ANALYSIS OF THE VISIBLE SPECTRA OF CONCENTRATED CHROMIC CHLORIDE SOLUTIONS

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INTRODUCTION

In the development of the NASA Redox Energy Storage System, the electrical storage efficiency has been low due to the complex chemical reaction of the chromium II and III species. This paper describes several studies dealing with the processes occurring at the catalyzed carbon electrode during the charging and discharging of the system.

The Redox Energy Storage System is an electrochemical device that employs the oxidation and reduction of two soluble redox couples for charging and discharging. In a Redox flow cell there are two active electrolyte solutions separated by a highly selective ion exchange membrane (fig. 1) (1). Each electrode consists of porous carbon felt, a few millimeters in width. On the chromium side, the carbon felt is catalyzed by trace amounts of gold and lead because the rate of reduction of Cr(III) to Cr(II) is slow on most surfaces (4,5, and 7). This catalyst also improves the cell discharge rate. On the iron side no catalyst is needed (1).

In the aqueous chromic chloride, the complex ions, $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_4Cl_2^{+}$, exist in equilibrium with $Cr(H_2O)_6^{+3}$ (3). Depending on whether the cell is being charged or discharged, there are distinctive differences observed at the same state of charge in the chromium solutions (9). In fig. 2 the complete charge cycle is observed using open-circuit voltage behavior. Above 50 percent state-of-charge, the charging rate decreases considerably.

$Cr(H_2O)_6^{+3}$ and $Cr(H_2O)_5Cl^{+2}$ have been identified as the predominant Cr(III) species present in the acidified $CrCl_3$ solutions of the NASA Redox System and are shown in figure 3 (1,6 and 8). The reactions occurring at the catalyzed carbon felt electrode during charge-discharge cycles have been followed spectrophotometrically and potentiometrically (1). Figure 4 is a typical spectrum and figure 5 shows the emf data plotted versus the ratios of Cr(II) to Cr(III) calculated from the spectra using Beer's Law.

The concentration of $Cr(H_2O)_5Cl^{+2}$ is found to decrease much more rapidly with the increasing state-of-charge than does the concentration of $Cr(H_2O)_6^{+3}$, indicating that $Cr(H_2O)_5Cl^{+2}$ is predominantly reduced during the charging cycle (1). There is a rapid rise in $Cr(H_2O)_5Cl^{+2}$ concentration, and a slow rise in the concentration of $Cr(H_2O)_6^{+3}$, as discharge takes place. Electrode potential data also indicates that $Cr(H_2O)_5Cl^{+2}$ is the primary electroactive species. This can be explained as the reduction of $Cr(H_2O)_5Cl^{+2}$ via an inner-sphere chloride-bridged electrode reaction and the oxidation of $Cr(H_2O)_5Cl^{+}$ via an inner-sphere chloride-bridged electrode reaction shown in fig. 7 (1). There is also a slowly attained equilibrium between $Cr(H_2O)_6^{+3}$ and $Cr(H_2O)_5Cl^{+2}$.

The spectra was analyzed using a DuPont 310 curve resolver and the visible spectra of the complex ions present in the solution which are shown in figure 6 (1).

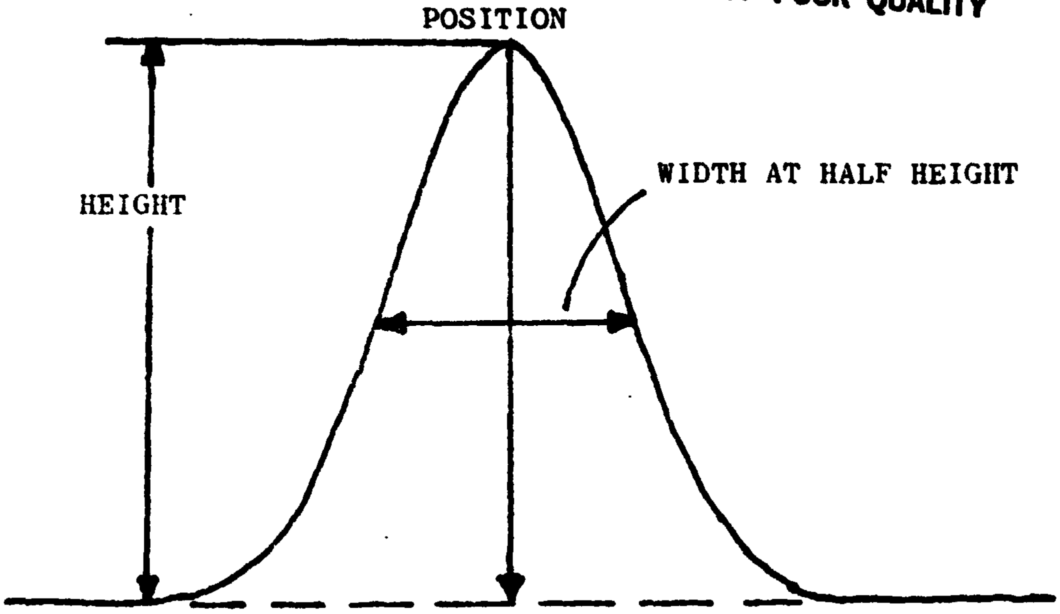
The Frank-Condon principle, which states that the motions of heavy atoms are negligibly slow with respect to the rapid motions of electrons dictates that the atomic geometry of $Cr(H_2O)_5Cl^{+2}$ during reduction should remain the same as well as the Cr(II) species during oxidation (4). The reaction pathway determined at a dropping mercury electrode and a catalyzed carbon electrode found the complexes $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6{}^{+3}$ to be involved in the oxidation and reduction reactions (1). The electrode potential data shows that $Cr(H_2O)_5Cl^{+2}$ and Cr^{+2} obey the Nernst equation in the discharge mode and in the charge mode. $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_5Cl^{+}$ appear to be the electroactive species. This activity can be explained by the unique atomic structure (octahedral) as well as the high activity of the chloride ion. The chloride ion forms a bridged inner-sphere pathway which is much more active than the H_2O pathway on the $Cr(H_2O)_6{}^{+3}$ (7). The ligands in the reactant's primary coordination sphere penetrate the layer of solvent molecules and ions specifically coordinated to the electrode surface. Thus, the crystal field that stabilized the octahedral $Cr(H_2O)_5Cl^{+2}$ is overcome. Reduction can now occur in the charge mode because the energy of activation is lowered.

The goal of this research was to analyze the visible spectra of acidified chromic chloride solutions using curve resolving techniques previously developed, to develop new computer techniques to analyze the spectra, and compare the resolts of the two methods. This comparison will be helpful in assessing the validity of using curve resolving techniques in previous studies and in carrying out future studies on the temperature dependence of chromium (III) complex concentrations.

EXPERIMENTAL PROCEDURES AND CALCULATIONS

Solutions of 1M $CrCl_3$ in 1N HCl and 1M $CrCl_3$ in 2N HCl were placed in 25°C, 40°C, 55°C, and 69.5°C water baths and the spectra recorded after 2, 4, 6, and 24 hours to detect any equilibrium changes in solution (3). Two samples were used, one 10ml and the other 25ml.

