

ABSTRACT OF THE THESIS OF

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Title CONTROLLED POTENTIAL COULOMETRY IN NONAQUEOUS SOLVENTS--APPLICATION TO THE KARL FISCHER DETERMINATION OF WATER AND TO AROMATIC NITRO COMPOUNDS IN DIMETHYLSULFOXIDE

Abstract approved   
(Major professor)

Aromatic Nitro Compounds. The n-values for the reduction of the isomers of nitrophenol and nitrobenzoic acid and for several other nitro compounds are determined in dimethylsulfoxide by controlled potential coulometry. A procedure is given in which one  $\mu$ mole of nitro compound may be determined with errors of less than  $\pm$  one percent. The associated background currents are quantitatively evaluated, and electrolysis conditions for their minimization are discussed. Controlled potential polarographic determinations are given for these nitro compounds in dimethylsulfoxide, and reaction schemes are proposed for the stepwise reductions.

Water. Microgram quantities of water are determined by rapid, controlled potential coulometry. Excess iodine is produced and removed coulometrically in a Karl Fischer system. By means of a special cell design, two  $\mu$ moles of iodine in methanol may be

reduced in 96 seconds. Ten to 74  $\mu\text{g}$ . of water in methanol and 18 to 82  $\mu\text{g}$ . of water in dimethylsulfoxide may be determined with an absolute standard deviation of  $\pm 0.2$  and  $0.3 \mu\text{g}$ . of water, respectively.

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DETERMINATION OF WATER AND TO AROMATIC  
NITRO COMPOUNDS IN DIMETHYLSULFOXIDE

by

MELVEN RAYMOND LINDBECK

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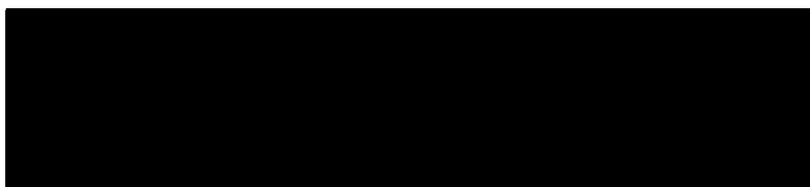
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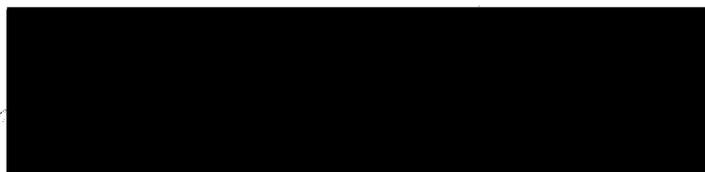
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PART I. THE CONTROLLED POTENTIAL COULOMETRIC  
AND CONTROLLED POTENTIAL POLAROGRAPHIC  
DETERMINATIONS OF SUBSTITUTED AROMATIC  
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I. INTRODUCTION

Electroanalysis of organic compounds in organic nonaqueous media has become more important with recent interest in electrochemical synthesis of organic compounds. There is a need for methods of analysis which allow in situ determinations and thereby offer a better understanding of the electrochemical processes that take place.

Coulometry supported by polarography is an invaluable method of electroanalysis in aqueous media. These methods, however, when applied to organic nonaqueous systems, are beset with many additional complications due to the need for special cell design, high electrical resistance of the solvent-electrolyte systems, the lack of suitable reference electrodes, and high background currents.

Recent developments in electronic control systems have paved the way for the development of new instrumentation for electroanalysis. Instruments have been developed which advantageously use the

"three-electrode" system for controlled potential coulometry

(5, 6, 48) and controlled potential polarography (16, 28, 29, 46).

Although these instruments have a great potential for electroanalysis in organic nonaqueous systems, there has been very little application to this field as yet.

Coulometry in general has been reviewed (2, 10, 11), and the theory of controlled potential coulometry has been discussed (14, 35, 43). The application of the latter method to analyses in organic nonaqueous media consists of determinations in acetonitrile (7, 37), dimethylformamide (37, 21), absolute methanol (15, 54), and dimethylsulfoxide (9, 34).

Only a few applications of controlled potential coulometry have been reported for the determination of aromatic nitro compounds. Kruse (33) employed the method for the determination of aromatic nitro compounds in methanol-water solvent. He reported that the major difficulty was the high background currents obtained during the determinations. Meites and Meites (39) reported a controlled potential coulometric method for the determination of picric acid in aqueous media. Ehlers and Sease (15) described a controlled potential coulometric determination of aromatic nitro compounds in absolute methanol. They were, however, unable to determine ortho and para nitrophenol in this solvent. Lindbeck and Young (34) have used dimethylsulfoxide as a solvent for the controlled potential

coulometric determination of the nitric acid oxidation products of humic acids.

Considerable attention has been given to secondary electrode processes and background currents associated with controlled potential coulometry in aqueous media (4, 5, 17, 18, 19, 27, 37, 38, 40, 41, 49). As yet there has been no study reported for these background currents in organic nonaqueous media.

Organic polarography in general has been reviewed (51, 53), and a review is given for organic nonaqueous polarography (23). Tensammetry and a. c. polarography have been investigated in organic nonaqueous media (8). The polarography of aromatic nitro compounds has been studied in dimethylformamide (26, 30), acetonitrile (20, 25, 26), and methanesulfonic acid (52). Dimethylsulfoxide has been employed as a solvent in polarography (12, 13, 24, 32, 34, 45, 47). However, the polarography of aromatic nitro compounds has not been investigated in this solvent.

Controlled potential coulometry and controlled potential polarography have not, as yet, been used for the electroanalysis of aromatic nitro compounds in dimethylsulfoxide. This investigation is concerned with the use of these methods for the determination of the electrochemical processes involved in the reduction of several substituted aromatic nitro compounds, including the isomers of nitrophenol and nitrobenzoic acid at a mercury electrode, using

dimethylsulfoxide as a solvent.

The research includes the use of this information in the development of a controlled potential coulometric procedure for the quantitative determination of these nitro compounds and a quantitative evaluation of the background currents associated with the determinations.

## II. EXPERIMENTAL

### Apparatus

#### Cell Design

The cell used for controlled potential coulometry and controlled potential polarography is shown schematically in Figures 1 and 2. The working electrode compartment is constructed from a 50 ml. glass stoppered Erleyneyer. The counter and reference electrode side-cells are made from 14/20 standard taper ground joint units, which are sealed at the bottom. The side-cells are connected to the center compartment by fine porosity frits. Nitrogen deaeration tubes are provided in each side-cell compartment for removal of dissolved oxygen. The mercury level of the working electrode is determined by the connection height of the capillary deaeration side-arm; any excess mercury is removed by vacuum. The maximum stirring rate as referred to in this work is defined as the rate at which any increase in the rate of the stirring motor causes the magnetic stirring bar to fall out of synchronization and stop. The maximum rate is dependent on the size of the magnetic stirring bar, cell solution volume, mercury volume, and the

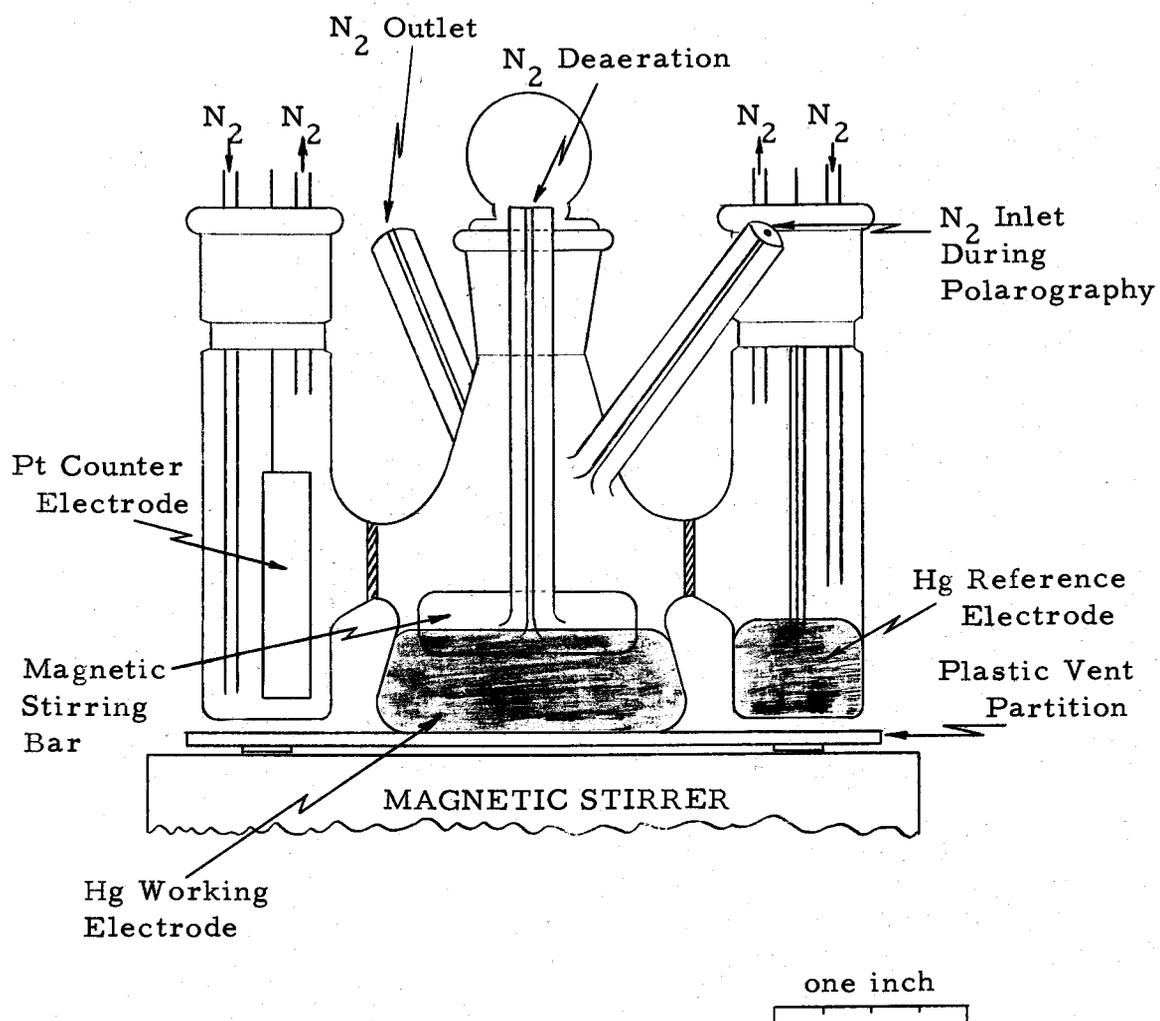


Figure 1. Controlled potential coulometry and polarography cell.

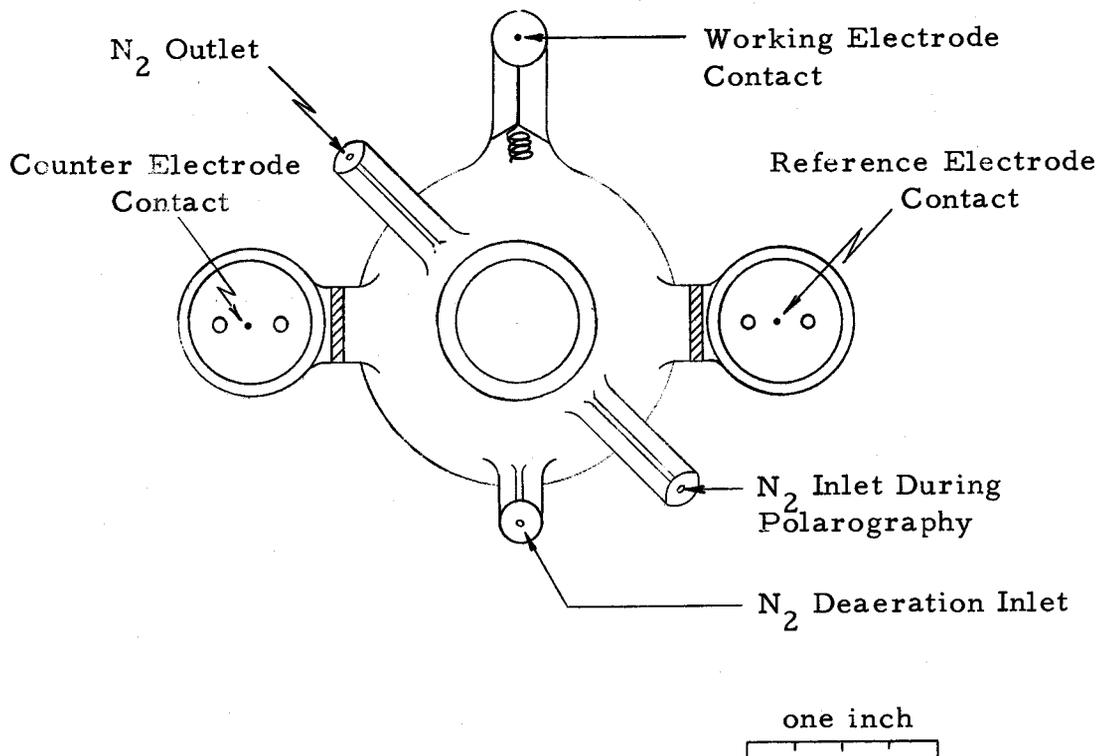
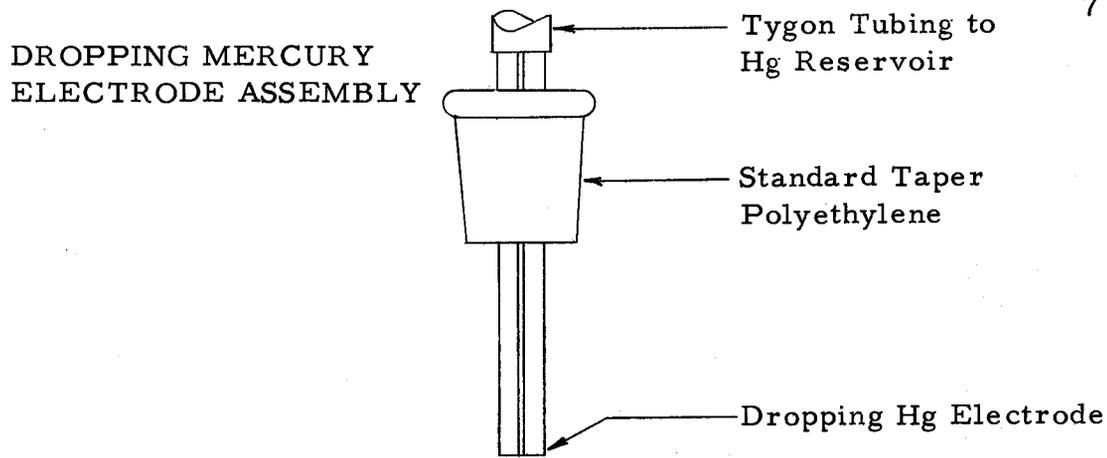


Figure 2. Controlled potential coulometry and polarography cell, top view and dropping mercury electrode assembly.

inside cell constrictions. For this particular cell and conditions, the maximum stirring rate was obtained at approximately 50 percent of the maximum dial adjustment on a Cenco magnetic stirrer (catalog no. 18851). The stirring bar is one and 1/8 inches long and 5/16 inch in diameter. It was found that stirring bars of shorter length fell out of synchronization at slower stirring rates.

