibit a significant deviation from "ideal" thin-layer behavior. While E°' was determined to be 0.228 V vs. SCE using Equation 15 (p. 46), in agreement with earlier results, the peak potential separation was observed to be 0.255 V , indicating a rather large iR drop across the OTE. As with the aqueous cell, ΔE_p was dependent upon supporting electrolyte concentration for $[\text{KCl}] = 0.5\text{-}1.0 \text{ M}$. The chronocoulometric response for controlled potential electrolysis of the ferricyanide solution and a blank KCl solution is shown in Figure 16. The Faradaic charge vs. time curve indicates that there is a considerable flux of electroactive species to the OTE even ten minutes after the potential step. This period is substantially longer than the time calculated for the diffusion layer to completely fill the 0.1 cm optical region (3.3 minutes) using Equation 17 (p. 52), indicating diffusion of reactant to the OTE from outside the thin-layer compartment.

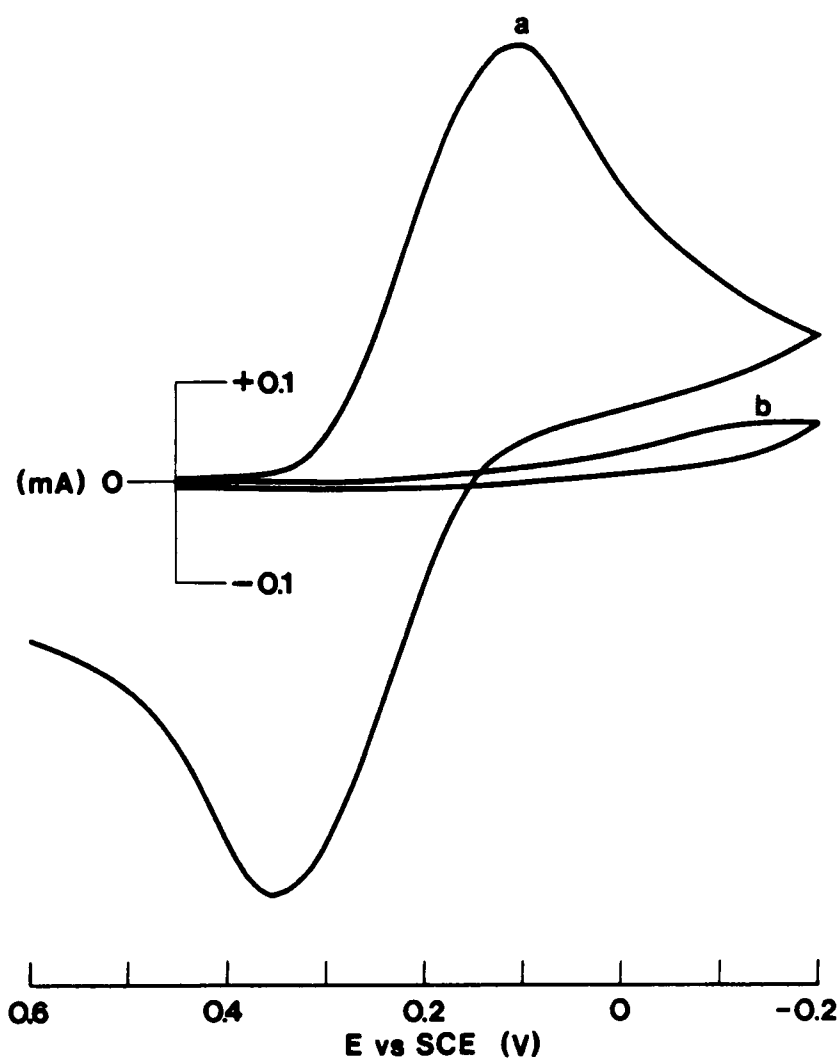


Figure 15. Test cyclic voltammograms using molten salt thin-layer cell:
 (a) $4 \times 10^{-3} \text{ M K}_3\text{Fe(CN)}_6$ in 1 M KCl , (b) 1 M KCl
 only; initial potential = 0.45 V vs. SCE ; initial scan
 direction negative; scan rate = $1 \text{ mV} \cdot \text{sec}^{-1}$.

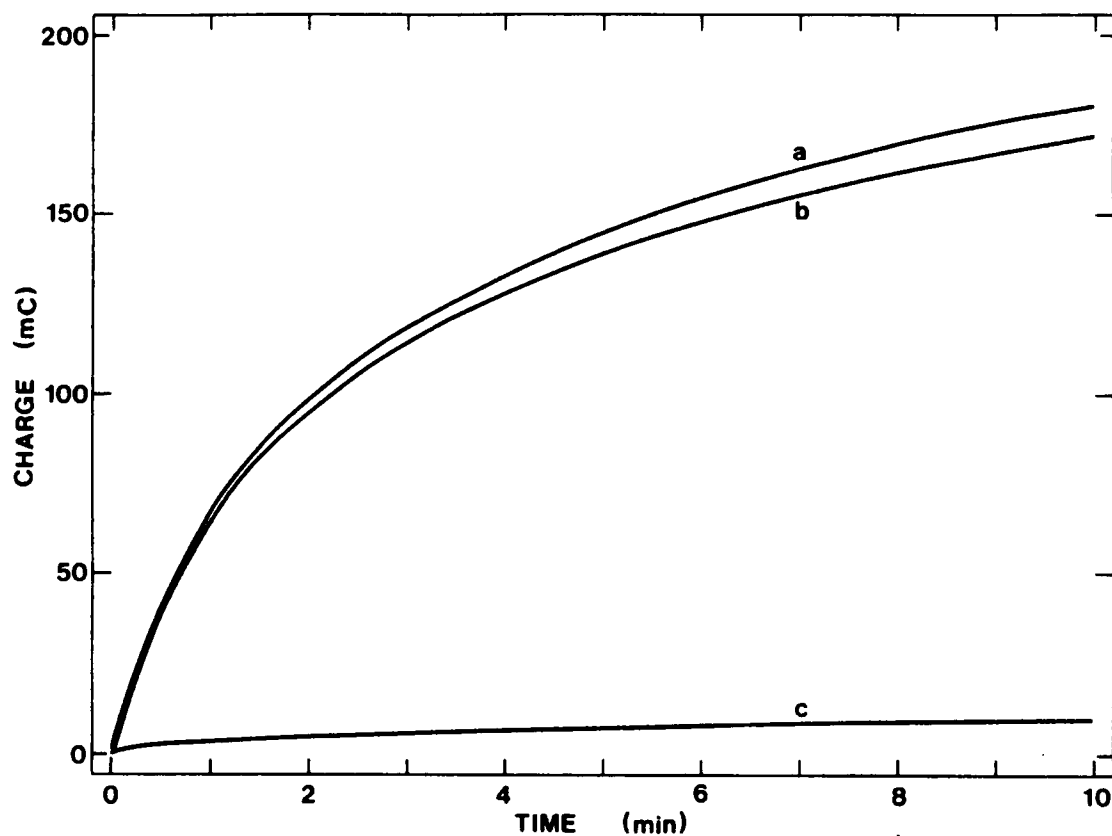


Figure 16. Chronocouloulogram for reduction of ferricyanide using molten salt thin-layer cell: (a) total charge, (b) Faradaic charge, (c) background charge; potential stepped from 0.45 to -0.20 V vs. SCE; $\text{K}_3\text{Fe}(\text{CN})_6$ concentration = 4.0×10^{-3} M in 1 M KCl.

Unfortunately, this "edge" effect precluded the determination of n -values for molten salt redox systems by thin-layer coulometry.

2. Sulfur Oxidation in Molten 63/37 AlCl_3 - NaCl

Interest in the electrooxidation of sulfur in molten chloroaluminates results primarily from the development of the rechargeable molten salt cell (109-113):



The oxidation of sulfur in molten AlCl_3 - NaCl has been investigated by electrochemical methods (114-120). Recently, the application of thin-layer transmission spectroelectrochemistry in the UV-visible region has illustrated the complexity of this redox system (91,121). The MPSEC technique was applied to the oxidation of sulfur in molten chloroaluminates to evaluate the technique with respect to molten salt studies and to obtain any additional spectral information which may be useful in understanding the system. Investigation was focused upon the initial oxidation of S_8 in the melt, resulting in sulfur species of low formal charge.

The cyclic voltammogram of 1.0×10^{-2} molal sulfur (as the monomer) in 63/37 AlCl_3 - NaCl at 150 °C taken immediately prior to spectroelectrochemical analysis is shown in Figure 17. The peak potentials and relative current magnitudes agree well with published data (118). The corresponding results for a 3-pass MPSEC investigation of the first oxidation wave of this system are shown in Figure 18. The spectrum for a single pass experiment for the same cell is included. Comparison with single pass measurements at normal incidence indicates

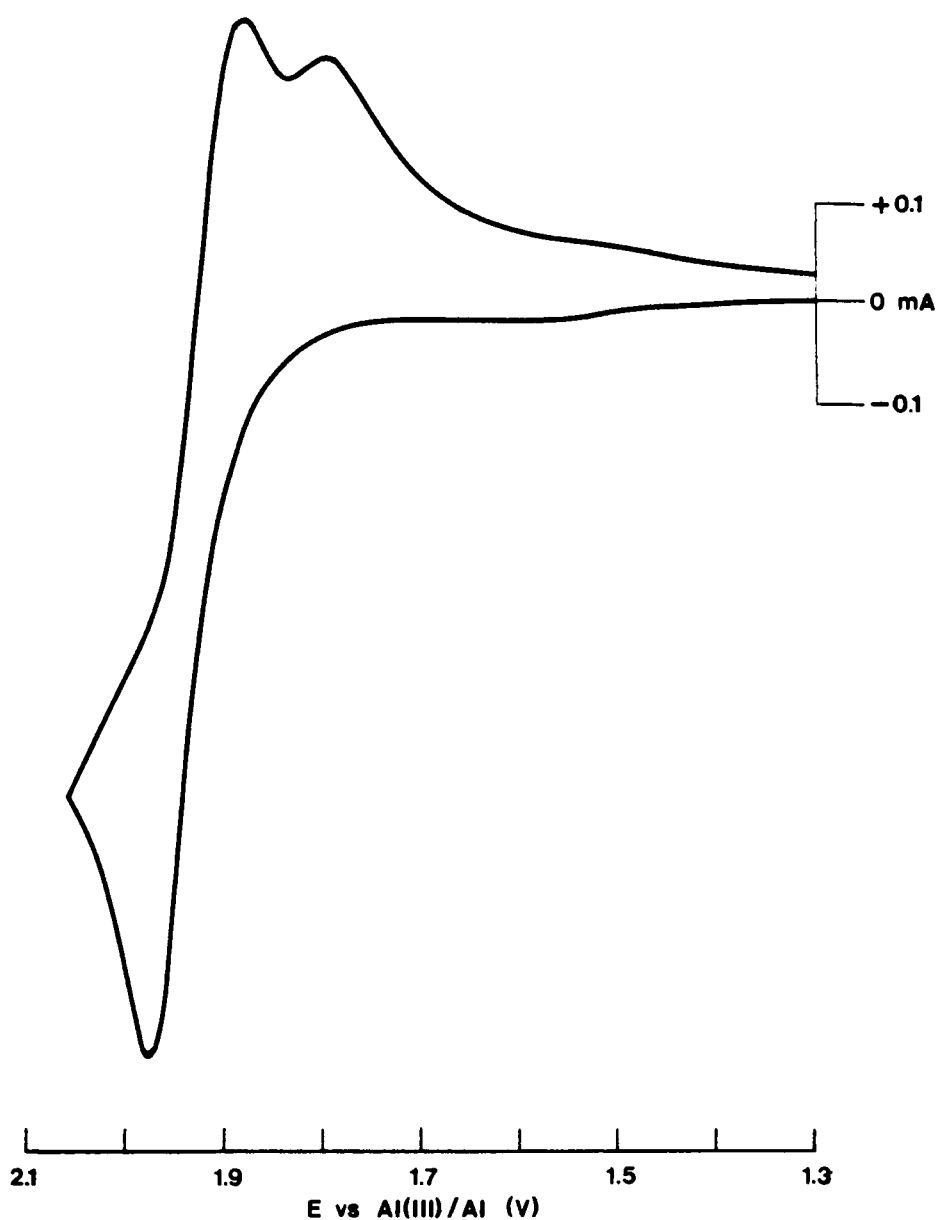


Figure 17. Cyclic voltammogram of sulfur in 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150°C : initial potential = 1.30 V vs. Al(III)/Al in 63/37 $\text{AlCl}_3\text{-NaCl}$; initial scan direction positive; scan rate = $50\text{ mV}\cdot\text{sec}^{-1}$; platinum electrode area = 0.10 cm^2 ; initial sulfur concentration = 1.0×10^{-2} molal (as the monomer).

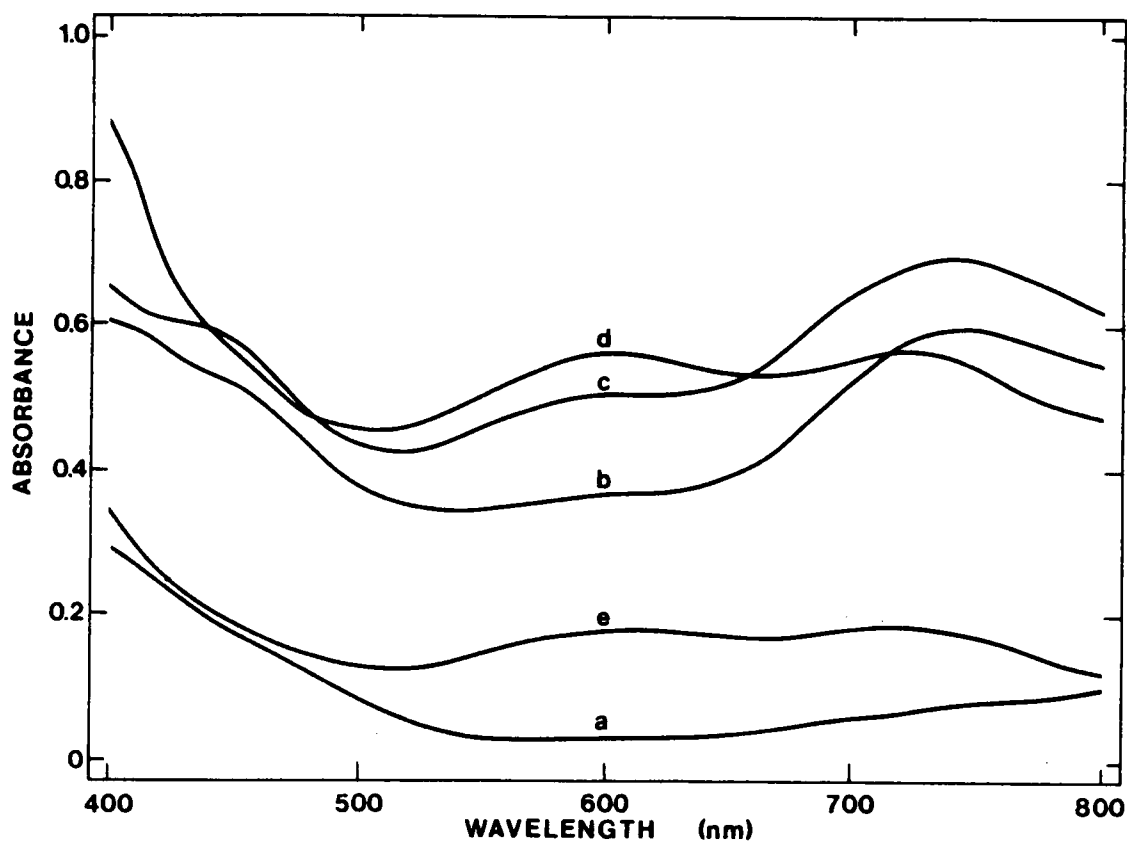


Figure 18. MPSEC (3-pass) absorption spectra of the products of the first sulfur oxidation wave after 10 minutes; E_{applied} (V) vs. Al(III)/Al : (a) 1.30; (b) 1.60; (c) 1.70; (d) 1.80; (e) 1.80, for single pass at normal incidence ($b = 0.1$ cm); sulfur concentration = 1.0×10^{-2} molal (as the monomer) in 63/37 AlCl_3 -NaCl at 150 °C.

an average gain of 3.0 for these studies. As reported in an earlier single pass study using a higher sulfur concentration and longer path-length (121), absorption bands with maxima at ~ 600 and ~ 730 nm appear when the potential applied to the OTE is varied between 1.60 and 1.80 V vs. the Al(III)/Al reference electrode. In addition, a band at ~ 440 nm is observed for $E_{\text{applied}} = 1.70$ V vs. Al(III)/Al. This spectral feature was not apparent from the previous single pass work and had been reported as a weak shoulder. The E_{applied} values used here are 0.1 V more positive than those used in the earlier study which resulted in a similar optical response. This result is attributed to the high iR drop of the MPSEC cell, arising from the placement of the Al(III)/Al reference electrode in the MPSEC cell out of the direct current path (as compared to the earlier cell arrangement) and significant diffusion currents due to poor isolation of the OTE from the bulk solution. This is reasonable if one considers the results of the initial electrochemical evaluation of the cell. A detailed analysis of the chronocoulometric response of the cell using the 4 mM ferricyanide system (Figure 16, p. 55) indicates a diffusion current of $\sim 167 \mu\text{A}$ (as estimated from dQ/dt) 5-10 minutes after application of the potential step. Using Ohm's Law, an iR drop of 0.128 V (as estimated from $\Delta E_p/2$) would result from an uncompensated resistance (between the reference and working electrodes) of ~ 763 ohms. The previously obtained UV-visible absorption and electron spin resonance (ESR) spectroelectrochemical results for the first oxidation step of this system (121) were rationalized in terms of a complex electrochemical and chemical reaction sequence:



In a more recent publication (122), steady-state UV-visible absorption and ESR spectra and potentiometric measurements indicate that the important low-oxidation sulfur species in acidic chloroaluminate melts are S_8^+ , S_4^+ , and S_{12}^{2+} . It was found from computer deconvolution of MPSEC steady-state absorption spectra, using the molar absorptivity data taken from Reference 122 (Table II) that the spectra in Figure 18 (p. 58) may be interpreted in terms of S_8^+ , S_4^+ , and S_{12}^{2+} only. These results are presented in Table III. For $E_{\text{applied}} = 1.60 \text{ V vs. Al(III)/Al}$, the predominant sulfur species is S_8^+ (89%), with only a small fraction (11%) present as S_{12}^{2+} . There is no evidence for the presence of S_4^+ or S_8 at this potential. Further oxidation at $E_{\text{applied}} = 1.70 \text{ V}$ results in the presence of all three sulfur species. S_{12}^{2+} and S_4^+ are present at approximately the same concentration and account for most (86%) sulfur species. The remaining sulfur is present as S_8^+ . At $E_{\text{applied}} = 1.80 \text{ V}$, S_4^+ is the predominant sulfur species (83%) with S_{12}^{2+} also present (17%); there is no evidence for S_8^+ at this potential. At $E_{\text{applied}} = 1.90 \text{ V}$, essentially all sulfur is present as S_4^+ .

Table II. Molar Absorptivities^a of Low Oxidation Sulfur Species
at Selected Wavelengths^b

Sulfur Species	Wavelength (nm)					
	440	500	550	600	670	740
S_4^+	331	257	333	386	327	231
S_{12}^{2+}	1059	909	1172	1365	1549	1921
S_8^+	856	605	539	514	613	896

^aIn $M^{-1}\cdot cm^{-1}$.

^bCalculated from Fehrmann, R.; Bjerrum, N. J.; Pedersen, E.
Inorg. Chem. **1982**, 21, 1497 (Figure 10).

Table III. Relative Concentration of Sulfur Species Present in
63/37 $\text{AlCl}_3\text{-NaCl}$ at 150 °C as Function of E_{applied}

E_{applied} [V <u>vs.</u> Al(III)/Al]	$\% \text{S}_8^+$	$\% \text{S}_{12}^{2+}$	$\% \text{S}_4^+$
1.60	89	11	--
1.70	14	43	43
1.80	--	17	83
1.90	--	--	100

An overall reaction sequence suggested by this interpretation of MPSEC results is given by:



The unequivocal confirmation of this simpler electrooxidation scheme should probably await the ESR hyperfine splitting measurements of the sulfur radical cations formed; such measurements to date have been unsuccessful (121,122).

3. Niobium (III) Reduction in Molten 65/35 AlCl₃-NaCl

The electroreduction of niobium pentachloride in molten chloroaluminates has been studied (123,124), and an ECE mechanism resulting in the formation of Nb₂⁶⁺ has been proposed for the first reduction wave in acidic chloroaluminate melts (123):



While thin-layer SEC investigations in the UV region have been reported (91), results in the visible region have provided little information concerning this reduction, primarily due to an absence of pronounced spectral features from 400 to 800 nm.

Previous SEC study of the second reduction wave using a single pass arrangement has indicated the presence of weak absorption bands in the visible region (94). The MPSEC technique was applied to study spectral features in the visible region associated with this reduction.

Prior to multipass SEC analysis of $1.0 \times 10^{-2} \text{ M NbCl}_5$ in 65/35 $\text{AlCl}_3\text{-NaCl}$ at 175°C , cyclic voltammetry was performed. The resulting CV agrees well with previously reported curves (123) and is presented in Figure 19. Initially, the potential applied to the OTE was stepped from 1.50 V to 0.60 V vs. Al(III)/Al in 65/35 $\text{AlCl}_3\text{-NaCl}$. After the cathodic current reached background levels and the absorption spectra ceased to change, indicating completion of the first reduction sequence, the potential was then stepped to 0.10 V; and spectral data acquisition was simultaneously begun.

The results obtained for a 3-pass MPSEC and single pass investigation of the second reduction wave of NbCl_5 in 65/35 $\text{AlCl}_3\text{-NaCl}$ at 175°C are shown in Figure 20. The spectra obtained for the three passes are much better defined than those obtained after a single pass and indicate a gain of ~ 3.0 . From steady-state spectra acquired 15 minutes after the potential step, a broad band at 540 nm and two well-defined isosbestic points at 600 and 750 nm are observed for $E_{\text{applied}} = 0.1 \text{ V vs. the } \text{Al(III)/Al} \text{ reference electrode}$. The band present initially at 630 nm disappears at this potential. There is no evidence for the previously suspected (94) isosbestic point at $\sim 440 \text{ nm}$.

These results indicate the formation of a soluble low oxidation state species of niobium, such as Nb_3^{8+} , and support the proposed reduction (124):

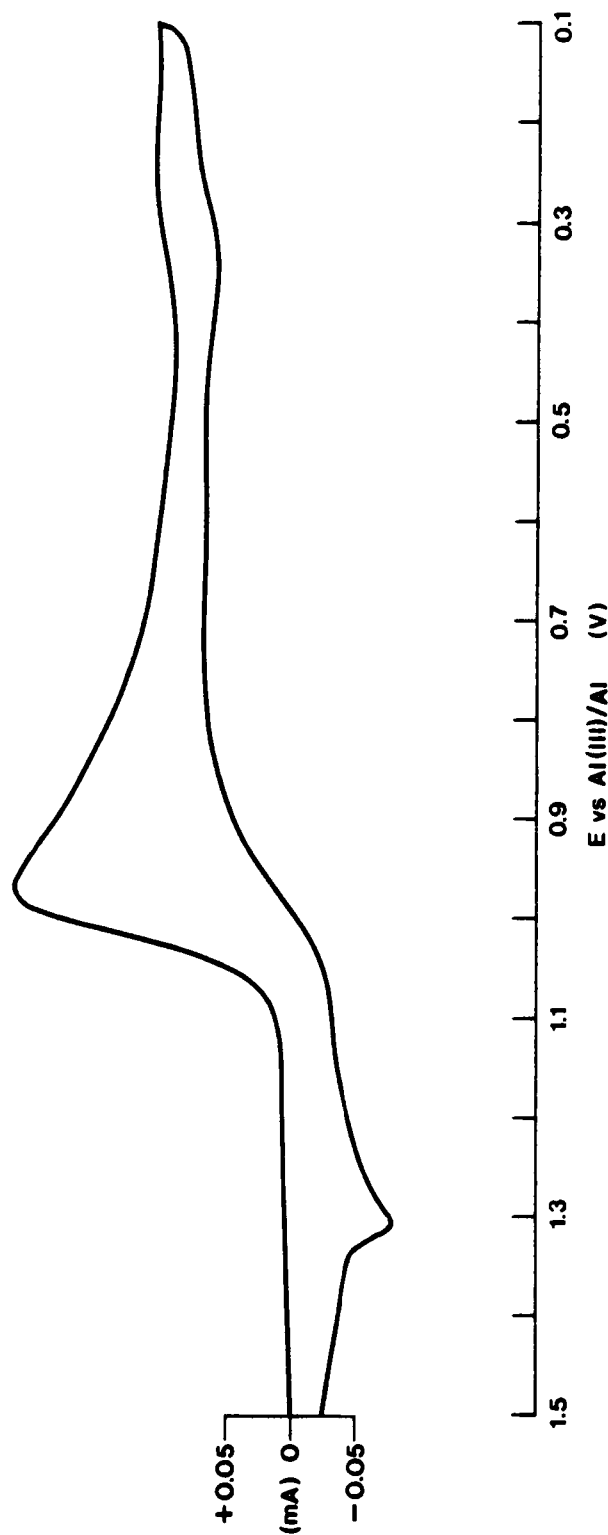


Figure 19. Cyclic voltammogram of niobium pentachloride in 65/35 $\text{AlCl}_3\text{-NaCl}$ at 175 °C: initial potential = 1.50 V vs. Al(III)/Al in 65/35 $\text{AlCl}_3\text{-NaCl}$; initial scan direction negative; scan rate = $50 \text{ mV}\cdot\text{sec}^{-1}$; platinum electrode area = 0.10 cm^2 ; NbCl_5 concentration = $1.0 \times 10^{-2} \text{ M}$.

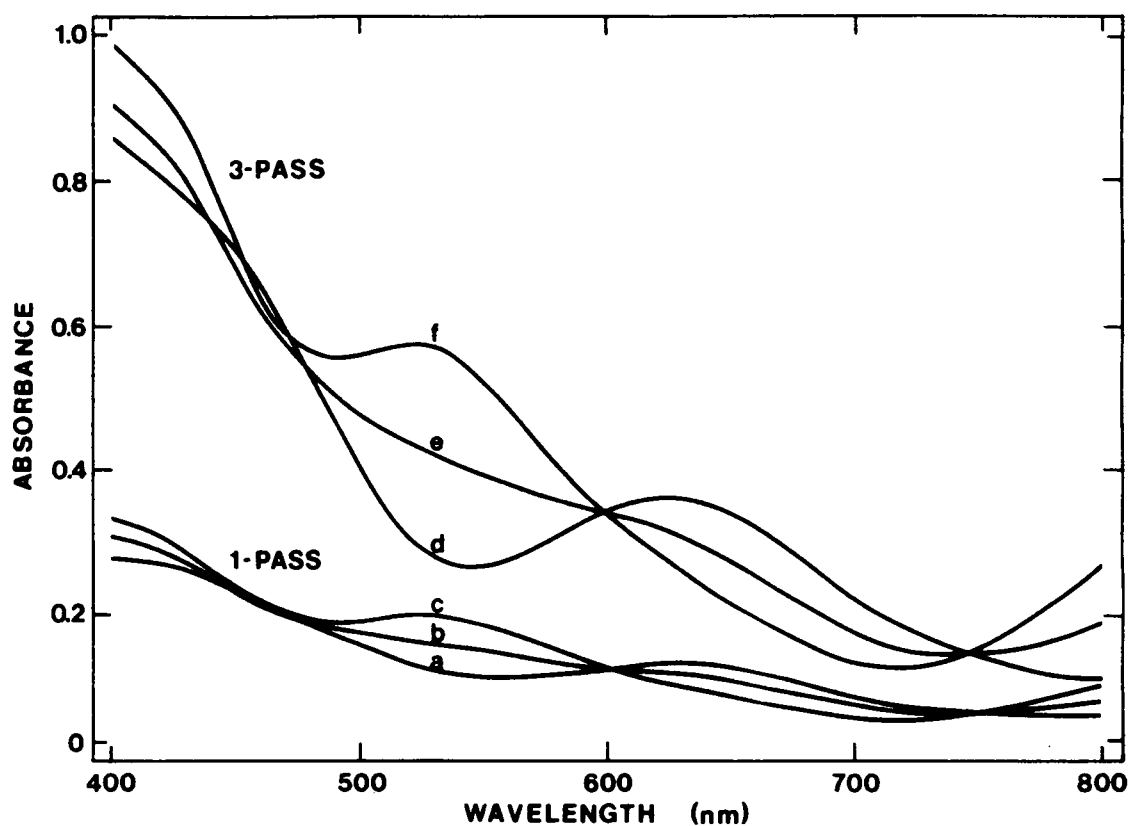


Figure 20. MPSEC (3-pass) and single pass absorption spectra of the product of the second Nb(V) reduction wave; time after potential stepped to 0.10 V vs. Al(III)/Al (minutes): (a,d) 0, (b,e) 4, (c,f) 15; $b = 0.1$ cm; NbCl_5 concentration = 1.0×10^{-2} M in 65/35 AlCl_3 -NaCl at 175 °C.