Analysis of the spectral data (figures 8-14) were first curved out with the Dupont 310 curve resolver. To resolve overlapping peaks, the instrument generates a series of component peaks and synthesizes a sum curve matching the original data. The resolver generates, on each of its function channels, peak shapes corresponding to many distributions. Since the visible spectrophotometer gives Guassian curve functions, the 310's individual peak parameters of height, width, and horizontal position are independently varied to fit this distribution. The data obtained from the spectrophotometer are displayed in some type of X-Y readout with the peak overlap occurring on the X-axis. For example, the Guassian function is illustrated in the figure below with important parameters shown;



TYPICAL DISTRIBUTION FUNCTION

The analog computer in the 310 adds the individual distribution functions together algebraically, and compares the resulting envelope with the actual experimental data. When resolving overlapping curve envelopes into their individual component curves, the 310 comes to within 1 percent (DuPont 310 Curve Resolver Manual, 1968).

The experimenter fits each curve to his satisfaction by varying each parameter independently. This can be achieved by viewing each component on the screen individually and making appropriate adjustments. When every component is combined on the screen, the readout should fit the total curve envelope.

When resolving each curve, data previously obtained from the spectra of the individual components was used. The maxima of the absorption of $Cr(H_2O)_5Cl^{+2}$ are 605 and 430, and $Cr(H_2O)_6{}^{+3}$ are 575 and 407. The molar absorptivity ratios of $Cr(H_2O)_5Cl^{+2}$ and the $Cr(H_2O)_6{}^{+3}$ are 0.824 liter $mol^{-1}cm^{-1}$ and 0.863 liter $mol^{-1}cm^{-1}$ respectively. Thus, the peaks were positioned and the heights determined according to the ratio of the molar absorptivities. Figures 8-14 show the spectra resolved into the $Cr(H_2O)_6{}^{+3}$ and $Cr(H_2O)_5Cl^{+2}$ peaks.

The calculation of the concentrations of the complexes utilize Beer's Law:

$A = abc$ or $c = A/ab$

A = absorbance

a = molar absorptivity (liter $mol^{-1}cm^{-1}$)

b = width of sample cell (cm)

c = concentration of sample (mol $liter^{-1}$)

The molar absorptivities of the individual species were calculated at arbitrary wavelengths from the spectra of $Cr(H_2O)_6{}^{+3}$ and $Cr(H_2O)_5Cl^{+2}$. The complex ions were prepared according to a procedure by Angelici and chromium concentrations determined by alkaline peroxide oxidation to chromate (9).

A computer program was developed to calculate the concentrations of the chromium (III) complexes from calculated molar absorptivities and is given in table 1. Absorbance values were obtained from the acidified chromium (III) solutions spectra. Using Beer's Law each set of data is compared against the other, giving a total of 45 possible combinations. These simultaneous equations are used to solve for the concentrations:

$$A_1 = a_{1H}b_1c_H + a_{1P}b_1c_P$$
$$A_2 = a_{2H}b_2c_H + a_{2P}b_2c_P$$

A_1 = absorbance at first wavelength
A_2 = absorbance at second wavelength
a_{1H} = molar absorptivity at first wavelength of $Cr(H_2O)_6^{+3}$
a_{1P} = molar absorptivity at first wavelength of $Cr(H_2O)_5Cl^{+2}$
a_{2P} = molar absorptivity at second wavelength of $Cr(H_2O)_5Cl^{+2}$
a_{2H} = molar absorptivity at second wavelength of $Cr(H_2O)_6^{+3}$
b_1 = b_2 = cell width used
c_H = concentration of $Cr(H_2O)_6^{+3}$
c_P = concentration of $Cr(H_2O)_5Cl^{+2}$

To avoid extremely erroneous values, a retaining sub-program was added. After the 45 concentration values are averaged, the sub-program is activated. Values greater than the average by an arbitrarily chosen retaining percentage are expelled. The final concentration value is then cal-

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culated from this new set of data.

To ensure the reliability of each of these methods, their concentrations must be compared. Since the peaks of the spectra relay the most accurate data, we chose these as our data points. For example, from spectra #82 we can calculate the concentration of each species as follows:

PENTA COMPLEX:

First Peak -

a = 17.8 liter $mol^{-1}cm^{-1}$
A = 0.897
b = 0.1cm

c = A/ab = 0.897/ 17.8liter/$mol^{-1}cm^{-1}$)(0.1cm)
= 0.5039 mol/liter

Second Peak -

a = 21.6 liter $mol^{-1}cm^{-1}$
A = 1.040
b = 0.1cm

c = A/ab = 1.040/(21.6 liter/$mol^{-1}cm^{-1}$)(0.1cm)
= 0.4815 mol/liter

average = 0.4927 mol/liter

Computed value for concentration of $Cr(H_2O)_5Cl^{+2}$ = 0.6207 mol/liter

Percent difference = 0.6207-0.4927/0.4927 x 100 = 25.9 percent

HEXA COMPLEX:

First Peak -

a = 13.9 liter $mol^{-1}cm^{-1}$
A = 0.597
b = 0.1cm

c = A/ab = 0.597/(13.9 liter $mol^{-1}cm^{-1}$)(0.1cm)
= 0.4295 mol/liter

Second Peak -

$a = 16.1$ liter mol^{-1}cm^{-1}
$A = 0.706$
$b = 0.1$cm

$c = A/ab = 0.706/(16.1$ liter mol^{-1}cm$^{-1})(0.1$cm$)$
$= 0.4385$ mol/liter

Average = 0.4340 mol/liter

Computed value for concentration of $Cr(H_2O)_6^{+3}$ = 0.3363 mol/liter

Percent difference = .4340-0.3363/.4340 x 100 = 22.5 percent

RESULTS AND DISCUSSION

Results obtained from the computer and curve resolver are shown in tables 2 and 3. In table 2, two sets of data are given at different retaining values for each spectrum. The differences in concentrations appear to be minimal with the exception of spectra #43. In other cases, the number of equations used in the computation of concentrations remain constant regardless of the retaining value. Spectra 36 and 86 illustrate this behavior. This problem could very well be caused by low concentrations of $Cr(H_2O)_6^{+3}$ On the other hand, the curve resolver appears to have given more accurate data. Curve resolve data used in a similar study of chromium (III) complexes agrees with the accepted values ("Spectrophotometric Analysis of Aqueous Mixtures of Some Chromium (III) Complexes", Greg Stevens, May, 1983).

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CONCLUSION

Table 4 compares the concentrations of the two methods. The discrepancy between these concentrations could have resulted from several factions. First of all, the temperature equilibrium data itself appears to be unreliable. Secondly, the computer analysis is inconsistant in its treatment of the data. The program may be unable to handle low concentrations of either species. Also, the selection of analytical wavelengths may have been poor. Consequently, it is desirable to chose wavelengths where one component absorbs strongly and the other weakly, or vice versa (2). The sharp slopeof the curve analyzed could have also caused some discrepancy by giving inaccurate absorbance and wavelength readings. The curve resolver could have also added to this error. Since there are three variables for each of the four component curves, the probability that one can fit each curve perfectly remains quite low. As a result, we find that the computer analysis is not applicable to the data available.