Several different electrolysis cells were designed and constructed for this work. The first attempts were with relatively large cells which held 75 to 150 ml. of solvent and 25 to 30 ml. of mercury. This size of cell is commonly used in aqueous coulometry. The continuous faradaic background currents from the nonaqueous system were 0.5 to one ma. This background is considerably higher than would be expected in an aqueous system; however, this is not uncommon for nonaqueous systems. The high background and the time necessary for analysis of a nitro compound, approximately 45 minutes, made it necessary to design a smaller cell. The electrolysis cell illustrated in Figures 1 and 2 is designed to handle small solution volumes of eight to ten ml. with a large mercury electrode area-to-solution-volume ratio for rapid electrolysis. The background currents are typically from 20 to 40  $\mu$ a., depending on the applied potential and stirring rate. The time necessary for analysis of a nitro compound is approximately eight minutes.

## Electrodes

The dropping mercury electrode assembly is shown in Figure 2. Typical capillary characteristics at open circuit in 0.5 molar lithium chloride solution in dimethylsulfoxide with 27.5 cm. mercury are:  $m = 0.820$  mg./sec. and  $t = 8.35$  sec.

The working electrode consists of 12.3 ml. of distilled mercury.

The mercury pool reference electrode in DMSO-electrolyte solvent (see Figure 1) was used for both controlled potential coulometry and controlled potential polarography. The potential of the mercury pool was measured against an aqueous saturated calomel electrode by means of an agar-potassium chloride salt bridge. The mercury pool reference was used during the determinations in order to prevent water contamination of the DMSO-electrolyte solvent. The increase in stability of mercury pool reference electrodes in halide-nonaqueous solvents is discussed by Given (22).

The counter electrode is made of heavy gauge platinum foil. The dimensions of the counter electrode are not important as long as the area is sufficient to carry the current.

## Instruments

The controlled potential coulometer used was constructed by Caton (6) and is similar to that described by Scott and Peekema (48). The instrument's electronic current integrator was continuously monitored by a 50-mv. recorder.

The controlled potential polarograph used is essentially the same as that described by Enke and Baxter (16).

## Reagents

### Solvent-Electrolyte System

In the early stages of this work both dimethylformamide and dimethylsulfoxide were considered for use as a solvent in the controlled potential coulometric determination of substituted aromatic nitro compounds. Preliminary determinations revealed that dimethylformamide gave a larger continuous faradaic background current than did dimethylsulfoxide when subjected to the same coulometric conditions. It was noted that a gray film formed on the surface of the mercury when dimethylformamide was allowed to stand in contact with the mercury for several days. The mercury was unchanged when allowed to remain in contact with dimethylsulfoxide for several weeks. From these preliminary results and the fact that dimethylsulfoxide is non-toxic, whereas

dimethylformamide is toxic, the former was chosen for this work.

The choice of lithium chloride as the supporting electrolyte was based on its availability and the fact that it had been used successfully for controlled potential coulometry in dimethylformamide (21). Tetrabutylammonium iodide was tried and found to give higher background currents than lithium chloride under the same coulometric conditions in dimethylsulfoxide.

It was observed that 0.5 molar tetrabutylammonium iodide solution in dimethylsulfoxide slowly turned yellow on standing. This is probably caused by the formation of iodine, which possibly accounts for the higher background currents.

The water content of the DMSO-electrolyte solvent was determined for each quantity prepared and several times during its usage. The water content was found to vary between 0.02 and 0.04 percent. The determinations were made by the controlled potential coulometric method described in Part II of this thesis.

### Chemicals

Lithium chloride, Baker and Adams, reagent grade.

Dimethylsulfoxide, Crown Zellerbach Chemical Products  
Division, spectro grade 40823.

Nitrogen, Matheson Co., Inc., prepurified; the nitrogen was passed through anhydrous magnesium perchlorate drying trains

before entering the electrolysis cell.

o-Nitrophenol, p-nitrophenol, and p-nitrobenzoic acid, Matheson Coleman and Bell Division, The Matheson Co., Inc., one degree melting point range.

o-Nitrobenzoic acid, m-nitrophenol, m-nitrobenzoic acid, p-nitroanisole, p-nitrobenzaldehyde, 3-nitrophthalic acid, and nitroterephthalic acid, Eastman Kodak Co., white label; where necessary these compounds were recrystallized from ethanol-water mixtures until the nitro compounds gave approximately one degree melting point range.

m-Nitrobenzoic acid sodium salt and p-nitrophenol sodium salt, Eastman Kodak Co., white label, used without further purification.

#### Procedure for Controlled Potential Coulometry

At the beginning of a series of determinations, the counter and reference electrode side-cells of the electrolysis cell, Figures 1 and 2, were charged with fresh 0.5 molar lithium chloride solution in dimethylsulfoxide (DMSO-electrolyte solvent). The solution level of the side-cells was maintained just above the level of the solution in the working compartment. Both side-cells were deaerated for ten minutes with nitrogen to remove the dissolved oxygen. Eight ml. of DMSO-electrolyte solvent was added to the working electrode

compartment. The magnetic stirrer was activated and the solution deaerated with nitrogen for five minutes. It was found by coulometric reduction of residual oxygen that the oxygen could be removed in less than two minutes. This fast deaeration was probably due to the added mixing of the nitrogen and solvent by the stirring. The faradaic reducible impurities in the 8.0 ml. of DMSO-electrolyte solvent were determined coulometrically. The controlled potential coulometric reduction was made at the same applied potential as that required for the nitro compound which was to be determined. An example of a chronocoulogram obtained from the recorder read-out of the instrument integrated current is given in Figure 3, curve 5. The extrapolation back to zero time gives the quantity of electricity due to the solvent impurities that are reducible at this applied potential. The DMSO-electrolyte solvent was removed from the electrolysis cell by means of a vacuum liquid trap which was attached to the nitrogen deaeration capillary side-arm. This capillary is attached at the bottom of the cell such that the solution was removed, leaving the mercury electrode in the cell. An 8.0 ml. DMSO-electrolyte solution which contained 1.00  $\mu$ mole of the nitro compound was then added to the working compartment, and the solution was deaerated for five minutes. After deaeration, the nitro compound was determined coulometrically at the same applied potential as the solvent impurities. Examples of chronocoulograms

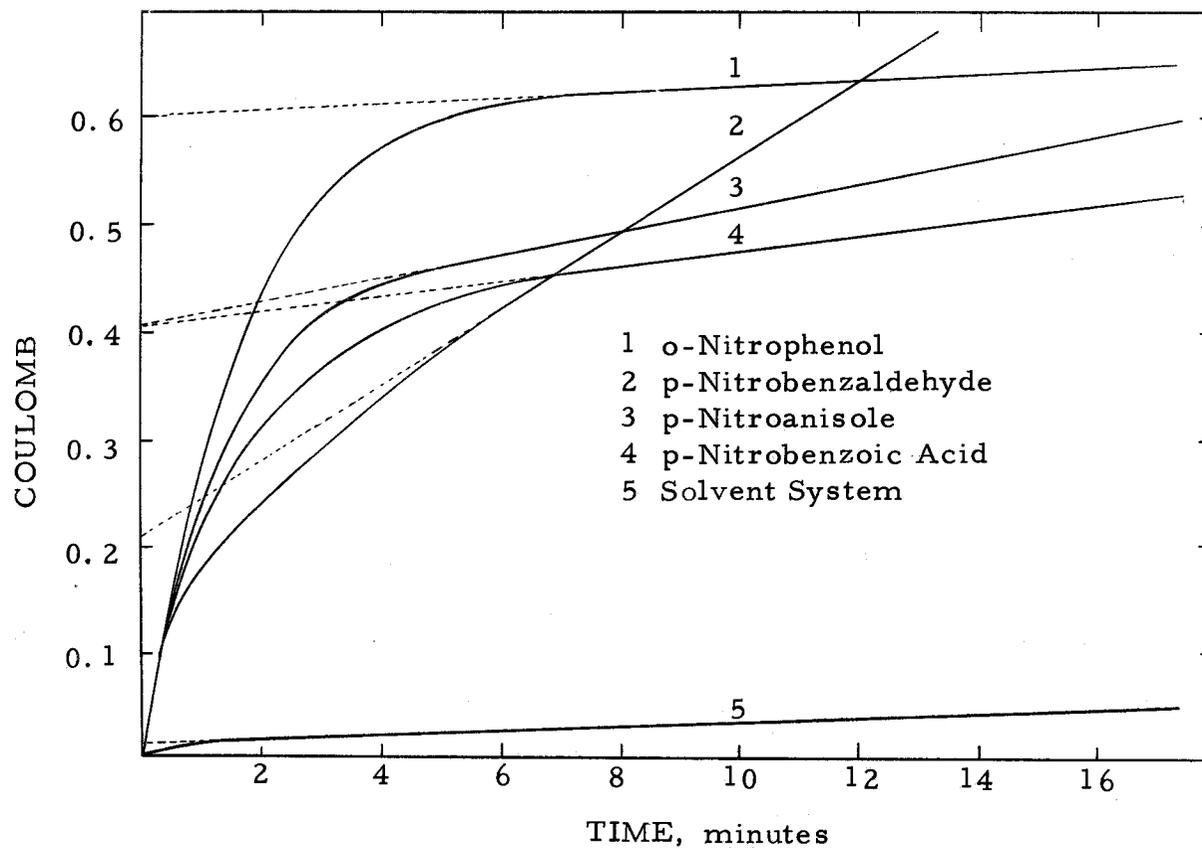


Figure 3. Typical Chronocoulograms.

Conditions: The results represent the determination of 1.00  $\mu$ mole of the nitro compound in 8.0 ml. of dimethylsulfoxide containing 0.5M lithium chloride at an applied potential of -1.6 volts vs. SCE.

obtained for the reduction of some of the nitro compounds are given in Figure 3. The quantity of electricity given by the reduction of the nitro compound was determined by extrapolating back to zero time and subtracting from this value the value found for the impurities in 8.0 ml. of DMSO-electrolyte solution.

The above demonstrates the procedure that would be necessary for an unknown nitro compound in dimethylsulfoxide at a low concentration such that an 8.0 ml. sample would be necessary for determination. For the n-value determinations, however, the procedure employs pre-electrolysis. This eliminated the necessity of correcting for the quantity of electricity due to the solvent impurities. After deaeration of the 8.0 ml. of DMSO-electrolyte solvent, it was pre-electrolyzed at the applied potential required for determination of the nitro compound until a continuous faradaic background current was attained. This continuous faradaic current corresponds to the final slope of curve 5 in Figure 3. After the pre-electrolysis, a 0.100 ml. sample of DMSO-electrolyte solvent containing 1.00  $\mu$ mole of the nitro compound was added by syringe. This was achieved by placing the needle of the syringe through one of the nitrogen outlet capillaries. One minute was allowed for nitrogen deaeration, and then the nitro compound was determined at the same applied potential as the pre-electrolysis. The quantity of electricity necessary for the reduction of the nitro compound was

obtained from the resulting chronocoulogram by extrapolation to zero time. The DMSO-electrolyte solvent containing the reduced nitro compound was then removed by vacuum and the cell rinsed with two 10 ml. volumes of fresh solvent by addition and removal. The mercury was changed only occasionally when the cell had remained unused for several weeks.

#### Procedure for Controlled Potential Polarography

The polarographic determinations were made in the same cell, Figures 1 and 2, used for the controlled potential coulometric determinations. The only changes were that the magnetic stirring bar was removed and the dropping mercury electrode assembly was placed in the top of the cell. The side-cells were filled to just above the frits with DMSO-electrolyte solvent, and deaerated with nitrogen for ten minutes to remove the oxygen. The 12.3 ml. of mercury comprising the coulometric working electrode was left in the cell so that the sample solution could be removed by vacuum through the nitrogen deaeration capillary side-arm after completion of the determination. Approximately ten ml. of the sample solution was added to the center compartment of the cell from a ten ml. syringe by placing the needle through one of the nitrogen outlets. The sample solution was deaerated for 15 minutes with nitrogen which had previously passed through DMSO-electrolyte solvent.

During the determination, the nitrogen stream was passed over the sample by means of the upper capillary nitrogen inlet. The height of the mercury surface in the reservoir was adjusted to exactly 27.5 cm. above the tip of the dropping mercury electrode and maintained at this height for all determinations. After completion of the determination, the sample solution was removed by vacuum, and the cell was rinsed with two consecutive ten ml. portions of DMSO-electrolyte solvent. These rinse additions were also made with a ten ml. syringe.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

#### Controlled Potential Polarography

The results from the controlled potential polarographic determinations of several substituted aromatic nitro compounds in dimethylsulfoxide are shown in Figures 4-6, and the half-wave potentials are summarized in Table 1. The polarograms are determined from millimolar solutions of the nitro compounds. The supporting electrolyte consisted of 0.5 molar lithium chloride. The polarograms are taken as the envelope of the maximum current. All half-wave potentials are versus a saturated calomel electrode. A plot of the residual current given by the DMSO-electrolyte solvent only is shown in Figure 5, curve 5. The overall n-values are taken from the controlled potential coulometric results.

On the basis of the experimentally determined n-values, along with existing information given for the electrochemical reduction of nitrobenzene in other media, the following electrochemical steps are proposed for the polarographic reduction of each nitro compound in dimethylsulfoxide.

The first one-electron electrochemical reduction for nitrobenzene and substituted nitrobenzene has been studied in acetonitrile and dimethylformamide (20, 30, 31, 36, 44). It has been shown that this reduction is reversible and is due to the

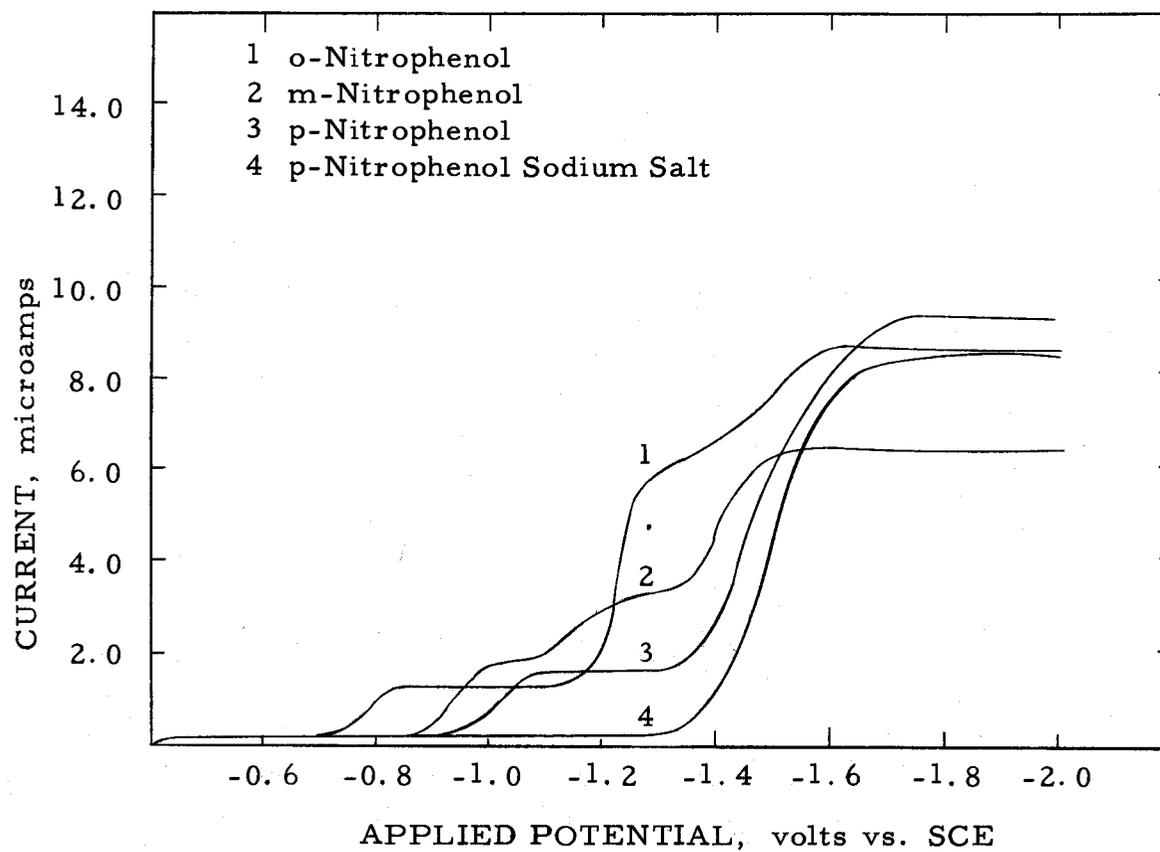


Figure 4. Polarograms of dimethylsulfoxide solutions, which are 1.0 mM in nitrophenol and 0.5 M in lithium chloride.