The visible spectra of this cluster ion in solution have not been previously reported.

CHAPTER IV

CONCLUSION

The MPSEC technique has been shown to be a useful optical enhancement method for studies in molten salts or similar media whose very nature precludes the application of many other approaches introduced to increase optical sensitivity. Due to the use of external optics, the enhancement is unaffected by changes in electrode reflectivity; the method is therefore considerably more tolerant of highly corrosive systems than internal reflectance methods. Alternative external optical systems based either upon right-angle prisms operated in a Porro configuration (redirection of the beam 180° using two total internal reflections) or reflective coatings on the cell windows were considered for achieving this effect, but these do not offer the flexibility of the mirror approach presented here. The MPSEC method may be performed with a low power continuum source, permitting simultaneous multiwavelength analysis. While the net gain in optical sensitivity is directly proportional to the number of passes through the cell, the accompanying stray reflections and attenuation of the light beam, resulting from the unavoidable presence of interfaces between media of different refractive indices, ultimately limit the gain to a practical value of 3-5. For multiple passes where α is substantially less than 90° , consideration should be given to a possible alteration in refractive index of the solution, especially when an intense source such as laser is used to monitor a strong absorber. The resulting thermally-induced change in refractive index alters the alignment of the beam, producing absorbances which are not related directly to concentration.

This is not a factor when using a low power continuum source. Perhaps the most significant advantage of the use of external optics is the ease with which one can convert from a high optical gain to a low optical gain experiment. In the study of redox systems with multiple steps, especially those involving species with greatly varying absorptivities, this allows the study of more than one electrochemical wave using the same cell and contents without a change in solute concentration. This advantage is more fully appreciated when operating with systems such as molten salts, where such a routine change in solute concentration usually encompasses a period of several days.

PART II
SPECTROSCOPIC AND ELECTROCHEMICAL INVESTIGATIONS
OF IRIIDIUM CARBONYLS

CHAPTER V

INTRODUCTION

The increasing costs and uncertainty of future petroleum supplies have revived interest in synthesis gas chemistry, particularly in technology related to conversion of coal to usable chemicals and fuel. Such efforts are directed toward the utilization of a vast domestic coal reserve and decreasing the dependence upon foreign energy resources.

Included in this renewed interest is the Fischer-Tropsch reaction, the catalytic reduction of carbon monoxide by hydrogen (both coal-derived gases) to produce hydrocarbons (125). In addition to advances in traditional Fischer-Tropsch chemistry using heterogeneous catalysts (126-129), there has been much interest in the homogeneous reduction of carbon monoxide (130-141). Advantages of homogeneous catalysts over their heterogeneous counterparts include the potential for increased product selectivity, greater control at the catalytic site, and greater tolerance to poisoning from sulfur-containing feedstocks.

A. Fischer-Tropsch Catalysis Using $\text{Ir}_4(\text{CO})_{12}$ in Molten $\text{AlCl}_3\text{-NaCl}$

Muettert et al. (142) discovered that dodecacarbonyltetra-iridium, $\text{Ir}_4(\text{CO})_{12}$, in molten 63/37 $\text{AlCl}_3\text{-NaCl}$ at 180 °C catalyzes the conversion of CO and H_2 at 1 atm to light hydrocarbons (primarily ethane). In a later study of the same system under flow conditions, heavier hydrocarbons ($\text{C}_3\text{-C}_6$) were observed along with some methane and ethane (143). Oxygenated or chlorinated products, typical of homogeneous catalysis, were not detected in either of these investigations.

In a recent detailed kinetic study of the Fischer-Tropsch activity of $\text{Ir}_4(\text{CO})_{12}$ in molten $\text{AlCl}_3\text{-NaCl}$, Collman et al. (144) identified methane, ethane, and chloromethane as the major carbon-containing products in both continuous flow and recycle experiments. Similar catalytic activity was observed for chlorotricarbonyliridium(I), $[\text{IrCl}(\text{CO})_3]_n$, suggesting that an iridium chlorocarbonyl complex may be the catalytic species in the melt.

Walters also investigated carbon monoxide reduction by $\text{Ir}_4(\text{CO})_{12}$ in molten $\text{AlCl}_3\text{-NaCl}$ (145). Primarily methane and ethane were observed using a batch reaction system. However, in a recycle-flow system, chloromethane was detected in addition to methane and ethane. These results indicate that chloromethane may be an intermediate product which is converted to hydrocarbons upon increased contact time with the catalytic system.

B. Proposed Research

The observation of Fischer-Tropsch catalytic activity by $\text{Ir}_4(\text{CO})_{12}$ (or a compound derived from it) in molten acidic $\text{AlCl}_3\text{-NaCl}$ is significant for several reasons: (a) it appears that the strong Lewis acidity of the melt allows the reduction of CO to occur at very low pressures, (b) the products of the reaction are saturated hydrocarbons and not oxygenated species, and (c) this reaction may offer some of the first chemical evidence for the similarity of metal clusters to metal surfaces in an actual catalytic system. No previous work has been directed toward the identification of the catalytic species.

This part of the dissertation is concerned with the application of spectroscopic and electrochemical methods to the determination of the iridium species resulting from addition of $\text{Ir}_4(\text{CO})_{12}$ to molten 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO and CO-H_2 (1:3). The analytical techniques used in this study include UV-visible spectroscopy, Raman spectroscopy, infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry, and normal pulse voltammetry.

CHAPTER VI

EXPERIMENTAL

A. Materials

Dodecacarbonyltetrairidium, more commonly known as iridium carbonyl, $\text{Ir}_4(\text{CO})_{12}$, and chlorotricarbonyliridium (I), $[\text{IrCl}(\text{CO})_3]_n$, were purchased from Strem Chemicals Inc. (Newburyport, MA) and were used without further purification. The physical properties of both compounds as given by the manufacturer are listed in Table IV. Ultra high purity (UHP) carbon monoxide (99.8%) and carbon monoxide-hydrogen gas mixture (1:3 mole ratio) were purchased from Air Products (Allentown, PA). Prepurified nitrogen (99.998%), silane (3% in hydrogen), and argon were purchased from MG Scientific Gases (Knoxville, TN).

ACS reagent grade acetonitrile, chloroform, and cyclohexane were purchased from Fisher Scientific Co. (Fair Lawn, NJ). Tetraethylammonium chloride (TEAC) was obtained from J. Q. Chambers at UTK.

Aluminum chloride and sodium chloride purification and melt preparation have been described in Part I.

B. Apparatus

1. Sample Isolation-Introduction Apparatus

Preliminary UV-spectroscopic studies of $\text{Ir}_4(\text{CO})_{12}$ in 63/37 AlCl_3 - NaCl under CO-H_2 (1:3) involved suspending the sample in a glass tube directly above the solid chloroaluminate during heating, and then introducing the carbonyl to the melt at 150 °C. This method of introduction was similar to that used in a recent catalytic study where

Table IV. Properties of Iridium Carbonyls^a

Property	Iridium Carbonyl	Chlorotricarbonyliridium (I)
Formula	$\text{Ir}_4(\text{CO})_{12}$	$[\text{IrCl}(\text{CO})_3]_n$
Molecular Weight (gfw):	1105.1	311.71 ^b
Color and Form:	yellow solid	brown solid
M.P. (°C):	230 ^c	235 ^c
Stability:	air-stable	air-stable
Typical Analysis (%C):	12.7	12.0

^aCatalog No. 10 (1982), Strem Chemicals, Inc.

^bAs monomer.

^cDecomposes.

the $\text{Ir}_4(\text{CO})_{12}$ was suspended above the melt in a hole bored in a Teflon stirring bar (144). Different results were obtained for solutions prepared by mixing the carbonyl with solid $\text{AlCl}_3\text{-NaCl}$ prior to heating (premix sample introduction).

Due to the apparent dependence upon initial contact with the chloroaluminate in the solid vs. liquid state, an apparatus to provide a more efficient means of isolating the compounds from the melt prior to introduction was developed and is presented in Figure 21. This device was fabricated from a 90° high vacuum Teflon stopcock (Part No. 8195-45, Ace Glass Inc.) and a 5-mm I.D. Flickit valve (Part No. 8200-05, Ace Glass Inc.), both equipped with Viton O-rings.

The Flickit valve is designed such that a 180° turn of the Teflon plug retracts it from the tube pathway, allowing clear passage through the stem. The lower 7-mm O.D. Pyrex stem of this apparatus was attached to the molten salt cell by a No. 7 threaded glass connector (Part No. 5027-05, Ace Glass Inc.).

The solute was positioned between the valve and stopcock in a 4-mm O.D. Pyrex tube supported by a glass-encased iron rod and external magnet. With the Flickit valve slightly opened, the entire cell may be evacuated through the 1/4-inch side arm of the vacuum stopcock and then pressurized with the desired fill gas. The valve and stopcock were then closed, isolating the sample from the solid $\text{AlCl}_3\text{-NaCl}$ mixture. After the melt is heated to the desired temperature, the Flickit valve is completely opened and the sample is lowered into the cell by removing the external magnet. The two-piece sample holder disconnects upon contact with the liquid, and the solute is quickly dispersed throughout the melt.

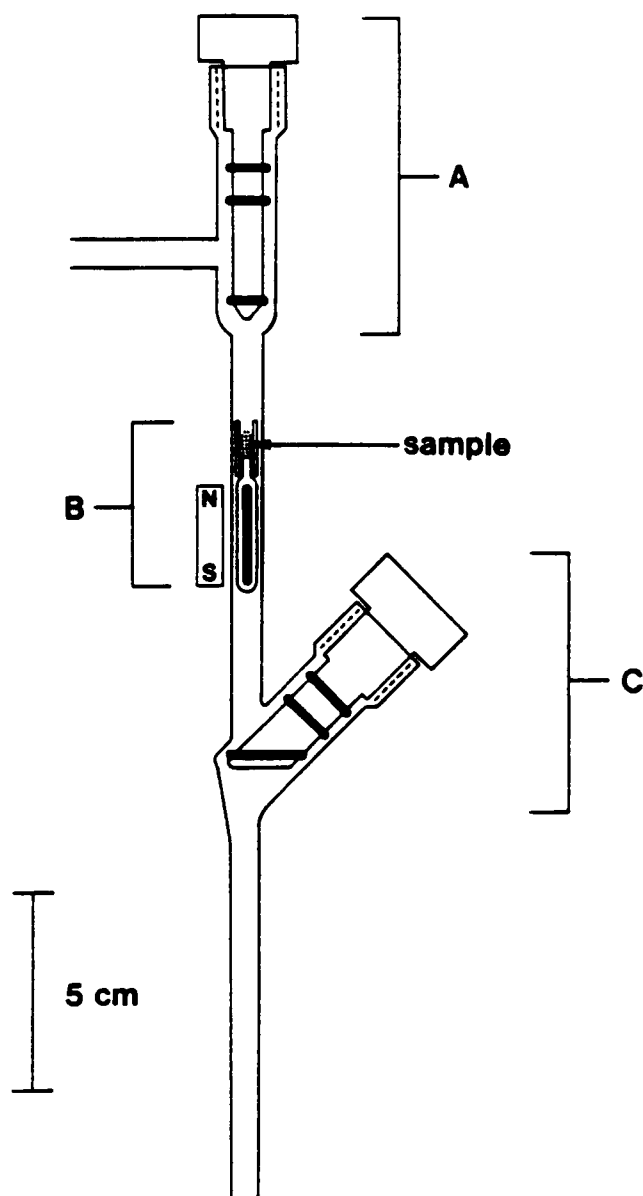


Figure 21. Sample isolation-introduction apparatus: (A) 90° high vacuum Teflon stopcock, (B) sample container and external magnet, (C) Flickit valve.

The solution may be stirred by further movement of the glass-encased iron rod with the external magnet.

Additionally, this apparatus allows the acquisition of a more accurate reference measurement, such as a 100 % T spectrum or a background cyclic voltammogram by utilizing the same cell and contents prior to sample introduction. Typically, such measurements in molten salt studies are made independently with a separate cell and solution. The Flickit valve introduction assembly also allows a more accurate determination of an initial ($t = 0$) measurement, since periods of 0.5-1 hour were required to heat the melt to the desired temperature.

For those studies of solutions resulting from premixing the sample and solid $\text{AlCl}_3\text{-NaCl}$, a similar device omitting the Flickit valve was used to evacuate and seal the cell under the selected conditions.

2. Molten Salt UV-Visible Absorption Cell

The 3-mm pathlength absorption cell used in this work is shown in Figure 22. The optical region was constructed from 3X9-mm I.D. rectangular quartz tubing (Part No. QR-0309, Vitro Dynamics Inc., Rockaway, NJ) and was connected to the main cell cavity (20-mm O.D. Pyrex) by a 3/8-inch O.D. graded quartz-to-Pyrex seal. The upper stem of the cell was terminated with a No. 7 threaded glass connector (Part No. 5027-05, Ace Glass, Inc.), which permitted attachment of the Flickit valve assembly or a similar device. Due to the apparent large molar absorptivities involved in these studies, a large cell volume (~ 25 ml) was required to allow a reasonably accurate determination of solute concentration. Typically <10 mg of sample was added to 25-40 g of 63/37 $\text{AlCl}_3\text{-NaCl}$.

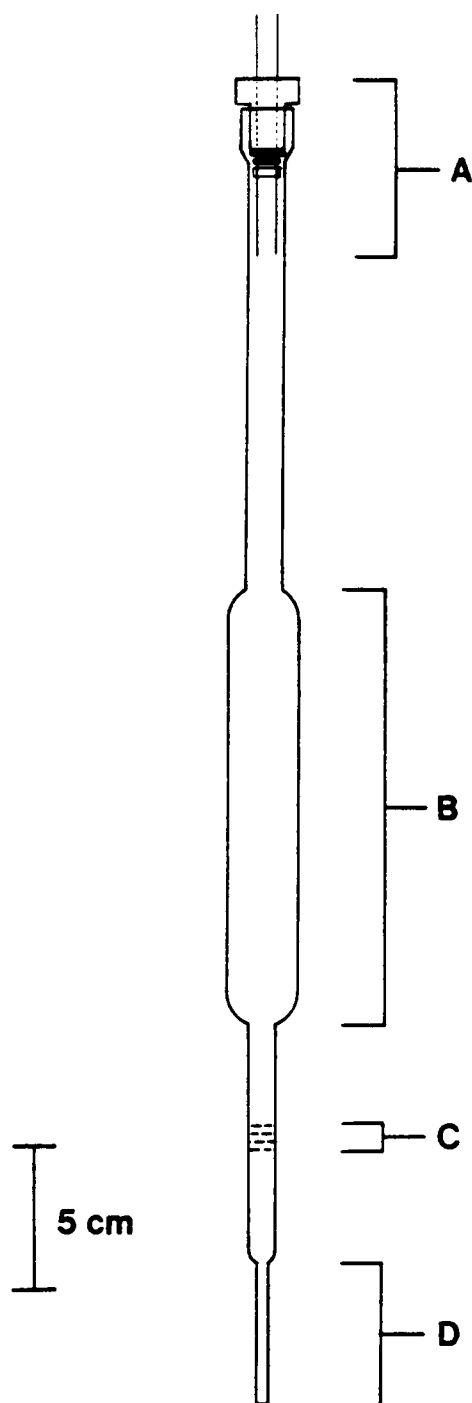


Figure 22. Molten salt UV-visible absorption cell: (A) No. 7 threaded threaded glass connector-Teflon bushing assembly, (B) 20-mm O.D. Pyrex tubing, (C) 3/8-inch O.D. graded quartz-to-Pyrex seal, (D) 3-mm pathlength quartz optical region.

3. Molten Salt Electrochemical Cell

The electrochemical cell used in this work is presented in Figure 23. The aluminum wire reference electrode and reticulated vitreous carbon (RVC) counter electrode (60 pores per inch; Fluorocarbon, Anaheim, CA) were isolated from the main cell compartment by a fine porosity (4-8 μm) glass frit (Ace Glass Inc.) The glassy carbon (GC) working electrode was fabricated from 3-mm diameter rod (GC-30, Tokai Carbon Co., Ltd., Tokyo, Japan).

Originally, working electrodes were prepared by shrinking Pyrex tubing onto the GC rod at 800 °C under vacuum (146). A durable leak-tight seal could not be obtained using this procedure due to (a) the inefficiency of glass to wet carbon and (b) the mismatch in thermal expansion coefficients between the GC and Pyrex below the set point of the glass. Electrodes constructed in this manner were frequently observed to leak after exposure to molten $\text{AlCl}_3\text{-NaCl}$ for several hours.

An improved method for fabricating GC electrodes suitable for molten salt studies was later adapted (147). The glassy carbon was first coated with a thin layer of silicon using the apparatus shown in Figure 24. The GC rod was positioned in a 1/2-inch Pyrex tube by a graphite rod and plug assembly. Electrical contact across the unit was made by a nickel spring compressed between the graphite and a 1/2-1/4-inch SS Ultra-Torr reducing union (Part No. SS-8-UT-6-4, Ridge Valve and Fitting Co., Knoxville, TN). The two unions were connected to the output of an 18-amp adjustable voltage transformer (Model 100-Q; General Radio, Cambridge, MA) and were electrically isolated from the rest of the assembly by 1/4-inch Pyrex tubing and 1/4-inch SS Ultra-Torr Unions

Figure 23. Molten salt electrochemical cell: (A) sample introduction tube; (B) No. 7 threaded glass connection with (a) Teflon bushing; (b) aluminum washer, (c) Viton O-ring, and (d) Teflon sleeve; (C) tungsten wire lead; (D) fill and vent hole; (E) thermocouple well; (F) aluminum wire reference electrode; (G) RVC counter electrode; (H) 3-mm diameter glassy carbon rod; (I) graded sealing cane No. 4; (J) Pyrex; (K) graphite rod lead.

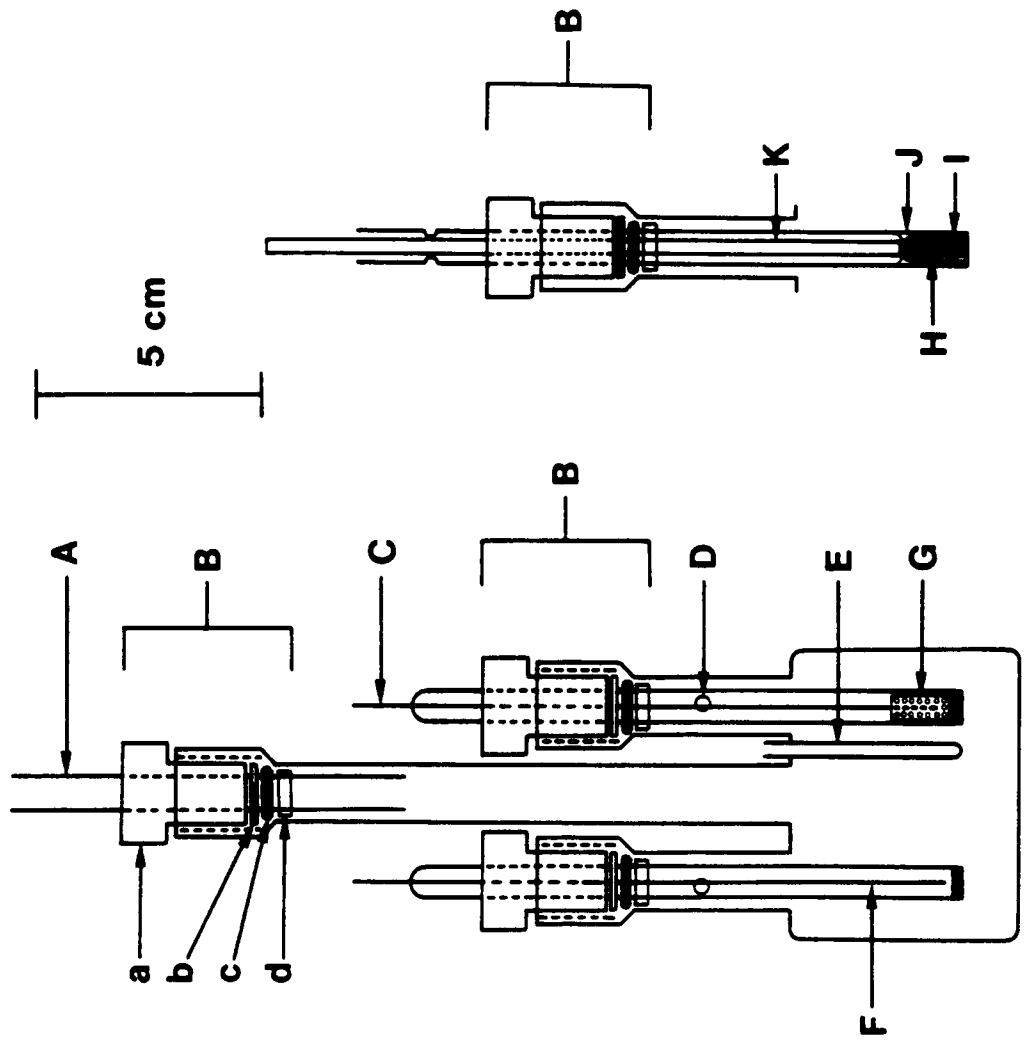


Figure 23.

Figure 24. Apparatus used to deposit silicon on glassy carbon:
(A) pressure gauge, (B) regulating and shut-off valve, (C) 1/4inch O.D. stainless steel tubing, (D) 1/4-1/4-inch SS Ultra-Torr union; (E) 1/4-inch O.D. Pyrex, (F) 1/2-1/4-inch SS Ultra-Torr reducing union, (G) 18-amp transformer (H) nickel spring, (I) graphite plug, (J) 1/2-inch O.D. Pyrex, (K) graphite rod, (L) glassy carbon rod.

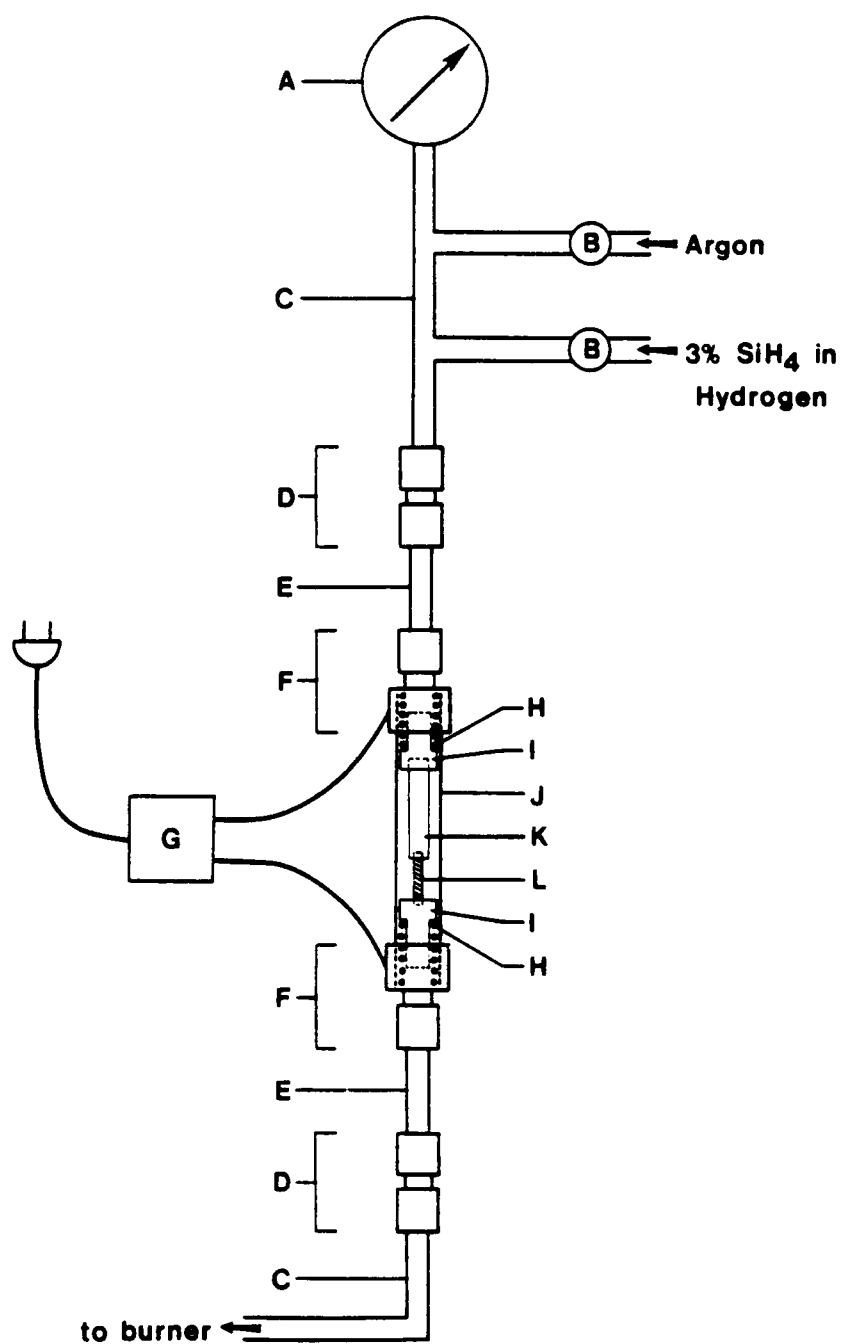


Figure 24.

(Part No. SS-4-UT-6, Ridge Valve and Fitting Co.). A stream of 3% silane (SiH_4) in hydrogen ($100 \text{ cm}^3 \cdot \text{min}^{-1}$), diluted with an equal flow of argon, was passed through the apparatus. The transformer was turned on for ~ 5 -10 sec at 10-20 volts (60 cycle a.c.), heating the GC rod to a red glow. Silane decomposed upon contact with the hot glassy carbon, depositing a thin film of silicon on the carbon surface. The unused SiH_4 , which is pyrophoric, was vented away from the unit and ignited by a gas burner. A pressure gauge was used to monitor a potential obstruction of the system due to the formation of SiO_2 .

The silicon-coated glassy carbon rod was then sealed in graded sealing cane No. 4 (GSC-4, National Scientific Co., Quakertown, PA), a borosilicate glass which more closely matches glassy carbon in expansion than Pyrex below 300°C . The thermal expansion coefficients (in the temperature range 0 - 300°C) for glassy carbon, GSC-4, and Pyrex are 2.2×10^{-6} , 2.7×10^{-6} , and $3.2 \times 10^{-6} \text{ cm/cm/}^\circ\text{C}$, respectively. A 7-mm O.D. Pyrex sleeve was then slipped over unit and sealed to the GSC-4. The end of the assembly was cut, exposing a flat, circular cross-section of the glassy carbon, which was then successively polished with 10, 1, and $0.1 \mu\text{m}$ alumina to a mirror finish. A 1/8-in graphite rod inserted inside the Pyrex tube permitted electrical contact to the glassy carbon.

A K-type thermocouple inserted in the thermocouple well permitted accurate monitoring of the temperature of the electrochemical cell's contents.

4. Molten Salt Raman Cell

The molten salt cell used for Raman measurements is shown in Figure 25. The optical region was constructed from 5-mm I.D. square

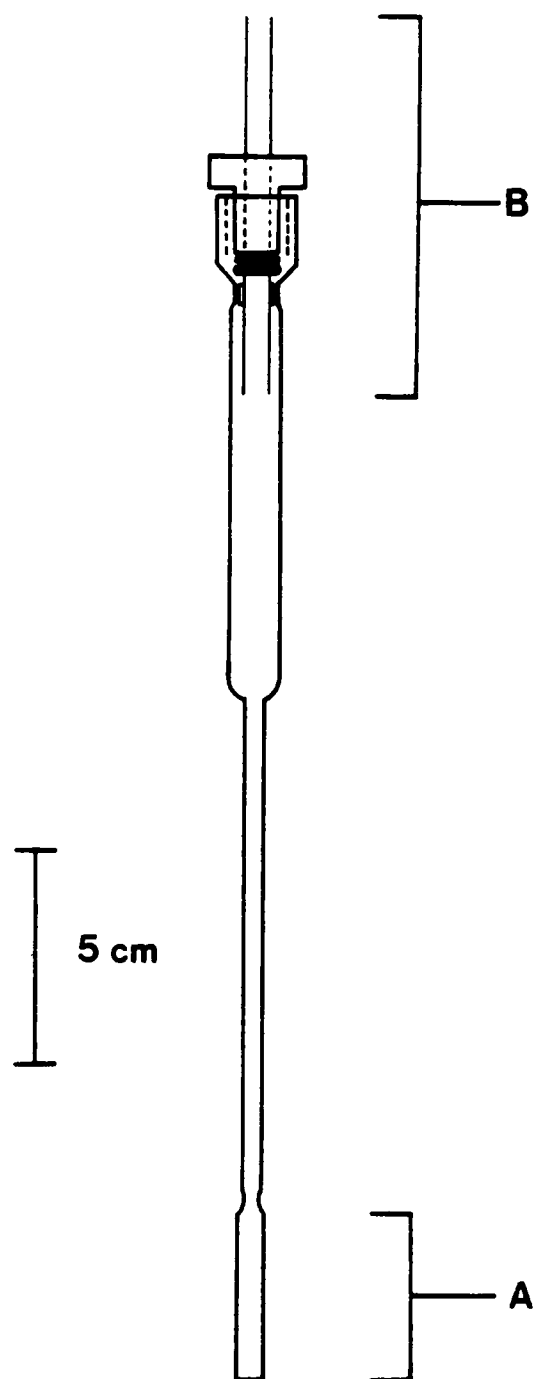


Figure 25. Molten salt Raman cell: (A) 5-mm I.D. square optical region, (B) No. 7 threaded glass connector-Teflon bushing assembly.