FIGURE. 1- PRINCIPLE OF OPERATION OF NASA-REDOX CONCEPT

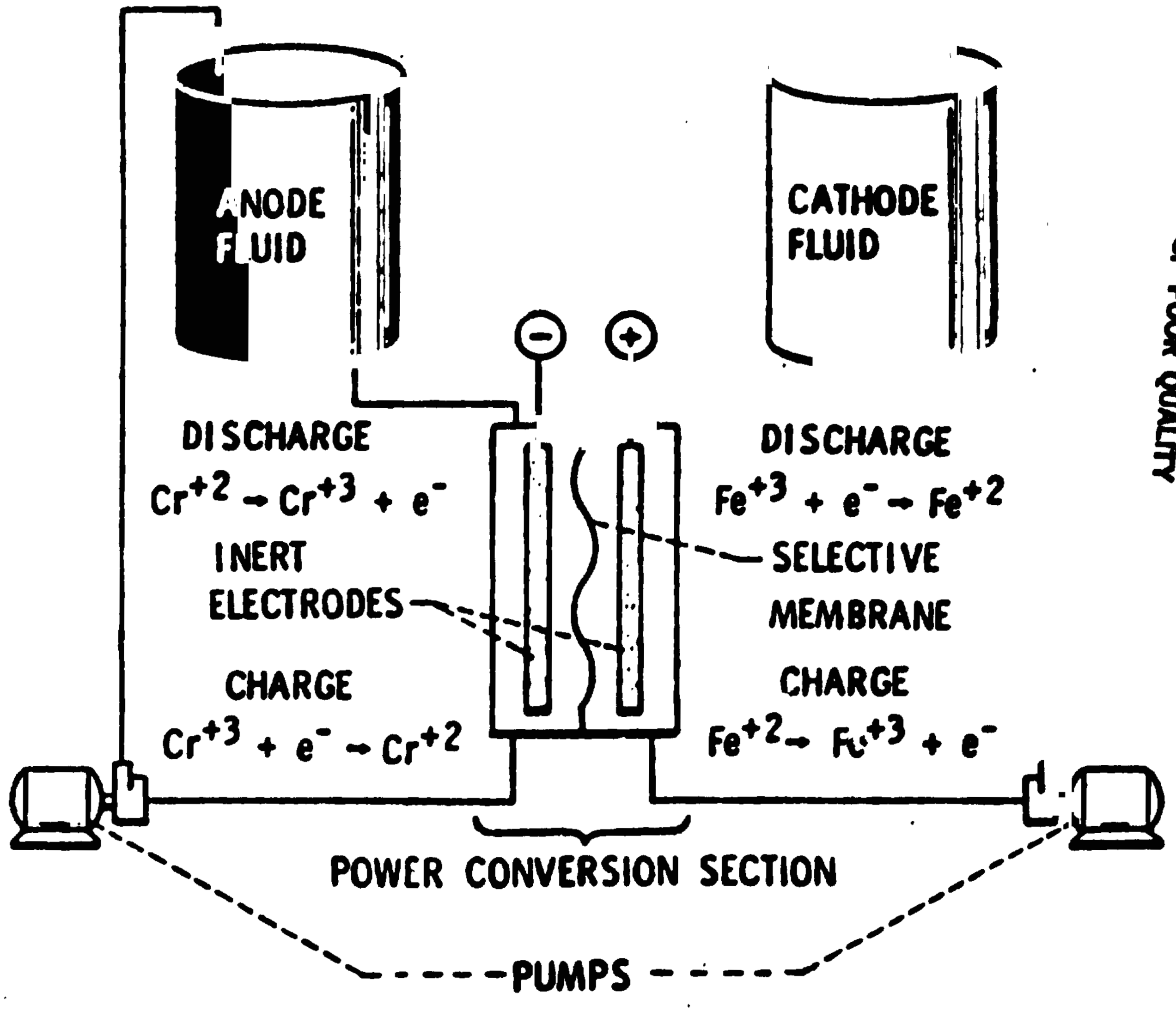


FIGURE. 2- OPEN-CIRCUIT VOLTAGE HYSTERESIS OF IRON/CHROMIUM REDOX CELL

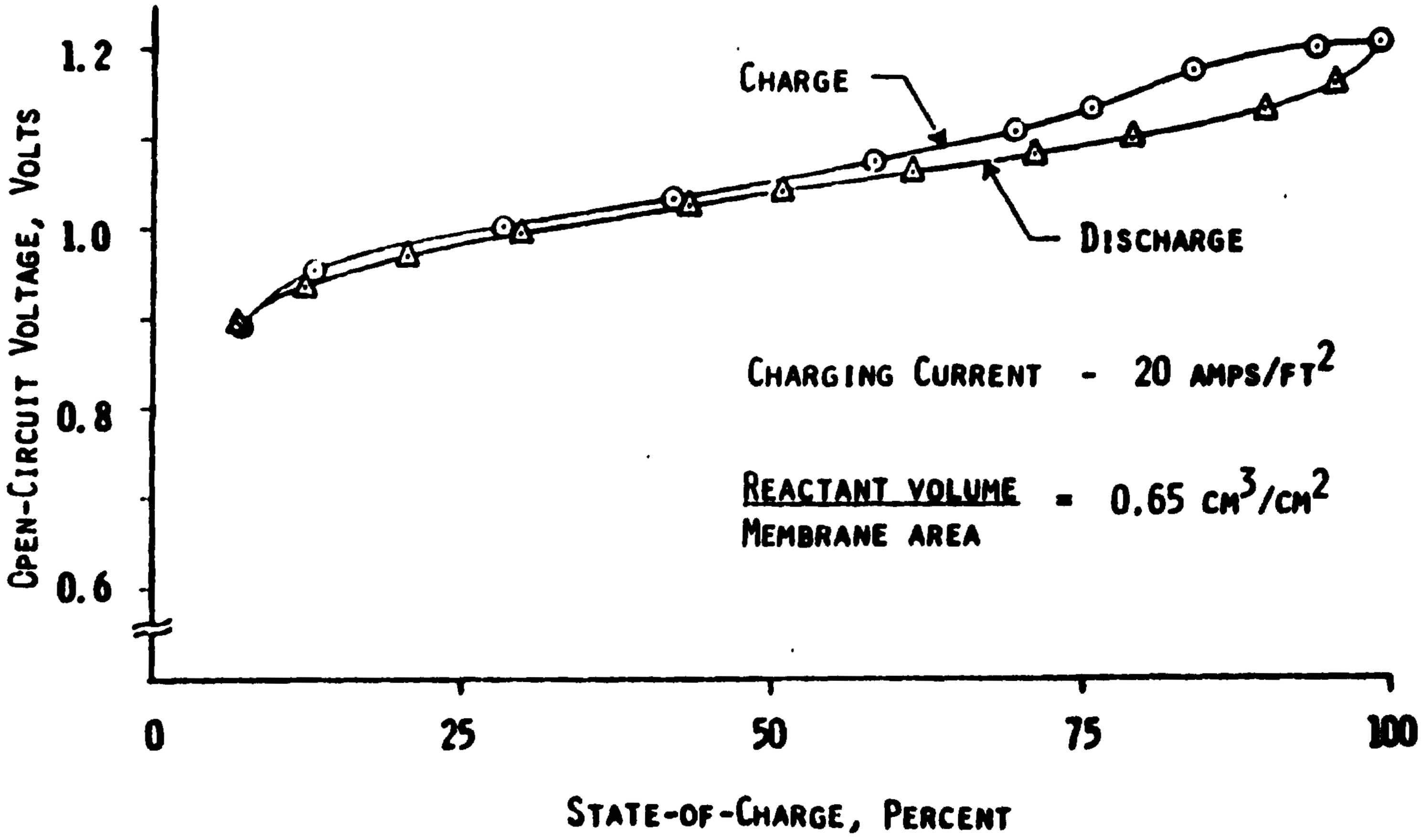
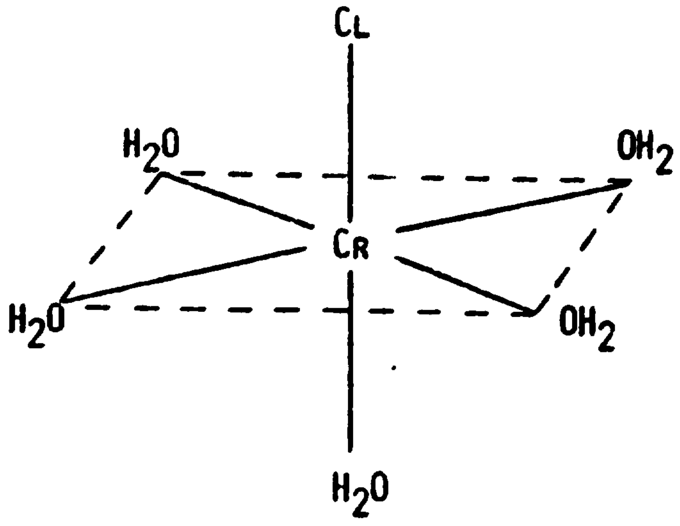
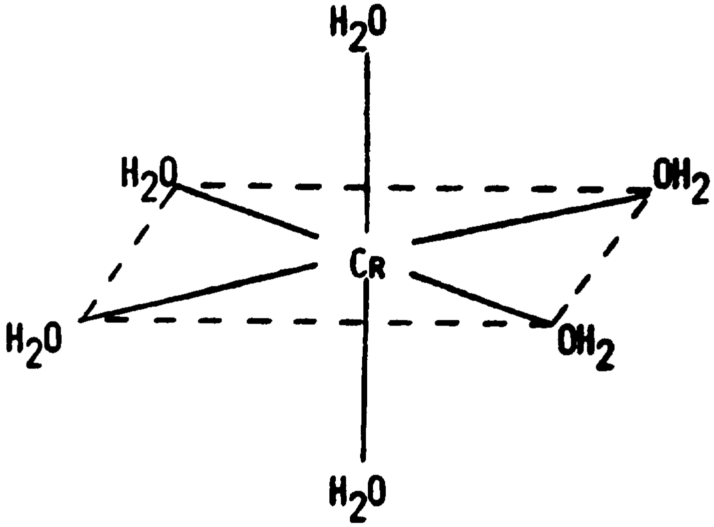