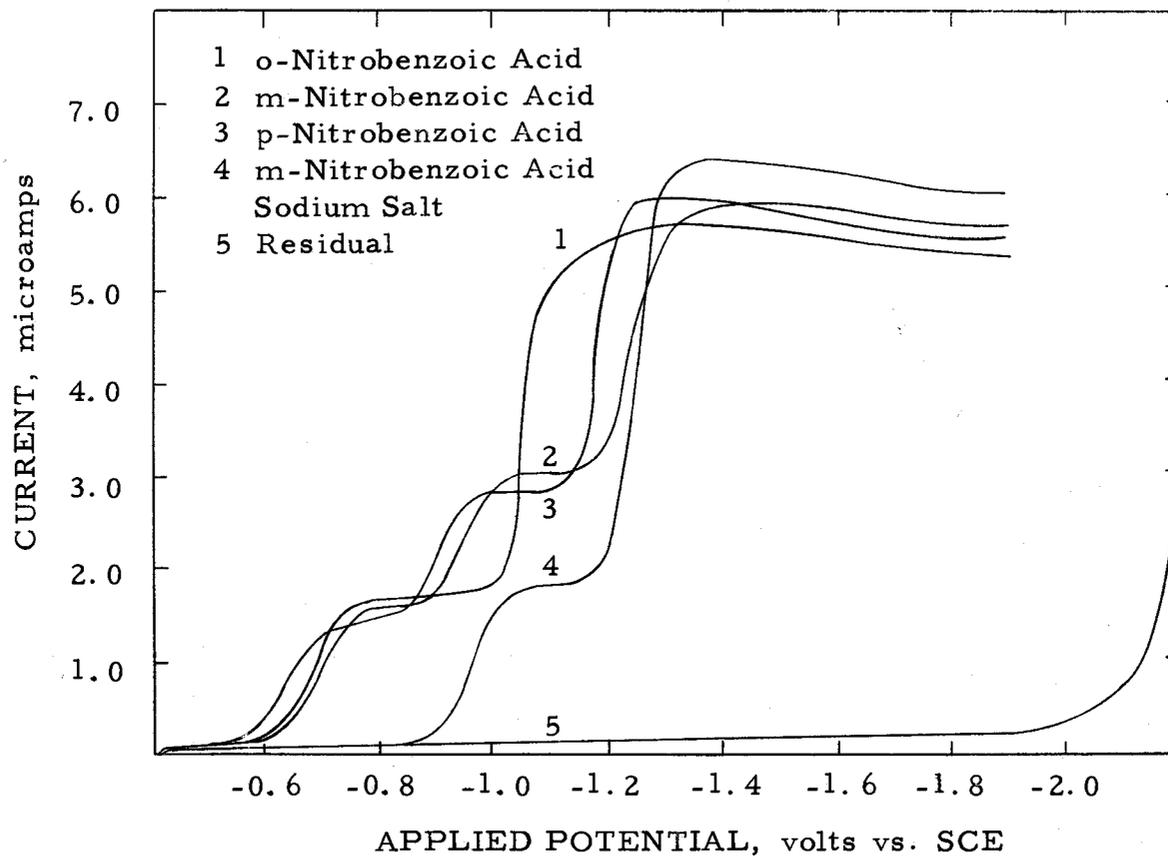


Figure 5. Polarograms of dimethylsulfoxide solutions, which are 1.0 mM in nitrobenzoic acid and 0.5 M in lithium chloride.

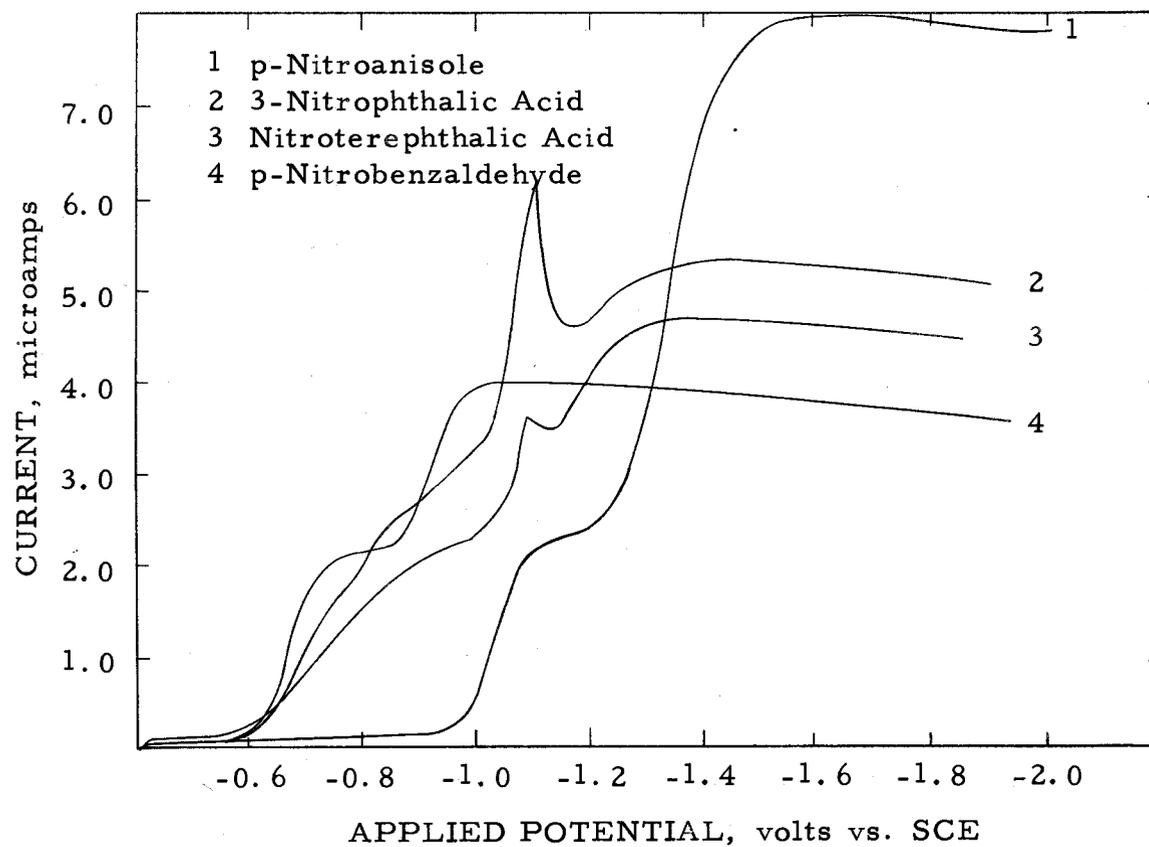


Figure 6. Polarograms of dimethylsulfoxide solutions, which are 1.0 mM in nitro compound and 0.5 M in lithium chloride.

Table 1. Summary of Polarographic Half-wave Potentials

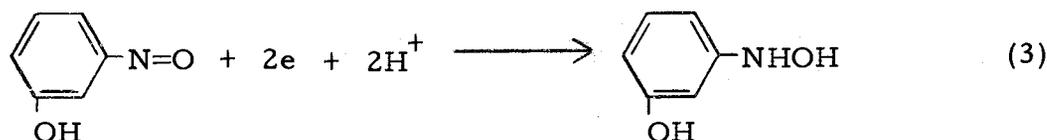
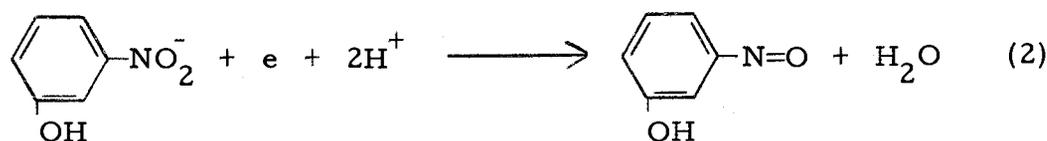
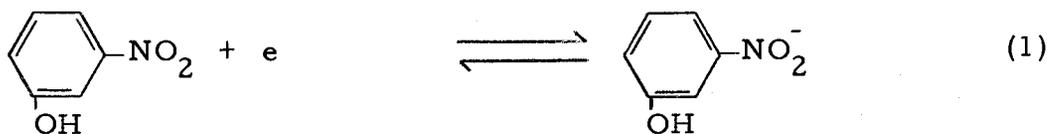
Nitro Compounds	-E <sub>1/2</sub> vs. SCE		
	1st.	2nd.	3rd.
o-Nitrophenol	0.785	1.223	1.502
m-Nitrophenol	0.943	1.146	1.405
p-Nitrophenol	1.025	1.485	
p-Nitrophenol Sodium Salt	1.500		
p-Nitroanisole	1.035	1.345	
o-Nitrobenzoic Acid	0.678	1.055	
p-Nitrobenzoic Acid	0.634	0.908	1.18
m-Nitrobenzoic Acid	0.697	0.942	1.246
m-Nitrobenzoic Acid Sodium Salt	0.955	1.247	
p-Nitrobenzaldehyde	0.680	0.931	

formation of an anion radical. It is assumed here that the same process takes place in dimethylsulfoxide.

The polarographic results for the p-nitrophenol sodium salt and the isomers of nitrophenol are shown in Figure 4.

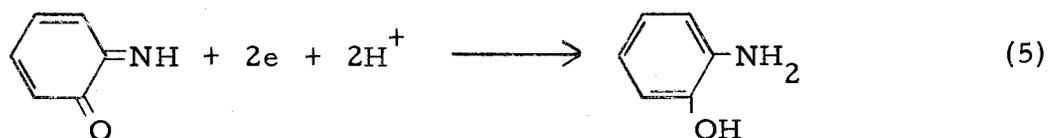
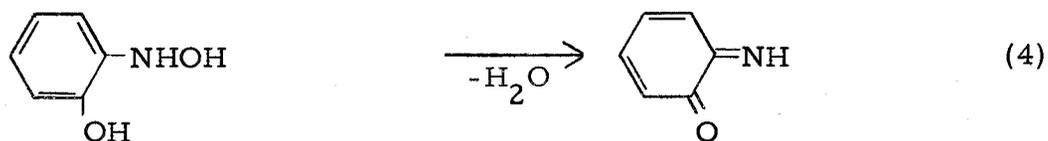
m-Nitrophenol, curve 2, gives an overall four-electron reduction.

The first wave at an  $E_{\frac{1}{2}}$  of -0.943 volt is due to a one-electron reduction of m-nitrophenol to the corresponding anion radical. The second wave at an  $E_{\frac{1}{2}}$  of -1.146 volts is due to a one-electron reduction of the anion radical to m-nitrosophenol. The third wave at an  $E_{\frac{1}{2}}$  of -1.405 is due to a two-electron reduction of m-nitrosophenol to m-hydroxylaminophenol.



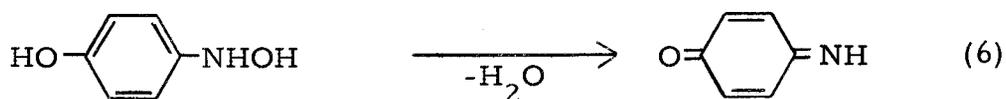
o-Nitrophenol, curve 1, gives an overall six-electron reduction. The first wave at an  $E_{\frac{1}{2}}$  of -0.785 is due to a one-electron reduction of o-nitrophenol to the corresponding anion radical. The second wave at an  $E_{\frac{1}{2}}$  of -1.223 is due to a three-electron reduction of the anion radical to o-hydroxylaminophenol. The third wave at

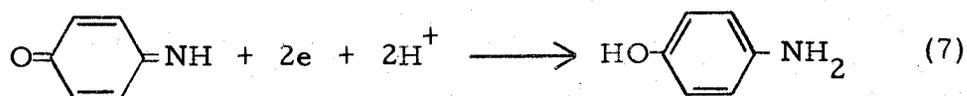
an  $E_{1/2}$  of -1.502 volts is due to a two-electron reduction of o-benzoquinoneimine to o-aminophenol. The o-benzoquinoneimine is formed by a chemical reaction involving the dehydration of o-hydroxylaminophenol.



A chemical reaction which takes place between two electron transfer reactions is referred to as the ECE mechanism (50) and has been established for the reduction of p-nitrosophenol in an aqueous system (1, 42).

p-Nitrosophenol, curve 3, also gives an overall six-electron reduction. The first wave at an  $E_{1/2}$  of -1.025 volts is due to a one-electron reduction to the p-nitrosophenol anion radical. The second wave at an  $E_{1/2}$  of -1.485 volts is due to a five-electron reduction to p-aminophenol. This is probably due, as with o-nitrosophenol, to the chemical reaction which produces p-benzoquinoneimine, which in turn gives a two-electron reduction to p-aminophenol.





The p-nitrophenol sodium salt gives an overall six-electron reduction. The polarographic curve 4 shows only one wave at an  $E_{\frac{1}{2}}$  of -1.500 volts. The reduction mechanism is probably the same as that proposed for p-nitrophenol, equations 6 and 7.

The polarographic results for the m-nitrobenzoic acid sodium salt and the isomers of nitrobenzoic acid are shown in Figure 5. These compounds all yield an overall four-electron reduction.

p-Nitrobenzoic acid, curve 3, gives a wave at an  $E_{\frac{1}{2}}$  of -0.634 volt which is due to a one-electron reduction to the anion radical. The second wave at an  $E_{\frac{1}{2}}$  of -0.908 volt is due to a one-electron reduction of the anion radical to p-nitrosobenzoic acid. The third wave at an  $E_{\frac{1}{2}}$  of -1.18 volts is due to a two-electron reduction of p-nitrosobenzoic acid to p-hydroxylaminobenzoic acid.

m-Nitrobenzoic acid, curve 2, follows the same stepwise process, producing the same corresponding reduction products as p-nitrobenzoic acid. The first, second, and third waves are shown at  $E_{\frac{1}{2}}$  values of -0.697, -0.942, and -1.246 volts respectively.

The polarographic reduction of p-nitrobenzoic acid and of m-nitrobenzoic acid probably follow the same stepwise reduction as shown in equations 1, 2, and 3 for m-nitrophenol.

o-Nitrobenzoic acid, curve 1, gives a one-electron reduction wave at an  $E_{\frac{1}{2}}$  of -0.678 volt, which is due to the formation of the corresponding anion radical. The second wave at an  $E_{\frac{1}{2}}$  of -1.055 volts is due to a three-electron reduction of the anion radical to o-hydroxylaminobenzoic acid.

The m-nitrobenzoic acid sodium salt, curve 4, produces a wave at an  $E_{\frac{1}{2}}$  of -0.955 volt which is due to a one-electron reduction to yield the anion radical. The second wave at an  $E_{\frac{1}{2}}$  of -1.247 volts is due to a three-electron reduction of the anion radical to the corresponding hydroxylamine benzoic acid sodium salt.