Pyrex tubing (Part No. S-105, Vitro Dynamics Inc.) and was connected to a No. 7 threaded glass connector (Part No. 5027-05, Ace Glass Inc.) by 6-mm O.D. Pyrex tubing. A small restriction immediately above the square tubing prevented the sample delivery tube from obstructing the optical region.

5. Vacuum-Pressure Manifold

The apparatus used to evacuate and pressurize molten salt cells with the desired fill gas is shown in Figure 26. Each cell was connected to the assembly by a 1/4-inch flexible stainless steel tubing (Part No. 321-4-X-6, Ridge Valve and Fitting Co.) equipped with 1/4-inch Ultra-Torr Unions (Part No. SS-4-UT-6, Ridge Valve and Fitting Co.). Evacuation of the system was monitored with a Veeco Model T6-70 TC vacuum gauge and Type DV-1M vacuum probe. The absolute pressure of the system during refilling with N_2 , CO, or $CO-H_2(1:3)$ was measured with a Matheson Model 63-5601 test gauge. Regulating and shut-off valves permitted isolation of the individual sections of the apparatus when required.

6. Liquid SO_2 Cleaning Apparatus

Preliminary results indicated that $Ir_4(CO)_{12}$ and $[IrCl(CO)_3]_n$ were not soluble in liquid SO_2 . An apparatus was developed for collecting compounds dissolved in the melt on a removable glass frit by removing the melt with liquid SO_2 . This apparatus, shown in Figure 27, functions similarly to an earlier design used to clean solid metal samples (148). Unfortunately, the species produced by $Ir_4(CO)_{12}$ in 63/37 $AlCl_3-NaCl$ were soluble in liquid SO_2 and therefore could not be isolated using this method.

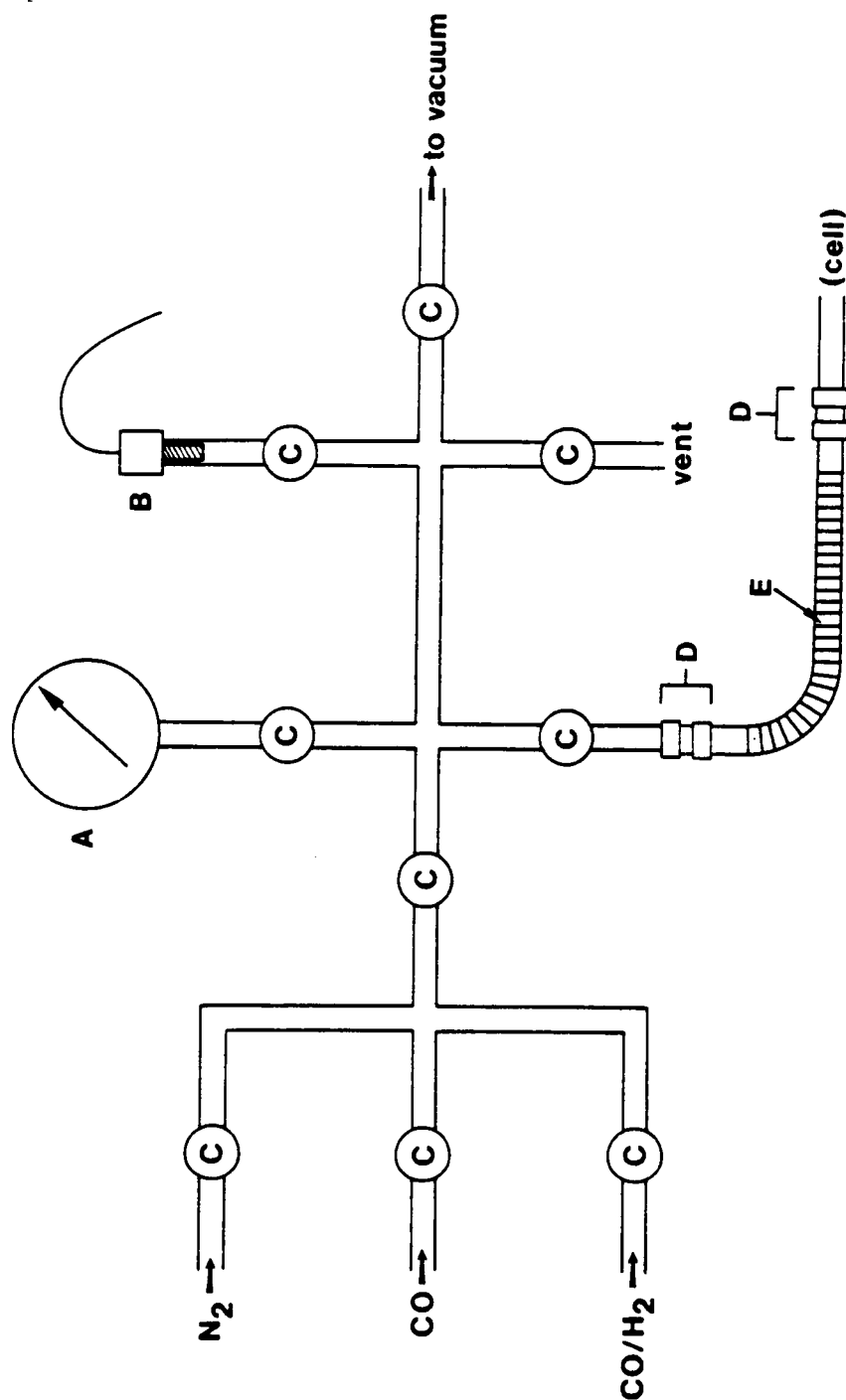


Figure 26. Vacuum-pressure manifold: (A) pressure gauge (B) vacuum probe, (C) regulating and shut-off valve, (D) 1/4-inch SS Ultra-Torr Union, (E) 1/4-inch flexible SS tubing.

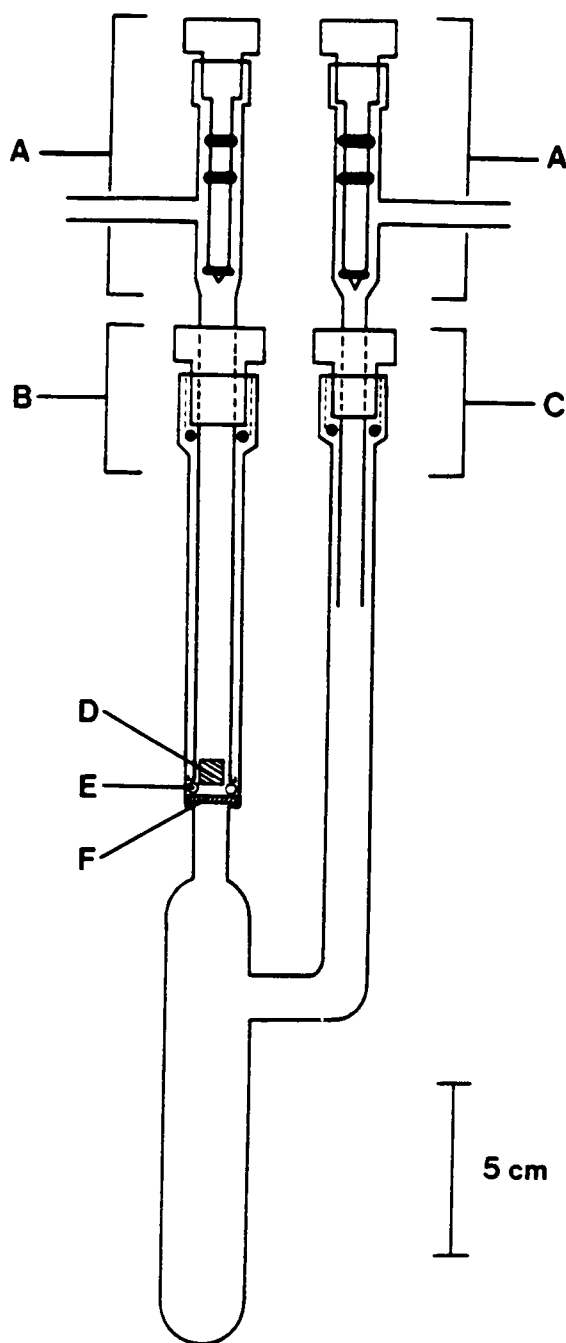


Figure 27. Liquid SO₂ cleaning apparatus: (A) 90° high vacuum Teflon stopcock; (B) No. 10 and (C) No. 7 threaded glass connector-Teflon bushing assembly; (D) sample in solid AlCl₃-NaCl; (E) Teflon O-ring; (F) coarse glass frit.

7. Reaction Cells for Preparing Solid Samples

To prepare samples for IR and XPS analysis, a reaction cell was fabricated by attaching a No. 7 threaded glass connector (Ace Glass Inc.) to a Pyrex tube and closing the other end.

C. Instrumentation

1. UV-Visible Spectroscopy

The instrumentation used to acquire molten salt spectra is described in Part I. The optical arrangement was identical to that used for multiwavelength single-pass SEC experiments. For measurements in the visible region, the spectral output of the quartz halogen lamp described earlier was modified with a Corning No. 5850 glass filter to optimize the source with respect to detector response in the 350-450 nm region. A deuterium lamp (Model EU-701-50, the Heath Co., Benton Harbor, MI) served as the light source for UV measurements.

To prevent continual irradiation of the sample, a Uniblitz Model 225S electronic shutter (placed between the light source and sample) and Model 310 shutter timer control (Vincent Associates, Rochester, NY) were used. The timer control was computer-actuated immediately prior to data acquisition. A period of 2 seconds was sufficient for acquisition of 8 spectral scans by the RSS.

To minimize variations in temperature over long periods (≤ 10 hours), an Omega Model 4201 resistance temperature detector (RTD) digital controller and platinum RTD probe (Omega Engineering Inc.) were used to regulate the power input to the optical furnace.

For conventional UV-visible absorption measurements using other solvents, a Cary Model 219 spectrophotometer was used.

2. Raman Spectroscopy

Raman measurements were acquired using a Jobin-Yvon Ramanor 2000M spectrometer equipped with an Instruments S.A. Inc. Model 980015 controller and a Pacific Model 126 photometer. The argon-ion laser line at 514.5 nm from a Spectra Physics Model 171 laser was used to illuminate the sample. Collection, storage and plotting of spectra were facilitated through use of a dedicated LSI 11/23+ based system.

Molten salt samples were heated using a 6-mm I.D. quartz tube wrapped with nichrome wire positioned in a fire brick. Raman spectra of weakly absorbing solids were acquired by sealing the sample in a glass capillary. For strongly absorbing solids, a rotation technique was employed to prevent thermal decomposition of the sample (149).

3. Infrared Spectroscopy

Infrared spectra were acquired with a Digilab FTS-20E Fourier Transform spectrometer equipped with a fast-scanning Michelson interferometer, KBr beam splitter, triglycine sulfate (TGS) pyroelectric bolometer detector, and nichrome wire source. Data acquisition and storage were performed with a Digilab 3280 Data system incorporating a Motorola 3800 based multiprocessor and Idris operating system. Typically, 1000 scans were collected at 4 cm^{-1} resolution.

4. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra were acquired with a Perkin-Elmer PHI 5100 ESCA spectrometer using a MgK_{α} source (1254 eV) operated at 300 watts. Spectra were calibrated with respect to the Ag $3d_{5/2}$ peak and Cu $2p_{3/2}$ peak at 267.9 and 932.4 eV, respectively.

5. Electrochemistry

Cyclic voltammetry and normal pulse voltammetry were performed using the instrumentation described in Part I.

D. Procedure

1. Conventional Solutions

Solutions of $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ in selected organic solvents were prepared by refluxing the solid in the solvent for several (3-5) hours. Typically, <10 mg of solid dissolved in 50 ml of all the organic solvents considered.

2. Analysis of Iridium Carbonyls in Molten $\text{AlCl}_3\text{-NaCl}$

Due to the similarity in procedures used for UV-visible, Raman, and electrochemical analysis of molten 63/37 $\text{AlCl}_3\text{-NaCl}$ samples, the following description is typical of all of these methods:

The molten salt cell was cleaned with concentrated HCl , rinsed with distilled H_2O and ethanol, and dried at 120°C for 24 hours. The cleaning of the aluminum wire reference electrode is described in Part I. The cell was then transferred to the dry box and loaded with an accurately weighed amount of the $\text{AlCl}_3\text{-NaCl}$ solid. The analyte was then weighed and positioned in the Flickit valve assembly using the external magnet. The introduction assembly was then attached to the main cell by a threaded glass connection. For premixed solutions, the sample was placed directly in the cell with the solid $\text{AlCl}_3\text{-NaCl}$. All stopcocks and connections were secured, and the assembly was transferred from the dry box to the vacuum-pressure manifold. The entire assembly was evacuated and pressurized with the selected fill gas to 1.0 atm

(25 °C). All stopcocks were reclosed, the cell was then transferred to the furnace and heated to the desired temperature.

After making a background measurement, the Flickit valve was opened and the sample was lowered into the melt. After a brief period of mixing (5-10 min.), an initial ($t = 0$) measurement was made. Data were then taken at selected intervals after this measurement. For premixed solutions, the initial measurement was made as soon as the contents had reached the experimental temperature and no undissolved material remained.

3. Analysis of Iridium Carbonyls in Solidified $\text{AlCl}_3\text{-NaCl}$

Infrared and X-ray photoelectron measurements were performed using solidified samples of the iridium species in the melt. The solutions were prepared in the same manner as those described above; however, after a selected period, the $\text{AlCl}_3\text{-NaCl}$ solution was frozen at room temperature. The cell was returned to the dry box, opened, and the solid material removed. The sample was then pulverized and stored in the dry box in a sealed glass container.

Samples for infrared analysis were prepared as KBr pellets inside the dry box using a mini-press (Wilks Scientific Corp., South Norwalk, CT) and adjustable torque wrench set at ~ 32 ft-lbs. To minimize exposure to the air, samples were transported to the spectrometer in a closed glass container and were only briefly exposed to the air during transfer to the sample chamber of the spectrometer, which was maintained under vacuum during analysis.

For XPS analysis, samples were run as powders on adhesive tape. An iridium metal sample was prepared by thermal decomposition of $\text{Ir}_4(\text{CO})_{12}$ on a glass frit under vacuum.

CHAPTER VII

RESULTS

A. General Observations

1. In 63/37 AlCl₃-NaCl under CO

Ir₄(CO)₁₂ formed a pale yellow solution when added to the 63/37 melt under 1 atm of CO. The color of the solution became more intense during the first 2 hours after addition. A light-brown solution resulted after prolonged periods at 150 °C (>10 hours). A similar color change was observed for solutions under vacuum in only several hours. Upon introduction of Ir₄(CO)₁₂ in a small tube to the melt under CO, the yellow solid was observed to slowly turn brown and then dissolve to form the yellow solution described above. This color change of the solid was not observed when the material was quickly dispersed throughout the melt.

For solutions $>3-4 \times 10^{-3}$ M in Ir₄(CO)₁₂, two distinct solution layers were formed within 1 hour after introduction of the solute to the melt under CO, an upper yellow layer and a more dense brown layer. Both solidified layers retained their color indefinitely in the dry box. When the yellow layer was exposed to air, a rapid color change to light blue was observed. When a small amount of water was then added to the light blue solid, a brown solution formed. Ir₄(CO)₁₂ was observed to be insoluble in AlCl₃-n-butylpyridinium chloride (mole ratio 2:1), which is a liquid at room temperature (150).

Iridium chlorotricarbonyl, [IrCl(CO)₃]_n, formed a yellow solution in the 63/37 melt under 1 atm CO. When [IrCl(CO)₃]_n was

introduced to the melt in a small tube, a rigorous reaction, coupled with gas evolution was observed. The black-brown $[\text{IrCl}(\text{CO})_3]_n$ solid turned reddish brown and then dissolved producing a yellow solution. This reaction was not observed when the solute was quickly dispersed throughout the melt. Saturated solutions ($>5 \times 10^{-3} \text{ M } [\text{IrCl}(\text{CO})_3]_n$, as the monomer) under CO produced only a single yellow solution layer and an undissolved brown solid in the melt. The solidified yellow layer displayed the same behavior as that observed for the $\text{Ir}_4(\text{CO})_{12}$ product when exposed to air and water.

For comparison, iridium trichloride, IrCl_3 , was observed to be insoluble in the 63/37 AlCl_3 - NaCl under CO.

2. In 63/37 AlCl_3 - NaCl under CO-H_2 (1:3)

$\text{Ir}_4(\text{CO})_{12}$ formed a pale yellow solution in the melt under CO-H_2 (1:3; 1 atm at 25 °C). Only the most concentrated solutions developed a more intense color. When $\text{Ir}_4(\text{CO})_{12}$ was introduced to the melt in a small tube, the yellow solid was observed to slowly turn brown and evolve gas. This brown solid slowly dissolved, producing a pale yellow solution. This reaction was not observed when the solute was quickly dispersed throughout the melt.

A difference in solubility, apparently dependent upon the method of sample introduction, was observed. Premixed (solute added to 63/37 solid prior to heating) samples ($>13 \times 10^{-3} \text{ M } \text{Ir}_4(\text{CO})_{12}$) yielded homogeneous solutions with no undissolved solid present. Using the Flickit introduction assembly, undissolved yellow solid was observed for solutions $>5 \times 10^{-3} \text{ M } \text{Ir}_4(\text{CO})_{12}$. The remaining yellow solid eventually turned brown; however, a corresponding brown solution layer did not form.

The solidified yellow layer displayed the same color change as that formed under CO when exposed to air and water and retained its color indefinitely in the dry box. For solidified yellow samples from solutions molten ≥ 2 hours, a pink discoloration was observed within several days inside the dry box.

When brown $[\text{IrCl}(\text{CO})_3]_n$ was introduced to the melt under CO-H₂ (1:3) in a small tube, the solid reacted with the melt to evolve gas and form a yellow solid which quickly dissolved to produce a pale yellow solution. As before, gas evolution and color change of the solid were not observed when the solute was quickly dispersed in the melt. A dependence upon the method of sample introduction similar to $\text{Ir}_4(\text{CO})_{12}$ was observed for the solubility of $[\text{IrCl}(\text{CO})_3]_n$ in the melt under CO-H₂ (1:3). The resulting yellow solid displayed the same color changes as described for the samples produced by $\text{Ir}_4(\text{CO})_{12}$ under CO-H₂ (1:3).

B. UV-Visible Spectroscopy

1. Conventional Solution and Solid-State Spectra

The absorption spectrum of $\text{Ir}_4(\text{CO})_{12}$ dissolved in acetonitrile by refluxing several hours is presented in Figure 28. Absorption bands with maxima at 210, 250, and 322 nm were observed. No additional bands were detected in the 500-900 nm region. Similar spectra were observed for solutions prepared using chloroform and cyclohexane. The absorption maxima and corresponding molar absorptivities for $\text{Ir}_4(\text{CO})_{12}$ in these solvents are listed in Table V.

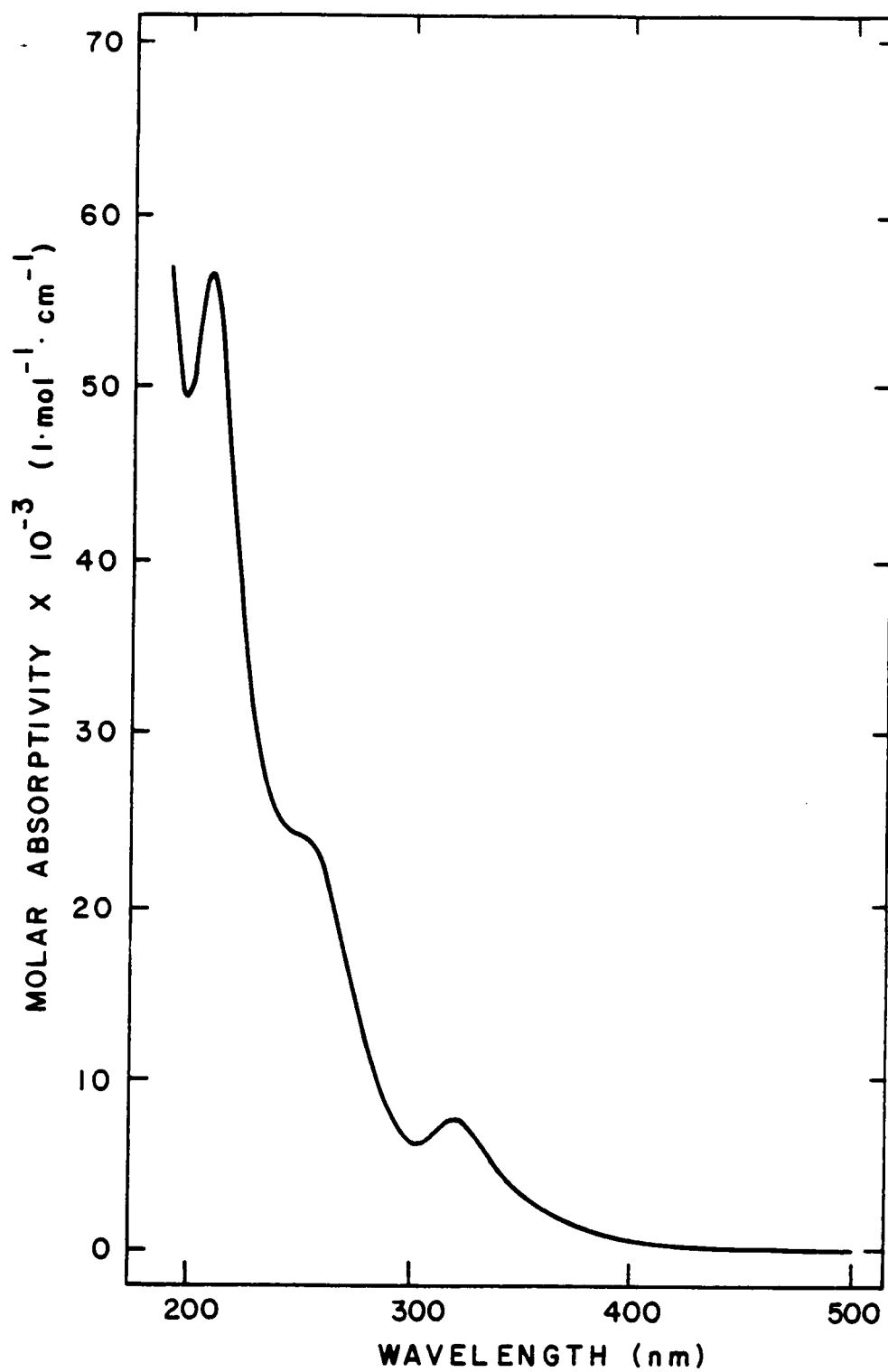


Figure 28. UV-visible spectrum of $\text{Ir}_4(\text{CO})_{12}$ in acetonitrile.

Table V. Absorption Maxima and Molar Absorptivities for $\text{Ir}_4(\text{CO})_{12}$ in Conventional Solvents and Solid State

Solvent	Wavelength in nm (molar absorptivity in $\text{M}^{-1}\cdot\text{cm}^{-1}$)
acetonitrile	210 (56,600); 250 (23,700); 322 (7,600)
cyclohexane ^a	250 (26,800); 322 (8,470)
chloroform ^a	322
solid in CaF_2	214, 315, 320
solid ^b	260, 315, 415

^aShorter wavelength bands not observed due to solvent UV limit.

^bDiffuse reflectance spectrum.

The absorption spectrum of solid $\text{Ir}_4(\text{CO})_{12}$ (diluted with calcium fluoride) indicated a broad band centered at 214 nm with two shoulders located at 315 and 320 nm. The diffuse reflectance spectrum of $\text{Ir}_4(\text{CO})_{12}$ featured absorption maxima at 260, 315, and 415 nm. The absorption maxima of solid $\text{Ir}_4(\text{CO})_{12}$ are included in Table V.

The absorption spectrum of $[\text{IrCl}(\text{CO})_3]_n$ dissolved in acetonitrile by refluxing several hours is presented in Figure 29. Well-defined bands were observed at 254, 315, and 364 nm. Much weaker bands appearing as shoulders were observed at 236 and 392 nm. When chloroform was used as the solvent, a yellow color developed immediately upon addition of the solid. The resulting spectrum featured bands at 314 and 430 nm. After refluxing the solution was almost colorless. Additional bands were then observed at 263, 350, 382, and 590 nm, indicating at least partial conversion of the original complex to another species. $[\text{IrCl}(\text{CO})_3]_n$ did not dissolve in cyclohexane but did form a brown aqueous solution exhibiting a single absorption band at 358 nm. Absorption maxima and molar absorptivities for $[\text{IrCl}(\text{CO})_3]_n$ in these solvents are included in Table VI.

The absorption spectrum of solid $[\text{IrCl}(\text{CO})_3]_n$ (diluted with calcium fluoride) was less defined than that of $\text{Ir}_4(\text{CO})_{12}$. A sharp peak was observed at 206 nm, with shoulders at 228 and 264 nm. The diffuse reflectance spectrum of $[\text{IrCl}(\text{CO})_3]_n$ indicated a sharp peak at 258 nm, with a broad band and shoulder located at ~ 368 and ~ 400 nm, respectively. The absorption maxima of solid $[\text{IrCl}(\text{CO})_3]_n$ are included in Table VI.

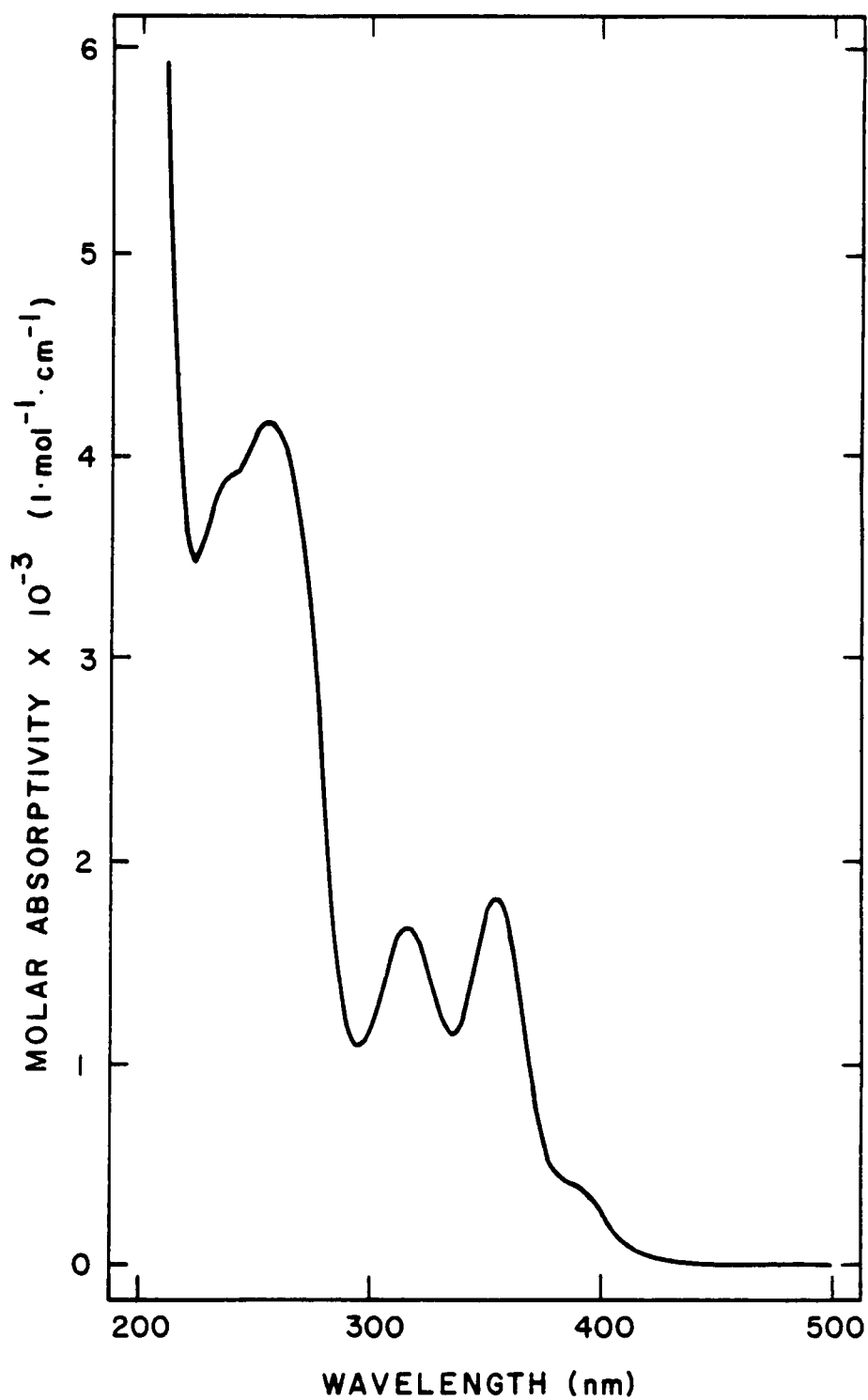


Figure 29. UV-visible spectrum of $[\text{IrCl}(\text{CO})_3]_n$ in acetonitrile.