FIGURE. 3- CR(III) COMPLEX IONS



$Cr(H_2O)_5Cl^{+2}$



$Cr(H_2O)_6^{+3}$

FIGURE. 4- SPECTRUM OF CHROMIUM REDOX SOLUTION

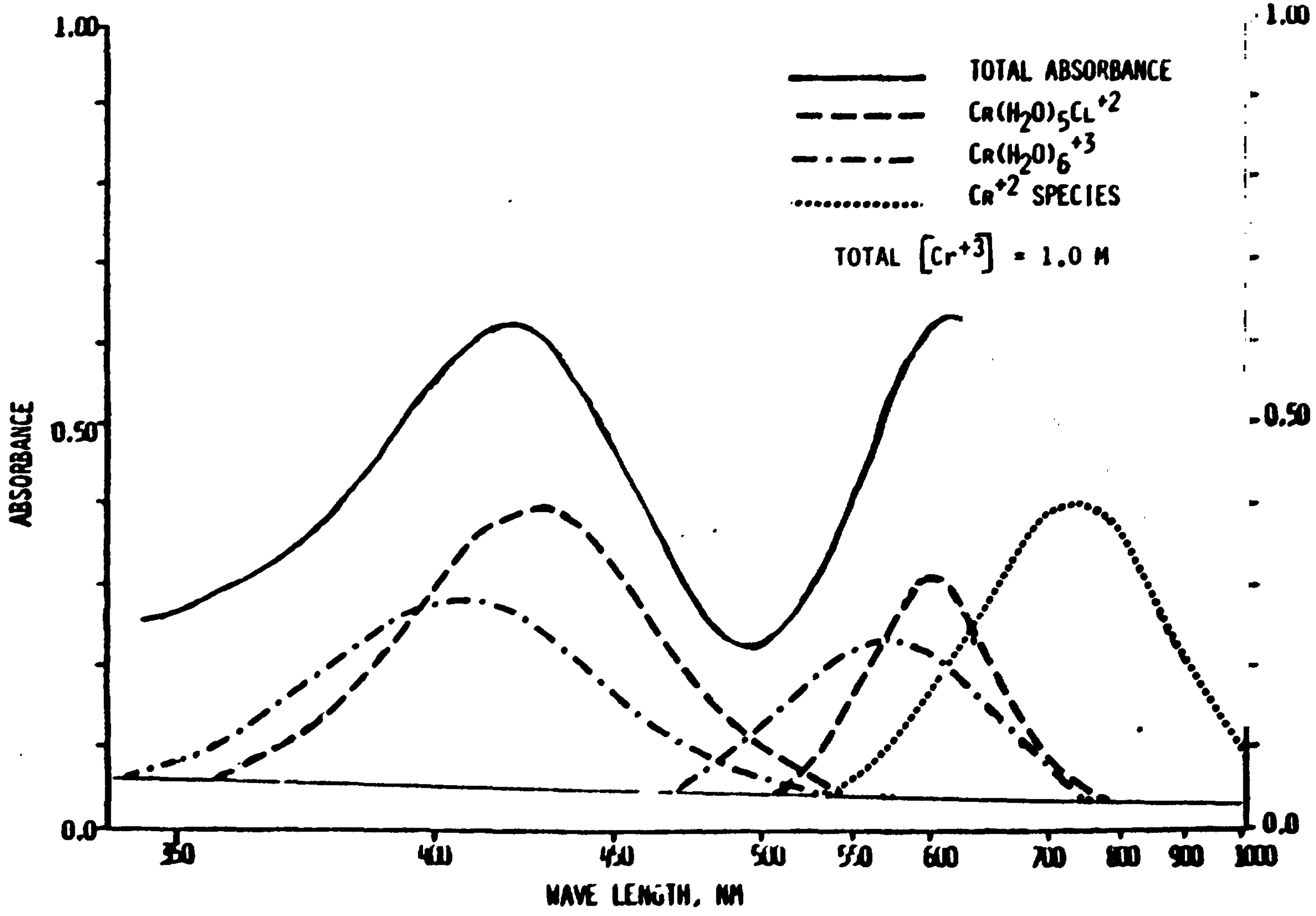