The polarographic results for 3-nitro- and terephthalic acids are shown in Figure 6, curves 2 and 3. Both acids give an overall four-electron reduction. The polarograms show what appear to be two 2-electron reduction waves for each compound, with maxima at the beginning of the second waves. It appears that the first one-electron reduction, which is given for the monoacids, coincides with the one-electron reduction to the corresponding nitrosophthalic acid. The final reduction product, as in the case of the monoacids, is the corresponding hydroxylaminophthalic acid. The diffusion coefficients of the diacids are probably smaller, which accounts for the smaller diffusion currents given by the diacids compared to the diffusion currents given by the monoacids.

p-Nitroanisole yields an overall four-electron reduction.

The polarographic results are shown by curve 1 in Figure 6. The first wave at an  $E_{\frac{1}{2}}$  of -1.035 is due to a one-electron reduction to the anion radical. The second wave at an  $E_{\frac{1}{2}}$  of -1.345 is due to a three-electron reduction of the anion radical to p-hydroxylaminoanisole. p-Nitroanisole gives a relatively higher diffusion current compared to those produced by the other nitro compounds.

The polarographic results shown by the nitrophenols, nitrobenzoic acids, nitrophthalic acids, and p-nitroanisole indicate that for a substituted aromatic nitro compound to be reduced to the amine in dimethylsulfoxide, the corresponding hydroxylamine compound must be able to undergo a chemical reaction to produce a quinoneimine as in equations 4, 5, 6 and 7.

p-Nitrobenzaldehyde appears to yield an overall two-electron reduction. On this basis the polarographic results shown by curve 4 in Figure 6 are interpreted as giving a one-electron reduction at an  $E_{\frac{1}{2}}$  of -0.680, which is due to the formation of the p-nitrobenzaldehyde anion radical. The second wave at an  $E_{\frac{1}{2}}$  of -0.931 is possibly caused by a one-electron reduction of the anion radical to p-nitrosobenzaldehyde. The latter reduction was not established by identification of the p-nitrosobenzaldehyde. Because of the peculiar coulometric results and the lack of an explanation for why the o-nitrosobenzaldehyde should not be polarographically reduced to the corresponding hydroxylamino compound, it appears

that a dimer or a nonelectroactive species may possibly be formed by a chemical reaction under these conditions.

Polarograms for the reduction of oxygen in air-saturated dimethylsulfoxide are shown in Figure 7. It was found that when 0.5 molar lithium chloride was used as the supporting electrolyte, only one wave is produced at an  $E_{\frac{1}{2}}$  of -0.585 volt. When 0.5 molar tetrabutylammonium iodide was used as the supporting electrolyte, two waves are produced at  $E_{\frac{1}{2}}$  of -0.510 and -0.735 volt. Kolthoff and Reddy (32) reported two drawn-out oxygen waves at  $E_{\frac{1}{2}}$  values of -0.72 and -1.13 volts versus a saturated calomel electrode obtained in dimethylsulfoxide using 0.1 molar sodium perchlorate as the supporting electrolyte. These results indicate that the supporting electrolyte has a considerable effect on the half-wave potentials given by the reduction of oxygen in dimethylsulfoxide.

It was found experimentally that the rate of scan, concentration of the electroactive species, and the drop time are considerable factors in obtaining well-defined polarograms in dimethylsulfoxide. If the scan rate is greater than 0.1 volt per minute, large maxima are observed. Quite often these maxima appear on the rising portion of the wave. Very erratic drop times and drop growths are observed when the concentration of the nitro compound exceeds  $5 \times 10^{-3}$  molar. The drop time of 8.35 seconds at open circuit, which is somewhat longer than employed in aqueous systems, is necessary

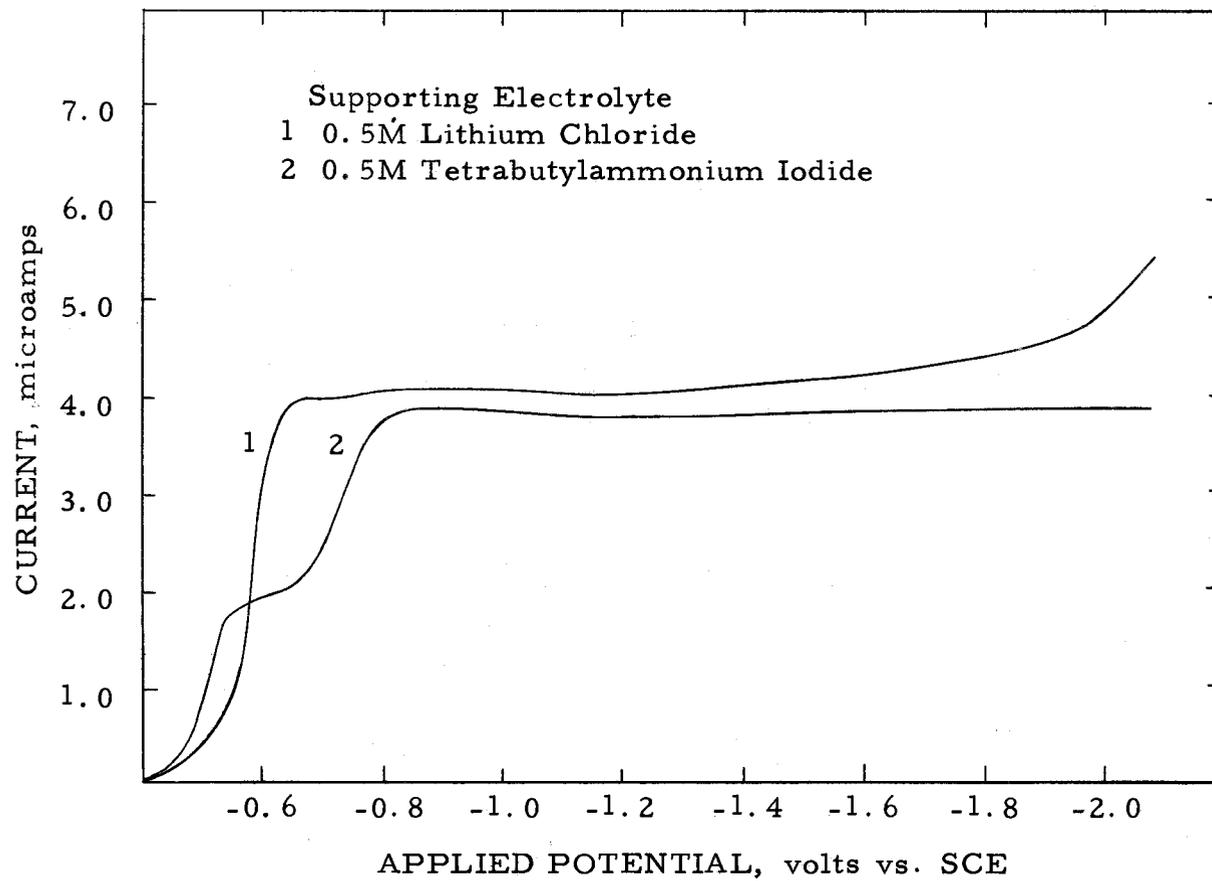


Figure 7. Polarograms of dimethylsulfoxide solutions, which are air saturated with oxygen.

because of the rate at which the drop time decreases during the polarographic determination. Erratic drop times are observed when the drop time is less than about four seconds. An electrocapillary curve for dimethylsulfoxide containing 0.1 molar sodium perchlorate is given by Kolthoff and Reddy (32).

### Controlled Potential Coulometry

#### n-Value Determinations

The results for the controlled potential coulometric determination of the n-values for the reduction of several substituted aromatic nitro compounds are given in Tables 2-5. The determinations were made from the reduction of 1.00  $\mu$ mole of the nitro compound in 8.0 ml. of dimethylsulfoxide containing 0.5 molar lithium chloride. The applied potentials employed for the reductions are given in Tables 2-5. Current-versus-potential curves were determined for the reduction of several of the nitro compounds at the mercury pool working electrode in the absence of stirring. The resulting curves were found to agree reasonably well with the polarograms given by the same nitro compounds. The choice of applied potential was made on the basis of the polarogram produced by the nitro compound (see Figures 4-6).

The n-values were calculated by the use of Faraday's law:

Table 2. Coulometric n-Values for the Reduction of the Isomers of Nitrophenol in Dimethylsulfoxide.

Nitrophenol	Experimental n-Value	Average Deviation	Applied Potential volts vs. SCE
o-Nitrophenol	5.92		-1.6
	5.98		
	5.96		
	5.98		
	5.96		
	<u>6.00</u>		
	mean	5.97	
m-Nitrophenol	3.99		-1.6
	4.08		
	3.90		
	4.03		
	4.01		
	<u>4.05</u>		
	mean	4.01	
p-Nitrophenol	6.15		-1.8
	5.98		
	6.14		
	6.01		
	5.99		
	<u>6.06</u>		
	mean	6.06	

Table 3. Coulometric n-Values for the Reduction of the Isomers of Nitrobenzoic Acid in Dimethylsulfoxide.

Nitrobenzoic Acid	Experimental n-Value	Average Deviation	Applied Potential volts vs. SCE
o-Nitrobenzoic Acid	3.94		-1.4
	4.06		
	3.92		
	4.02		
	4.01		
	<u>3.99</u>		
mean	3.99	±0.04	
m-Nitrobenzoic Acid	3.94		-1.4
	4.03		
	3.92		
	3.92		
	4.06		
	<u>3.96</u>		
mean	3.97	±0.05	
p-Nitrobenzoic Acid	4.19		-1.4
	4.12		
	4.15		
	4.03		
	4.15		
	<u>4.10</u>		
mean	4.12	±0.04	

Table 4. Coulometric n-Values for the Reduction of Nitroterephthalic Acid and 3-Nitrophthalic Acid in Dimethylsulfoxide.

Nitrophthalic Acid	Experimental n-Value	Average Deviation	Applied Potential volts vs. SCE
Nitroterephthalic Acid	3.96		-1.4
	3.85		
	4.01		
	4.01		
	3.99		
	<u>4.01</u>		
	mean	3.97	
3-Nitrophthalic Acid	3.92		-1.4
	3.96		
	4.06		
	4.06		
	4.05		
	<u>4.03</u>		
	mean	4.01	

Table 5. Coulometric n-Values for the Reduction of p-Nitroanisole and the Sodium Salts of m-Nitrobenzoic Acid and p-Nitrophenol in Dimethylsulfoxide.

Nitro Compound	Experimental n-Value	Average Deviation	Applied Potential volts vs. SCE
m-Nitrobenzoic Acid	4.05		-1.4
Sodium Salt	4.10		
	4.19		
	4.10		
	3.99		
	<u>4.07</u>		
mean	4.08	±0.05	
p-Nitrophenol	6.22		-1.8
Sodium Salt	6.24		
	6.01		
	6.10		
	5.96		
	<u>6.01</u>		
mean	6.09	±0.10	
p-Nitroanisole	4.08		-1.6
	4.01		
	3.96		
	3.96		
	4.03		
	<u>4.06</u>		
mean	4.02	±0.04	

$$Q = nFN \quad (8)$$

where  $Q$  is the quantity of electricity (number of coulombs) consumed in the reduction of the nitro compound,  $n$  is the number of equivalents per mole for the reduction of the nitro compound ( $n$ -value or number of electrons appearing in the halfreaction),  $F$  is the Faraday of electricity (96493 coulombs per equivalent), and  $N$  is the number of moles of the nitro compound.

The reductions of the isomers of nitrophenol, Table 2, do not yield the same  $n$ -value. *m*-Nitrophenol gives an  $n$ -value of four, which indicates that this compound is reduced to the *m*-hydroxylaminophenol. *m*-nitrophenol produces a slight yellow-brown color in the solvent and the reduction product is colorless. Ortho and para nitrophenols give  $n$ -values of six, which indicate that these compounds are reduced to the corresponding aminophenols. This further two-electron reduction is probably due to a chemical reaction which yields the corresponding benzoquinoneimine, which in turn is reduced to the corresponding aminophenol. Ortho and para nitrophenol are yellow in the solvent and the reduction products are colorless.

Reduction of the isomers of nitrobenzoic acid, Table 3, give  $n$ -values of four, indicating that these nitro compounds are reduced to the corresponding hydroxlyaminobenzoic acids. The nitrobenzoic acids are colorless both in the oxidized and reduced states in the

solvent.

The reduction of 3-nitrophthalic and nitroterephthalic acids, Table 4, both give n-values of four, which indicate that these compounds are reduced to the corresponding hydroxylamine compound. As with the nitrobenzoic acids, these compounds are also colorless in both the oxidized and reduced form.

The n-values for the reduction of the sodium salts of m-nitrobenzoic acid and p-nitrophenol, Table 5, are four and six, respectively, which agree with the n-values given for the reduction of the corresponding acids. The sodium salts were determined primarily for the purpose of comparing the continuous kinetic background currents with those produced by the acids. It was found that the sodium salts also give approximately the same kinetic background currents. This comparison made it possible to rule out the proton donation from the acids as the cause of the kinetic background currents.

The n-value for the reduction of p-nitroanisole, Table 5, is four, which indicates that this compound is reduced to p-hydroxylaminoanisole. p-Nitroanisole is colorless in the solvent, turning slightly purple during reduction, and colorless after complete reduction.

An attempt was made to determine the n-value for the reduction

of p-nitrobenzaldehyde, but this compound was found to yield results which differed considerably from the other nitro compounds. An example is shown in Figure 3 by chronocoulogram 2, which on extrapolation to zero time appears to give an n-value of two. However, because of the large background, which very slowly decreases with time, the quantitative determination is questionable. An attempt to improve these results by a change in applied potential, addition of benzoic acid as a proton donor, and concentration variations was unsuccessful. p-Nitrobenzaldehyde is colorless in the DMSO-electrolyte solvent, but as soon as the reduction is initiated, the solution turns bright blue. The blue color is followed by intermediate shades of blue-green. After approximately five minutes of reduction, the solution is bright green; this color very slowly changes to a light yellow after several hours of reduction.

The analytical significance of the results given in Tables 2-5 is that integral values of four or six, depending on the nitro compound being determined, can be used for n in equation 8. The precision in the measurement would then apply to the determination of the quantity of the nitro compound. This means that under these conditions one  $\mu$ mole of the nitro compound can be determined with an approximate precision of  $\pm$  one percent.

## Background

The background quantity of electricity consumed in a controlled potential coulometric analysis may be defined as the difference between the theoretical and the actual quantity consumed. This difference is considered to arise from the passage of currents that can be classified as charging, impurity faradaic, continuous faradaic, kinetic, and induced. These phenomena are discussed in detail by Meites and Moros (40). All five types of background quantities of electricity are observed in the controlled potential coulometric reduction of substituted aromatic nitro compounds in DMSO-electrolyte solvent.

The quantity of electricity related to the charging current is that quantity required to charge the working electrode and the electrical double layer at its surface. It is determined by the extrapolation to zero time of a chronocoulogram of the DMSO-electrolyte solvent taken after removal of the trace impurities by pre-electrolysis. For the cell and conditions used in this work, the charging background is insignificant.

The impurity faradaic quantity of electricity is consumed by the reduction of trace impurities. It is determined by the extrapolation to zero time of a chronocoulogram of the DMSO-electrolyte solvent. An example of this determination is given by chronocoulogram 5

in Figure 3. Eight ml. of DMSO-electrolyte solvent typically gave impurity faradaic backgrounds of from 0.01 to 0.02 coulomb, depending on the applied potential.