Table VI. Absorption Maxima and Molar Absorptivities^a for $[\text{IrCl}(\text{CO})_3]_n$ in Conventional Solvents and Solid State

Solvent	Wavelength in nm (molar absorptivity in $\text{M}^{-1}\cdot\text{cm}^{-1}$)
acetonitrile	236 (3,900); 254 (4,160); 315 (1,680); 354 (1,820); 392 (376)
chloroform ^{b,c}	314; 430
chloroform ^{b,d}	263, 314, 350, 382, 430, 590
water	358
solid in CaF_2	206, 228, 264
solid ^e	258, 368, 400

^aCalculated for monomer.

^bSolvent UV limit = 245 nm.

^cBefore refluxing.

^dAfter refluxing.

^eDiffuse reflectance spectrum.

2. In 63/37 AlCl₃-NaCl under CO

Spectra of Ir₄(CO)₁₂ introduced to 63/37 AlCl₃-NaCl at 150 °C under CO (1 atm at 25 °C) are shown in Figure 30. Bands located at 278, 326, and 430 nm are observed to grow in with time. A shoulder on the long-wavelength side of the 278 nm band is also observed. Plots of absorbance vs. time for 278, 326, and 430 nm are presented in Figure 31. It appears that most of the changes occur in the first 2-3 hours after introduction. From these curves, the values of the original concentration of reactant A (a) and remaining concentration (a-x) after x amount of B has been produced from the reaction (151):



were determined. Plots of $\ln[a/(a-x)]$ vs. time (Figure 32) were nearly linear (for $t \leq 3$ hours) indicating a first order reaction according to:

$$\ln[a/(a-x)] = k_1(t) \quad (34)$$

where k_1 is the first order rate constant. Values for k_1 from the slope of these curves for 278, 326, and 430 nm are 1.62×10^{-4} , 1.16×10^{-4} , and $1.18 \times 10^{-4} \text{ sec}^{-1}$, respectively. Similar results were obtained for Ir₄(CO)₁₂ mixed with the 63/37 solid prior to melting. Bands at 278, 326, and 430 nm developed with a similar time dependence. No absorption bands were observed in the 500-800 nm region for Ir₄(CO)₁₂ in the melt under CO for either method of sample introduction. A comparison of molar absorptivities for the Flickit and premixed samples is presented in Table VII. The close agreement of these values indicates that the formation of the ultimate iridium species under CO is not dependent upon sample introduction.

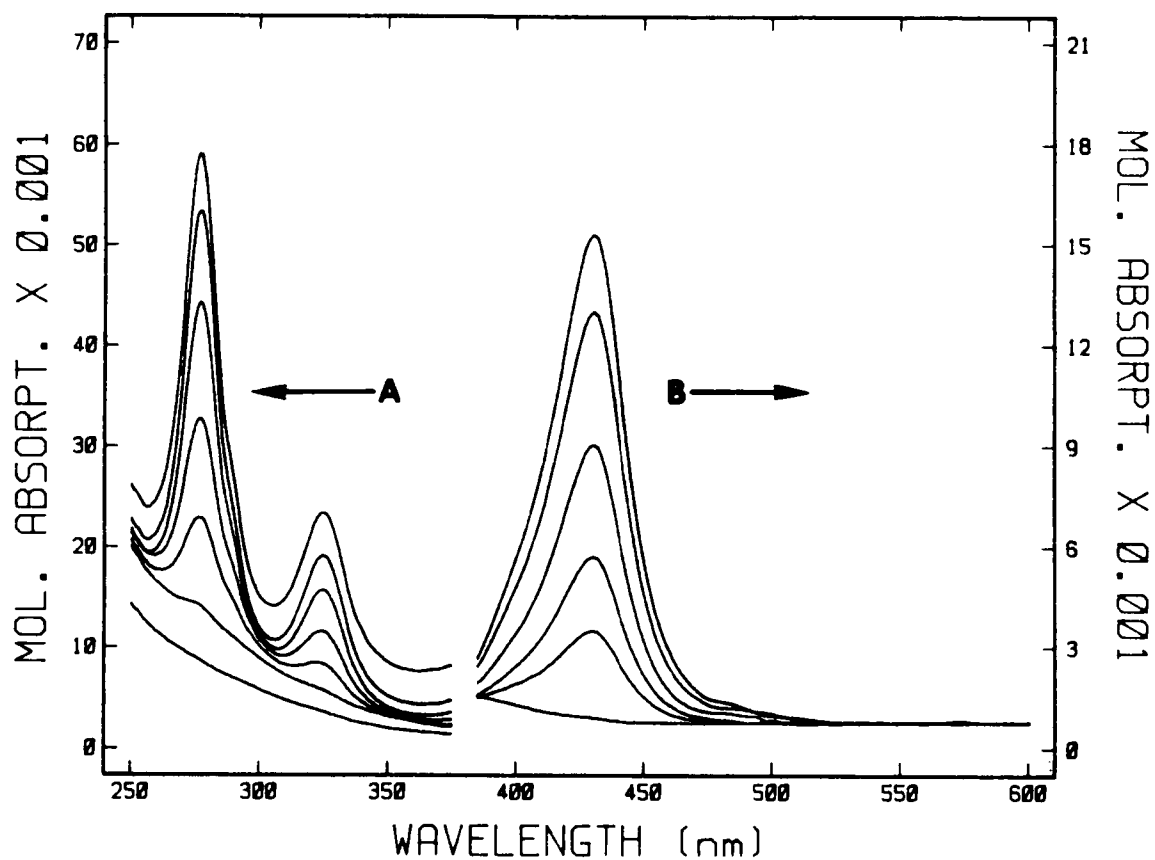


Figure 30. UV-visible spectra of $\text{Ir}_4(\text{CO})_{12}$ in 63/37 AlCl_3 - NaCl at 150°C under CO : (A) $5.73 \times 10^{-5} \text{ M}$; (B) $2.48 \times 10^{-4} \text{ M}$.

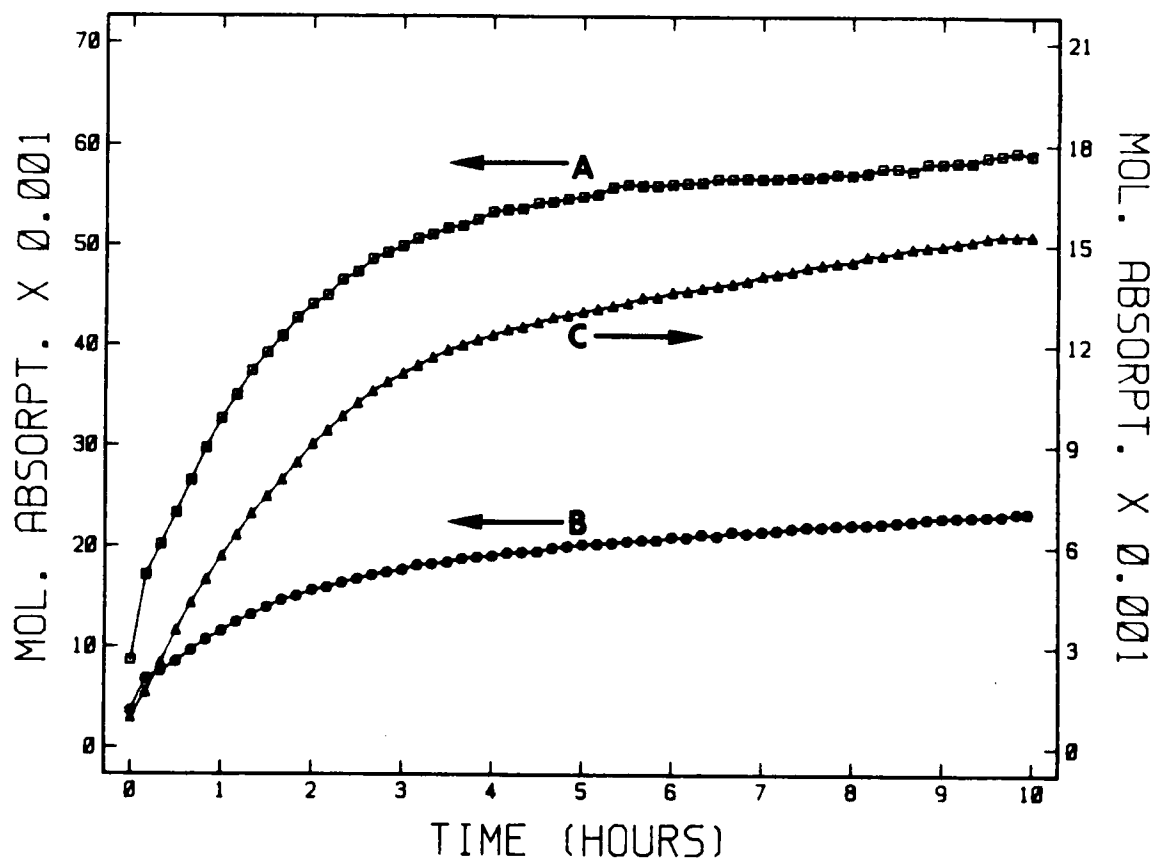


Figure 31. Absorbance vs. time for $\text{Ir}_4(\text{CO})_{12}$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150°C under CO: (A) 278 nm, (B) 326 nm, (C) 430 nm.

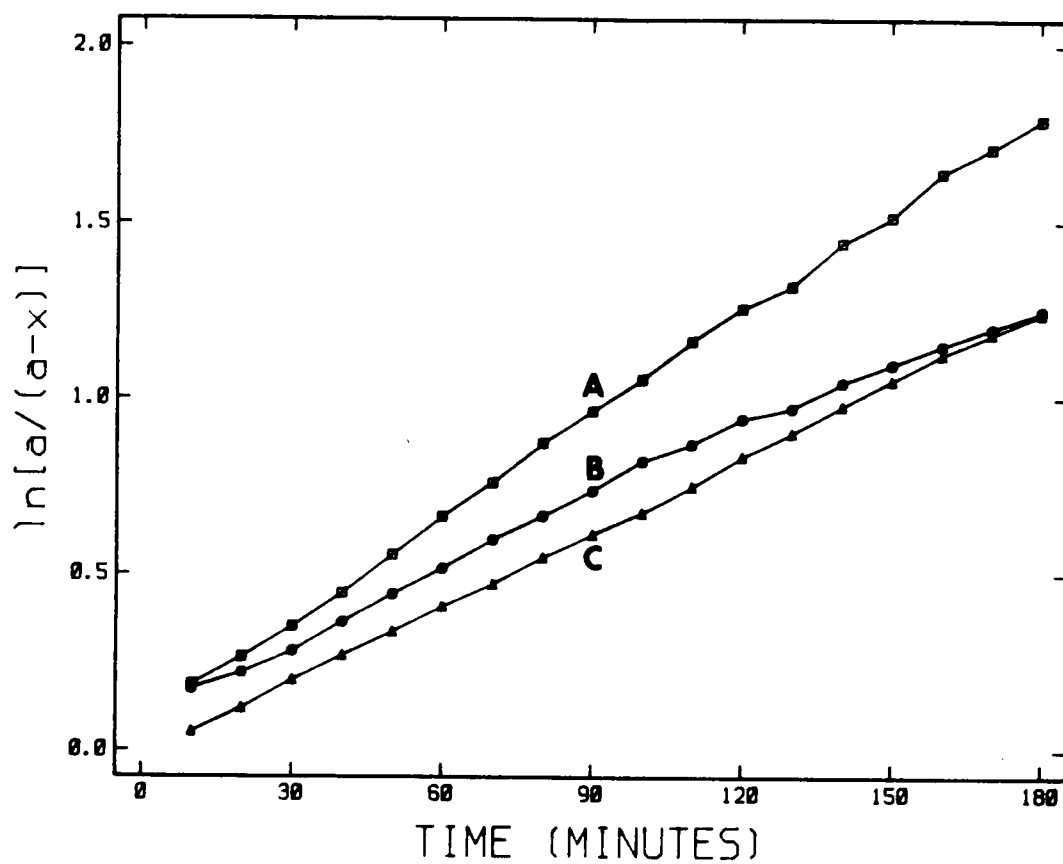


Figure 32. Plots of $\ln[a/(a-x)]$ vs. time for $\text{Ir}_4(\text{CO})_{12}$ in 63/37 AlCl_3 - NaCl at 150 °C under CO: (A) 278 nm, (B) 326 nm, (C) 430 nm.

Table VII. Absorption Maxima and Molar Absorptivities^a for Ir₄(CO)₁₂ in 63/37 AlCl₃-NaCl at 150 °C under CO after 10 Hours

Introduction Method	Wavelength (nm)		
	278	326	430
Flickit Valve	59020	23400	15300
Premix	60800	23000	15200
Average Value	59910	23200	15250
% Deviation	2.97	1.72	0.66

^aIn M⁻¹·cm⁻¹.

The spectra of $[\text{IrCl}(\text{CO})_3]_n$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150 °C under CO (1 atm at 25 °C) are shown in Figure 33. The solution was prepared by introduction of the sample to the melt using the Flickit valve assembly. Similar results were obtained using premixed solutions.

The spectrum acquired after 10 hours is identical to that obtained using $\text{Ir}_4(\text{CO})_{12}$, with bands observed at 278, 326, and 430 nm. One significant difference is the early appearance of these bands, even in the initial spectrum. The absorbance vs. time curves for the three wavelengths are presented in Figure 34. These plots differ from those using $\text{Ir}_4(\text{CO})_{12}$, with a 1-2 hour induction period preceding a major period of change observed after 2 hours. The sharp increase in absorbance during the first 0.5 hour is probably due to dissolution of the solid in the melt and was not observed for premixed solutions. The same time dependence after 0.5 hour and same molar absorptivities were observed for both methods of sample introduction.

These results indicate that $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ ultimately form the same iridium complex in 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO. A comparison of molar absorptivities at 278, 326, and 430 nm for $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ in the melt under CO is presented in Table VIII. The ratio of molar absorptivities for $\text{Ir}_4(\text{CO})_{12}$ vs. $[\text{IrCl}(\text{CO})_3]_n$ (as the monomer) after 10 hours is 4:1.

3. In 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO-H_2 (1:3)

The spectra resulting from addition of $\text{Ir}_4(\text{CO})_{12}$ to 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150 °C under CO-H_2 (1:3) using the Flickit assembly are presented in Figure 35. Bands are observed at 272, 322, 406, and 430 nm. The position and relative intensity of the bands at 272, 322,

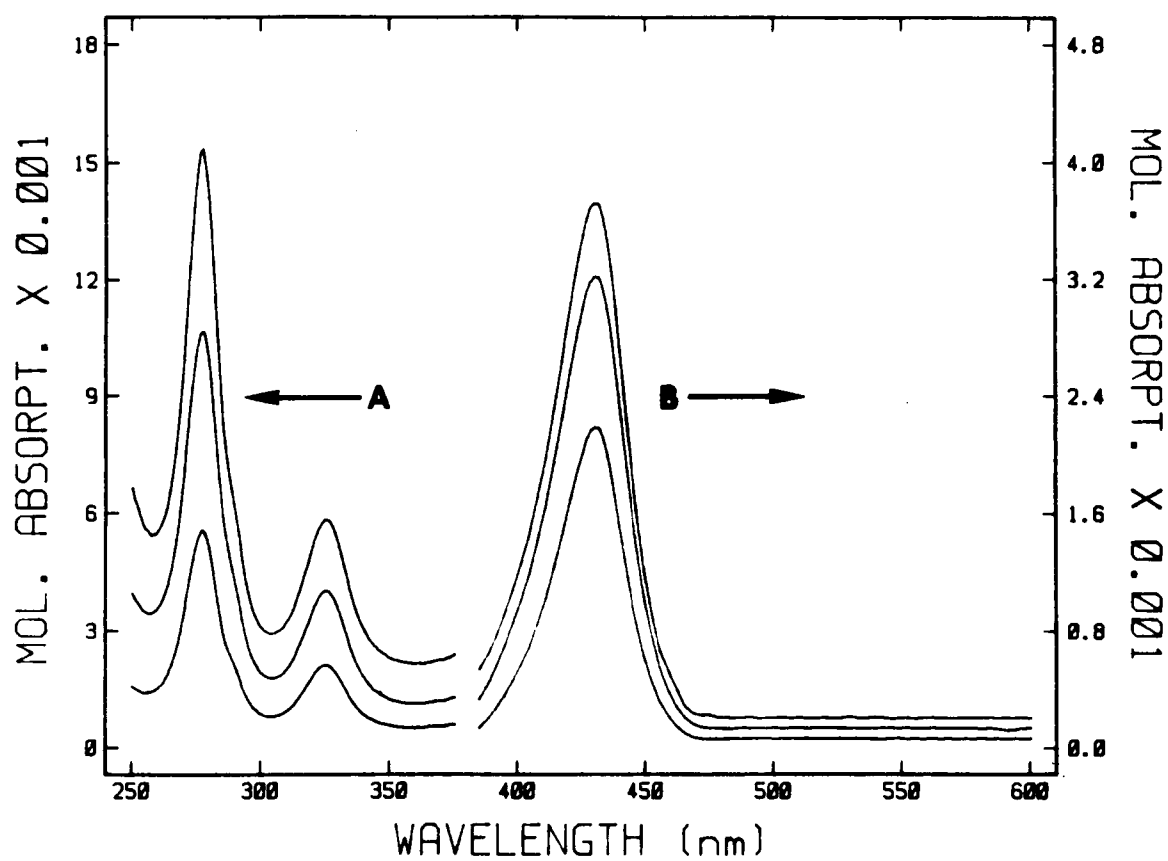


Figure 33. UV-visible spectra of $[\text{IrCl}(\text{CO})_3]_n$ in 63/37 AlCl_3 - NaCl at 150°C under CO ; concentration (as monomer): (A) $2.45 \times 10^{-4} \text{ M}$, (B) $8.04 \times 10^{-4} \text{ M}$.

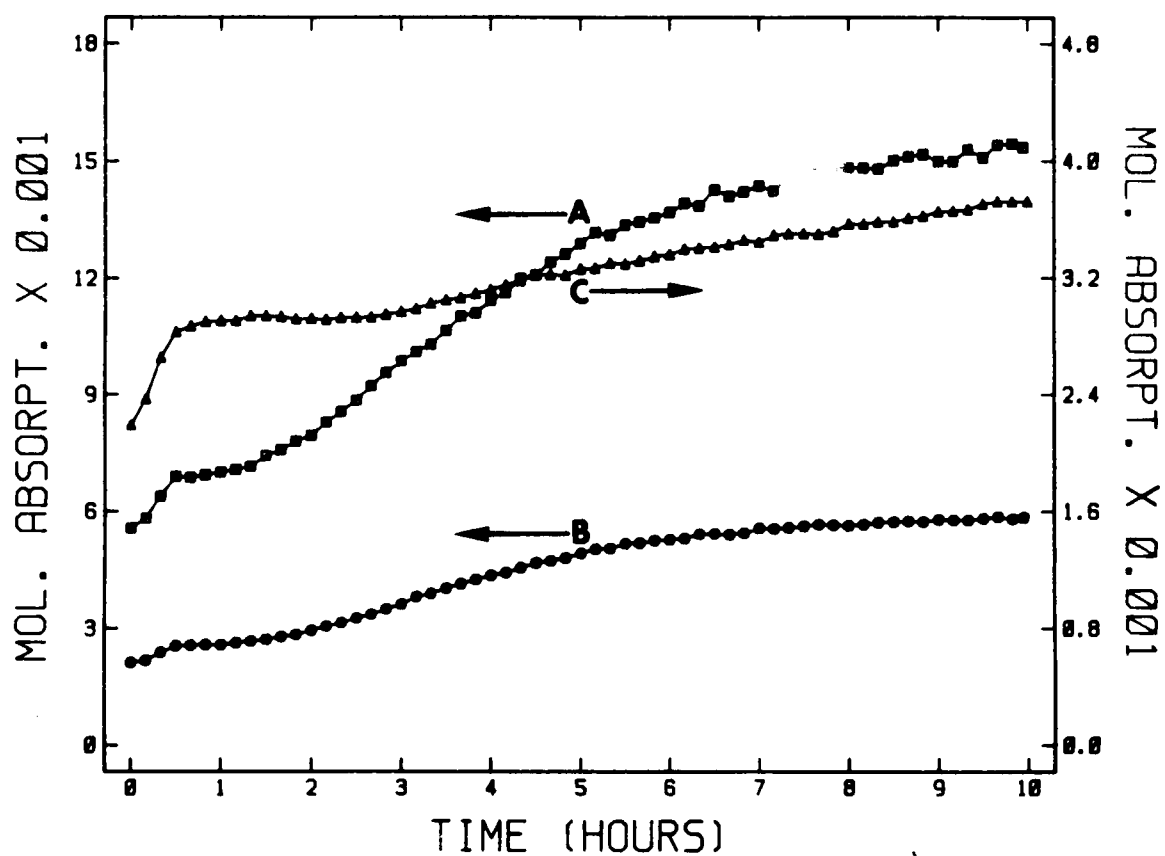


Figure 34. Absorbance vs time for $[\text{IrCl}(\text{CO})_3]_n$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150 °C under CO: (A) 278 nm, (B) 326 nm, (C) 430 nm.

Table VIII. Molar Absorptivities^a at 278, 326, and 430 nm for $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ ^b in 63/37 AlCl_3 - NaCl at 150 °C under CO after 10 Hours

Wavelength (nm)	(I)	(II)	I:II
	$\text{Ir}_4(\text{CO})_{12}$	$\text{IrCl}(\text{CO})_3$	
278	59910	15300	3.92:1
326	23200	5830	3.98:1
430	15250	3710	4.11:1

^aIn $\text{M}^{-1}\cdot\text{cm}^{-1}$.

^bAs the monomer.

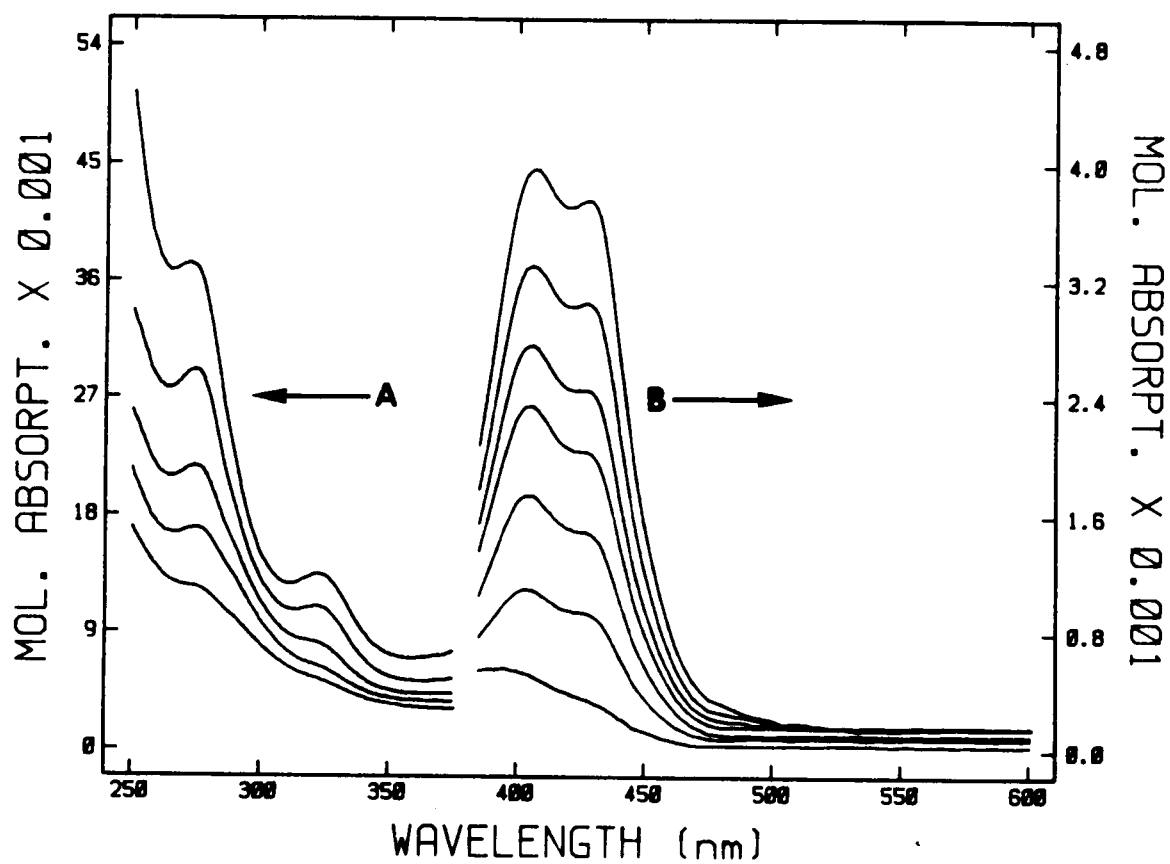


Figure 35. UV-visible spectra of $\text{Ir}_4(\text{CO})_{12}$ in 63/37 AlCl_3 - NaCl at 150°C under CO-H_2 (1:3): (A) $6.69 \times 10^{-5} \text{ M}$, (B) $4.33 \times 10^{-4} \text{ M}$.

and 430 nm indicate a strong similarity with the spectra resulting from $\text{Ir}_4(\text{CO})_{12}$ in the melt under only CO. The superposition of the two shorter wavelength bands on a broader, more intense band centered below 250 nm results in their appearance as shoulders with a slight decrease in maxima from 278 and 326 nm. The presence of two new bands (<250 and 406 nm) suggests the formation of at least one additional complex in the melt under CO- H_2 (1:3) than under only CO. The absorbance vs. time curves for 272, 322, 406, and 430 nm are presented in Figure 36. The time dependence for 406 and 430 nm bands resembles the results obtained for $\text{Ir}_4(\text{CO})_{12}$ under CO. However, the bands at 272 and 322 nm are observed to develop much more slowly and displayed a time response more similar to that observed for $[\text{IrCl}(\text{CO})_3]_n$ in the melt under CO. This discrepancy may be due to the ~ 6.5 -fold increase in concentration of solution used to monitor the 406 and 430 nm bands from that used to monitor the two lower wavelengths.

A comparison of the $\text{Ir}_4(\text{CO})_{12}$ concentration calculated using the molar absorptivities for 278 and 326 nm (Table VII, p. 107) and the actual concentration indicates that only $\sim 33\%$ of the sample undergoes the same chemistry as under CO. Using the Flickit sample introduction system, the fraction of $\text{Ir}_4(\text{CO})_{12}$ converted to the same products in the melt as under only CO decreases as the amount of material added is increased. This trend is illustrated in Table IX. These results indicate that the % conversion of $\text{Ir}_4(\text{CO})_{12}$ in CO- H_2 (1:3) to the same species formed under CO is inversely related to the amount of iridium carbonyl introduced to the system. The relative amounts of $\text{Ir}_4(\text{CO})_{12}$:CO: H_2 used in these studies (1:29:87; on mole basis) suggest that the limiting reagent is not related to fill gas.