FIGURE. 5- POTENTIOMETRIC STUDIES

TEST OF NERNST EQUATION IN CHROMIUM
REDOX SOLUTIONS

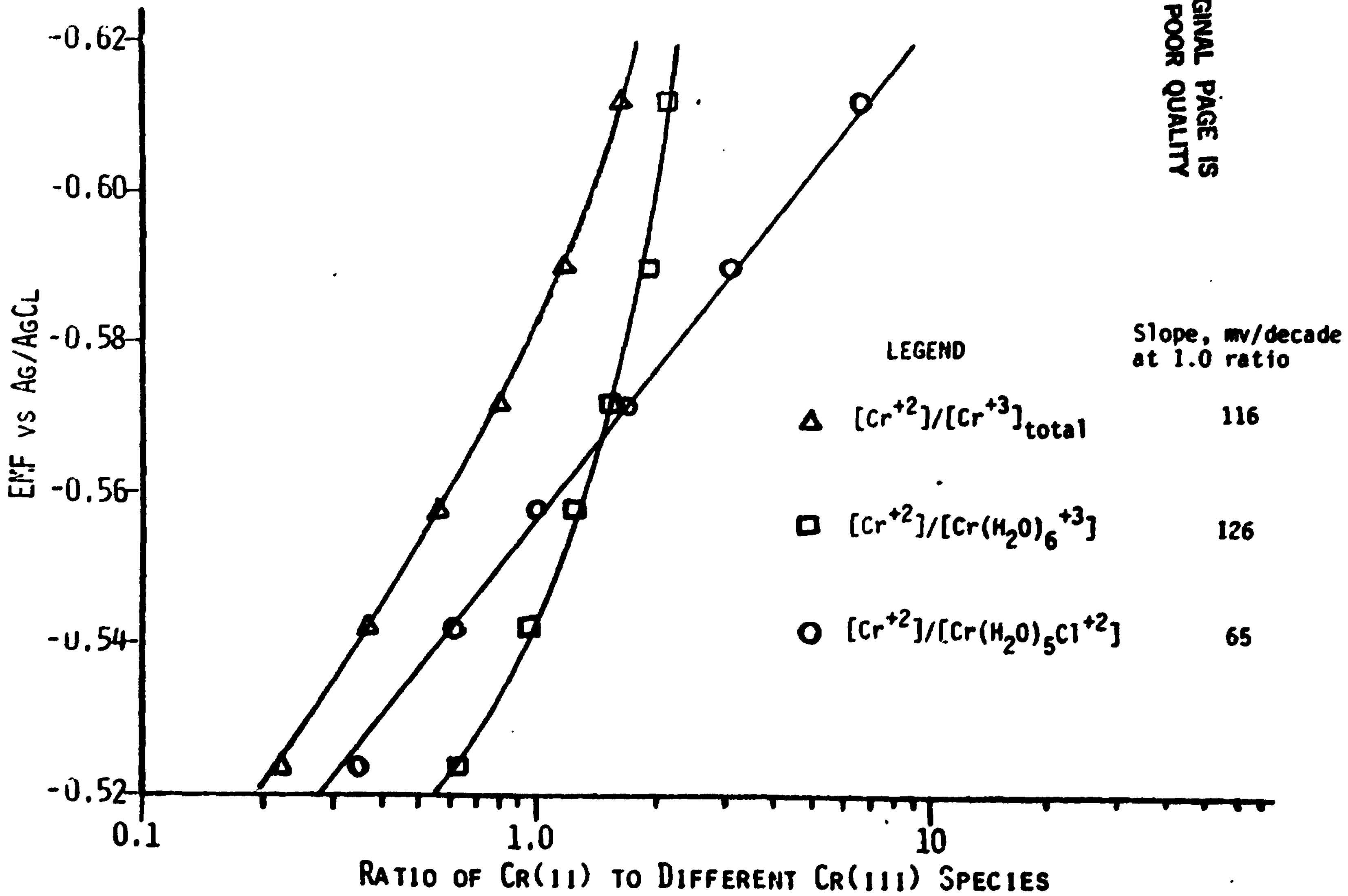
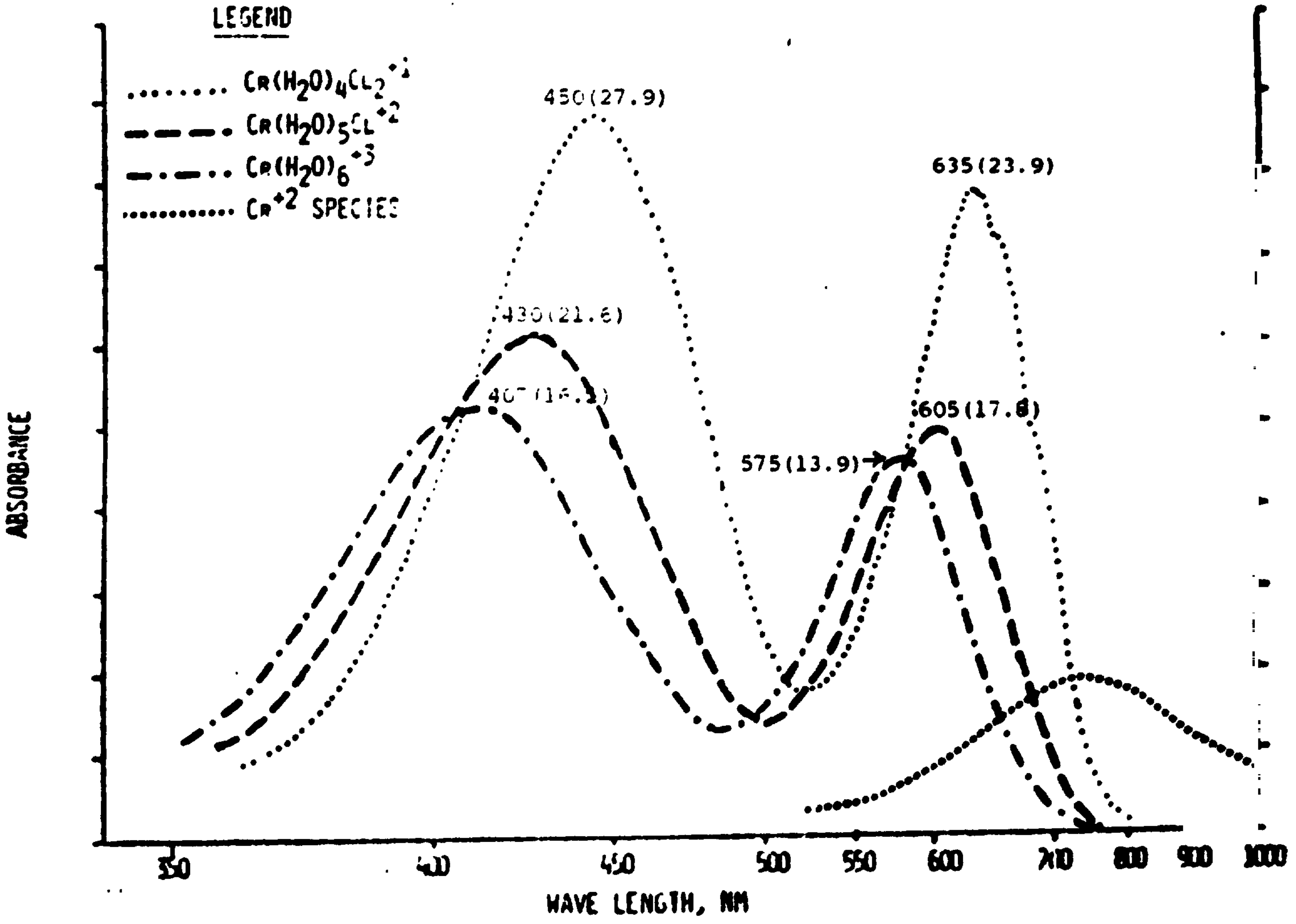