The continuous faradaic quantity of electricity is that quantity continuously consumed by the reduction of lithium ions. The continuous current is determined from the slope of the plateau of a chronocoulogram of the DMSO-electrolyte solvent (see Figure 3, chronocoulogram 5). This background is dependent on the area of the working electrode and the applied potential. The dependence on the former is shown in Table 6. The larger increase in current at the higher stirring rates is due to the larger mercury surface area which is caused by the magnetic stirring bar spinning closer to the bottom of the cell, spreading the mercury up the sides of the cell. The dependence on applied potential is shown in Table 7.

The kinetic quantity of electricity is that quantity consumed by reduction of an electroactive species which is produced by a slow chemical reaction of the reduced product with the solvent or some constituent of the solvent. The kinetic quantity of electricity being consumed is dependent on the concentration of the reduced product and increases during the reduction. The continuous kinetic current, after complete reduction of the nitro compound, is determined by the increase in slope of the plateau of a chronocoulogram of the nitro compound compared to a chronocoulogram of the

Table 6. Variation of the Continuous Faradaic Background Current with Stirring Rate.

Percent Maximum Stirring Rate	Faradaic Background, $\mu\text{a}$
0	2.0
25	7.1
50	18.8
75	42.5
100	73.0

Conditions: Values were taken in 8.0 ml. of dimethylsulfoxide containing 0.5 M lithium chloride at an applied potential of -1.8 volts vs. SCE.

Table 7. Variation of the Continuous Faradaic Background Current with Applied Potential.

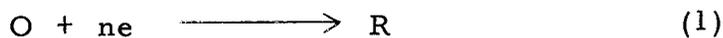
Applied Potential volts vs. SCE	Faradaic Background, $\mu\text{a}$
-1.0	11.5
-1.1	14.0
-1.2	15.6
-1.3	16.5
-1.4	17.7
-1.5	19.7
-1.6	26.0
-1.7	36.4
-1.8	42.5

Conditions: Values were taken in 8.0 ml. of dimethylsulfoxide containing 0.5 M lithium chloride with 75 percent of the maximum stirring rate.

DMSO-electrolyte solvent, all other parameters being the same.

It was found that the continuous kinetic background for the nitro compounds is independent of the applied potential and stirring rate changes between 50 and 75 percent of the maximum stirring rate.

The process that occurs probably involves the following steps:



Where (2) is the rate determining step, O is the nitro compound, and R is the corresponding reduced compound. O' may or may not be the original oxidized state, and S may be dimethylsulfoxide or hydrogen ion.

The magnitude of the continuous kinetic current is different for different substituted aromatic nitro compounds, and also varies among different isomers. This variation and the increase in continuous kinetic current with increase in the cell concentration of the reduced product is given in Table 8. The cell concentration of the reduced product is assumed to correspond to the initial cell concentration of the nitro compound. The ortho isomers of nitrophenol and nitrobenzoic acid give smaller continuous kinetic background currents compared to those given by the corresponding para and meta nitro compounds. This may be caused by a steric hindrance in the case of the ortho isomers, which causes a slower chemical

Table 8. Effect of the Initial Cell Concentration on the Continuous Kinetic Background Current.

Nitro Compound	Initial Cell Concentration			
	0.125mM	0.250mM	0.375mM	0.500mM
	Background Current, $\mu\text{a}$			
o-Nitrophenol	12	12	12	19
m-Nitrophenol	23	38	49	60
p-Nitrophenol	20	50	79	162
p-Nitrophenol Sodium Salt	15	42	57	84
p-Nitroanisole	135	195	212	227
o-Nitrobenzoic Acid	19	27	38	42
p-Nitrobenzoic Acid	88	110	125	144
m-Nitrobenzoic Acid	79	105	124	143
m-Nitrobenzoic Acid Sodium Salt	76	121	140	162
Nitroterephthalic Acid	27	34	56	68
3-Nitrophthalic Acid	27	42	53	68

regeneration of the electroactive species.

The induced quantity of electricity is that quantity consumed by a secondary reduction which is induced by the reduction of the nitro compound, and is dependent on the rate of the latter. It is determined by the increase in total quantity of electricity consumed over the theoretical quantity required for reduction of the nitro compound after the other background quantities of electricity have been accounted for. The effect of the rate of reduction of different nitro compounds on the induced background is given in Table 9. The increase in rate of reduction is achieved by increase in initial cell concentration, all other parameters being the same. Different values of induced background are found for different nitro compounds and, in the case of the isomers of nitrobenzoic acid and of nitrophenol, the ortho isomers give the smallest and the para isomers give the largest. A smaller value than expected is given by p-nitroanisole, which is probably due to cancellation by a kinetic background. The most important observation, however, is that no induced background is found at the lower rates of reduction.

The kinetic and induced backgrounds cannot be completely corrected for by extrapolation of the chronocoulograms to zero time, which gives an overcorrection in the case of the kinetic background and an undercorrection in the case of the induced background. These errors were, however, decreased by careful choice

Table 9. Effect of the Initial Cell Concentration on the Induced Background.

Nitro Compound	Initial Cell Concentration*			
	0.125mM	0.250mM	0.375mM	0.500mM
o-Nitrophenol			0.017	0.069
m-Nitrophenol	0.003	0.014	0.027	0.139
p-Nitrophenol		0.127	0.266	0.428
p-Nitrophenol Sodium Salt	0.004	0.062	0.054	0.135
p-Nitroanisole		0.007	0.031	0.101
o-Nitrobenzoic Acid				0.019
p-Nitrobenzoic Acid	0.007	0.019	0.073	0.134
m-Nitrobenzoic Acid		0.007	0.042	0.116
m-Nitrobenzoic Acid Sodium Salt		0.023	0.104	0.205
Nitroterephthalic Acid			0.024	0.069
3-Nitrophthalic Acid		0.024	0.062	0.093

\*Cell solution volumes are 8.00 ml.

of electrolysis conditions. The electrolysis cell parameters were adjusted such that the time necessary for complete reduction was as short as possible. This shortens the extrapolation and thus decreases the error due to the kinetic background. The initial cell concentration of the nitro compound was kept low enough to avoid any detectable induced background. The lower initial cell concentration also decreases the error from kinetic background.

## IV. CONCLUSIONS

It is possible to obtain well-defined controlled potential polarograms of the isomers of nitrophenol and nitrobenzoic acid in dimethylsulfoxide, provided that the scan rate is not greater than 0.1 volt per minute, the concentration of the nitro compound is less than  $5 \times 10^{-3}$  molar, and the initial drop time is not less than eight seconds.

One  $\mu$ mole of nitro compound can be determined by controlled potential coulometry from cell concentrations of approximately  $10^{-4}$  molar in nitro compound in dimethylsulfoxide solution, with errors of less than  $\pm 1$  percent. The nitrobenzoic acids and m-nitrophenol give a four-electron reduction, which indicates that these compounds are reduced to the corresponding hydroxylaminobenzoic acids. Ortho and para nitrophenol both give a six-electron reduction, which indicates that the corresponding hydroxylaminophenol undergoes a chemical reaction to give the corresponding benzoquinoneimine which in turn is reduced to the corresponding aminophenol.

The nitrophenols and nitrobenzoic acids give both kinetic and induced backgrounds when determined by controlled potential coulometry. The ortho isomers give smaller backgrounds than do the meta and para isomers. This may be caused by a steric hindrance in the case of the ortho isomers. The backgrounds can be decreased

to insignificant values by proper choice of the electrolysis conditions, of which the most important are a shorter electrolysis time and lower initial cell concentrations.

## V. BIBLIOGRAPHY

1. Alberts, Gene S. and Irving Shain. Electrochemical study of kinetics of a chemical reaction coupled between two charge transfer reactions. Potentiostatic reduction of p-nitrosophenol. *Analytical Chemistry* 35:1859-1866. 1963.
2. Bard, Allen J. Electroanalysis and coulometric analysis. *Analytical Chemistry* 34:57R-64R. 1962; 36:70R-80R. 1964.
3. Bard, Allen J. and Jaspal S. Mayell. Secondary reactions in controlled potential coulometry. II. Secondary electrode reactions. *Journal of Physical Chemistry* 66:2173-2179. 1962.
4. Bard, Allen J. and Emanuel Solon. Secondary reactions in controlled potential coulometry. II. Preceding and simultaneous chemical reactions. *Journal of Physical Chemistry* 67:2326-2330. 1963.
5. Booman, Glenn L. Instrument for controlled potential electrolysis and precision coulometric integration. *Analytical Chemistry* 29:213-218. 1957.
6. Caton, Roy Dudley, Jr. Controlled potential coulometric and polarographic investigation of metallic ions in fused salts. Ph.D. thesis. Corvallis, Oregon State University, 1963. 129 numb. leaves.
7. Cokal, E. J. and E. M. Wise. Determination of sodium by controlled-potential coulometry. *Analytical Chemistry* 35:914-915. 1963.
8. Gupta, S. L., M. K. Chatterji and S. K. Sharma. Organic a. c. polarography and tensammetry in non-aqueous media. *Journal of Electroanalytical Chemistry* 7:81-84. 1964.
9. Dapo, Roland F. and Charles K. Mann. Anodic oxidation of triethylamine. *Analytical Chemistry* 35:677-680. 1963.
10. DeFord, Donald D. Electroanalysis and coulometric analysis. *Analytical Chemistry* 30:613-619. 1958; 32:31R-37R. 1960.
11. \_\_\_\_\_ . Electroanalysis. *Analytical Chemistry* 28:660-666. 1956.

12. Dehn, H. et al. Gaspolarographie. Monatshefte für Chemie 93:1348-1352. 1962.
13. Dehn, H., V. Gutmann und G. Schöber. Polarographische Untersuchungen in wasserfreiem Dimethylsuloxid. Monatshefte für Chemie 93:453-454. 1962.
14. Delahay, Paul. New instrumental methods in electrochemistry. New York, Interscience, 1954. 437 p.
15. Ehlers, Vivian B. and John W. Sease. Constant-potential coulometric reduction of organic nitro and halogen compounds. Analytical Chemistry 31:16-22. 1959.
16. Enke, C. G. and R. A. Baxter. A versatile and inexpensive controlled potential polarographic analyzer. Journal of Chemical Education 41:202-209. 1964.
17. Gelb, Robert I. and Louis Meites. Polarographic characteristics and controlled-potential electroreduction of  $\alpha$ -furildioxime. Journal of Physical Chemistry 68:2599-2607. 1964.
18. Geske, David H. The electrooxidation of the tetraphenylborate ion; an example of a secondary chemical reaction following the primary electrode process. Journal of Physical Chemistry 63:1062-1070. 1959.
19. Geske, David H. and Allen J. Bard. Evaluation of the effect of secondary reactions in controlled potential coulometry. Journal of Physical Chemistry 63:1057-1062. 1959.
20. Geske, David H. and August H. Maki. Electrochemical generation of free radicals and their study by electron spin resonance spectroscopy; the nitrobenzene anion radical. Journal of the American Chemical Society 82:2671-2676. 1960.
21. Given P. H. and M. E. Peover. Investigation of carbonyl groups in solvent extracts of coals. Journal of the Chemical Society, 1960, p 394-399.
22. \_\_\_\_\_ . Polarography of iodide and chloride ions in dimethylformamide. Journal of the Chemical Society, 1959, p. 1602-1607.

23. Gutmann V. and G. Schöber. Die Polarographie in nichtwässrigen Lösungen. *Angewandte Chemie* 70:98-104. 1958.
24. \_\_\_\_\_ . Polarographische Untersuchungen in wasserfreiem Dimethylsulfoxyd. *Zeitschrift für Analytische Chemie* 171:339-343. 1959.
25. Holleck, L. , R. Schindler and O. Löhr. Polarographische Untersuchungen meta-substituierter Nitrobenzolderivate in wasserfreiem Acetonitril. *Die Naturwissenschaften* 46: 625-626. 1959.
26. Holleck, Ludwig und Dieter Becher. Untersuchungen über den Einfluss der Leitsalzionen auf die Polarographische reduktion aromatischer Nitroverbindungen in Acetonitril und Dimethylformamid. *Journal of Electroanalytical Chemistry* 4:321-331. 1962.
27. Karp, Stewart and Louis Meites. The voltammetric characteristics and mechanism of electrooxidation of hydrazine. *Journal of the American Chemical Society* 84:906-912. 1962.
28. Kelley, M. T., D. J. Fisher and H. C. Jones. Controlled-potential Polarographic polarizing unit with electronic scan and linear residual current compensation. *Analytical Chemistry* 32:1262-1265. 1960.
29. Kelley M. T., H. C. Jones and D. J. Fisher. Controlled-potential and derivative polarograph. *Analytical Chemistry* 31:1475-1485. 1959.
30. Kemula, Wiktor and Roman Sioda. Electrochemical generation and visible spectrum of nitrobenzene free radical anion in dimethylformamide. *Nature* 197:588-589. 1963.
31. Kitagawa, Toyokichi, Thomas P. Layloff and Ralph N. Adams. Voltammetry and electron paramagnetic resonance spectra of halonitrobenzene anion radicals. *Analytical Chemistry* 35:1086-1087. 1963.
32. Koltoff, I. M. and T. B. Reddy. Polarography and voltammetry in dimethylsulfoxide. *Journal of the Electrochemical Society*. 108:980-985. 1961.

33. Kruse, Jurgen M. Determination of organic nitro compounds by controlled-potential coulometry. *Analytical Chemistry* 31:1854-1857. 1959.
34. Lindbeck, M. R. and J. L. Young. Polarography and coulometry in dimethylsulfoxide of nitric acid oxidation products from soil humic acid. *Soil Science* (Accepted for publication June 29, 1965).
35. Lingane, James J. *Electroanalytical chemistry*. 2d ed. New York, Interscience, 1958. 669 p.
36. Maki, August H. and David H. Geske. Electron spin resonance and polarographic investigation of substituted nitrobenzene negative ions. *Journal of the American Chemical Society* 83:1852-1860. 1961.
37. Mayell, Jaspal S. and Allen J. Bard. The electroreduction of quaternary ammonium compounds. *Journal of the American Chemical Society* 85:421-425. 1963.
38. Meites, Louis. Experimental evaluation of rate constants for dimerization of intermediates formed in controlled-potential electrolysis. *Journal of Electroanalytical Chemistry* 5:270-280. 1963.
39. Meites, Louis and Thelma Meites. Assay of picric acid by coulometry at controlled potential. *Analytical Chemistry* 28:103-106. 1956.
40. Meites, Louis and Stephen A. Moros. Background corrections in controlled-potential coulometric analysis. *Analytical Chemistry* 31:23-28. 1959.
41. Moros, Stephen A. and Louis Meites. Electrochemical characteristics of manganese in cyanide solutions. II. Background corrections in controlled-potential coulometric determination of manganese (II). Kinetics of the oxidation of manganese (I) by hydrogen cyanide. *Journal of Electroanalytical Chemistry* 5:103-113. 1963.