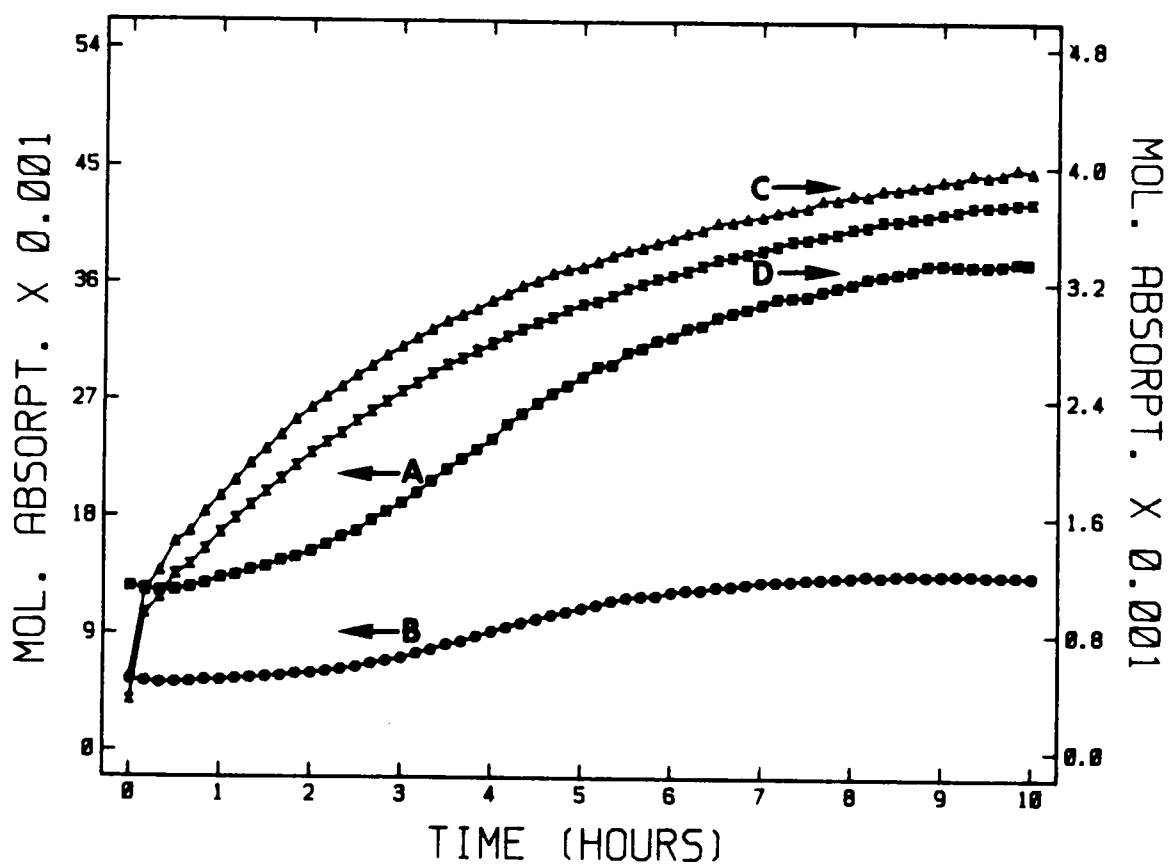


Figure 36. Absorbance vs. time for $\text{Ir}_4(\text{CO})_{12}$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150 °C under CO-H_2 (Flickit Introduction Method): (A) 272 nm, (B) 322 nm, (C) 406 nm, (D) 430 nm.

Table IX. Original $\text{Ir}_4(\text{CO})_{12}$ Concentration and % Converted to Products Resulting from Reaction under CO (Flickit Introduction Method)^a

$[\text{Ir}_4(\text{CO})_{12}], \text{ M}$	% Converted
6.7×10^{-5}	33%
8.6×10^{-5}	20% ^b
1.5×10^{-4}	12%
4.3×10^{-4}	10%

^aCalculated using spectra acquired after 10 hours.

^b $T = 175^\circ\text{C}$.

Much higher concentrations of $\text{Ir}_4(\text{CO})_{12}$ were required to produce similar spectra using premixed samples. An approximate 3-fold increase in concentration was used to produce absorbances at 272 and 322 nm (after 10 hours) comparable to those observed using the Flickit valve assembly. The absorbance vs. time curves for bands at 272, 322, 406, and 430 nm for $\text{Ir}_4(\text{CO})_{12}$ premixed in $\text{AlCl}_3\text{-NaCl}$ are shown in Figure 37. The bands at 406 and 430 nm developed in the first several hours, while bands at 272 and 322 nm showed more increase after 6 hours. This difference may be due to the higher concentration of $\text{Ir}_4(\text{CO})_{12}$ used to monitor the 406 and 430 nm bands vs. the 272 and 322 nm bands. Also an inversion in relative peak intensity was observed for the two higher wavelength bands (compare with Figure 36, p. 114). A comparison of the apparent molar absorptivities and absorbance-time response for the four absorption maxima indicates a dependence upon the method of introduction of $\text{Ir}_4(\text{CO})_{12}$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO-H_2 (1:3).

Calculation of the % $\text{Ir}_4(\text{CO})_{12}$ undergoing chemistry similar to that in the melt under CO indicates a less obvious relationship for the premix method as compared to the Flickit method. These results are presented in Table X. Except for the most dilute solution, it appears that approximately 10% of the original material is converted to products derived under CO fill gas conditions over the concentration range studied. This is approximately the same % observed for the most concentrated solution prepared using the Flickit valve assembly. These results indicate that for premixed solutions, only a small fraction (<12 %) of $\text{Ir}_4(\text{CO})_{12}$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO-H_2 (1:3) undergoes the same chemistry as under CO.

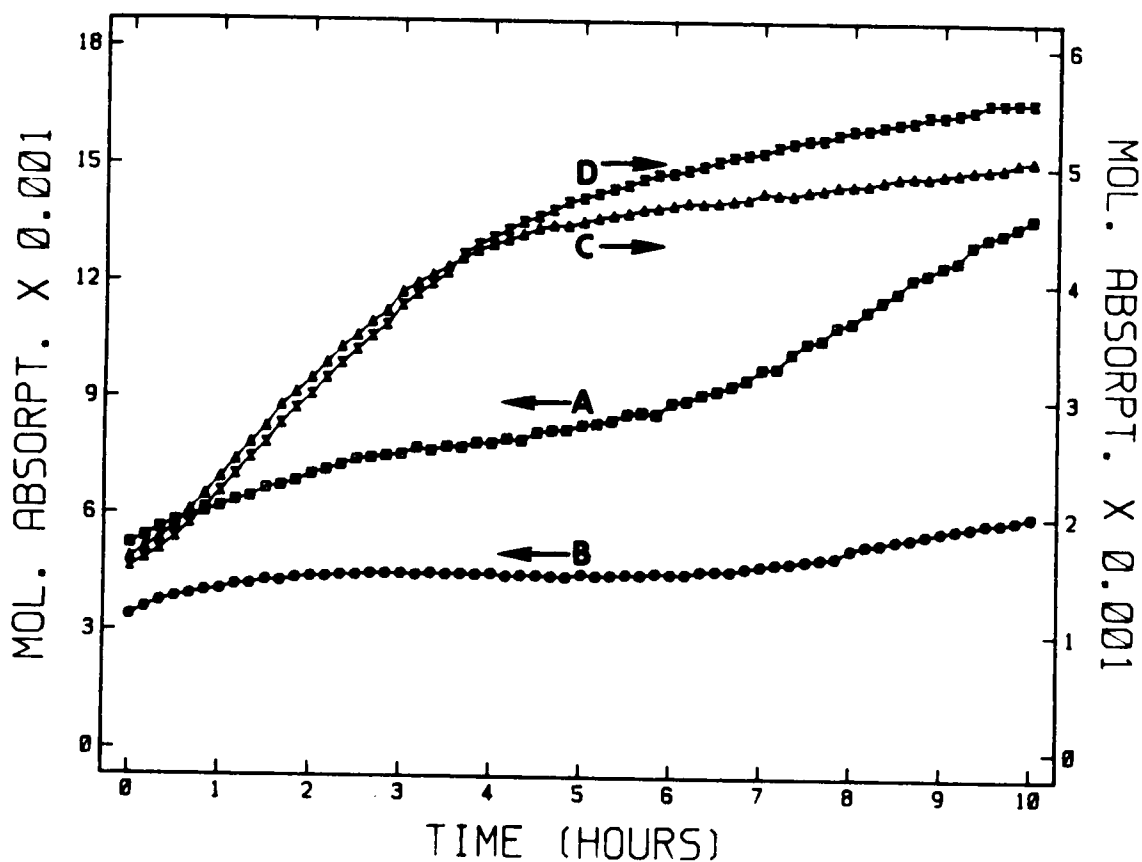


Figure 37. Absorbance vs. time for $\text{Ir}_4(\text{CO})_{12}$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150°C under CO-H_2 (Premix Introduction Method); $1.83 \times 10^{-4} \text{ M}$: (A) 272 nm, (B) 322 nm; $4.46 \times 10^{-4} \text{ M}$: (C) 406 nm, (D) 430 nm.

Table X. Original $\text{Ir}_4(\text{CO})_{12}$ Concentration and % Converted to Products
Resulting from Reaction under CO (Premix Introduction Method)^a

$[\text{Ir}_4(\text{CO})_{12}], \text{M}$	% Converted
1.52×10^{-4}	<5%
1.83×10^{-4}	12%
4.46×10^{-4}	10%
5.56×10^{-4}	9%

^aCalculated using spectra acquired after 10 hours.

Similar spectra were observed for $[\text{IrCl}(\text{CO})_3]_n$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150 °C under CO-H_2 (1:3). Calculations using the molar absorptivities for $\text{IrCl}(\text{CO})_3$ in Table VIII (p. 111) and spectra acquired after 10 hours indicated that for solutions $1\text{-}2 \times 10^{-3} \text{ M}$ (as the monomer), only 15-20% of the original material was observed to produce the same products as under only CO, regardless of the method of sample introduction used.

C. Raman Spectroscopy

1. Pure Solids

The Raman spectra of solid $\text{Ir}_4(\text{CO})_{12}$ in the (A) metal-metal ($25\text{-}250 \text{ cm}^{-1}$), (B) metal-carbonyl stretching ($350\text{-}600 \text{ cm}^{-1}$) and (C) carbonyl stretching ($1900\text{-}2150 \text{ cm}^{-1}$) regions are presented in Figure 38. These results are in agreement with those found in the literature (152-155). Band positions and mode assignments for these spectra are presented in Table XI. Of major importance is the assignment of bands at 207, 162, and 131 cm^{-1} with the A_1 , T_2 , and E vibrational modes of the Ir_4 metal tetrahedron (T_d), respectively (155). Attempts to acquire Raman spectra of $\text{Ir}_4(\text{CO})_{12}$ in solution using various organic solvents were unsuccessful due to the low solubility of the compound in such media.

The Raman spectrum of solid $[\text{IrCl}(\text{CO})_3]_n$ up to 700 cm^{-1} is shown in Figure 39. Bands are observed at 325, 500, 536, and 568 cm^{-1} . There is an additional weak band at 209 cm^{-1} , which may indicate some metal-metal interaction in the solid. From comparison with the Raman spectra of other halogenocarbonyls of iridium (156),

Figure 38. Raman spectra of $\text{Ir}_4(\text{CO})_{12}$: (A) metal-metal region, (B) metal-carbonyl region, (C) carbonyl stretching region.

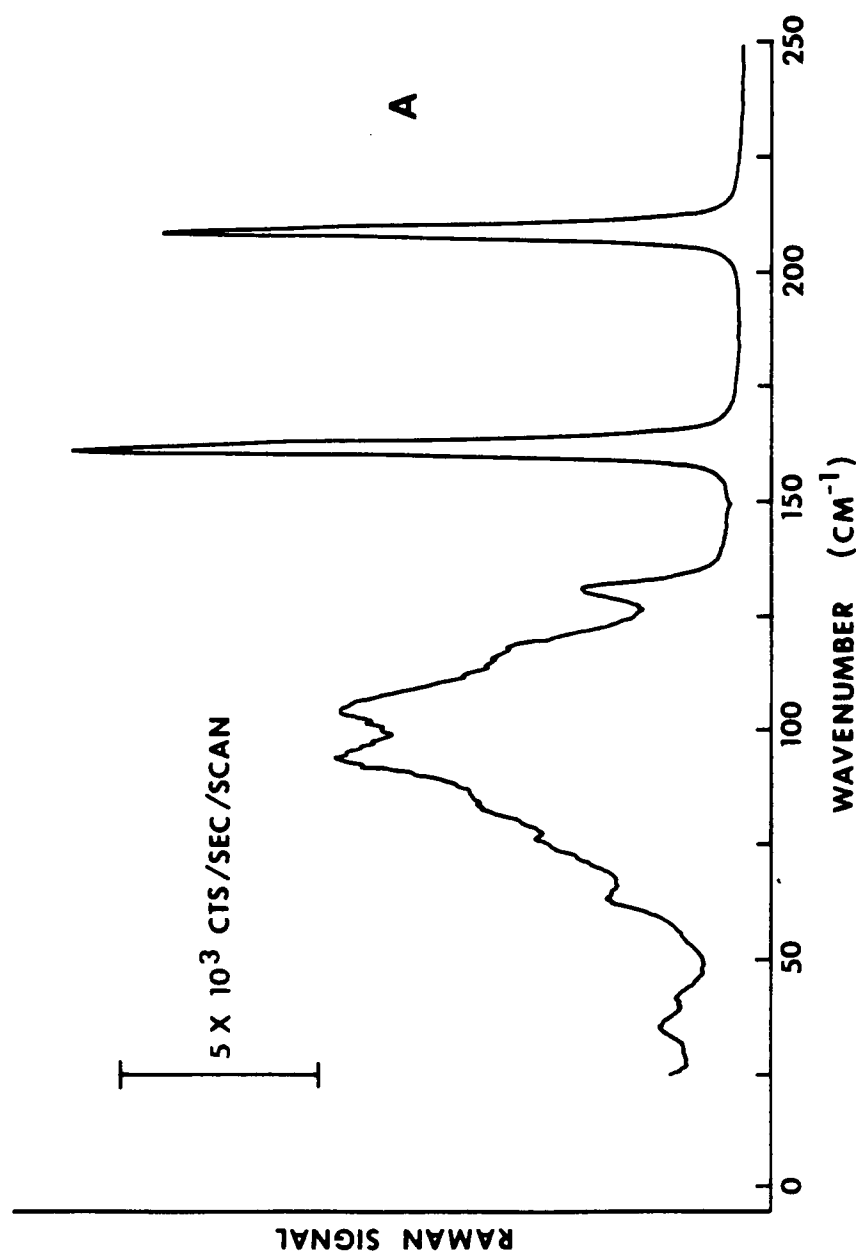


Figure 38.

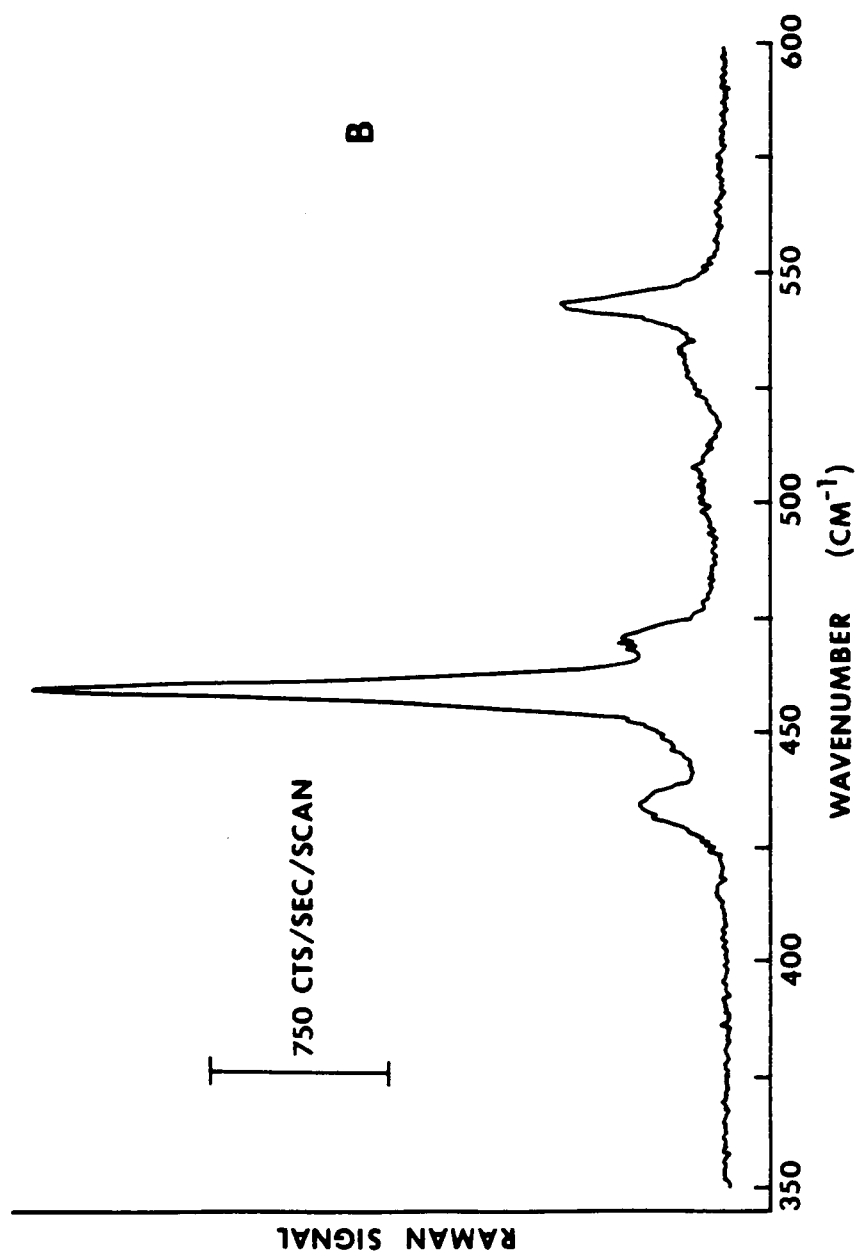


Figure 38. (continued)

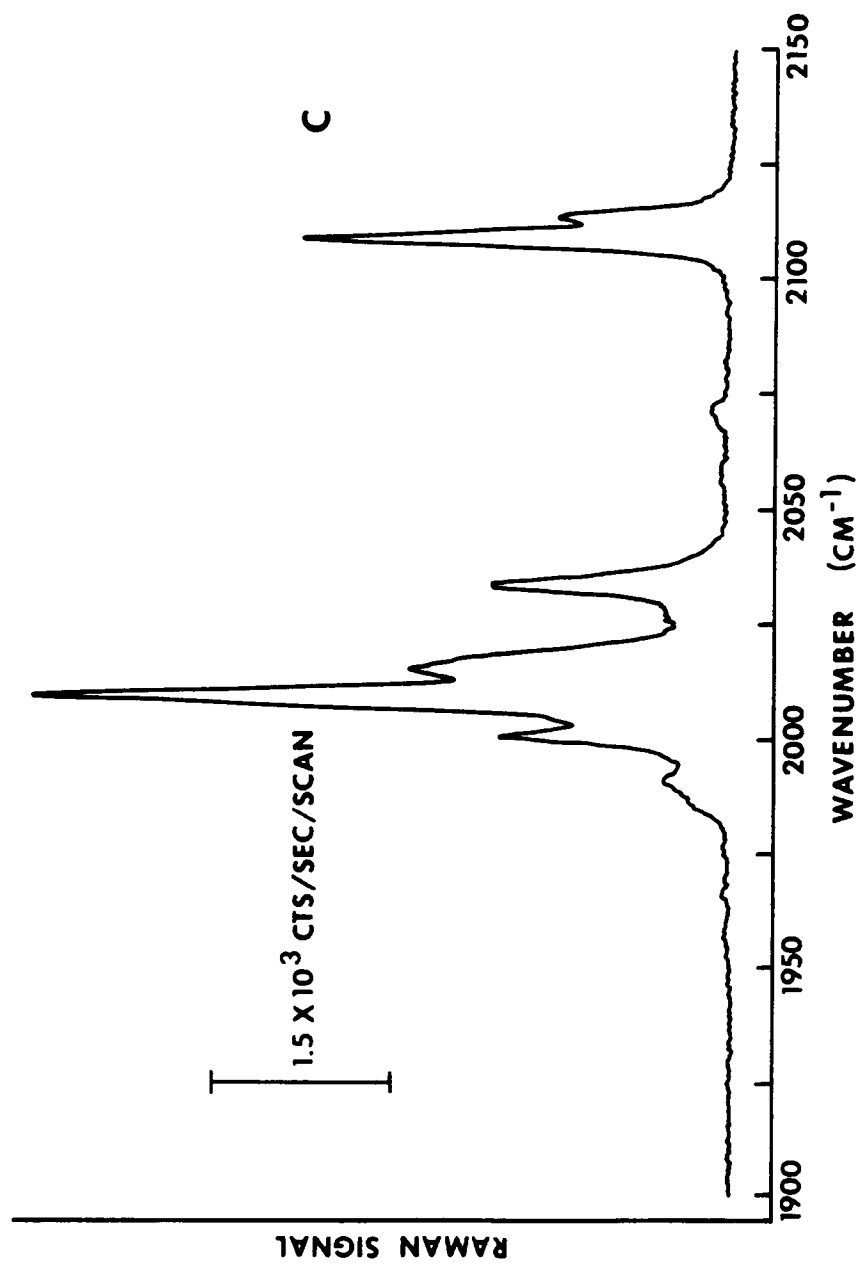


Figure 38. (continued)

Table XI. Raman Bands (cm^{-1}) and Mode Assignments for $\text{Ir}_4(\text{CO})_{12}$

This work	Ref. 152	Ref. 153	Ref. 154	Ref. 155	Assignment ^a
2113		2112	2111		A_1
2109	2106.5				"
	2100.5				"
2072	2070	2076	2070		$T_2(1)$
2034	2036	2036			$T_2(2)$
	2030	2030			"
	2022				"
2016	2017				"
2010	2010.5	2012	2010		E
2001	2002.5	2004	2004		E
1989	1989	1992			T_1
543		544	542		A_1 or E
529		532	530		T_2
505		484	513		E or A_1
470		472	470		T_2
460		460	459		A_1
			450		$T_1(?)$
434		435	437		T_2
			430		"
207		210	208	207	A_1
162		163	164	161	T_2
131		131	131	131	E
116 ^b		112			
105		107	102	102	A_1
94		97	94	94	T_2
84		89	85	85	"
76 ^b			72	72	
63 ^b		67	68		
42			40	40	lattice modes
35					" "

^aAssignment given in Ref. 152.^bPlasma line.

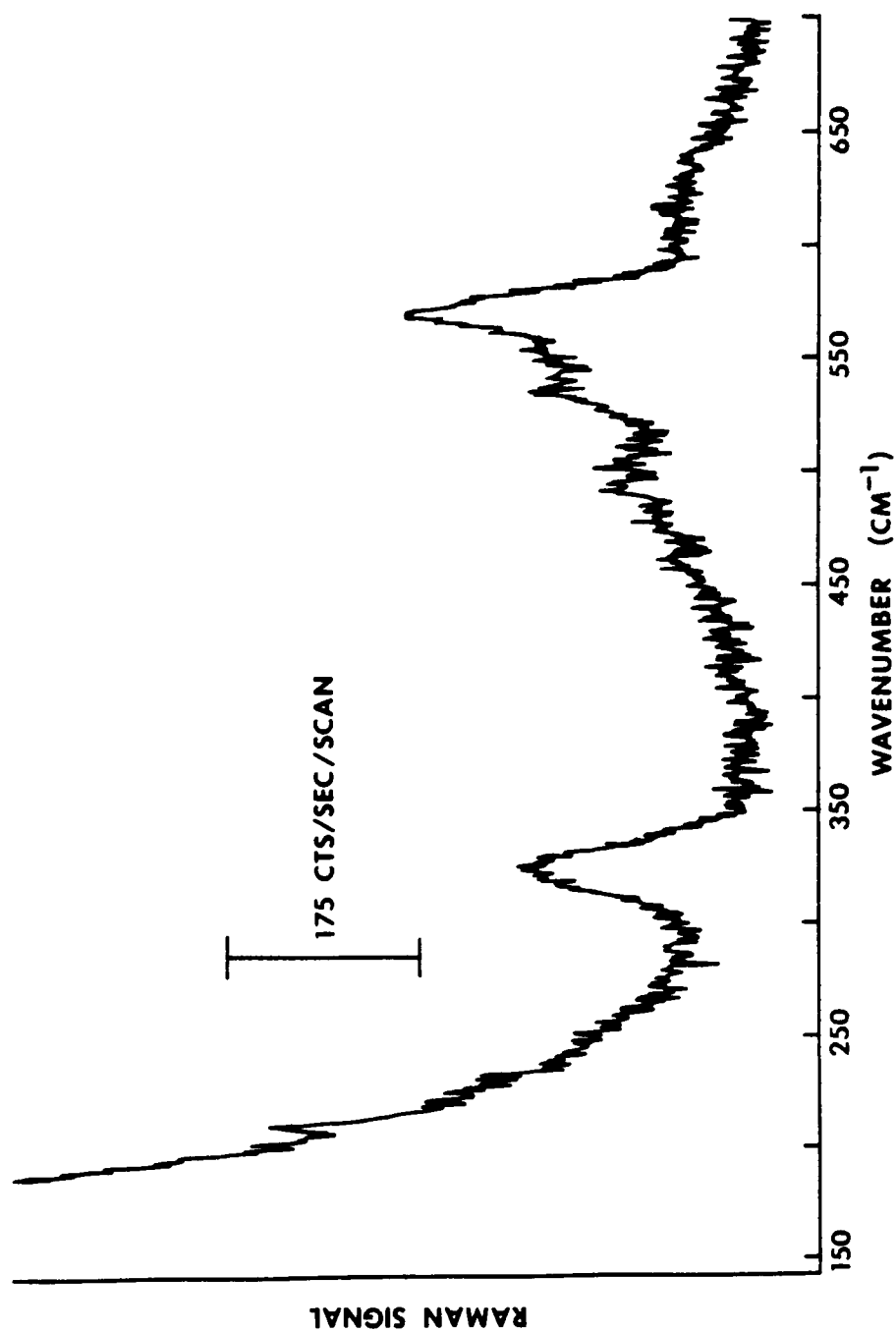


Figure 39. Raman spectrum of $[\text{IrCl}(\text{CO})_3]_n$.

bands at 325 and 500-568 cm^{-1} are probably due to Ir-Cl and Ir-C vibrational modes, respectively.

2. In 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO and CO- H_2 (1:3)

The Raman spectra of 63/37 $\text{AlCl}_3\text{-NaCl}$ at 150 $^\circ\text{C}$ under CO before and immediately after introduction of $\text{Ir}_4(\text{CO})_{12}$ are shown in Figure 40. The background spectrum (A) agrees well with published data (157). After addition of sufficient $\text{Ir}_4(\text{CO})_{12}$ to saturate the melt ($> 5 \times 10^{-3} \text{ M}$), an intense yellow solution formed with undissolved yellow solid remaining on the bottom of the cell. The resulting Raman spectrum of this solution (B) showed a single additional weak band at 202 cm^{-1} . No other new bands are observed below 500 cm^{-1} . The band at 202 cm^{-1} is highly polarized (disappears when the polarization of the laser beam is changed from parallel to perpendicular with respect to the direction of observation) and disappeared within 1 hour after introduction of the solid to the melt. It was not possible to investigate above 500 cm^{-1} due to the presence of a high background signal resulting after addition of the $\text{Ir}_4(\text{CO})_{12}$ to the melt. Examination of the solution after Raman analysis revealed that a brown dense layer had formed. This may be due to photolysis or pyrolysis of the sample from absorption of light, resulting in decomposition of the carbonyl complex under prolonged exposure to the intense laser source (158). Attempts to limit irradiation of the sample during the first hour of contact with the melt produced the same results. The same band and its disappearance were also observed for premixed solutions.