FIGURE. 6- SPECTRA OF CHROMIUM COMPLEX IONS



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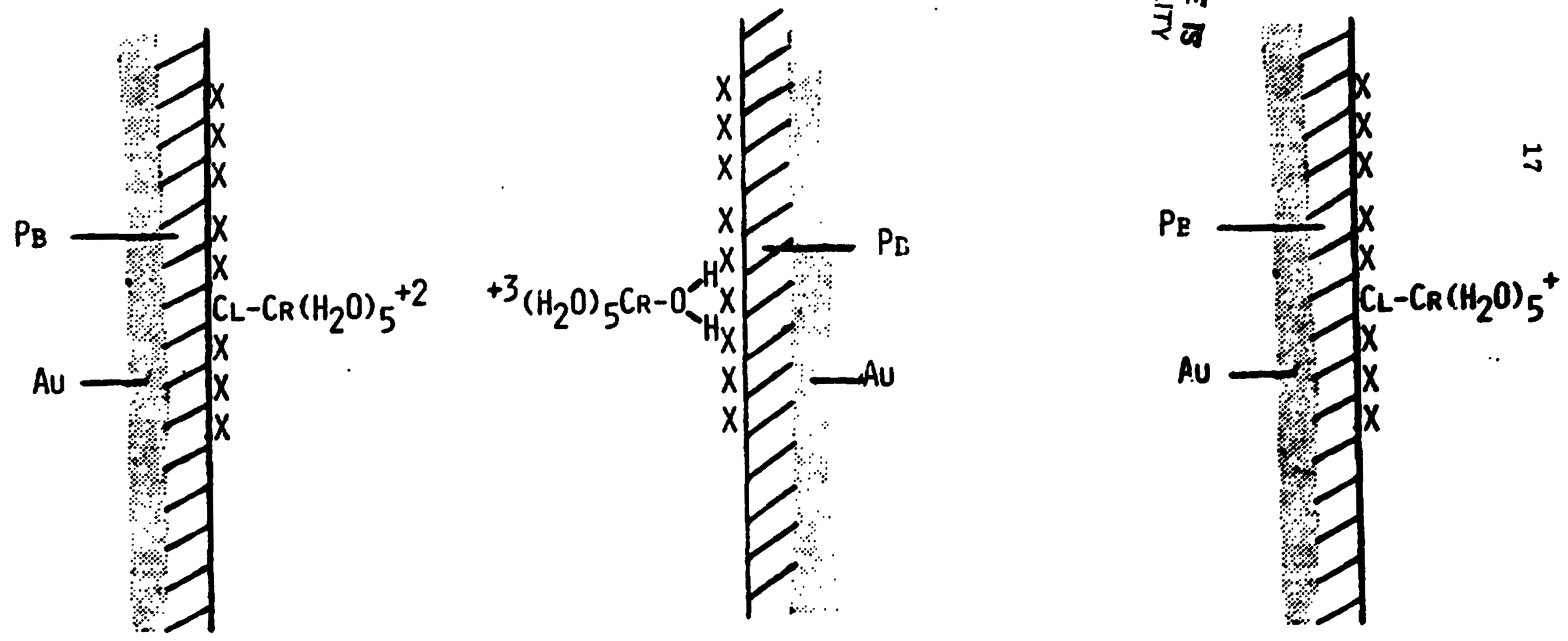

FIGURE. 7- ELECTRODE REACTION MECHANISMS

TABLE. 1-

```
5 CLS
10 REM    PROGRAM TO DETERMINE CONCENTRATIONS OF 2 COMPONENTS
20 REM    IN MIXTURE FROM UV-VIS SPECTROSCOPY DATA
21 REM
22 REM     BY   GREG STEVENS    3/83
23 REM
25 FOR I=20 TO 6 STEP -1:SET(0,I):NEXT
26 FOR I=0 TO 127:SET(I,6):NEXT
27 FOR I=6 TO 20:SET(127,I):NEXT
28 FOR I=127 TO 0 STEP -1:SET(I,20):NEXT
40 PRINT@197,"DETERMINATION OF CONCENTRATIONS OF TWO SPECIES IN";
50 PRINT@330,"SOLUTION USING UV-VIS SPECTROSCOPY DATA";
60 FOR T=1 TO 2000:NEXT
70 PRINT@914,"HIT ANY KEY TO CONTINUE"
80 Z$=INKEY$:IF Z$="" THEN 80 ELSE 90
90 CLS
100 LPRINT"*************************************************"
110 LPRINT" "
120 LPRINT"  DETERMINATION OF CONCENTRATIONS OF TWO SPECIES"
130 LPRINT"     IN SOLUTION USING UV-VIS SPECTROSCOPY DATA"
140 LPRINT" "
150 LPRINT"*************************************************"
160 LPRINT" ":LPRINT" "
165 GOTO 3000
170 REM     INPUT DATA
175 CLS
180 PRINT"ENTER THE NUMBER OF WAVELENGTHS FROM WHICH"
190 PRINT"DATA IS TAKEN"
200 INPUT L
210 IF L<2 THEN 220 ELSE 235
220 PRINT"YOU MUST ENTER AT LEAST 2 WAVELENGTHS."
230 GOTO 180
235 CLS
240 GOSUB [illegible]
245 CLS
250 PRINT
260 [illegible]
270 FOR I=1 TO L
280 PRINT"ENTER WAVELENGTH ";I
290 INPUT W(I)
300 PRINT""
310 PRINT"ENTER ABSORBANCE AT WAVELENGTH";W(I)
320 INPUT A(I)
330 PRINT""
340 PRINT"ENTER MOLAR ABSORPTIVITY OF FIRST"
350 PRINT"COMPONENT AT WAVELENGTH";W(I)
360 INPUT M(I,1)
370 PRINT""
380 PRINT"ENTER MOLAR ABSORPTIVITY OF SECOND"
390 PRINT"COMPONENT AT WAVELENGTH";W(I)
400 INPUT M(I,2)
410 PRINT""
420 PRINT"ENTER THE CELL WITH USED (IN CM)"
430 INPUT B(I)
440 CLS
445 PRINT"PLEASE WAIT"
450 NEXT I
460 REM      PRINTED OUTPUT OF DATA
470 LPRINT"WAVELENGTH","ABSORBANCE","MOLAR ABSORPTIVITY 1,2",
480 LPRINT"CELL WIDTH"
490 LPRINT" "
500 F$="#.###"
510 G$="##.##"
520 H$="#.#"
530 FOR I=1 TO L
540 LPRINT TAB(4) W(I);
550 LPRINT TAB(18);:LPRINT USING F$;A(I);
560 LPRINT TAB(33);:LPRINT USING G$;M(I,1);
570 LPRINT TAB(48);:LPRINT USING G$;M(I,2);
575 LPRINT" ";
580 LPRINT USING H$;B(I)
590 NEXT I
595 REM     COMPUTATIONS
600 N=0
610 S(1)=0
620 S(2)=0
630 [illegible]
640 FOR I=1 TO L
650 FOR J=1 TO 2
```