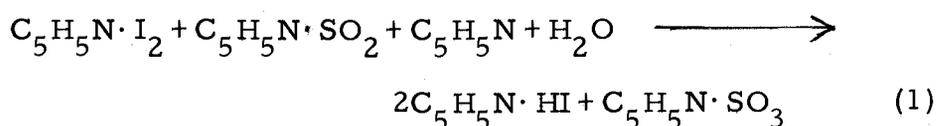
42. Nicholson, Richard S. and Irving Shain. Experimental verification of an ECE mechanism for the reduction of p-nitrosophenol, using stationary electrode polarography. *Analytical Chemistry* 37:190-195. 1965.
43. Rechnitz, Garry A. *Controlled-potential analysis*. New York, Pergamon, 1963. 85 p.
44. Rieger, Philip H. and George K. Fraenkel. Analysis of the electron spin resonance spectra of aromatic nitrosubstituted anion radicals. *Journal of Chemical Physics* 39:609-629. 1963.
45. Roberts, J. L., Jr. and D. T. Sawyer. Voltammetric determination of carbon dioxide using dimethylsulfoxide as a solvent. *Journal of Electroanalytical Chemistry* 9:1-7. 1965.
46. Schaap, Ward B. and Peter S. McKinney. Resistance compensation in polarography. Application to high resistance nonaqueous systems and to high current-density aqueous systems. *Analytical Chemistry* 36:1251-1258. 1964.
47. Schöber, G. und G. Rehak. Polarographische Untersuchungen in wasserfreiem Dimethylsulfoxid. *Monatshefte für Chemie*. 93:445-452. 1961.
48. Scott, F. A. and R. M. Peekema. Analysis for plutonium by controlled potential coulometry. In: *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1958. Vol. 28. Geneva, United Nations, 1958. p. 573-578. (Paper no. 914).
49. Spritzer, Michael and Louis Meites. Polarographic characteristics and controlled-potential electro-reduction of dimethylglyoxime. *Analytica Chimica Acta* 26:58-65. 1962.
50. Testa, A. C. and W. H. Reinmuth. Stepwise reactions in chronopotentiometry. *Analytical Chemistry* 33:1320-1324. 1961.
51. Wawzonek, S. Organic polarography. *Analytical Chemistry* 28:638-649. 1956; 30:661-674. 1958; 32:144R-161R. 1960; 34:182R-200R. 1962.

52. Wawzonek, S., R. Berkey and D. Thomson. Polarographic behavior of organic compounds in methanesulfonic acid. *Electrochemical Society Journal* 103:513-518. 1956.
53. Wawzonek, S. and D. J. Pietrzyk. Organic polarography. *Analytical Chemistry* 36:220R-239R. 1964.
54. Wise, Edward N. and Edward J. Cokal. Coulometric determination of europium and ytterbium at controlled potential. *Analytical Chemistry* 32:1417-1419. 1960.

PART II. MICROANALYSIS FOR WATER, USING  
RAPID CONTROLLED POTENTIAL COULOMETRY  
IN A KARL FISCHER SYSTEM

I. INTRODUCTION

The Karl Fischer method is, without question, the most widely applied technique for the quantitative determination of water in organic materials. The method was first developed by Karl Fischer (4) primarily for the determination of moisture in petroleum chemicals and sulfur dioxide. The method is based on the reaction of water with a solution of sulfur dioxide, pyridine, and iodine in methanol. The stoichiometry of the reaction was established by Smith, Bryant, and Mitchell (14) and requires one mole of water for each mole of iodine consumed. They proposed the following two-step reaction:



The quantitative determination of water is accomplished volumetrically, with a methanol titrant containing a known concentration of iodine and an excess of pyridine and sulfur dioxide. The equivalence point is taken as the visual appearance of iodine or by electrometric methods.

The Karl Fischer method has proven extremely useful in

determining moisture in both organic and inorganic materials and in quantitatively determining functional groups in organic systems. The latter is achieved by determining the water liberated or consumed in a stoichiometric organic reaction. There are several publications (7, 8, 19) which cover these applications in detail.

Perhaps the most perplexing problem associated with the Karl Fischer method is the instability of the reagent. The iodine concentration decreases with time, even in the absence of moisture, and the reagent must be standardized just prior to usage. The parasitic reaction or reactions responsible for the consumption of iodine have not as yet been elucidated. Many modifications of the reagent have been proposed for increasing its stability, yet, the instability problem remains. An example of such a modification is given by Peters and Jungnickel (11). They found that a Karl Fischer reagent prepared with methanol as the major constituent lost 22 percent of its iodine concentration over a period of 30 days, whereas a reagent in which methyl cellosolve was substituted for methanol lost only nine percent of its iodine concentration over the same period.

A coulometric method in which the Karl Fischer reagent is produced in situ at the time of analysis has the advantage of eliminating the necessity for preparation, storage, and standardization of the reagent. The use of coulometry in the Karl Fischer water determination has only recently been considered. A constant

current coulometric titration method in which electrolytic generation of iodine provides the titrant in a depleted Karl Fischer reagent was first developed by Meyer and Boyd (6). It was necessary, however, to provide a supplementary generating current that could be adjusted to maintain the depleted Karl Fischer reagent at the end-point before addition of the sample. This was reported as necessary because of side-reactions which continuously consumed the iodine. The absolute standard deviation was reported as approximately  $\pm 2 \mu\text{g.}$  of water. Swensen and Keyworth (16) employed the coulometric titration method to determine water below 10 ppm. in benzene and related solvents. However, they used from one to five gram samples, and no evaluation of the precision of the method was given. Přebyl and Slovák (12) reported a coulometric titration method which gave an approximate error in determination of  $\pm 2 \mu\text{g.}$  of water in the range from 10 to 550  $\mu\text{g.}$  of water.

It is very difficult to achieve a precision of only  $\pm 2 \mu\text{g.}$  of water in a conventional Karl Fischer microdetermination. Bastin, Siegel, and Bullock (2) developed a direct microtitration method which was scaled down to 1/100 of the conventional Karl Fischer macromethod. They determined from 10 to 3000  $\mu\text{g.}$  of water, with a standard deviation of  $\pm 3 \mu\text{g.}$  for determinations of samples containing less than 300  $\mu\text{g.}$

Otterson (10) has described a spectrophotometric method for determination of microgram quantities of water. He used the color of the Karl Fischer reagent to determine from 11 to 26  $\mu\text{g}$ . of water in  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , reporting an average error of about  $\pm 2 \mu\text{g}$ . of water.

An advantage of controlled potential coulometry for micro-determinations is that an end-point determination is not necessary. The determination is terminated by the completion of the oxidation or reduction, and assuming 100 percent current efficiency, the addition of excess titrant (electrons) is not possible. The precision of the method is not limited by the absolute error in reproduction of an end-point. A disadvantage, however, is that controlled potential coulometric determinations usually require from twenty minutes to several hours. Bard (1), by taking advantage of a large electrode area-to-solution volume, ultrasonic and nitrogen stirring, designed a high speed electrolysis cell. He has determined from 2.5 to 25  $\mu\text{moles}$  of silver (I) and iodide by electrodeposition of silver and silver iodide, respectively, in less than 100 seconds.

This research applies rapid, controlled potential coulometry to the microdetermination of water in liquid solvents, in which coulometric control of iodine is achieved in a Karl Fischer reagent. The absolute standard deviation is decreased to  $\pm 0.2 \mu\text{g}$ . of water, a substantial improvement over existing methods. In addition, a

rapid electrolysis method is given, and some of the related parameters are discussed.

## II. EXPERIMENTAL

### Apparatus

#### Electrolysis Cell

The three-compartment cell used for controlled potential electrolysis is illustrated in Figure 1. The reference and isolated side-cells are connected by fine porosity frits. The nitrogen inlet frit at the bottom of the working compartment is of medium porosity. The working compartment is closed to the atmosphere by a Teflon top with a silicone rubber seal. The sample inlet system consists of a silicone rubber septum held in position by a 5/16 inch stainless steel cap screw with a 1/8 inch hole through the center. The nitrogen outlet connection may be removed from the Teflon top for addition and removal of the cell solution. The cell solution is added with a 10 ml. graduated syringe fitted with 0.03 inch diameter Teflon tubing, and removed with a 0.03 inch diameter Teflon tubing by means of vacuum.

#### Electrodes

The working electrode is shaped into a tightly wound spiral consisting of 7.6 g. of 52 mesh platinum gauze. The counter electrode is made of heavy gauge silver foil. The dimensions of the counter electrode are not important as long as the area is sufficient

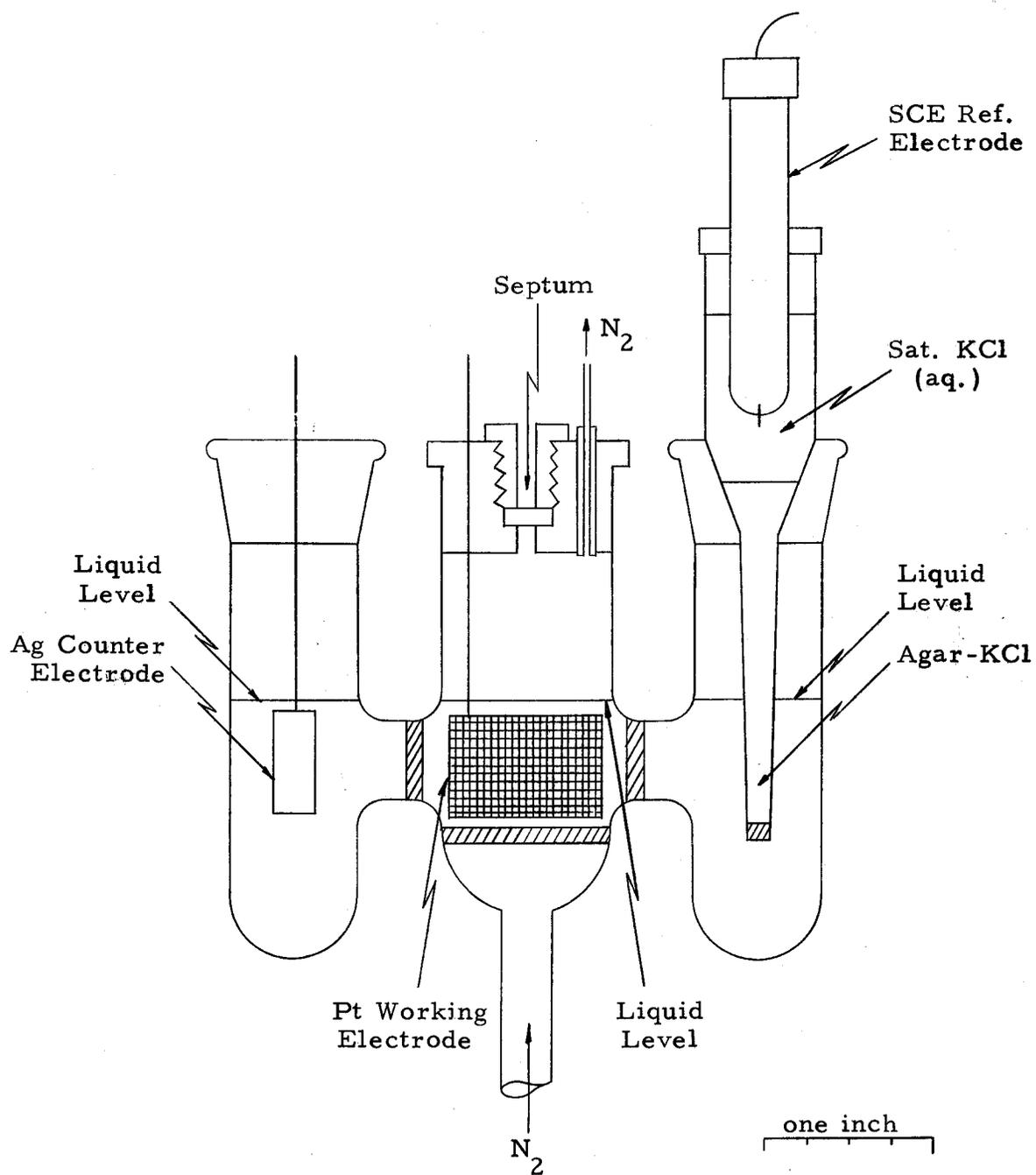


Figure 1. Electrolysis Cell

to carry the current. The reference electrode is a saturated calomel electrode. All voltages reported are versus this electrode. The electrolytic continuity from aqueous to nonaqueous systems is established by an agar-potassium chloride salt bridge and frit, as shown in Figure 1.

### Controlled Potential Coulometer

The instrument used was constructed by Caton (3) similar to that described by Scott and Peekema (13). The instrument's electronic current integrator was continuously monitored by a 50-mv. recorder.

### Preparation of Reagents

#### Karl Fischer Reagents

These reagents are prepared in volumetric flasks by addition of sodium iodide, sulfur dioxide, and pyridine to give the desired concentration when the system is made to volume with methanol. The sulfur dioxide is added through addition of a standard sulfur dioxide solution in methanol which in turn is prepared by adding 200 g. of gaseous anhydrous sulfur dioxide to one liter of methanol. The water in the system is removed by addition of iodine. An excess of iodine is added to yield a solution 0.01 molar in iodine. A premixed stabilized Karl Fischer reagent (Matheson Coleman and

Bell, catalog no. KX10, B806) was made to approximately 0.01 molar in iodine by careful addition of water. At the time of use, the reagents are converted to spent Karl Fischer reagents inside the electrolysis cell by controlled potential reduction of the excess iodine.

### Standard Additions

Standards containing as little as 0.01 percent water in methanol and dimethylsulfoxide cannot be prepared feasibly by a quantitative addition of water to the solvents because of the difficulty of conveniently preparing anhydrous solvents. A common practice in preparing water standards is to add water to the solvent to approximate the desired concentration and to standardize the resulting solution with a Karl Fischer reagent which has previously been standardized against sodium tartrate dihydrate or pure water. It is felt, however, that because of the low level of water concentrations involved, the standard addition method is a more suitable approach. The methanol and dimethylsulfoxide solutions with standard additions of water are prepared inside volumetric flasks and in the absence of air by fitting the volumetric flasks with serum-type rubber septums, and performing additions and removals with gas-tight syringes. The volumetric flasks are filled to the top and sealed with the rubber septums, leaving no air inside the flasks. Then the initial water

content of the solvent is determined on samples removed from the volumetric flasks by syringe. This technique is employed so that the determinations at zero water addition are not subject to errors from water picked up in solvent handling-i. e., from the flasks, transfer, etc. Dry nitrogen is added by syringe to replace the volume of liquid removed. After the initial water content of the solvent is determined, each solvent volume is adjusted by further removal of solvent until the addition of the water brings the final volume to the calibrated volume of the flask. Water is added by syringe, either as pure water, ten percent water in methanol, or ten percent water in dimethylsulfoxide, depending on the volume being prepared.

### Chemicals

Pyridine, Baker and Adamson, reagent grade.

Methanol, Baker and Adamson, reagent grade absolute.

Dimethylsulfoxide, Crown Zellerbach Chemical Products  
Division, spectro grade 40823.

Nitrogen, Matheson Co., Inc., prepurified; the nitrogen was passed through anhydrous magnesium perchlorate drying trains before entering the electrolysis cell.

Sodium Iodide, Baker and Adamson, reagent grade.

Sulfur Dioxide, Matheson Co., Inc., Anhydrous grade,  
purity 99.99 percent.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

#### Iodine Coulometry in Methanol

A current versus potential plot showing the oxidation of iodide to iodine at positive potentials versus a saturated calomel electrode and the decomposition of methanol at negative potentials in a 0.1 molar sodium iodide solution in methanol is given in Figure 2, curve 4. The measurements were made in the electrolysis cell described above. The solution was first deaerated by nitrogen, after which the measurements were made in the absence of stirring. The applied potential was adjusted to give the desired value, and the current recorded after a ten second interval.