Under CO- H_2 (1:3), the highly-polarized band at 202 cm^{-1} was observed at similar intensity for $\text{Ir}_4(\text{CO})_{12}$ in the acidic melt,

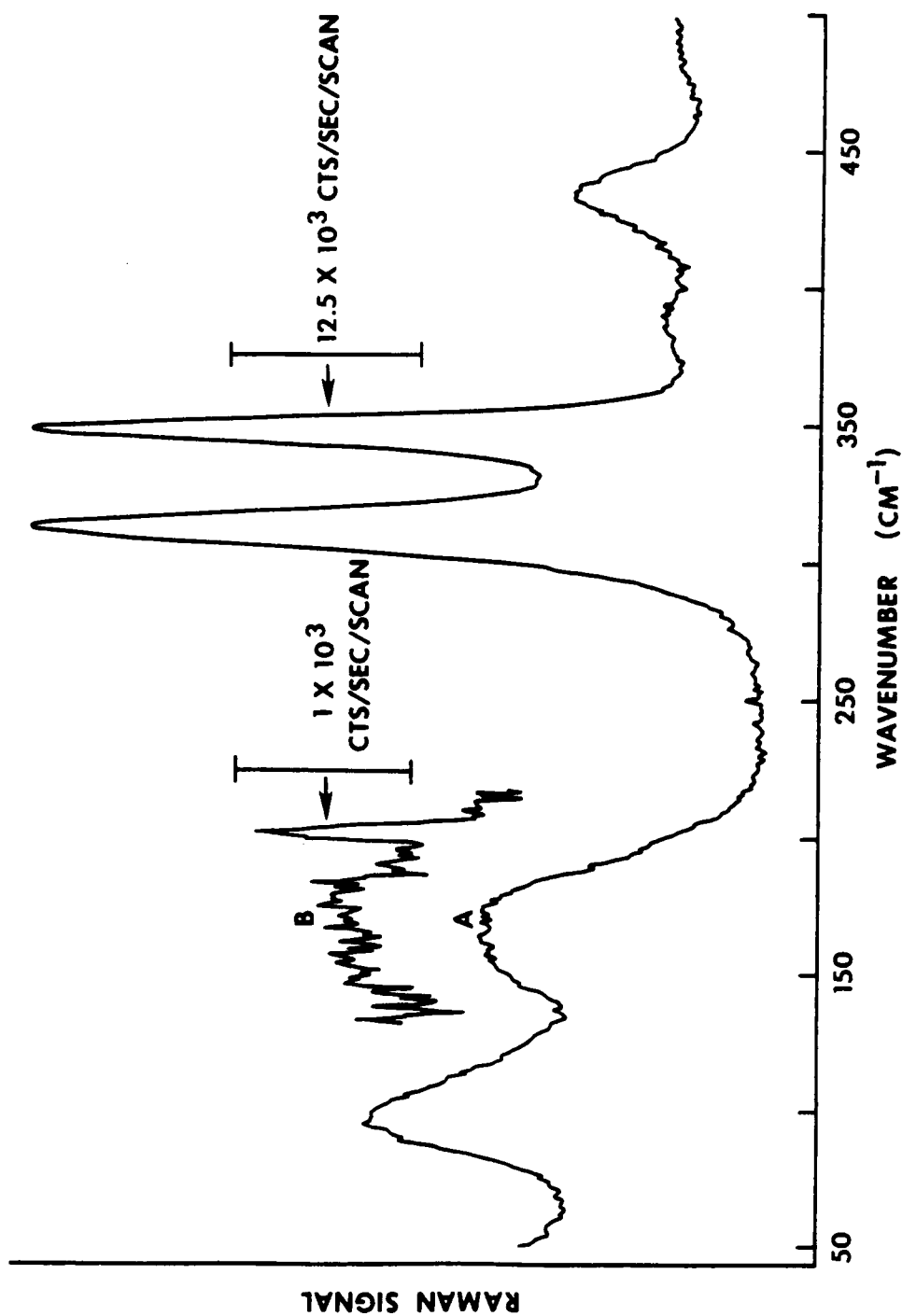


Figure 40. Raman spectra of 63/37 AlCl₃-NaCl at 150 °C under CO:
(A) before addition of Ir₄(CO)₁₂, (B) after addition of Ir₄(CO)₁₂.

regardless of the method of sample introduction used. This band also disappeared within one hour after introduction of $\text{Ir}_4(\text{CO})_{12}$.

Upon freezing both CO and CO- H_2 (1:3) solutions after data acquisition, distinct separate light brown and dark brown layers were observed beneath the larger yellow layer. Undissolved solid was also present. These results indicate that more than one species may be formed by $\text{Ir}_4(\text{CO})_{12}$ in the melt under these conditions.

Only Raman bands attributed to the melt were observed for $[\text{IrCl}(\text{CO})_3]_n$ in the melt under CO or CO- H_2 (1:3) using either sample introduction method. However, the resulting intense yellow solution did not change color even after prolonged laser irradiation.

D. Infrared Spectroscopy

1. Pure Solids

The infrared spectrum of $\text{Ir}_4(\text{CO})_{12}$ in KBr is shown in Figure 41. Major bands in the CO stretching frequency region are observed at 2056 and 2023 cm^{-1} . Additional weak shoulders are observed at 2112, 2090, and 2006 cm^{-1} . In the metal-carbon (M-C) stretching region, bands are located at 530, 496, 470, and 440 cm^{-1} . These results are in agreement with those found in the literature (152, 154). Band positions and mode assignments for these spectra are presented in Table XII.

The infrared spectrum of $[\text{IrCl}(\text{CO})_3]_n$ in KBr is shown in Figure 42. Bands are observed at 2145, 2133, 2109, and 2078 cm^{-1} in the CO stretching region. Major bands in the M-C stretching region are located at 527, 507, and 483 cm^{-1} . Additional weak shoulders are observed at 580, 562, 483, and 465 cm^{-1} .

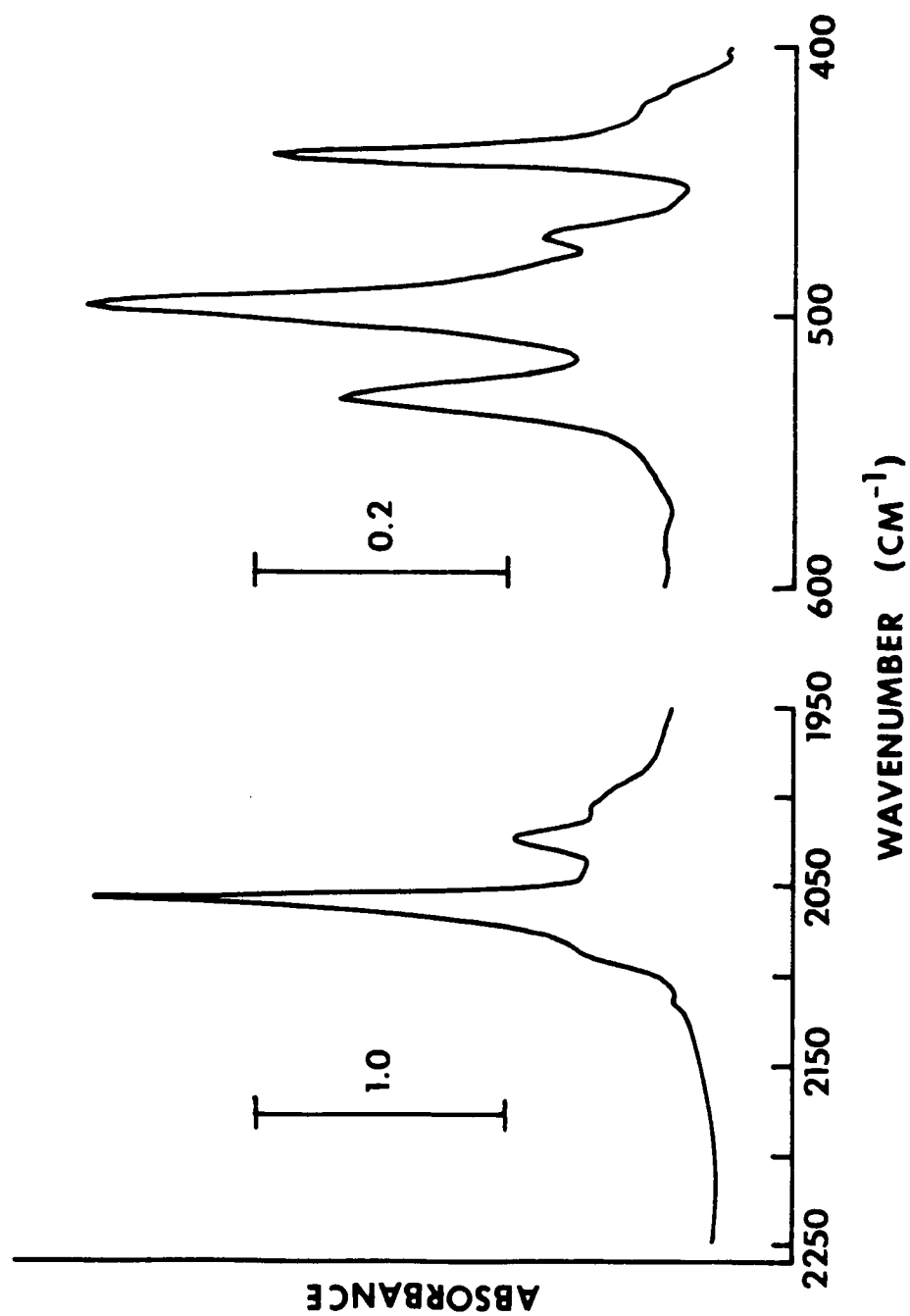


Figure 41. Infrared spectrum of $\text{Ir}_4(\text{CO})_{12}$ in KBr.

Table XII. Infrared Bands (cm^{-1}) and Mode Assignments for $\text{Ir}_4(\text{CO})_{12}$

This work	Ref. 152	Ref. 154	Assignment ^a
2112w	2112	2110	A ₁
2090sh	u.sh	2075sh	T ₂ (1)
2065vs	2054	2066	"
	2040	2030	T ₂ (2)
2023m	2022	2010	"
2006sh	2004	2005	E
530	531	529	T ₂ (IrCO)
496	497	494	"
	486sh		"
	483sh	480	"
470	472.5	467	T ₂ (Ir-C)
440	442.5	439	"

^aAssignment given in Ref. 152 (w = weak; sh = shoulder; u.sh = unresolved shoulder; vs = very strong; m = medium).

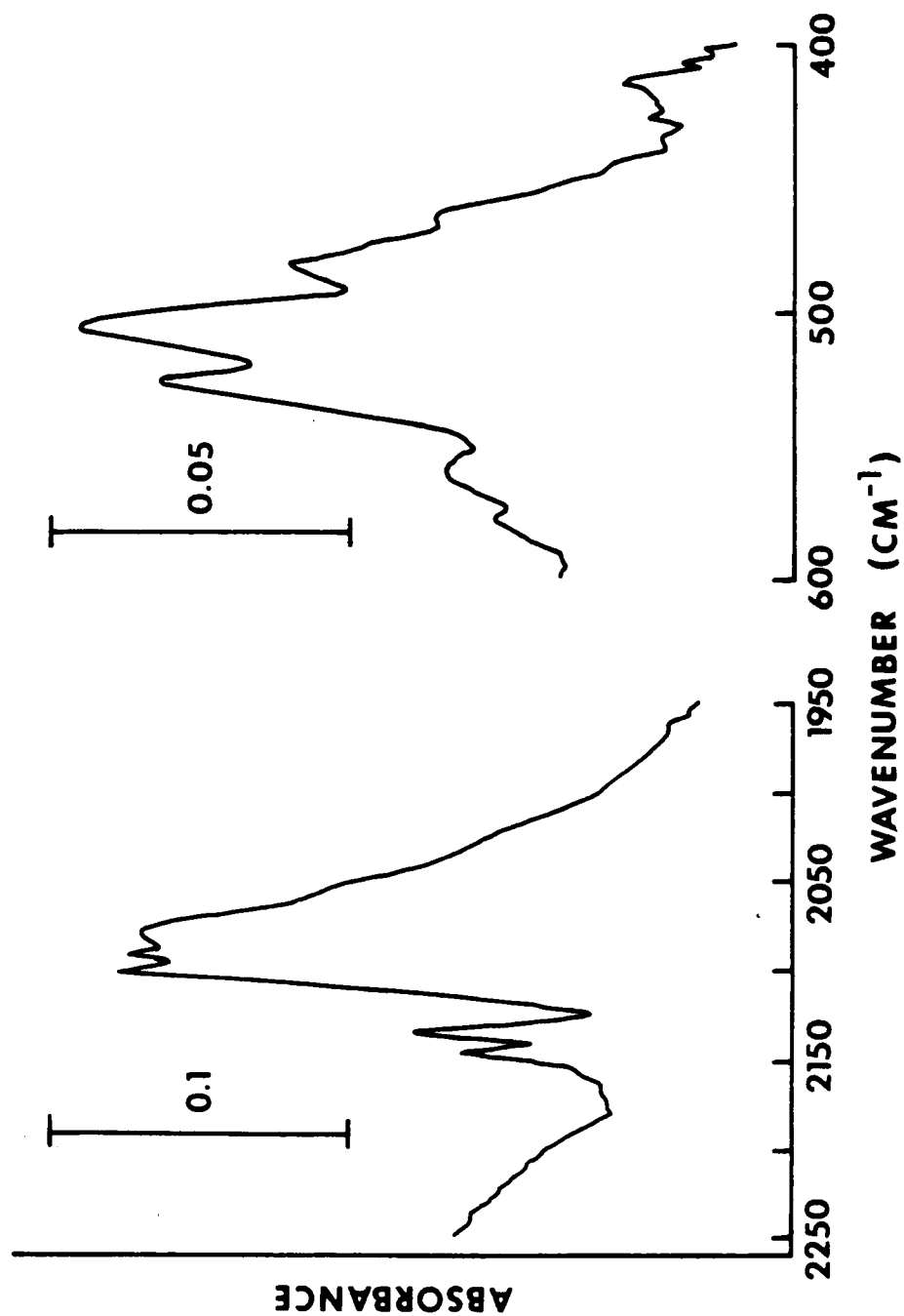


Figure 42. Infrared spectrum of $[\text{IrCl}(\text{CO})_3]_n$ in KBr.

2. In 63/37 AlCl₃-NaCl under CO

The infrared spectrum of the sample resulting from freezing the 63/37 AlCl₃-NaCl melt 1 hour after introduction of Ir₄(CO)₁₂ under CO is shown in Figure 43. This spectrum is more complex than that observed for solid Ir₄(CO)₁₂ in KBr. Strong bands are located at 2158, 2143, 2120, and 2085 cm⁻¹. An additional shoulder is observed at 2105 cm⁻¹. A broadband centered at ~1630 cm⁻¹ was observed for this sample and for a background spectrum of solid 63/37 AlCl₃-NaCl under CO. This band is most likely due to H₂O contamination of the acidic melt (159). Similar bands have been reported for H₂O adsorbed by LiCl and NaCl dispersed in a matrix of alkali metal halides (160). No other bands were observed in the 1600-2000 cm⁻¹ region. The background spectrum of the melt contained only one additional band at 2227 cm⁻¹, which may be due to adsorbed CO. However, this band is ~81 cm⁻¹ higher in wavenumber than that reported for free CO (161). Strong infrared bands associated with the melt precluded examination of the 400-600 cm⁻¹ (M-C) region.

3. In 63/37 AlCl₃-NaCl under CO-H₂ (1:3)

The infrared spectrum of the sample resulting from freezing the 63/37 AlCl₃-NaCl melt 10 minutes after introduction of Ir₄(CO)₁₂ under CO-H₂(1:3) is shown in Figure 44. Strong bands are observed at 2156, 2145, and 2124 cm⁻¹. Weaker bands are observed at 2188, 2114, 2103, and 2030 cm⁻¹. The large broad band centered at ~1630 cm⁻¹ attributed to H₂O contamination was also observed. No other bands were observed in the 1600-2000 cm⁻¹ region. There is no evidence for the strong 2120 and 2085 cm⁻¹ bands observed for Ir₄(CO)₁₂ in the

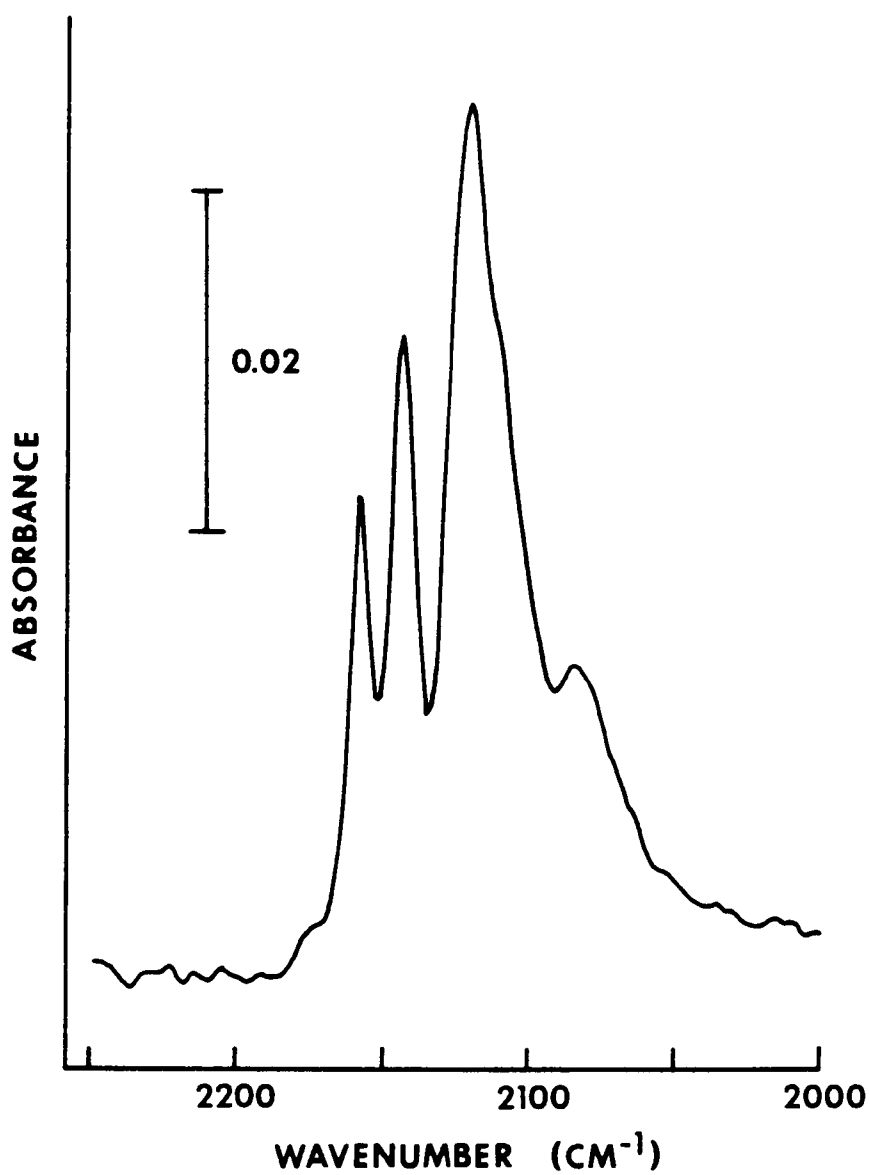


Figure 43. Infrared spectrum of 63/37 AlCl₃-NaCl frozen 1 hour after addition of Ir₄(CO)₁₂ under CO.

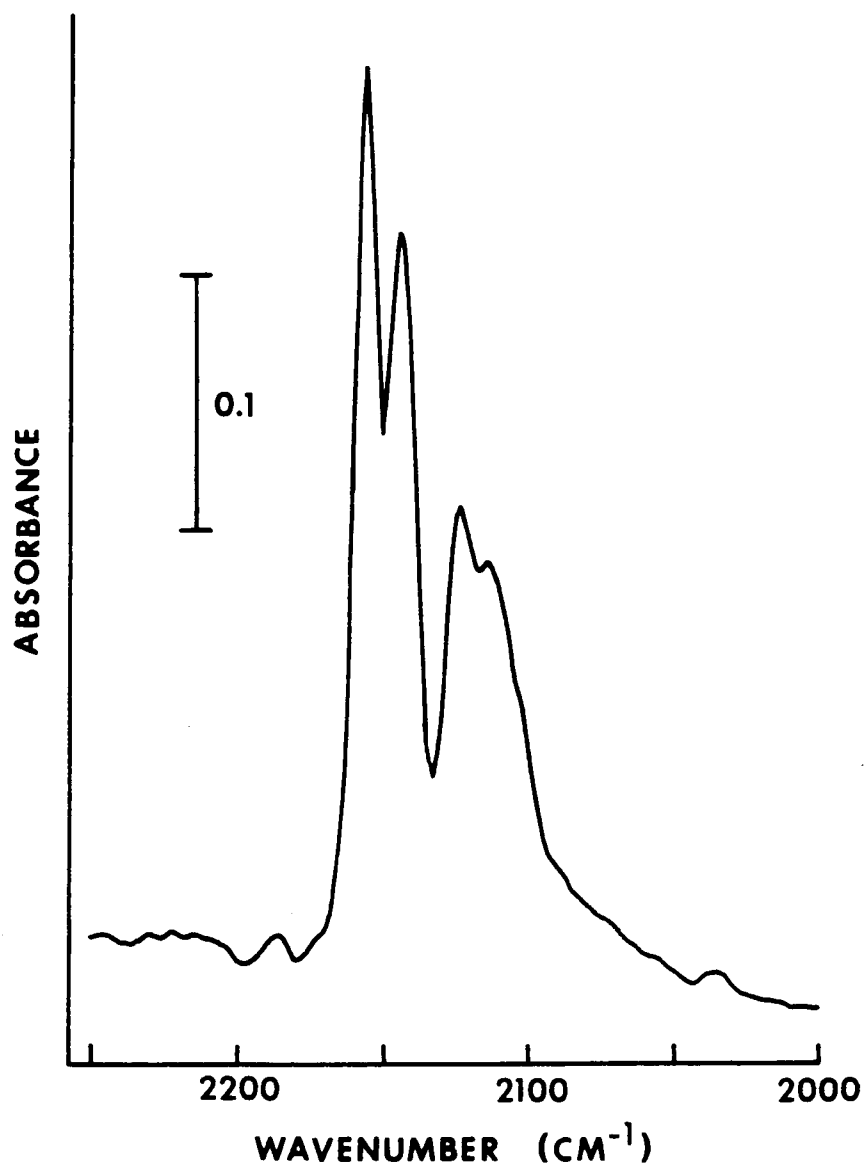


Figure 44. Infrared spectrum of 63/37 AlCl₃-NaCl frozen 10 minutes after addition of Ir₄(CO)₁₂ under CO-H₂ (1:3).

melt under only CO, indicating the formation of a different iridium carbonyl complex in the melt under CO-H₂ (1:3).

The infrared spectrum of the sample resulting from freezing the 63/37 AlCl₃-NaCl melt 5 hours after introduction of Ir₄(CO)₁₂ under CO-H₂ (1:3) is shown in Figure 45. Bands are observed at 2188, 2156, 2125, and 2112 cm⁻¹. Weak shoulders are also observed at 2148 and 2103 cm⁻¹. In addition to an overall decrease in band intensities, a relative increase in band intensity at 2188 and 2156 cm⁻¹ and decrease in bands at 2145-2103 cm⁻¹ were observed. Similar spectra were obtained using premixed solutions.

The infrared spectrum of the sample resulting from freezing the 63/37 AlCl₃-NaCl melt 1 hour after introduction of [IrCl(CO)₃]_n under CO-H₂ (1:3) is shown in Figure 46. Bands observed at 2145, 2134, 2100, and 2090 cm⁻¹ agree well with those obtained for the solid [IrCl(CO)₃]_n in KBr. Additional bands at 2188 and 2157 cm⁻¹, and a weak shoulder at 2125 cm⁻¹ indicate the formation of at least one new carbonyl complex from [IrCl(CO)₃]_n in the 63/37 melt under CO-H₂ (1:3).

E. X-Ray Photoelectron Spectroscopy

1. Pure Solids

A partial X-ray photoelectron spectrum of Ir₄(CO)₁₂ is shown in Figure 47. The iridium 4f_{7/2} and 4f_{5/2} peaks are located at 61.7 and 64.6 eV, respectively. A grey discoloration of the yellow solid was observed after prolonged exposure to the X-ray source, indicating long-term instability of the material under these conditions.

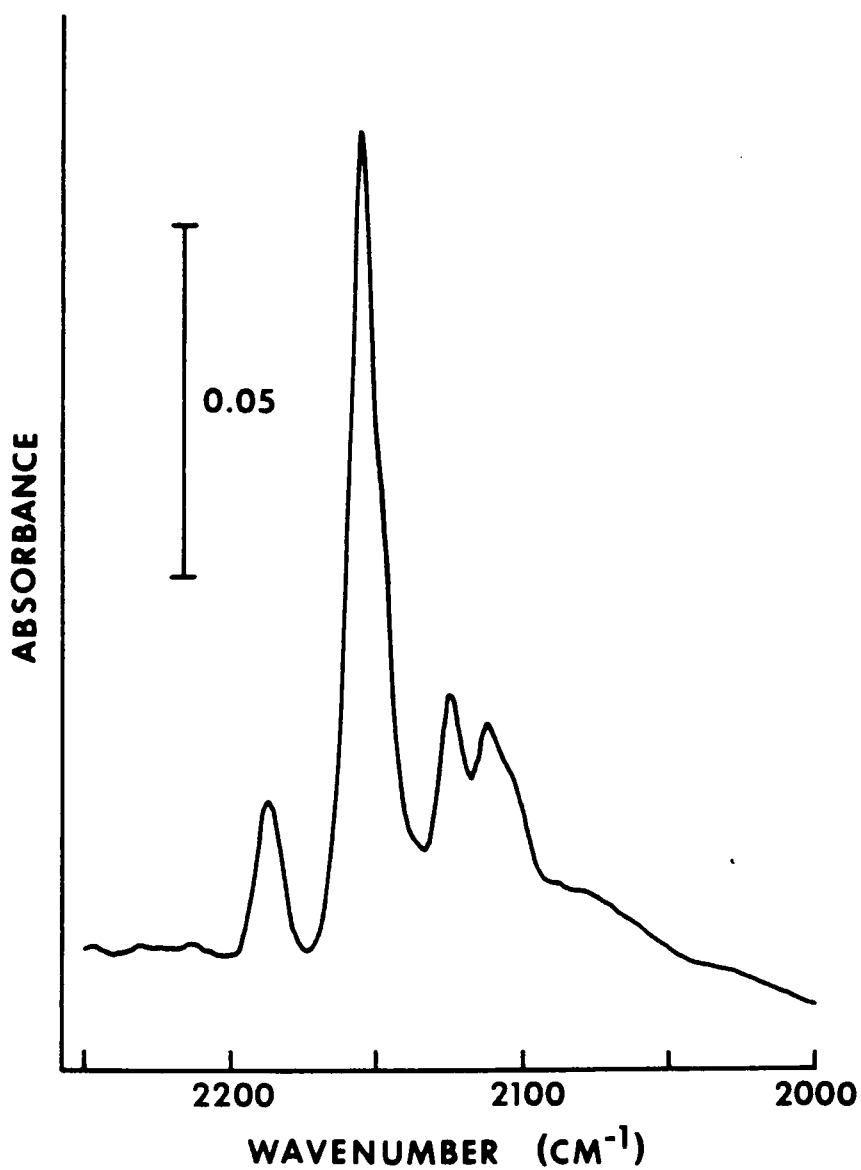


Figure 45. Infrared spectrum of 63/37 AlCl₃-NaCl frozen 5 hours after addition of Ir₄(CO)₁₂ under CO-H₂ (1:3).

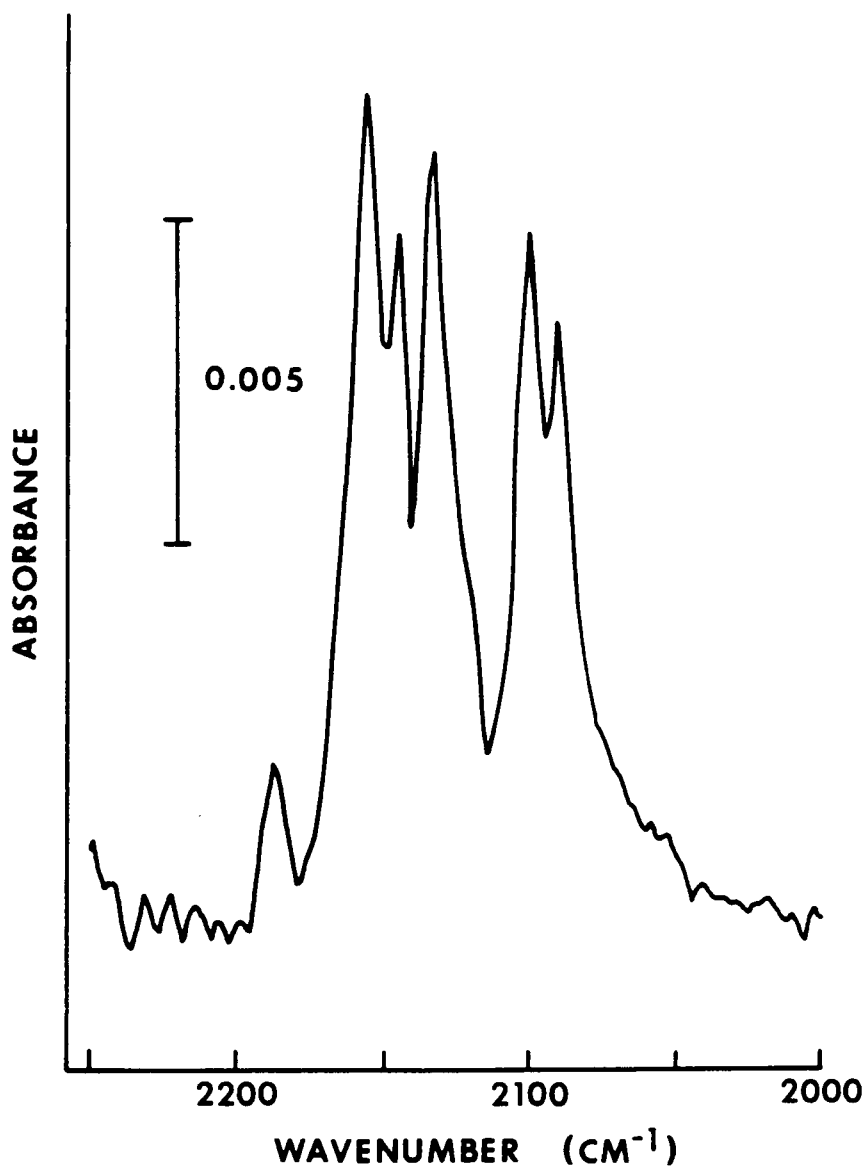


Figure 46. Infrared spectrum of 63/37 AlCl₃-NaCl frozen 1 hour after addition of [IrCl(CO)₃]_n under CO-H₂ (1:3).