TABLE 1-(con't)

```
660 C(I,J,1)=A(I)*M [illegible]
670 C(I,J,2)= [illegible]
680 E(1)=E(1)+C(I,J,1)
690 E(2)=E(2)+C(I,J,2)
700 N=N+1
710 NEXT J
720 K=K+1
730 IF K=(D+1) THEN 750
740 NEXT I
750 X=E(1)/N
760 Y=E(2)/N
770 X=INT(X*10000+.5)/10000
780 Y=INT(Y*10000+.5)/10000
785 GOSUB 2000
790 REM      PRINT OUTPUT CONCENTRATIONS
800 LPRINT" ":LPRINT" "
810 LPRINT"THE CONCENTRATION OF THE FIRST SPECIES IS";X;"MOLAR"
820 LPRINT" "
830 LPRINT"THE CONCENTRATION OF THE SECOND SPECIES IS";Y;"MOLAR"
835 LPRINT" ":LPRINT" "
840 LPRINT"FIRST SPECIES STANDARD DEVIATION IS ";:LPRINT USING F$;F(1)
850 LPRINT"SECOND SPECIES STANDARD DEVIATION IS ";:LPRINT USING F$;F(2)
855 LPRINT" "
860 LPRINT"FIRST SPECIES RELATIVE AVERAGE DEVIATION IS ";:LPRINT USING G$;G(1);:LPRINT"%"
870 LPRINT"SECOND SPECIES RELATIVE AVERAGE DEVIATION IS ";:LPRINT USING G$;G(2);:LPRINT"%"
890 REM  PRINT OUT COMPUTED CONCENTRATIONS AND THEIR
891 REM  STANDARD DEVIATION AND RELATIVE AVERAGE DEVIATION
900 LPRINT" ":LPRINT" "
905 LPRINT" ","DATA":LPRINT" "
910 LPRINT"CONCENTRATION #1","CONCENTRATION #2"
915 LPRINT" "
1010 K=1
1020 FOR I=1 TO I
1030 FOR J=1 TO I
1040 LPRINT C(I,J,1),[illegible]C(I,J,2)
1050 N3=N3+1
1100 SD(1,1)=(C(I,J,1)-X)^2
1110 SD(2,1)=SD(1,1)+SD(2,1)
1120 RAD(1,1)=ABS(C(I,J,1)-X)
1130 RAD(2,1)=RAD(1,1)+RAD(2,1)
1140 SD(1,2)=(C(I,J,2)-Y)^2
1150 SD(2,2)=SD(1,2)+SD(2,2)
1160 RAD(1,2)=ABS(C(I,J,2)-Y)
1170 RAD(2,2)=RAD(1,2)+RAD(2,2)
1200 NEXT J
1210 K=K+1
1220 IF K=(D+1) THEN 1245
1230 NEXT I
1240 LPRINT" ":LPRINT"THERE WERE";N3;"TOTAL PAIRS OF CONCENTRATION C[illegible]
1245 N2=N
1252 IF N<2 THEN N=2
1255 IF N>2 THEN N=2
1256 X2=X:Y2=Y
1257 IF X=0 OR Y=0 THEN X=1:Y=1
1260 F(1)=(SD(2,1)/(N-1))^.5
1270 G(1)=(RAD(2,1)/((N-1)*X))*100
1280 F(2)=(SD(2,2)/(N-1))^.5
1290 G(2)=(RAD(2,2)/((N-1)*Y))*100
1292 N=N2
1293 X=X2:Y=Y2
1295 LPRINT" ":LPRINT" "
1300 LPRINT"THERE WERE";N;"SIMULTANEOUS EQUATIONS USED FOR THE CONCENTRATION DETERMINAT[illegible]
1310 LPRINT" "
1320 LPRINT"TOTAL STANDARD DEVIATION FOR FIRST SPECIES IS ";:LPRINT USING F$;F(1)
1330 LPRINT"TOTAL STANDARD DEVIATION FOR SECOND SPECIES IS ";:LPRINT USING F$;F(2)
1340 LPRINT" "
1350 LPRINT"TOTAL RELATIVE AVERAGE DEVIATION FOR FIRST SPECIES IS ";:LPRINT USING G$;G(1);:LPRINT"%"
1360 LPRINT"TOTAL RELATIVE AVERAGE DEVIATION FOR SECOND SPECIES IS ";:LPRINT USING G$;G(2);:LPRINT"%"
1400 INPUT"DO YOU WANT TO RUN THE PROGRAM AGAIN (YES OR NO)";Z$
1410 IF Z$="YES" THEN LPRINT CHR$(12):GOTO5
1415 CLS
1420 FOR I=46TO68:SET(I,10):NEXT
1430 FOR I=10TO15:SET(68,I):NEXT
1440 FOR I=68TO46 STEP -1:SET(I,15):NEXT
1450 FOR I=15TO10 STEP -1:SET(46,I):NEXT I
1460 IF Z$="NO" PRINT@280,"THANK YOU": ELSE PRINT@280,"TRY AGAIN"
1470 PRINT@800," "
1480 FOR I=1TO3000:NEXT
1490 IFZ$="NO" THEN 9000 ELSE 1400
```