#### Induced Background Current

Theoretically it should be possible to oxidize iodide to iodine at a controlled potential to give a quantity of iodine corresponding to a readout in coulombs, and to reduce that quantity of iodine at a controlled potential to give the same readout in coulombs. It was found, however, that this was the case only when the applied potential was maintained at potentials more positive than -0.08 volt. If the reduction was carried out at more negative applied potentials, there was an increase in the number of coulombs required for reduction with respect to the number of coulombs required for

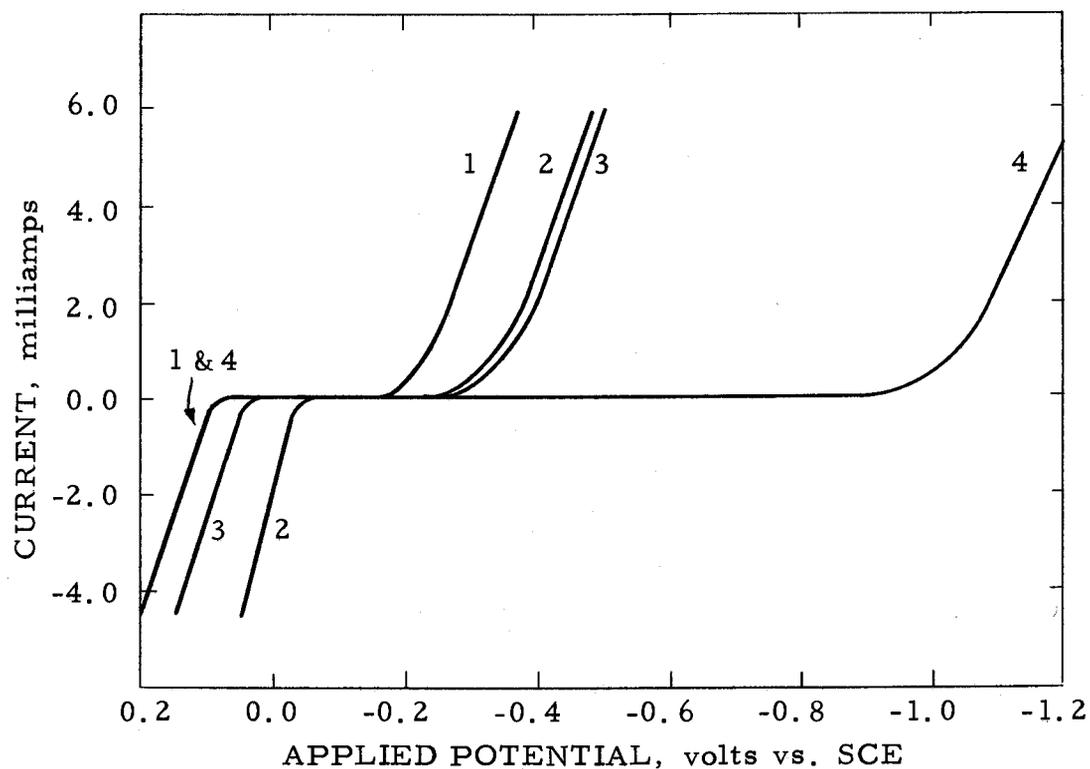


Figure 2. Variation of electrolysis current with applied potential.

- (1) 0.1 M NaI, 0.15 M  $\text{SO}_2$  solutions in methanol.
- (2) M. C. & B. stabilized Karl Fischer reagent.
- (3) 0.1 M NaI, 0.15 M  $\text{SO}_2$ , and 0.6 M pyridine solutions in methanol.
- (4) 0.1 M NaI solution in methanol.

oxidation. This increase in the coulombs ratio for reduction over oxidation corresponding to reductions at more negative applied potentials is shown in Figure 3. The increase in the number of coulombs for reduction was found to be more a function of the initial current (initial rate of reduction) than the applied potential. The ratio of coulombs remained at unity if the initial current was not allowed to exceed ten ma., regardless of the applied potential. This was demonstrated by adjusting the applied potential from -0.05 to -0.32 volt during the reduction at a rate such that the current never exceeded ten ma. Another approach was to reduce the nitrogen stirring such that the reduction at -0.2 volt gave an initial current below ten ma.

It seems reasonable to suspect the reduction step as causing the deviation of the coulombs ratio from unity because the system contains 0.1 molar iodide and any secondary oxidation should be insignificant. However, the possibility of the oxidation step causing the deviation was checked by making all reductions at an applied potential of -0.05 volt and the oxidations were made at applied potentials between +0.2 volt (with an initial current of five ma.) and +0.7 volt (with an initial current of 25 ma.). No deviation from unity was observed for the ratio of the number of coulombs given by the reduction and oxidation processes.

These results indicate that at higher initial currents a different

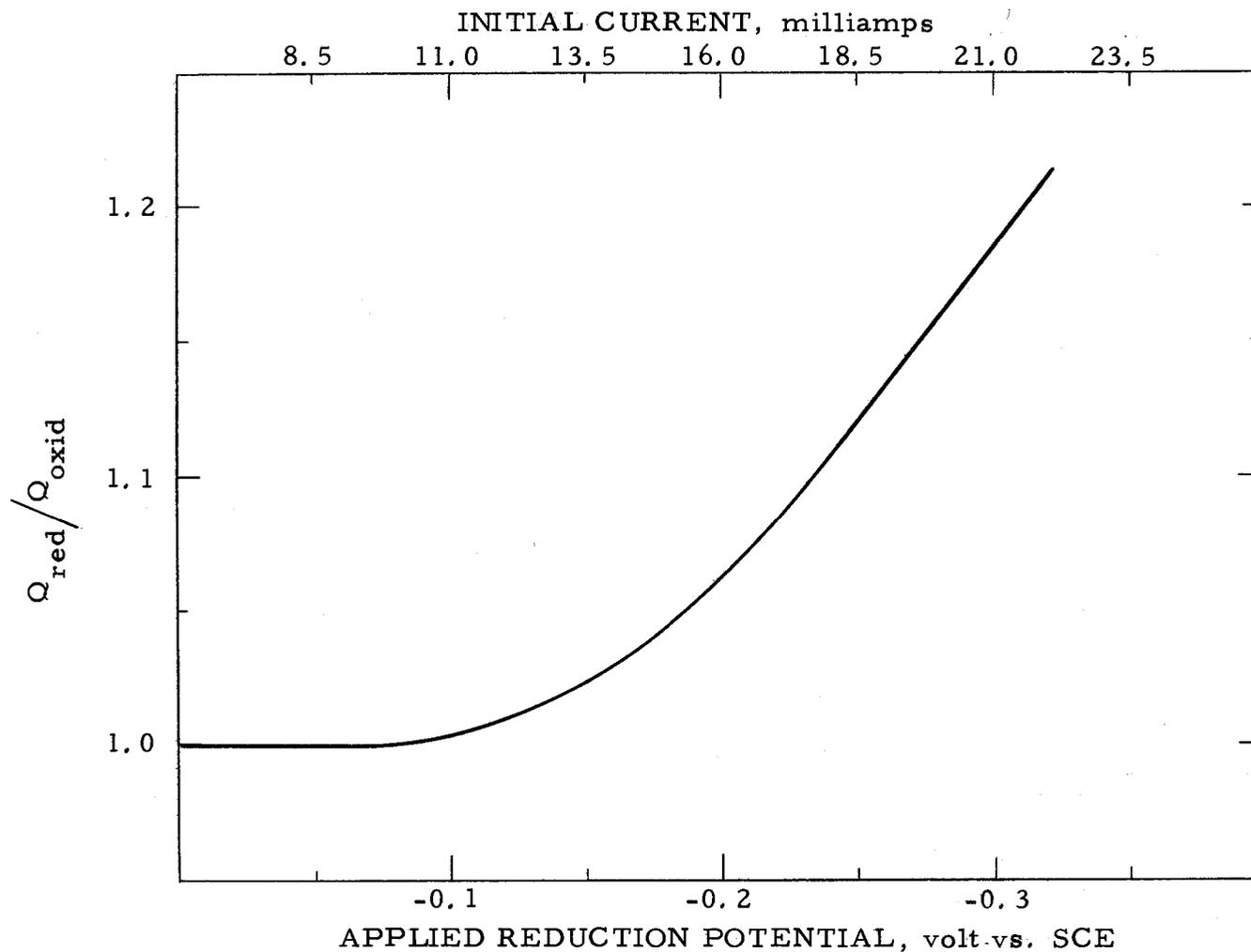


Figure 3. Ratio of coulombs for iodine reduction to iodide oxidation as a function of the iodine reduction potential. Conditions: Iodide oxidations were maintained at +0.4 volt to give  $2\mu$  moles of iodine in 5 ml. of methanol containing 0.1 M NaI.

reduction mechanism for iodine occurs, or an induced reduction of some other substance also takes place. A localized voltage excursion at the working electrode was considered unlikely. If this were the case, the Karl Fischer reagent would be expected to show a greater reduction-oxidation coulombs ratio change, because this reagent contains substances which are reduced more easily than methanol. However, it was found that the Karl Fischer reagent did not show any change in the reduction-oxidation coulombs ratio when subjected to the same applied potential variations described for iodine in methanol. There may have been an induced hydrogen reduction at the higher initial currents. This seems plausible in view of the fact that the 0.1 molar sodium iodide solution in methanol contained 0.05 percent water, whereas the Karl Fischer reagent was absolutely water-free. Background currents involving the induced reduction of hydrogen in controlled potential coulometry of aqueous systems have been discussed by Meites and Moros (5).

#### Rapid Controlled Potential Coulometry

The electrolysis cell (see Figure 1) was designed to provide a large electrode area-to-solution volume ratio and efficient nitrogen stirring in order to decrease the time necessary for electrolysis. The nitrogen stirring efficiency was evaluated by noting the change in the time necessary for complete iodine reduction at different

nitrogen flow rates, maintaining the other parameters constant. The results are given in Figure 4. The time of complete reduction was taken as the time at which the current had decayed to 0.1 percent of its initial value. No significant amount of iodine was lost from the solution due to nitrogen stirring. This was established by subjecting two  $\mu$ moles of iodine in five ml. of methanol containing 0.1 molar sodium iodide to nitrogen stirring with 20 ml./min. for ten minutes before reduction. No change in iodine concentration was observed. The loss of iodine was expected to be less likely from a Karl Fischer reagent because, in addition to the 0.1 molar sodium iodide, the system also contains pyridine which forms an addition compound with iodine. The effect of pyridine addition on the redox potential of iodine in methanol can be seen by comparing curve 3 with curve 4 in Figure 2. The oxidation of iodide to iodine with pyridine present was easier, and consequently the reduction of iodine was more difficult.

Figure 5 illustrates the effect of change in the electrolysis cell solution volume upon the time necessary to completely reduce 2.0  $\mu$ moles of iodine in a 0.1 molar sodium iodide solution in methanol. The cell solution was just level with the top of the working electrode at a volume of 3.5 ml. The relatively small increase in iodine reduction time with increase in the cell solution volume demonstrates the high efficiency of nitrogen stirring from a large

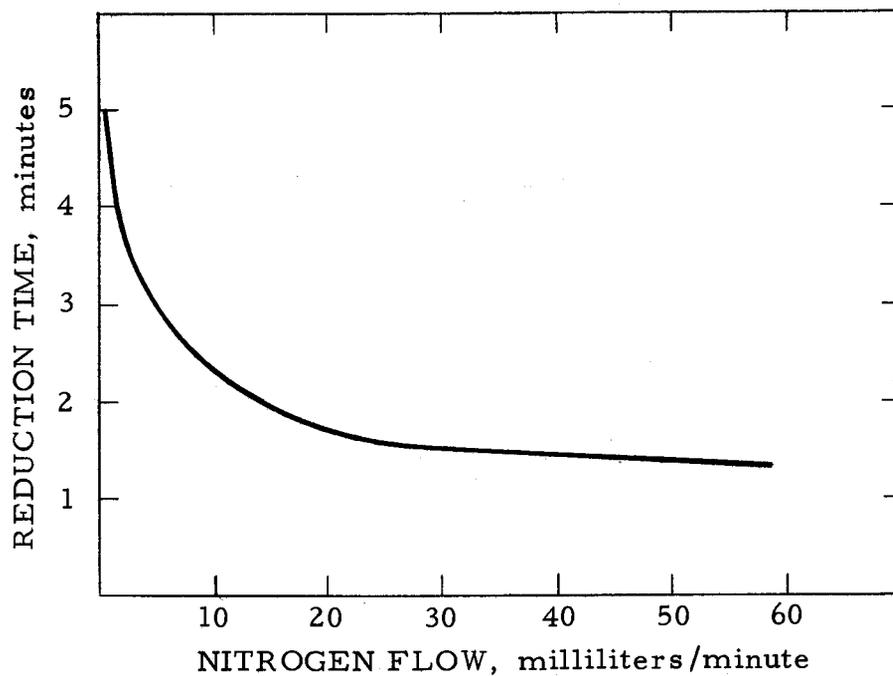


Figure 4. Effect of nitrogen stirring on the time necessary to reduce  $2 \mu$  moles of iodine. Conditions: Reductions were made at  $-0.1$  volt applied potential in  $5$  ml. of methanol containing  $0.1$  M NaI.

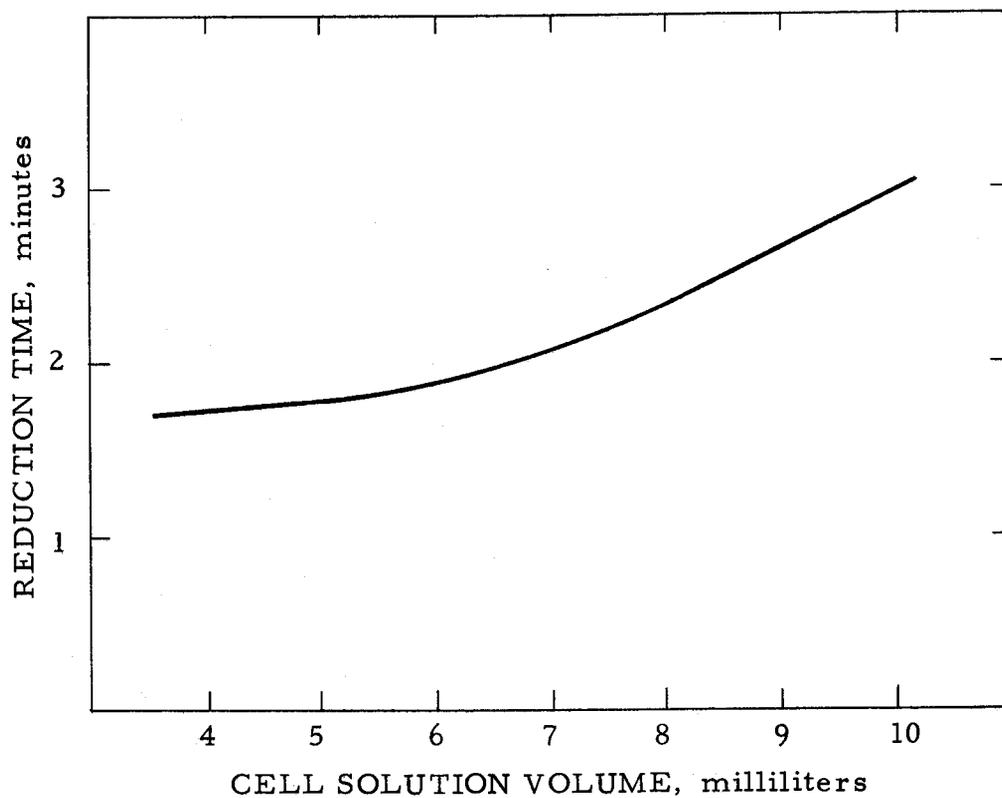


Figure 5. Effect of the cell solution volume on the time necessary to reduce  $2\mu$  moles of iodine. Conditions: Reductions were made at  $-0.1$  volt applied potential in cell solutions of methanol containing  $0.1$  M NaI, and with a nitrogen stirring rate of  $20$  ml./min.

frit placed in the bottom of the cell.