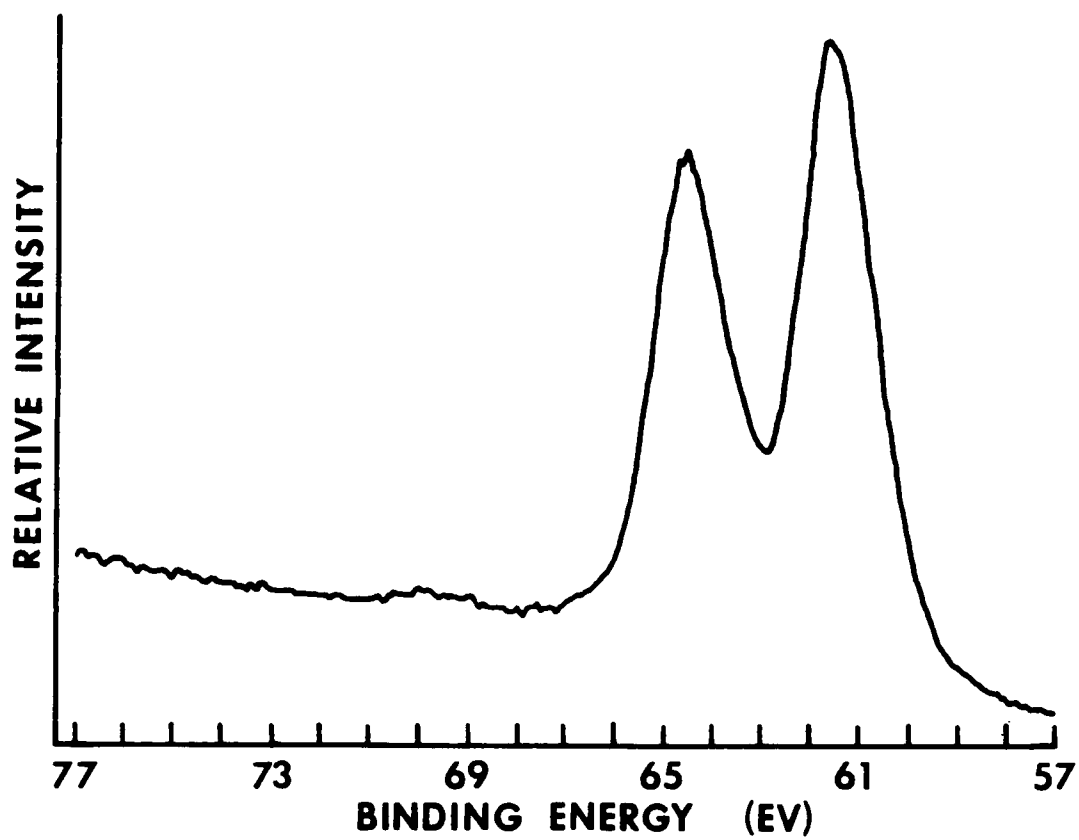


Figure 47. X-ray photoelectron spectrum of $\text{Ir}_4(\text{CO})_{12}$.

The X-ray photoelectron spectrum of $[\text{IrCl}(\text{CO})_3]_n$ is shown in Figure 48. The iridium $4f_{7/2}$ and $4f_{5/2}$ peaks are observed at 62.3 and 65.2 eV, respectively. For comparison, the spectrum of the iridium metal sample prepared by thermal decomposition of $\text{Ir}_4(\text{CO})_{12}$ under vacuum is shown in Figure 49. The iridium $4f_{7/2}$ and $4f_{5/2}$ peaks are located at 60.4 and 63.3 eV, respectively. An increase in binding energy of the iridium 4f peaks was observed in the order Ir metal < $\text{Ir}_4(\text{CO})_{12}$ < $[\text{IrCl}(\text{CO})_3]_n$. A comparison of these results with the literature is presented in Table XIII.

2. In 63/37 AlCl_3 -NaCl under CO-H_2 (1:3)

The X-ray photoelectron spectrum of the sample resulting from freezing the 63/37 AlCl_3 -NaCl 1 hour after introduction of $\text{Ir}_4(\text{CO})_{12}$ under CO-H_2 (1:3) is shown in Figure 50. Many peaks are observed, indicating the presence of more than one iridium complex. Major peaks at 64.5 and 66.4 eV are slightly higher in energy than those for $\text{Ir}_4(\text{CO})_{12}$ or $[\text{IrCl}(\text{CO})_3]_n$, suggesting the presence of a new complex. A comparison with literature values for Ir(I), Ir(II), and Ir(III) compounds is presented in Table XIII.

A more detailed XPS investigation of $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ in the melt under CO and CO-H_2 (1:3) was precluded by an apparent attack of the ESCA spectrometer detector by AlCl_3 vapor produced by heating of the sample during irradiation.

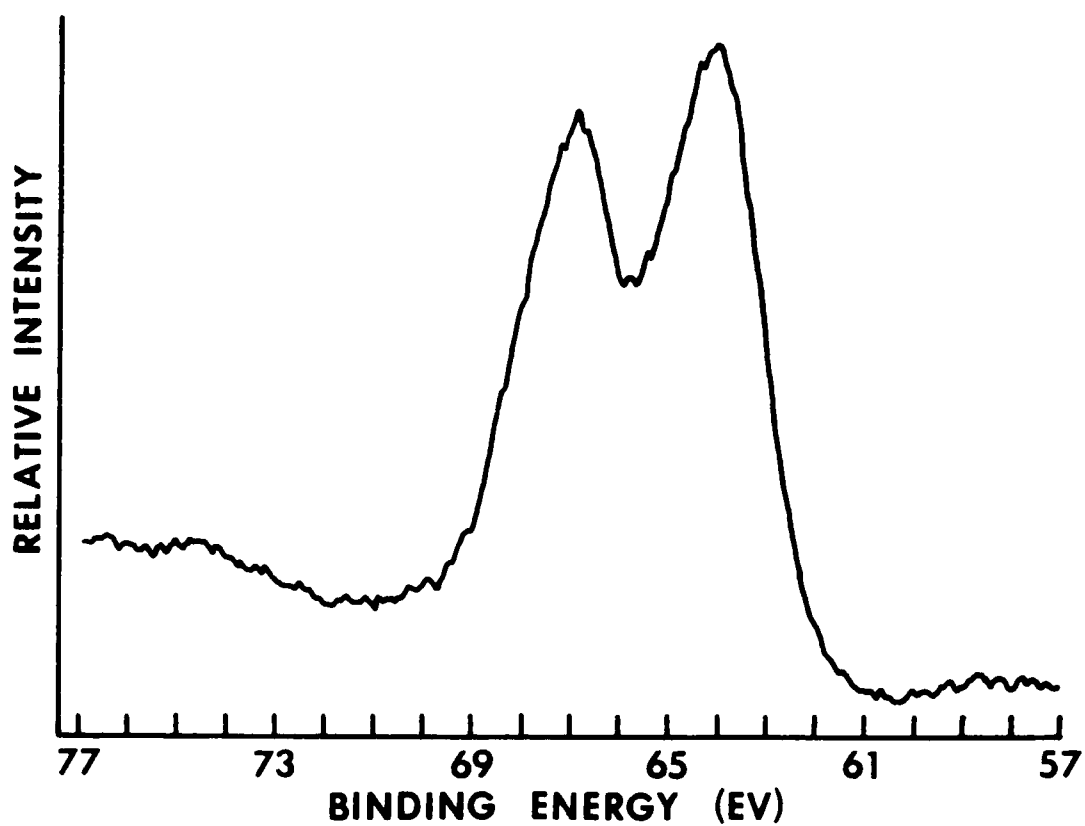


Figure 48. X-ray photoelectron spectrum of $[\text{IrCl}(\text{CO})_3]_n$.

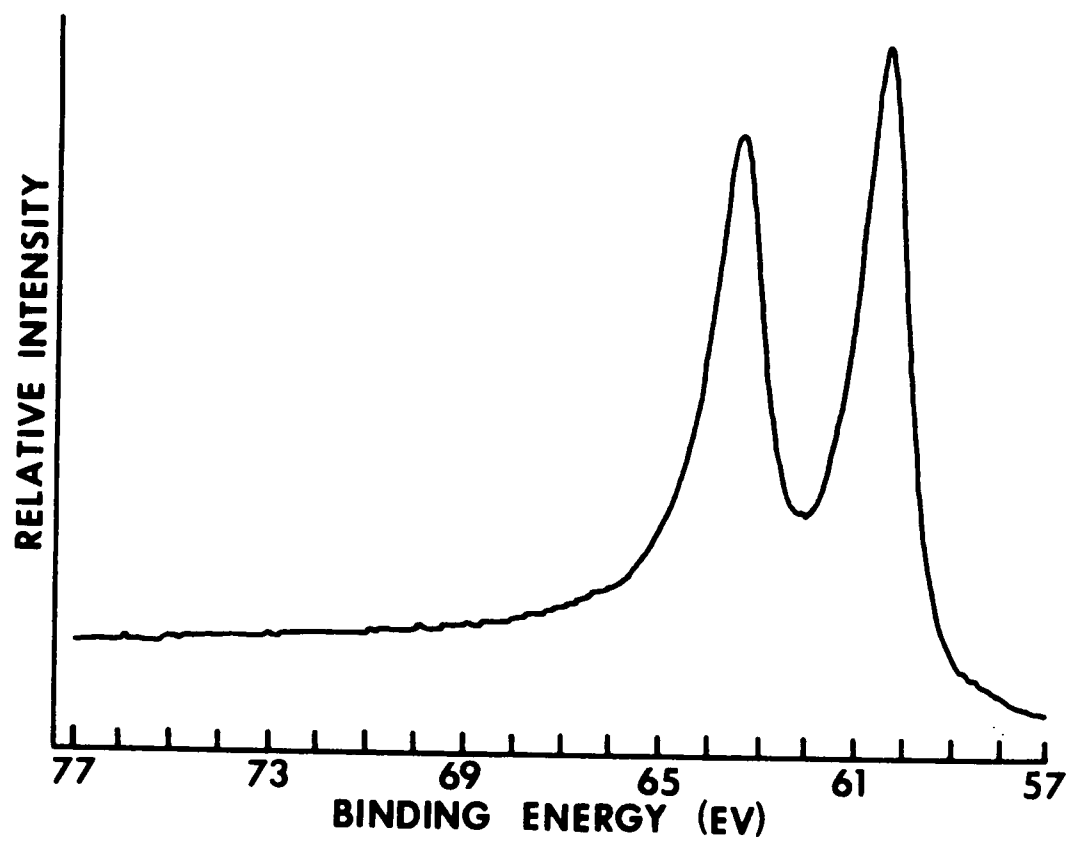


Figure 49. X-ray photoelectron spectrum of iridium metal.

Table XIII. Iridium 4f Binding Energies^a

Sample	4f _{7/2}	4f _{5/2}	Source
Ir metal	60.4	63.3	This work
Ir metal	60.1-60.8		Refs. 162-166
Ir ₄ (CO) ₁₂	61.7	64.6	This work
Ir ₄ (CO) ₁₂	62.5	65.6	Ref. 167
Ir ₄ (CO) ₁₂	62.8		Ref. 162
Ir ₄ (CO) ₁₂ ^b	62.3		Ref. 162
Ir ₄ (CO) ₁₂ ^c	61.9		Ref. 162
[IrCl(CO) ₃] _n	62.3	65.2	This work
[IrCl(CO) ₃] _n	63.6		Ref. 168
K ₂ [Ir ₂ (CO) ₄ Cl ₅]	63.2		Ref. 168
K[Ir ₂ (CO) ₄ Cl ₄]	62.9		Ref. 168
K ₂ IrCl ₆	63.7		Ref. 168

^aIn eV.^bOn SiO₂.^cOn Al₂O₃.

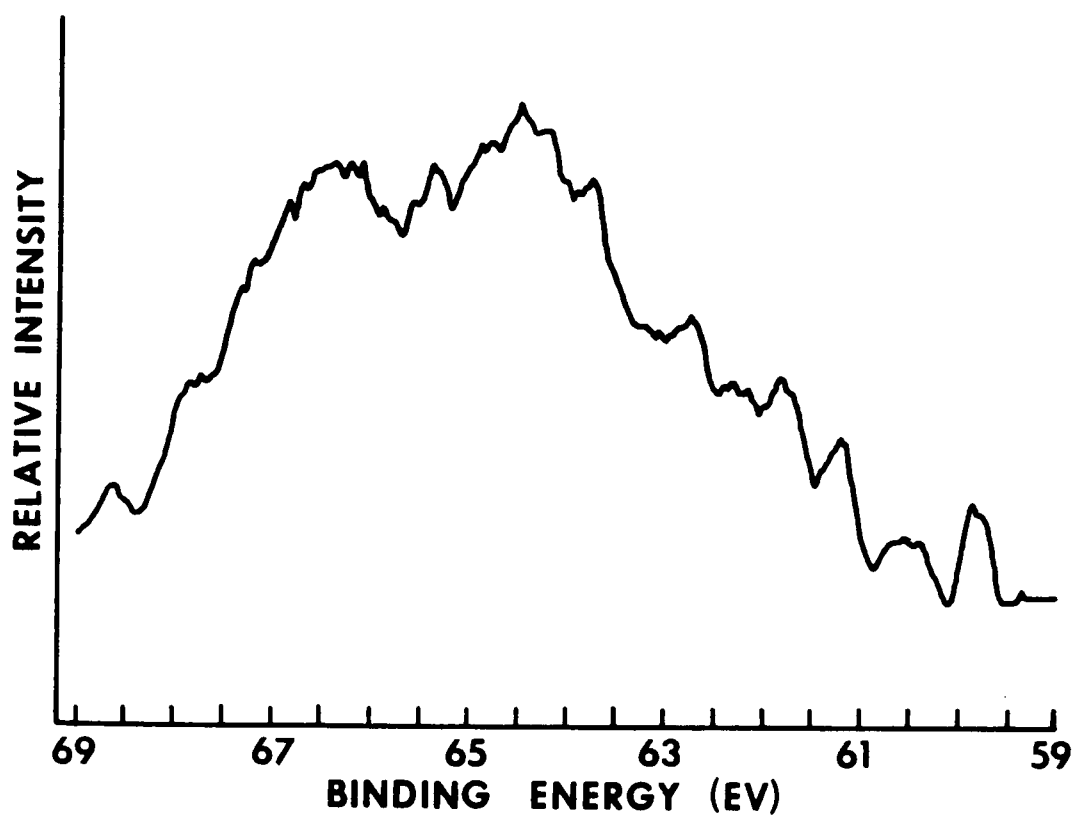


Figure 50. X-ray photoelectron spectrum of 63/37 $\text{AlCl}_3\text{-NaCl}$ frozen 1 hour after addition of $\text{Ir}_4(\text{CO})_{12}$ under CO-H_2 (1:3).

F. Electrochemistry

1. In Acetonitrile with 0.05 Molar TEAC

Cyclic voltammograms of $\text{Ir}_4(\text{CO})_{12}$ refluxed in CH_3CN containing 0.05 M TEAC displayed ill-defined reduction from -1.5 to -2.5 V vs. SCE, which increased with prolonged refluxing. A change in solution color from yellow to amber during refluxing was observed, suggesting a conversion of the original species to a complex which may be reduced.

For $[\text{IrCl}(\text{CO})_3]_n$ in the same solution, cathodic and anodic waves were observed at -2.21 and -1.63 V vs. SCE, respectively.

2. In 63/37 AlCl_3 -NaCl under CO

Cyclic voltammograms acquired using a $20 \text{ mV}\cdot\text{sec}^{-1}$ scan rate of $\text{Ir}_4(\text{CO})_{12}$ in the acidic melt under CO at selected periods after introduction using the Flickit assembly are presented in Figure 51. Broad reduction and oxidation waves observed at approximately 0.4 and 0.6 V vs. Al(III)/Al , respectively, developed with time. The weak anodic peak was not observed when the scan was reversed at 0.3 V (instead of 0.0 V), indicating that the reoxidation is dependent upon reduction of species near the cathodic limit. Cyclic voltammograms acquired using 50 and $100 \text{ mV}\cdot\text{sec}^{-1}$ scan rates showed similar but less-defined features, perhaps indicating slow kinetics of the reduction at glassy carbon.

A normal pulse voltammogram (NPV) of $\text{Ir}_4(\text{CO})_{12}$ in the melt under CO after 2 hours was acquired. A $\log [(i_d-i)/i]$ vs. E plot was constructed from the NPV response, and an n-value of 0.69 and $E_{1/2}$ of 0.34 V vs. Al(III)/Al were determined from the slope and y-intercept,

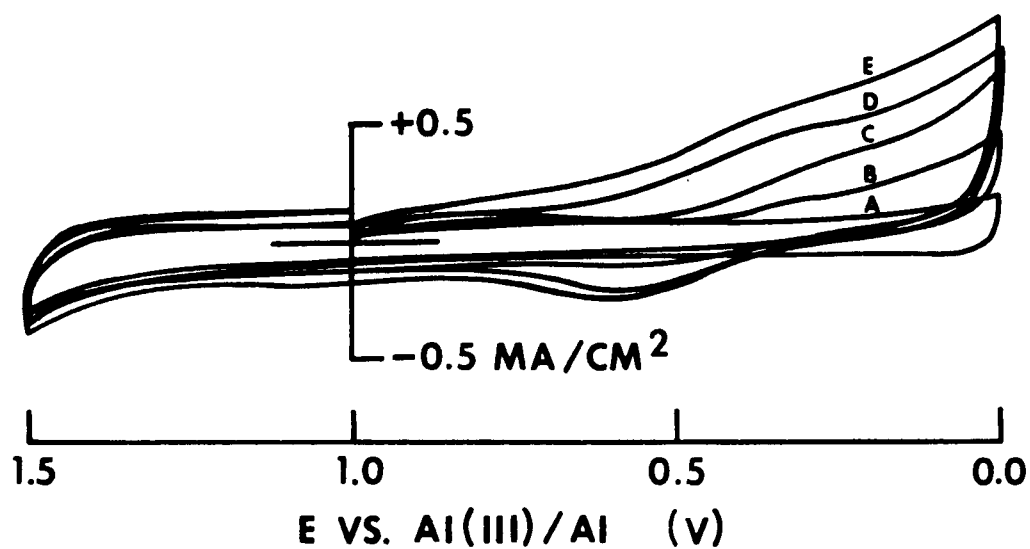


Figure 51. Cyclic voltammograms of $\text{Ir}_4(\text{CO})_{12}$ in 63/37 AlCl_3 - NaCl at 150 °C under CO at glassy carbon: (A) background, (B) initial, (C) 30 minutes, (D) 1 hour, (E) 2 hours; initial potential = 1.0 V vs. Al(III)/Al ; initial scan direction negative; scan rate = $20 \text{ mV} \cdot \text{sec}^{-1}$.

respectively, by least squares analysis of this plot. However, this plot was not truly linear, indicating that one is not dealing with a simple reversible process (169). Thus, the above values are estimates at best. Efforts to repeat the NPV analysis after the first scan at $2 \text{ mV} \cdot \text{sec}^{-1}$ were unsuccessful. The resulting response and irreproducibility indicated that a change in the electrode surface had occurred. Attempts to reoxidize any adsorbed reduced species by holding the electrode potential at 1.5 V for several minutes were unsuccessful. Examination of the glassy carbon after terminating the experiment revealed a dull gray coating on the electrode surface. X-ray fluorescence analysis of the electrode surface indicated the presence of iridium. It, therefore, appears that reduction of an iridium species in the 63/37 melt under CO at slow scan rates resulted in the deposition of iridium metal or adsorption of an iridium complex. At higher scan rates no evidence for this process was observed.

An electrochemical investigation of $[\text{IrCl}(\text{CO})_3]_n$ under the same conditions was performed. An identical response for cyclic voltammograms acquired at 20, 50, and $100 \text{ mV} \cdot \text{sec}^{-1}$ as for $\text{Ir}_4(\text{CO})_{12}$ was observed. However, the NPV was better-defined than that observed for $\text{Ir}_4(\text{CO})_{12}$. The resulting $\log [(i_d - i)/i]$ vs. E plot exhibited a linear segment for $E \leq 0.33 \text{ V vs. Al(III)/Al}$. The corresponding n -value and $E_{1/2}$ were determined to be 2.27 and 0.31 V, respectively. However, this plot did deviate from a straight line for potentials $> 0.33 \text{ V vs. Al(III)/Al}$, indicating that the reduction is not truly a reversible process. NPV measurements at $2 \text{ mV} \cdot \text{sec}^{-1}$ were reproducible. Unlike for $\text{Ir}_4(\text{CO})_{12}$, no evidence for the formation of an adsorbed species at slow scan rates was observed.

The similarity of cyclic voltammograms (at scan rates ≥ 20 $\text{mV}\cdot\text{sec}^{-1}$) for $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ suggests the formation of the same $\text{Ir}(+n)$ complex from both compounds in 63/37 AlCl_3 - NaCl under CO . The deposition of an iridium species at slow scan rates for $\text{Ir}_4(\text{CO})_{12}$ and not for $[\text{IrCl}(\text{CO})_3]_n$ may indicate the presence of an additional iridium complex resulting from $\text{Ir}_4(\text{CO})_{12}$ in the melt under CO .

3. In 63/37 AlCl_3 - NaCl under CO-H_2 (1:3)

Cyclic voltammetry of $\text{Ir}_4(\text{CO})_{12}$ introduced to the melt under CO-H_2 (1:3) indicated almost no electrochemical activity in the region 1.5-0.0 V. vs. Al(III)/Al . Only a slight increase in the current response near the cathodic limit is observed, indicating that most of the $\text{Ir}_4(\text{CO})_{12}$ undergoes different chemistry than under CO . The resulting species are apparently electrochemically inactive at glassy carbon in the potential range studied.

A similar study of $[\text{IrCl}(\text{CO})_3]_n$ in the melt under CO-H_2 (1:3) indicated the development of a sharp peak which, if observed, would be centered at a more negative potential than the cathodic limit. The broad cathodic wave observed at 0.4 V under only CO was not present, indicating the reduction of a different system. Only a small reoxidation wave at ~ 0.6 V vs. Al(III)/Al was observed, indicating that the reduction is almost totally irreversible under these conditions. The proximity of the NPV response to the cathodic limit precluded construction of $\log[(i_d-i)/i]$ vs. E plots to determine n and $E_{1/2}$ for this process.

CHAPTER VIII

DISCUSSION AND CONCLUSION

A. Reaction in 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO

UV-visible spectroscopy indicates that $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ ultimately form the same iridium complex in 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO. There is evidence that the formation of this complex from $\text{Ir}_4(\text{CO})_{12}$ proceeds by a first order process. The spectrum of this product does not agree well with spectra of either of the original compounds, suggesting the formation of a new iridium species. The high intensities of bands observed at 278, 326, and 430 nm are typical of metal-to-ligand-charge-transfer (MLCT) modes (170). A survey of the literature indicates a somewhat closer agreement with MLCT spectra for iridium (I) and rhodium (I) carbonyl complexes (171,172). Absorption maxima and molar absorptivities for these complexes are presented in Table XIV.

The 4:1 ratio of molar absorptivities calculated for $\text{Ir}_4(\text{CO})_{12}$ vs. $[\text{IrCl}(\text{CO})_3]_n$ (as the monomer), the intensity of UV-visible bands, and correlation with other spectra suggest that the final product in the 63/37 melt under CO is an iridium (I) chlorocarbonyl complex, possibly similar to $[\text{IrCl}_2(\text{CO})_2]^-$. However, due to the very low concentration of free Cl^- in 63/37 $\text{AlCl}_3\text{-NaCl}$ (See Table I, p. 5), the chloride ligand is probably coordinated with AlCl_3 as AlCl_4^- . This may account for the closer agreement with the MLCT spectrum of $[\text{IrBr}_2(\text{CO})_2]^-$ than for the analogous dichloro complex.

To produce an Ir(I) complex from $\text{Ir}_4(\text{CO})_{12}$, a suitable oxidizing agent must be present in the melt. One explanation may be the reduction

Table XIV. Absorption Maxima and Molar Absorptivities for Iridium (I) and Rhodium (I) Carbonyl Complexes^{a,b}

Compound	Wavelength in nm (molar absorptivity in $\text{M}^{-1}\cdot\text{cm}^{-1}$)
$[\text{IrCl}_2(\text{CO})_2]^-$	259 (4700); 351 (2380); 384 (530)
$[\text{IrBr}_2(\text{CO})_2]^-$	263 (6350); 319 (2450); 353 (2500)
$[\text{Ir}(\text{CN})_2(\text{CO})_2]^-$	290 (5030); 346 (1980); 401 (2960)
$[\text{RhCl}(\text{CO})_2]_2$	260 (13400); 318 (8300); 365
$[\text{RhCl}_2(\text{CO})_2]^-$	270 (5400); 336 (2700)
$[\text{RhBr}_2(\text{CO})_2]^-$	275 (6600); 337 (2900)

^aRef. 171.

^bRef. 172.

of H^+ , resulting from H_2O contamination according to (173):



The presence of H^+ in the melt is indicated in the background cyclic voltammogram (See Figure 4, p. 24), where the reduction wave at approximately -0.5 V vs. platinum QRE (~ 1.0 V vs. Al(III)/Al) has been attributed to the reduction of H^+ in the 63/37 melt at platinum (174). Recently developed electrochemical methods have indicated a minimum oxide concentration of $2-5 \times 10^{-3}$ M in chloroaluminate melts prepared using purified $AlCl_3$ (88,175). If the oxide contamination were due solely to H_2O according to Equation 35, the corresponding $[H^+]$ would be at least $4-10 \times 10^{-3}$ M. This is approximately one order of magnitude greater than that of $[Ir_4(CO)_{12}]$ in the most concentrated melt solution studied.

The observation of a single, highly-polarized Raman band at 202 cm^{-1} for $Ir_4(CO)_{12}$ in the 63/37 melt under CO indicates the presence of a binuclear complex with metal-metal bonding (176). Due to the absence of a more intense band at 162 cm^{-1} , it appears that the original $Ir_4(CO)_{12}$ cluster is quickly converted to an Ir_2 complex, such as $[Ir(CO)_n]_2$. This Raman band was also observed for $Ir_4(CO)_{12}$ in 63/37 $AlCl_3$ -NaCl under N_2 , suggesting that formation of this Ir_2 complex does not require uptake of CO. This suggests that the binuclear species is not $Ir_2(CO)_8$.

The disappearance of the band at 202 cm^{-1} indicates that the Ir_2 species is converted to a new complex which does not have metal-metal bonding. Allowing for the less sensitive nature of Raman measurements as compared to absorption spectroscopy, the disappearance of the

202 cm^{-1} Raman band roughly coincides with the development of MCLT bands in the UV-visible spectrum.

The absence of similar low frequency Raman bands for $[\text{IrCl}(\text{CO})_3]_n$ in 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO indicates that only species without metal-metal bonding are formed from this Ir(I) complex.

A comparison of IR spectra for $\text{Ir}_4(\text{CO})_{12}$ as the original solid and the sample resulting from exposure to the 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO for 1 hour indicates that a more complex system exists in the melt. The overall shift in CO bands to higher frequencies (due to a decrease in M-CO bonding) may reflect oxidation of the metal center (143) and/or adduct formation with AlCl_3 (177). The formation of adducts with transition metal carbonyl complexes and AlCl_3 has been reported to result in a shift to higher frequency of CO stretching modes of more than 100 cm^{-1} (177).