Determinations in which 2.04  $\mu$ moles of iodine were produced by oxidation gave an iodine reduction of  $2.05 \pm 0.002$   $\mu$ moles. The standard deviation is based on ten determinations which were made in five ml. of 0.1 molar sodium iodide solution in methanol with a nitrogen stirring flow of 20 ml./min. Oxidations and reductions were made at controlled potentials of +0.4 and -0.08 volt, respectively. Each reduction of 2.04  $\mu$ moles of iodine was accomplished in 96 seconds. This rapid controlled potential electrolysis time compares closely with those reported by Bard (1). The reduction time could have been decreased by reducing the iodine at more negative applied potentials; however, as pointed out above, because of the induced background current the results were not quantitatively reliable.

#### Iodine Coulometry in Karl Fischer Reagents

Current versus potential curves resulting from spent Karl Fischer reagents are shown in Figure 2, curves 2 and 3. The conditions and procedure for the measurements were the same as those reported above for iodine in methanol. Oxidation at positive applied potentials corresponds to the oxidation of iodide to iodine, and the reduction at negative potentials was probably due to the reduction of pyridinium ion. Spritzer, Costa, and Elving (15) have shown that

pyridinium ion undergoes polarographic reduction at a dropping mercury electrode in a pyridine system.

### Reagent Stability

It was found that when 2.04  $\mu$ moles of iodine was produced by oxidation at +0.4 volt, the reduction at -0.2 volt gave  $1.98 \pm 0.004$   $\mu$ moles recovered. The standard deviation is based on 15 determinations. The oxidation and reduction times were 27 and 92 seconds, respectively. The loss of iodine was found to be continuous and constant throughout a series of determinations in the same cell solution reagent. Determinations were made after 2.04  $\mu$ moles of iodine had remained in the system for five minutes, and the loss of iodine was found to correspond to  $0.53 \pm 0.01$   $\mu$ g. of water per minute. Approximately the same loss was observed when the iodine was not produced in the system until just before the end of the five minute waiting period. This indicated that the cause of the iodine loss was continuous even in the absence of iodine. The loss was no doubt due to both water getting into the system and to side-reactions which continuously produced water or a product which could reduce iodine.

Changes in the nitrogen flow rate had very little effect on the amount of iodine lost per minute. A further check was made on the possible water contribution from the nitrogen by placing a dummy

cell immediately ahead of the electrolysis cell. The dummy cell contained 20 ml. of Karl Fischer reagent approximately 0.01 molar in iodine with a bubbling path four times that of the electrolysis cell. There was very little decrease in the loss of iodine per minute when this nitrogen pretreatment by the dummy cell was employed. This indicated that the nitrogen was not contributing a significant amount of water. A contribution of water from the isolated and reference cell compartments was eliminated by maintaining the Karl Fischer reagent in these cells at a slight iodine concentration. A contribution of oxidizable or reducible species from the cell containing the isolated electrode was not possible because the silver (I) oxidation product was insoluble in the iodide system, and the reduction product was iodide from the slight excess of iodine in the cell solution.

The loss of iodine was observed to vary considerably with the Karl Fischer reagent composition and age. Karl Fischer reagents gave a greater loss of iodine with increasing concentrations of sulfur dioxide. The reagent purchased from Matheson Coleman and Bell (see Figure 2, curve 2) and other stabilized reagents containing large ratios of pyridine-to-methanol were found to give somewhat smaller losses of iodine per minute; however, the iodine reduction time was greatly increased. This lack of improvement from the stabilized reagents, coupled with the tendency for them to plug the nitrogen inlet frit of the electrolysis cell, discouraged the use of

these reagents. Many Karl Fischer reagents with different compositions were checked, and the one found most satisfactory consisted of 0.1 molar sodium iodide, 0.15 molar sulfur dioxide, and 0.6 molar pyridine solutions in methanol. The loss of iodine from this reagent was found to be constant and did not interfere with the analysis for water, as the loss of iodine per minute was treated as a blank which was determined before and after each analysis.

#### Water Determination Procedure

The controlled potential coulometric procedure for determination of water, employing spent Karl Fischer reagent, closely resembles the Karl Fischer back titration procedure. In the back titration procedure a known excess of iodine is added to the sample in the form of Karl Fischer reagent, whereas in the controlled potential coulometric procedure a known excess of iodine is produced coulometrically in a spent Karl Fischer reagent containing the sample. In the back titration procedure the excess iodine is determined by titrating with a standard water-methanol titrant. In the controlled potential coulometric procedure the excess iodine is determined coulometrically.

#### Procedure:

- (a) Add five ml. of Karl Fischer reagent containing approximately 0.01 molar in iodine and adjust

the nitrogen flow rate to 20 ml./min.

- (b) After several minutes reduce the excess iodine at -0.2 volt applied potential.
- (c) Adjust the applied potential to +0.4 volt and oxidize 2.00  $\mu$ moles of iodide to iodine.
- (d) Add the 0.1 ml. sample which should contain less than one  $\mu$ mole of water. Allow one-half minute for complete reaction.
- (e) Reduce the excess iodine at -0.2 volt applied potential and subtract this value from the original 2.00  $\mu$ moles.
- (f) Determine the system loss of iodine (blank) by oxidation of iodide and reduction of iodine in the absence of a sample, maintaining the iodine quantity and time the same as above. The determination time can be obtained from the distance that the recorder chart paper travels. Add this loss of iodine to the value found in (e).
- (g) Convert the  $\mu$ moles of iodine consumed by the water in the sample to  $\mu$ grams of water on a one-to-one mole basis.

For samples which contained in excess of 20  $\mu\text{g}$ . of water, a change in procedure is necessary in order to maintain a sufficient excess of iodine in step (d) after addition of the sample. This is accomplished by producing a recorded amount of iodine after the sample addition, equal approximately to the iodine consumed by the sample. The increase in value for iodine produced is added to the original 2.00  $\mu\text{moles}$  of iodine produced. The remaining procedure is the same.

Maintaining an excess of iodine was found to be necessary in the determination of water in dimethylsulfoxide in order to obtain complete recovery. Also, the reaction time in (d) was increased to three minutes. This lack of complete recovery was demonstrated by determining consecutive blanks after a water determination. The blank immediately after a water determination, in which the reaction time in (d) was only one-half minute, would be considerably larger than the following blanks. This effect was not observed for water determinations in methanol.

If the electrolysis cell was not used for several days, the time in (b) was increased by 15 or 20 minutes. If moisture came into contact with the frits, the absorbed moisture was removed very slowly, yielding larger blanks which decreased with time. This problem was eliminated by keeping the frits in contact with Karl Fischer reagent when the cell was not in use. In consecutive sample

determinations the overall time of determination was kept constant, and a blank was determined before and after the sample.

#### Water Determination Results

The results of standard additions are given in Figure 6. The intersection at zero water addition agreed with the water content found for the solvents before standard water additions. This demonstrates that the method was absolute in that one mole of iodine consumed corresponded to one mole of water.

Tenth milliliter samples of methanol containing ten to 74  $\mu\text{g}$ . of water were determined. The absolute standard deviation was  $\pm 0.2 \mu\text{g}$ . of water. Tenth milliliter samples of dimethylsulfoxide containing from 18 to 82  $\mu\text{g}$ . of water were determined. The absolute standard deviation was  $\pm 0.3 \mu\text{g}$ . of water. The number of samples of dimethylsulfoxide determined in the same electrolysis cell solution reagent had a considerable effect on the reaction time necessary in (d) for 100 percent recovery. For three minute reaction times only four 0.1 ml. samples could be determined per cell solution reagent. This number was increased to eight 0.1 ml. samples by increasing the reaction time in (d) to five minutes. This effect was not observed for methanol, and from ten to twenty 0.1 ml. samples were determined for each cell solution reagent.

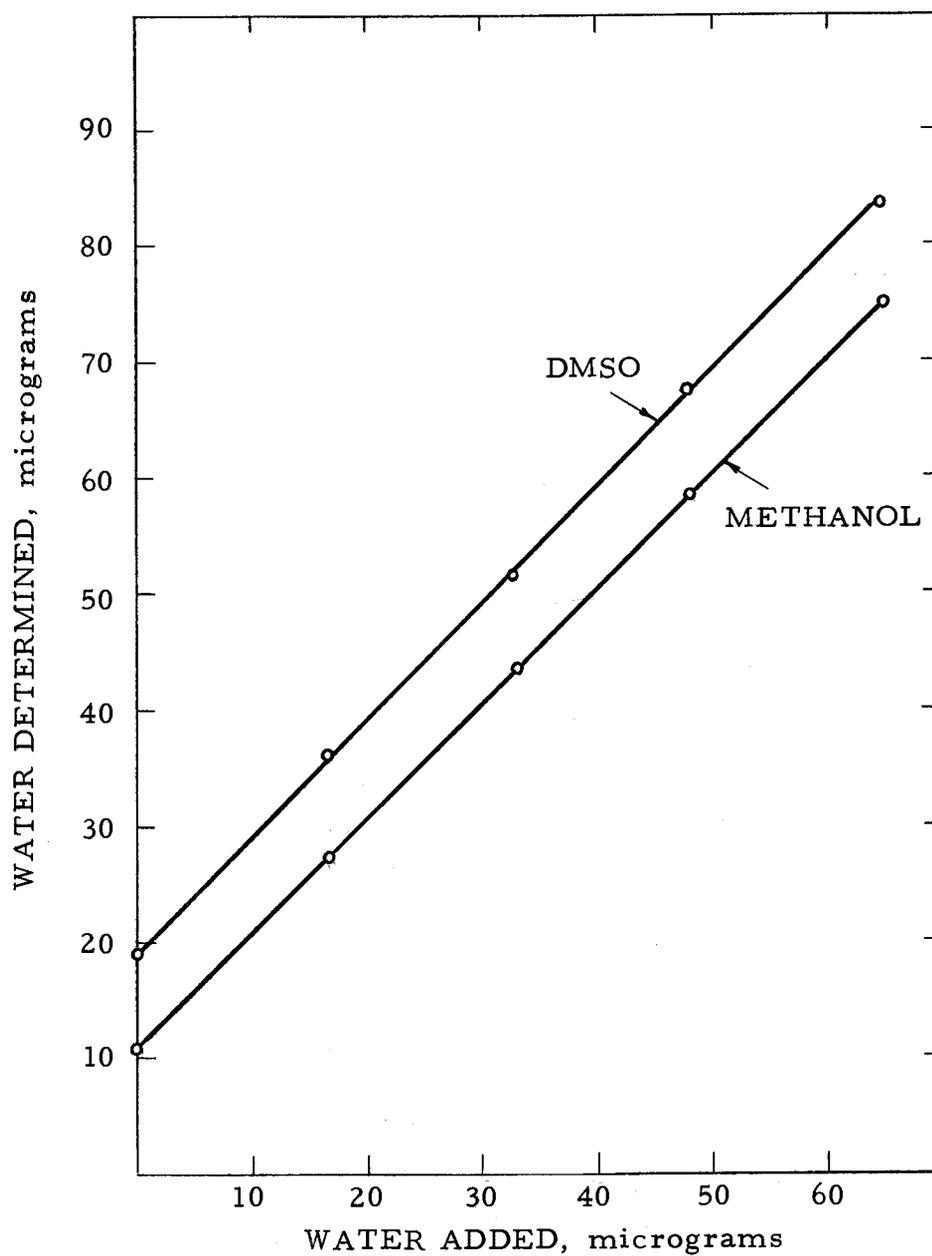


Figure 6. Standard addition determinations of water in 0.1 ml. solvent samples.

The dimethylsulfoxide appears to have a greater affinity for water than methanol. This demonstrates the advantage of a back titration type of procedure for solvents which release water slowly to the Karl Fischer reagent. Also, this shows that such solvents should be determined in a manner such that the sample volume to reagent volume is kept as small as possible.

#### IV. CONCLUSIONS

In comparison with other water determination methods developed on the basis of the Karl Fischer reaction, the proposed controlled potential coulometric method appears to have the greatest sensitivity. The method is not limited by the sensitivity of a conventional end-point detection. The ability to measure microgram quantities of water and thus decrease the solvent sample size is not only important where sample availability is limited, but also a small solvent sample size should decrease the effect of interfering side reactions given by the solvent and the Karl Fischer reagent. The method has the advantage of permitting excess iodine to remain in the system a predetermined time, thereby assuring complete reaction in the case of solvents which slowly give up the last traces of water. The development of a rapid electrolysis system allows the method to be competitive with other methods as far as overall time of analysis is concerned.

The results from iodine coulometry in Karl Fischer reagents demonstrate the utility of a rapid, controlled potential coulometric method for precise, controlled in situ addition and removal of a species for evaluating the parameters of a complicated system. The method has proven valuable for rapid evaluation of the stability of Karl Fischer reagents of different composition and age.

It should also prove useful for establishing the reaction kinetics and effect of interfering side reactions for different solvent-reagent systems.

## V. BIBLIOGRAPHY

1. Bard, Allen J. High speed controlled potential coulometry. *Analytical Chemistry* 35:1125-1128. 1963.
2. Bastin, E. L., Herbert Siegel and A. B. Bullock. Micro-determination of water by titration with Fischer reagent. *Analytical Chemistry* 31:467-473. 1959.
3. Caton, Roy Dudley, Jr. Controlled potential coulometric and polarographic investigation of metallic ions in fused salts. Ph. D. thesis. Corvallis, Oregon State University, 1963. 129 numb. leaves.
4. Fischer, Karl. Neues Verfahren zur massanalytischen Bistimmung des Wassergehaltes von Flüssigkeiten und festen Körpern. *Angewandte Chemie* 48:394-396. 1935.
5. Meites, Louis and Stephen A. Moros. Background corrections in controlled-potential coulometric analysis. *Analytical Chemistry* 31:23-28. 1959.
6. Meyer, A. S. Jr. and C. M. Boyd. Determination of water by titration with coulometrically generated Karl Fischer reagent. *Analytical Chemistry* 31:215-219. 1959.
7. Mitchell, John, Jr. Aquametric methods in organic analysis. *Analytical Chemistry* 36:2050-2052. 1964.
8. Mitchell, John, Jr. Karl Fischer reagent titration. *Analytical Chemistry* 23:1069-1075. 1951.
9. Mitchell, John, Jr. and M. Donald Smith. *Aquametry*. New York, Interscience, 1948. 444p.
10. Otterson, Dumas A. Spectrophotometric determination of microgram quantities of vaporizable water from solids using Karl Fischer reagent. *Analytical Chemistry* 33:450-453. 1961.
11. Peters, E. D. and J. L. Jungnickel. Improvements in Karl Fischer method for determination of water. *Analytical Chemistry* 27:450-453. 1955.

12. Přibyl, M. and Z. Slovák. Coulometrische Bistimmung kleiner Wassermengen nach dem Prinzip der Karl-Fischer-Reaktion. *Microchimica et Ichnoanalytica Acta*, 1965, no. 2, p. 1097-1105.
13. Scott, F. A. and R. M. Peekema. Analysis for plutonium by controlled potential coulometry. *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1958. Vol. 28. Geneva, United Nations, 1958. p. 573-578. (Paper no. 914).
14. Smith, D. M., W. M. D. Bryant and John Mitchell Jr. Analytical procedures employing Karl Fischer reagent. I. Nature of the reagent. *Journal of the American Chemical Society* 61:2407-2412. 1939.
15. Spritzer, Michael S., Jose M. Costa and Philip J. Elving. Polarographic reduction of pyridinium ion in pyridine. Application to the determination of Bronsted and Lewis acids. *Analytical Chemistry* 37:211-217. 1965.
16. Swensen, R. F. and D. A. Keyworth. Determination of water below 10 p. p. m. in benzene and related solvents, using coulometrically generated iodine. *Analytical Chemistry* 35:863-867. 1963.