The peak separation (35 cm^{-1}) and relative intensity of IR bands at 2120 and 2085 cm^{-1} for the 63/37 melt frozen 1 hour after introduction of $\text{Ir}_4(\text{CO})_{12}$ under CO resemble those observed for pure $\text{Ir}_4(\text{CO})_{12}$ in KBr (at 2056 and 2023 cm^{-1}) and may indicate the presence of an $[\text{Ir}(\text{CO})_3]_n$ complex. Poor agreement with the IR spectrum of $\text{Ir}_2(\text{CO})_8$ suggests that the octacarbonyl is not present (178). The increase in CO stretching frequencies of 64 cm^{-1} from $\text{Ir}_4(\text{CO})_{12}$ bands may be due to formation of an adduct with AlCl_3 coordinated at the iridium (0) center.

While the peak separation (15 cm^{-1}) for bands at 2158 and 2143 cm^{-1} does not agree well with that for the 2056 and 1970 cm^{-1} bands observed for $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$ in 2-methoxyethanol at

120°C (179), similar separation is observed for bands at 2044 and 2029 cm^{-1} for $[\text{Ir}(\text{CO})_2\text{Br}_2]^-$ isolated as the tetraphenylarsonium salt (180). Formation of an adduct with AlCl_3 coordinated at the metal center is unlikely due to the poor Lewis basicity of iridium in the positive (+1) state. However, interaction of the Lewis acid with the halide ligand of a carbonyl complex may occur (181,182). Such halide-Lewis acid adduct formations are observed to increase CO stretching frequencies by 30-50 cm^{-1} .

The absence of IR bands at 1600-1850 cm^{-1} due to the solute indicates that the final iridium complex does not contain bridging CO ligands. This strongly suggests that the resulting iridium species is not a substituted complex such as $\text{Ir}_4(\text{CO})_{11}\text{L}$ or $\text{Ir}_4(\text{CO})_{10}\text{L}_2$ (L=ligand), where a structural change from no bridging CO's in $\text{Ir}_4(\text{CO})_{12}$ to bridging CO's in the substituted forms normally occurs (183-186). Also precluded is the formation of iridium carbonyl species of higher nuclearity, such as $\text{Ir}_6(\text{CO})_{16}$, which have structures containing bridging CO ligands (187,188). While adduct formation with a Lewis acid coordinated to the oxygen atom of bridging CO groups is known (177,189), such interactions result in a marked decrease in frequencies for the resulting CO stretching vibrations. It, therefore, appears that an $\text{Ir}_n\text{CO-A}$ (A = Lewis acid) complex is not produced from $\text{Ir}_4(\text{CO})_{12}$ in 63/37 AlCl_3 -NaCl under CO. Thus, this interpretation of the IR spectrum suggests the presence of an iridium carbonyl species $[\text{Ir}(\text{CO})_3]_n$ and a chlorocarbonyl iridium (I) complex after 1 hour. To account for increases in CO stretching frequencies, it appears that both complexes probably exist as adducts with AlCl_3 coordinated at the Ir(0) metal in $[\text{Ir}(\text{CO})_3]_n$ and at the chloride ligand of the Ir(I) complex (as AlCl_4^-).

Electrochemical analysis of the system provided limited information regarding $\text{Ir}_4(\text{CO})_{12}$ in the melt under CO. The similarity of cyclic voltammograms at $\geq 20 \text{ mV} \cdot \text{sec}^{-1}$ for $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ suggests that the same reducible $\text{Ir}(+n)$ carbonyl complex is formed in 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO. However, the deposition of an iridium species on glassy carbon at slower scan rates for $\text{Ir}_4(\text{CO})_{12}$ and not for $[\text{IrCl}(\text{CO})_3]_n$ indicates some difference in the corresponding solutions. One such explanation may be the formation of an additional complex from $\text{Ir}_4(\text{CO})_{12}$.

A survey of the literature indicates that primarily the electrochemistry of Ir(III) and Ir(IV) species, mainly as the halide complexes, has been studied (190,191). However, the electrochemistry of binary carbonyls $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn, Re}$) has been reported (192). The reduction of these complexes proceeds by:

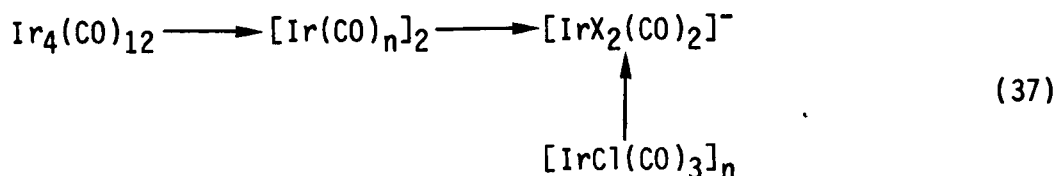


The peak potential separations for the anodic and cathodic reactions are quite large, 1.63 V and 2.26 V for $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, respectively. These separations are greater than the electrochemical window of the 63/37 melt observed in this study using the glassy carbon electrode. This may explain why the reduced complex adhering to the electrode was not removed by reoxidation. One additional explanation for the presence of an adsorbed product could be the formation of a carbide species with the carbon electrode. Although not known for iridium, several carbide carbonyl clusters of Group VIII transition metals ($\text{Fe, Ru, Os, Co, Rh}$) have been reported (193-195). The simplest

structure known for the rhodium complex is the anion $[\text{Rh}_6(\text{CO})_{15}\text{Cl}]^{2-}$, which is prepared from $\text{Rh}_4(\text{CO})_{12}$ (196).

It appears that the formation of an analogous iridium carbonyl carbide is possible by the reaction of the $[\text{Ir}(\text{CO})_n]^-$ species produced according to Equation 36 (p. 153) and unreduced $[\text{Ir}(\text{CO})_3]_n$ at the carbon electrode surface. The observation of an adsorbed species only at slow scan rates would support the formation of such a complex, where both the anion $[\text{Ir}(\text{CO})_n]^-$ and $[\text{Ir}(\text{CO})_3]_n$ would be present at the electrode surface. This explanation is consistent with the absence of the formation of such a complex for $[\text{IrCl}(\text{CO})_3]_n$ under similar conditions, where evidence for a proposed neutral species $[\text{Ir}(\text{CO})_3]_n$ is not observed.

The simplest reaction scheme suggested by all the spectral and electrochemical results is given by:



where $\text{X} = \text{Cl}^-$ is coordinated with AlCl_3 as AlCl_4^- . All evidence indicates that this or a similar iridium (I) chlorocarbonyl species is formed as the ultimate species in the 63/37 AlCl_3 - NaCl melt under CO. There is no evidence for a long-lived Ir_n metal carbonyl cluster in the melt under these conditions.

A similar breakdown of $\text{Rh}_4(\text{CO})_{12}$ in anhydrous C_6H_6 or tetrahydrofuran upon addition of AlBr_3 has been reported (197). The same IR spectrum was obtained when $\text{Rh}_4(\text{CO})_{12}$ was replaced by

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in the system. $[\text{Rh}(\text{CO})_2\text{X}_2]^-$ ($\text{X}=\text{Cl}^-, \text{Br}^-$) was proposed as the final species.

In an earlier study by Whyman (198), no evidence for the direct action of CO at 550 atm on $\text{Ir}_4(\text{CO})_{12}$ in liquid paraffin at 200 °C for 16 hours was observed. The results in this work indicate that the strong Lewis acidity of the 63/37 AlCl_3 -NaCl melt apparently plays a major role in the chemistry of $\text{Ir}_4(\text{CO})_{12}$ observed in this system.

B. Reaction in 63/37 AlCl_3 -NaCl under CO-H_2 (1:3)

UV-visible spectroscopy indicates that only a small fraction (10-30%) of $\text{Ir}_4(\text{CO})_{12}$ or $[\text{IrCl}(\text{CO})_3]_n$ in the 63/37 melt under CO-H_2 (1:3) undergoes the same chemistry as under only CO. The development of a large band below 250 nm and a new band at 406 nm (both with lower molar absorptivities than bands attributed to the products formed under CO) indicates that at least one additional iridium complex is formed under CO-H_2 (1:3). A much higher concentration of total iridium species is permitted using the premix vs. the Flickit valve introduction method, which may be due to a greater availability of the gas mixture during heating of the crushed solid vs. that dissolved in the melt at 150 °C. This may explain the >4-fold increase in concentration for the catalytic system used by Muetterties et al. (143), where the $\text{Ir}_4(\text{CO})_{12}$ was premixed with the AlCl_3 -NaCl solid, as compared to the catalytic study by Collman et al. (144), where the solute was introduced to the melt at 180 °C. The presence and disappearance of the highly-polarized Raman band at 202 cm^{-1} of approximately the same intensity as under only CO indicates that a similar initial reaction under CO-H_2 (1:3) producing the same $[\text{Ir}(\text{CO})_n]_2$ complex occurs.

The IR spectrum of the solution frozen 10 minutes after introduction of $\text{Ir}_4(\text{CO})_{12}$ to the 63/37 melt under CO-H_2 (1:3) was quite different from that acquired under CO after 1 hour. The two bands previously assigned to an Ir(I) chlorocarbonyl complex at 2158 and 2143 cm^{-1} were observed, however an inversion in intensity from the CO study indicates the contribution of an additional complex. The IR spectrum of the solution frozen 5 hours after digestion in 63/37 $\text{AlCl}_3\text{-NaCl}$ under CO-H_2 (1:3) indicated a long-lived species with bands at 2188, 2156, and 2125 cm^{-1} . The same bands were observed for $[\text{IrCl}(\text{CO})_3]_n$ under the same conditions, along with those attributed to the original solid. The peak separations and relative intensities for these bands are very similar to those proposed for $\text{HIr}(\text{CO})_4$ produced by the reaction of CO and H_2 at high pressure with $\text{Ir}_4(\text{CO})_{12}$ in hydrocarbon solvents (198,199). This comparison is presented in Table XV. The increase in CO stretching frequencies is probably due to adduct formation with AlCl_3 coordinated at the metal center (177). If such an adduct is formed, the iridium is most likely in the (-1) oxidation state. The corresponding anion $\text{Ir}(\text{CO})_4^-$ has been reported as the sodium and both tetramethyl- and tetraethylammonium salts (188).

The broad band observed at 1630 cm^{-1} for both sample and background IR spectra has been assigned to the O-H bending resulting from adsorbed H_2O (160). Muetterties et al. (143) interpreted this band as a carbonyl stretching vibration for an $\text{Ir}_n\text{CO-A}$ adduct (A = Lewis acid), suggesting the presence of an intact iridium metal cluster. In this work, no bands resulting from $\text{Ir}_4(\text{CO})_{12}$ were observed in this region which could be attributed to formation of a carbonyl cluster-Lewis acid adduct.

Table XV. Infrared Spectra of $\text{HIr}(\text{CO})_4$ and $\text{Ir}_4(\text{CO})_{12}$ in 63/37 AlCl_3 - NaCl under CO-H_2 (1:3)

Compound	Wavenumber (cm^{-1})		
$\text{Ir}_4(\text{CO})_{12}^{\text{a}}$	2188m	2156s	2125m
$\text{HIr}(\text{CO})_4^{\text{b}}$	2054m	2031s	1999w
$\text{HIr}(\text{CO})_4^{\text{c}}$	2070m	2030s	1995w

^aMelt frozen 5 hours after introduction of $\text{Ir}_4(\text{CO})_{12}$ under CO-H_2 (1:3).

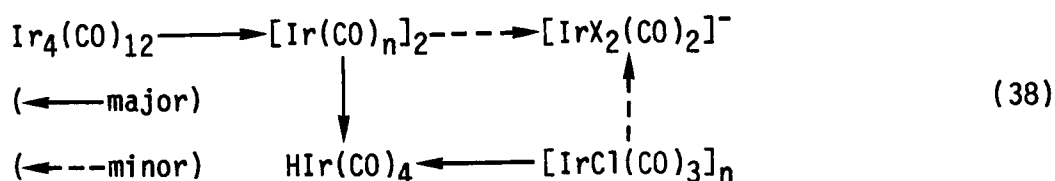
^bRef. 198 (dodecane solvent used).

^cRef. 199 (heptane solvent used).

XPS measurements indicated many chemical shifts for the iridium 4f peaks, suggesting the presence of more than one iridium complex.

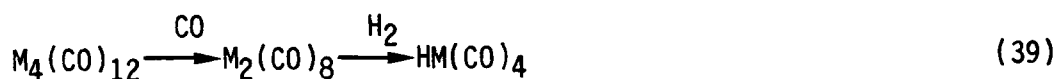
Electrochemical analysis revealed that the major product(s) resulting from addition of $\text{Ir}_4(\text{CO})_{12}$ to the 63/37 melt under CO-H_2 (1:3) were electrochemically inactive in the potential region studied. This indicates that different chemistry occurs under CO than under CO-H_2 (1:3) for $\text{Ir}_4(\text{CO})_{12}$ in the 63/37 melt.

All these results suggest that the reaction of $\text{Ir}_4(\text{CO})_{12}$ and $[\text{IrCl}(\text{CO})_3]_n$ in the 63/37 melt under CO-H_2 (1:3) may be best described by:



where $\text{X} = \text{AlCl}_4^-$.

A similar reaction has been proposed for $\text{M}_4(\text{CO})_{12}$, where $\text{M} = \text{Co}, \text{Rh}$ (199):



The intermediacy of an iridium octacarbonyl species was not detected in the studies of the formation $\text{HIr}(\text{CO})_4$ from $\text{Ir}_4(\text{CO})_{12}$ (198,199); however, $\text{Ir}_2(\text{CO})_8$ has been found under more favorable conditions (178).

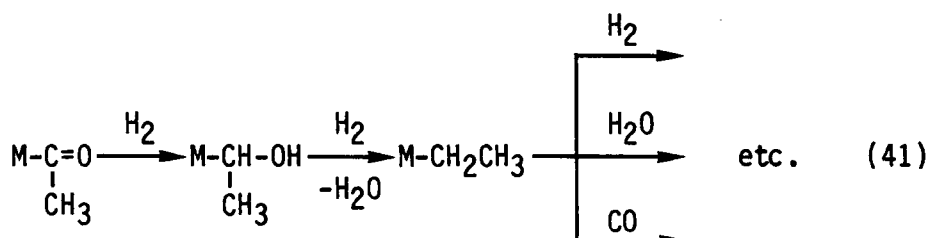
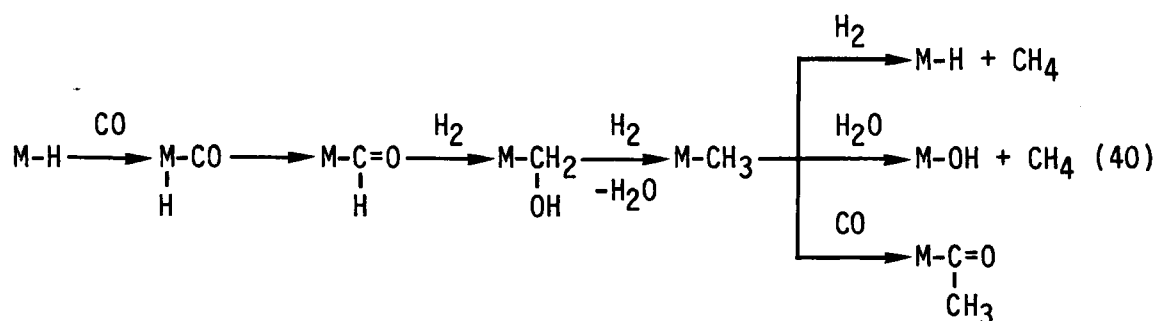
The species $\text{HM}(\text{CO})_4$ ($\text{M} = \text{Co}, \text{Rh}$) has been recently mentioned or proposed as the active species in several catalytic reactions involving metal carbonyl complexes (200-203). Therefore, the analogous iridium

complex $\text{HIr}(\text{CO})_4$ or system incorporating this species may be responsible for Fisher-Tropsch activity in the melt. There is no evidence in this work to support the existence of a long-lived iridium carbonyl cluster in 63/37 AlCl_3 -NaCl melt under CO-H_2 (1:3).

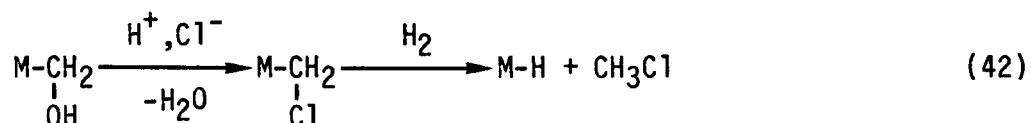
The proposed formation of $\text{HIr}(\text{CO})_4$ or similar species is in agreement with the conclusion presented by Collman et al. (144) that an iridium mononuclear carbonyl complex may be responsible for catalytic activity in the melt. However, evidence in this work indicates the formation of $\text{HIr}(\text{CO})_4$ in the 63/37 melt under CO-H_2 (1:3) instead of an iridium chlorocarbonyl complex (as under only CO). The observations from catalytic studies (144,145), such as unaccounted CO consumption, reduced conversion rate with addition of HCl, positive dependence upon H_2 pressure, and increased conversion rates with addition of aluminum, further support the formation of $\text{HIr}(\text{CO})_4$ or similar iridium complex.

C. Summary

The results in this work support the conclusion presented by Collman et al. (144) that the species responsible for homogeneous Fischer-Tropsch activity in the acidic AlCl_3 -NaCl melt is probably a mononuclear iridium complex and not a metal cluster. The formation of $\text{HIr}(\text{CO})_4$ or a similar species is consistent with the reaction mechanism proposed by Olive et al. (203) for the synthesis of hydrocarbons from CO and H_2 using a M-H catalyst according to:



This mechanism is similar to that proposed by Collman (144) which involves a Ir-H complex, where the additional production of CH_3Cl may be explained by:



Further work to confirm the formation of $\text{HIr}(\text{CO})_4$ or a similar Ir-H complex should include:

- A. a comparison of these results with those resulting from the addition of $\text{HIr}(\text{CO})_4$ to the 63/37 melt under CO-H_2 ;
- B. isolation of the iridium species from the melt for further analysis, such as mass spectrometry and X-ray crystallography;
- C. analysis by proton nuclear magnetic resonance to observe hydride protons;

D. the effect of adding a reducing agent, such as NaBH_4 or LiAlH_4 , which would enhance the formation of an $\text{Ir}(-1)$ complex in the melt;

E. the effect on the rate of formation of the final iridium species by varying the original $\text{Ir}_4(\text{CO})_{12}$ concentration or CO-H_2 ratio and pressure;

F. investigation of the initial reaction with the melt by introducing $\text{Ir}_4(\text{CO})_{12}$ dissolved in a volatile solvent, such as CH_2Cl_2 , thereby avoiding any complications due to the dissolution of the solid.

As noted by Collman et al. (144), a catalytic process which consumes AlCl_3 has no technological significance. However, the chloroaluminate system presented here may offer a potential route to the synthesis of a catalyst for use in other media.

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APPENDIX
FOCRSS PROGRAMS

C 240

01.10 C SPECTROELECTROCHEMICAL PROGRAM

01.20 C SPECTRAL DATA

02.10 C ACQUIRE DARK CURRENT

02.20 S A=43;S B=8;S C=9;S D=0;X FP(2,11876,0)

02.30 A "READY TO ACQUIRE D.C.?",Q

02.40 X FUID(A,B,C,D)

02.50 I [FP(2,11876)]2.6,2.5,2.6

02.60 X FUID(1566)

03.10 C ACQUIRE 100 %T

03.20 S A=100;S B=8;S C=9;S D=0;X FP(2,11620,0)

03.30 A "READY TO ACQUIRE 100 %T?",Q

03.40 X FUID(A,B,C,D)

03.50 I [FP(2,11620)]3.6,3.5,3.6

03.60 X FUID(1566);X FBMU(13,15);L P D 0

04.10 C ACQUIRE INITIAL SPECTRUM

04.20 S A=206;S B=8;S C=9;S D=0;X FP(2,12132,0)

04.30 A "READY TO ACQUIRE SPECTRUM?",Q

04.40 X FUID(A,B,C,D)

04.50 I [FP(2,12132)]4.6,4.5,4.6

04.60 X FUID(1566);L P D 1

05.10 C SPECTRA AFTER POTENTIAL STEP

05.20 S A=206;S B=1;S D=0;X FP(2,12132,0);S BN=2

05.30 A "SCANS SKIPPED PARAMETER",C

05.40 A "TOTAL NUMBER SPECTRA?",ZZ

05.50 A "READY TO BEGIN?",Q

05.60 X FUID(A,B,C,D);X FCST(4095)

05.70 I [FP(2,12132)]5.8,5.7,5.8

05.80 L P D BN;I [ZZ-BN]6.1;S BN=BN+1;X FP(2,12132,0);G 5.7

06.10 X FUID(1566);S T=FCST(0)

06.20 T T/100/60," MIN",!;Q

C 241

01.10 C SPECTROELECTROCHEMICAL PROGRAM

01.20 C ELECTROCHEMICAL DATA

02.10 C VOLTAMMETER SETTINGS

02.20 A "CURRENT RANGE",CR

02.30 A "VARIABLE SETTING(0-100)",US

02.40 S $ZX=CR*(100/US)$

03.10 C ACQUISITION PARAMETERS

03.20 A "SAMPLING PERIOD(SEC)",SP;S $CP=SP*100$ 03.30 A "SAMPLING DURATION(SEC)",SD;S $SD=SD*100$ 03.40 S $TX=SD/CP$;T %8,"TOTAL NUMBER OF SAMPLES : ",TX,!

03.50 A "STARTING ADDRESS FOR DATA STORAGE",M

04.10 C DATA ACQUISITION

04.20 S A=206;S B=8;S C=4095;S D=0;S Z=0;S ZZ=0

04.30 A "READY TO BEGIN",Q

04.40 X $FCST(4095)$;X $FUID(A,B,C,D)$ 04.50 X $FP(1,Z+M,FADCE1)$;S $ZZ=ZZ+CP$;S $Z=Z+1$ 04.60 I $[TX-Z]5.1$ 04.70 I $[FCST(-9)-ZZ]4.7$;G 4.505.10 S $T=FCST[0]$;X $FUID(1566)$

05.20 T "EXPERIMENT COMPLETE",!

05.30 T "TOTAL TIME ELAPSED(SEC)", $T/100$;T %8.04,!

05.40 Q

C 242

01.10 C PROGRAM TO INTEGRATE CURRENT AND PLOT CHARGE VS TIME

02.10 C INSTRUMENTAL PARAMETERS

02.20 A "CURRENT RANGE",CR

02.30 A "VARIABLE(0-100)",US

02.40 S $ZX=CR*(100/US)$

02.45 A "ADC OUTPUT FOR NO CHARGE",NC

02.50 A "STARTING ADDRESS",M

02.60 A "SAMPLING PERIOD",SP

02.70 A "TOTAL SAMPLES ",TX

02.80 A "BACKGROUND CORRECTION",BC

02.85 I [BC-15]2.9;A "STARTING ADDRESS FOR BACKGROUND DATA",N

02.90 A "MILLICOULOMBS FULL SCALE",ZM

02.95 S $KI=FP(1,M+10)-FP(1,M+15);S KI=FSGN(KI)$ 03.10 S $IT=0;S IB=0;S II=0$

03.15 I [BC-15]3.2;G 3.4

03.20 F $J=1,TX;D 4;D 6$

03.30 G 3.5..

03.40 F $J=1,TX;D 4;D 5;D 6$

03.50 T "COMPLETE",!;Q

04.10 S $T1=[FP(1,M+J-1)-NC]*0.00488$ 04.20 S $T2=[FP(1,M+J)-NC]*0.00488$ 04.30 S $IT=0.5*[(T1+T2)*ZX/10]*SP;R$ 05.10 S $B1=[FP(1,N+J-1)-NC]*0.00488$ 05.20 S $B2=[FP(1,N+J)-NC]*0.00488$ 05.30 S $IB=0.5*[(B1+B2)*ZX/10]*SP;R$ 06.10 S $II=II+(IT-IB)$ 06.20 X $FDIS[J*4095/TX,KI*II*4095/ZM];R$

C 240

01.10 C PROGRAM TO ACQUIRE SPECTRA AT SELECTED TIME INTERVALS
 01.20 C USING REAL TIME CLOCK

02.10 C ACQUIRE DARK CURRENT
 02.20 S A=43;S B=8;S C=9;S D=0;X FP(2,11876,0)
 02.30 A "READY TO ACQUIRE DC",Q
 02.40 X FUID(A,B,C,D)
 02.50 I [FP(2,11876)]2.6,2.5,2.6
 02.60 X FUID(1566)

03.10 C ACQUIRE 100 %T
 03.20 S A=100;X FP(2,11620,0)
 03.30 A "READY TO ACQUIRE 100 %T",Q
 03.40 X FUID(A,B,C,D)
 03.50 I [FP(2,11620)]3.6,3.5,3.6
 03.60 X FUID(1566)

04.10 C SAMPLING PARAMETERS
 04.20 S A=206;S B=8;S C=3;S D=0;S BN=0;S ZZ=0
 04.30 X FP(2,12132,0)
 04.40 A "SAMPLING PERIOD(SEC)",SP;S CP=SP*100
 04.50 A "TOTAL SAMPLES TO BE ACQUIRED",TS
 04.60 A "READY TO BEGIN",Q

05.10 C DATA ACQUISITION ROUTINE
 05.20 X FCST[4095]
 05.30 I [FCST(-9)-ZZ]5.3;X FDIS(0,0);X FUID(A,B,C,D)
 05.40 I [FP(2,12132)]5.5,5.4,5.5
 05.50 X FUID(1566);L P D BN;\$ P BN
 05.60 I [TS-BN-2]6.1;S BN=BN+1;X FP(2,12132,0)
 05.70 S ZZ=ZZ+CP;G 5.3

06.10 S T=FCST(0)
 06.20 T "TOTAL TIME ",(T/100)/60," MIN",!
 06.30 X FBMU(13,15);\$ P BN+1;\$
 06.40 Q

C 245

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01.10 C PROGRAM TO PLOT ABSORBANCE AT SELECTED WAVELENGTH
01.20 C AS A FUNCTION OF TIME;
01.30 C OPERATION BASED UPON 100 %T LOCATED IN BLOCK NO. 13

02.10 A "INITIAL BLOCK NUMBER",SB
02.20 A "FINAL BLOCK NUMBER",EB
02.30 A "ABSORBANCE UNITS FULL SCALE",AU
02.35 A "OFFSET",OS
02.40 A "DATA HARDCOPY?",DH
02.50 A "SAMPLING PERIOD",SP

03.05 A "POINT TO BE PLOTTED",P
03.10 S R=FP(1,11520+P)
03.15 I [DH-15]3.20;A "READY FOR OUTPUT?",Q;T "POINT ",P,!,!
03.16 T "          TIME          ABSORBANCE",!,!
03.20 F I=SB,EB;D 4
03.30 G 3.05

04.10 L G D,I;S Z=FP(1,12032+P)
04.20 S AB=FLOG(R/Z)/2.303
04.30 S X=(I-SB)*4095/(EB-SB)
04.40 S Y=(AB+OS)*4095/AU
04.50 X FDIS(X,Y)
04.60 I [14-DH]4.7;R
04.70 T "          ",I*SP,".....",AB,!

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C 246

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01.10 C PROGRAM TO SMOOTH AND PLOT DATA
01.20 C OPERATION BASED UPON 100 %T IN BLOCK 13

02.20 A "DATA TO BE SMOOTHED",SM;S R=11520
02.30 I [SM-25]3.1;S SA=R;S SB=10240
02.40 F I=3.246;D 8
02.50 S R=SB

03.10 A "ABSORBANCE UNITS FULL SCALE",N
03.20 A "OFFSET",OS
03.30 A "INITIAL POINT",P1
03.40 A "FINAL POINT",P2
03.50 A "DATA HARDCOPY",DH

04.10 A "SPECTRUM NO",J;L G D J;S A=12032
04.12 I [DH-15]4.2;A "READY FOR OUTPUT?",Q
04.15 T "SPECTRUM NO. ",J,!,!
04.16 T "          WAVELENGTH(NM)          ABSORBANCE",!,!
04.20 I [SM-25]5.1;S SA=A;S SB=10496;D 7
04.30 S A=SB

05.10 F I=P1,P2;D 6
05.20 X FDIS(0,0);G 4.1

06.10 S AB=OS+FLOG[FP(1,R+I)/FP(1,A+I)]/2.303
06.20 S X=I*4095/249;S Y=AB*4095/N
06.30 X FDIS[X,Y]
06.40 I [14-DH]6.5;R
06.50 T "          ",(I*200/250)+200,".....",AB,!

07.10 F I=P1,P2;D 8
07.20 R

08.10 S P=0;S P=7*FP(1,SA+I)+6*[FP(1,SA-1+I)+FP(1,SA+1+I)]
08.20 S P=P+3*[FP(1,SA-2+I)+FP(1,SA+2+I)]
08.30 S P=P-2*[FP(1,SA-3+I)+FP(1,SA+3+I)];X FP(1,SB+I,P/21)
08.40 R

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VITA

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