TABLE. 1-(con't)

```
2000 REM   LINES 2000-2190 ELIMINATE ERRONEOUS CONCENTRATION VALUES
2005 L=0
2010 K=0:N=0:S1=0:S2=0
2020 FOR I=1 TO E
2030 FOR J=1 TO E
2040 IF ABS(C(I,J,1)-X)>(.25*X) OR ABS(C(I,J,2)-Y)>(.25*Y) THEN 2080
2045 N=N+1
2050 S1=S1+C(I,J,1)
2060 S2=S2+C(I,J,2)
2070 IF L=9 THEN GOSUB 4000
2080 NEXT J
2090 K=K+1
2100 IF K=(D+1) THEN 2115
2110 NEXT I
2112 N2=N
2115 IF N=0 THEN N=1
2120 X=S1/N
2130 Y=S2/N
2135 N=N2
2140 X=INT(X*10000+.5)/10000
2150 Y=INT(Y*10000+.5)/10000
2160 L=L+1
2170 IF L=10 THEN 2190
2180 GOTO 2010
2190 RETURN
3000 REM     INPUT TITLE
3005 CLEAR 64
3010 INPUT "ENTER THE TITLE:  ";T$
3020 LPRINT T$
3030 LPRINT" ":LPRINT" "
3040 GOTO 170
4000 REM     COMPUTE SD AND RAD FOR REMAINING VALUES
4020 SD(1,1)=(C(I,J,1)-X)↑2
4030 SD(2,1)=SD(1,1)+SD(2,1)
4040 RAD(1,1)=ABS(C(I,J,1)-X)
4050 RAD(2,1)=RAD(1,1)+RAD(2,1)
4060 SD(1,2)=(C(I,J,2)-Y)↑2
4070 SD(2,2)=SD(1,2)+SD(2,2)
4080 RAD(1,2)=ABS(C(I,J,2)-Y)
4090 RAD(2,2)=RAD(1,2)+RAD(2,2)
4095 N2=N
4100 IF N<2 THEN N=2
4105 IF X=0 OR Y=0 THEN X=1:Y=1
4110 F(1)=(SD(2,1)/(N-1))↑.5
4120 G(1)=(RAD(2,1)/((N-1)*X))*100
4130 F(2)=(SD(2,2)/(N-1))↑.5
4140 G(2)=(RAD(2,2)/((N-1)*Y))*100
4150 N=N2
4190 RETURN
6000 PRINT"DO YOU WISH TO USE THE SPECIFIED WAVELENGTHS FOR"
6010 PRINT"CHROMIUM ANALYSIS--652,629,592,556,532,460,442,415,"
6020 INPUT"388, AND 370";K$
6030 IF K$="YES" THEN 6040 ELSE RETURN
6040 CLS
6050 FOR I=1TO10
6070 READ W(I),M(I,1),M(I,2),B(I)
6080 PRINT"ENTER ABSORBANCE AT WAVELENGTH";W(I)
6085 INPUT A(I)
6110 NEXTI
6115 PRINT"PLEASE WAIT"
6120 GOTO460
8900 DATA 652,11.15,3.76,.1,629,15.25,7.3,.1,592,15.56,2.02,.1
8901 DATA 556,6.93,12.81,.1,532,5.04,5.95,.1,460,13.21,6.25,.1
8902 DATA 442,15.91,10.56,.1,415,19.62,16.93,.1,388,7.78,16.16
8903 DATA .1,370,2.58,11.93,.1
9000 END
```

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Table 2.- Computer Output for Spectra Obtained From Equilibrium Temperature Study

Spectra #	Number of equations used	Retaining value	C_P(mol/l)	C_H(mol/l)	SD_P	SD_H	RAD_P(%)	RAD_H(%)
88	17	0.25	0.6135	0.3377	0.050	0.029	6.64	7.31
88	25	0.50	0.6389	0.3274	0.082	0.073	9.32	16.17
36	2	0.25	0.8103	0.0761	0.018	0.015	3.07	27.66
36	5	0.75	0.8190	0.0667	0.028	0.033	3.20	45.48
52	18	0.25	0.5607	0.3245	0.035	0.039	5.16	11.04
52	34	0.50	0.5606	0.3483	0.088	0.088	11.53	21.67
86	2	0.25	0.7720	0.0699	0.013	0.015	2.31	29.59
86	2	0.75	0.7720	0.0699	0.013	0.015	2.31	29.59
82	18	0.25	0.6207	0.3363	0.048	0.033	6.38	7.77
82	26	0.50	0.6436	0.3262	0.081	0.074	9.19	16.87
43	5	0.25	0.8753	0.0756	0.091	0.006	9.25	7.00
43	38	0.75	0.7668	0.1870	0.072	0.062	6.96	24.21
66	20	0.25	0.5212	0.3602	0.036	0.047	5.93	11.62
66	33	0.50	0.4962	0.4118	0.071	0.101	11.54	21.04
92	18	0.25	0.5275	0.3989	0.047	0.034	6.33	6.88
92	33	0.50	0.5171	0.1213	0.079	0.102	11.87	20.15

C_P = concentration of $Cr(H_2O)_5Cl^{+2}$

C_H = concentration of $Cr(H_2O)_6^{+3}$

SD_P = standard deviation of $Cr(H_2O)_5Cl^{+2}$

SD_H = standard deviation of $Cr(H_2O)_6^{+3}$

RAD_P = relative average deviation of $Cr(H_2O)_5Cl^{+2}$

RAD_H = relative average deviation of $Cr(H_2O)_6^{+3}$

Table 3.- Curve Resolve Data for Spectra Obtained from Equilibrium Temperature Study

Spectra #	C_P(mol/l)	C_H(mol/l)	A_{P1}	A_{P2}	A_{H1}	A_{H2}
88	0.5187	0.3825	0.930	1.112	0.540	0.606
36	0.7052	0.1503	1.258	1.520	0.194	0.259
52	0.2900	0.3710	0.888	1.039	0.522	0.590
86	0.5987	0.5660	1.087	1.267	0.540	0.592
82	0.4927	0.4340	0.897	1.040	0.597	0.706
43	0.7485	0.1136	1.351	1.594	0.150	0.192
66	0.3794	0.4900	0.684	0.809	0.680	0.790
92	0.3921	0.5018	0.688	0.859	0.705	0.799

A_{P1} = absorbance of $Cr(H_2O)_5Cl^{+2}$ at first peak

A_{P2} = absorbance of $Cr(H_2O)_5Cl^{+2}$ at seccnd peak

A_{H1} = absorbance of $Cr(H_2O)_6^{+3}$ at first peak

A_{H2} = absorbance of $Cr(H_2O)_6^{+3}$ at second peak

Table 4.- Comparison of Data Obtained From Computer and Curve Resolver

	Computer		Resolver	
Spectra #	C_p(mol/l)	C_H(mol/l)	C_p(mol/l)	C_H(mol/l)
88	0.6135	0.3377	0.5187	0.3825
36	0.8103	0.0761	0.7052	0.1503
52	0.5606	0.3483	0.4900	0.3710
86	0.7720	0.0699	0.5987	0.5660
82	0.6207	0.3363	0.4927	0.4340
43	0.7668	0.1870	0.7485	0.1136
66	0.4962	0.4118	0.3794	0.4900
92	0.5171	0.4213	0.3921	0.5018

FIGURE. 8- SPECTRA # 82

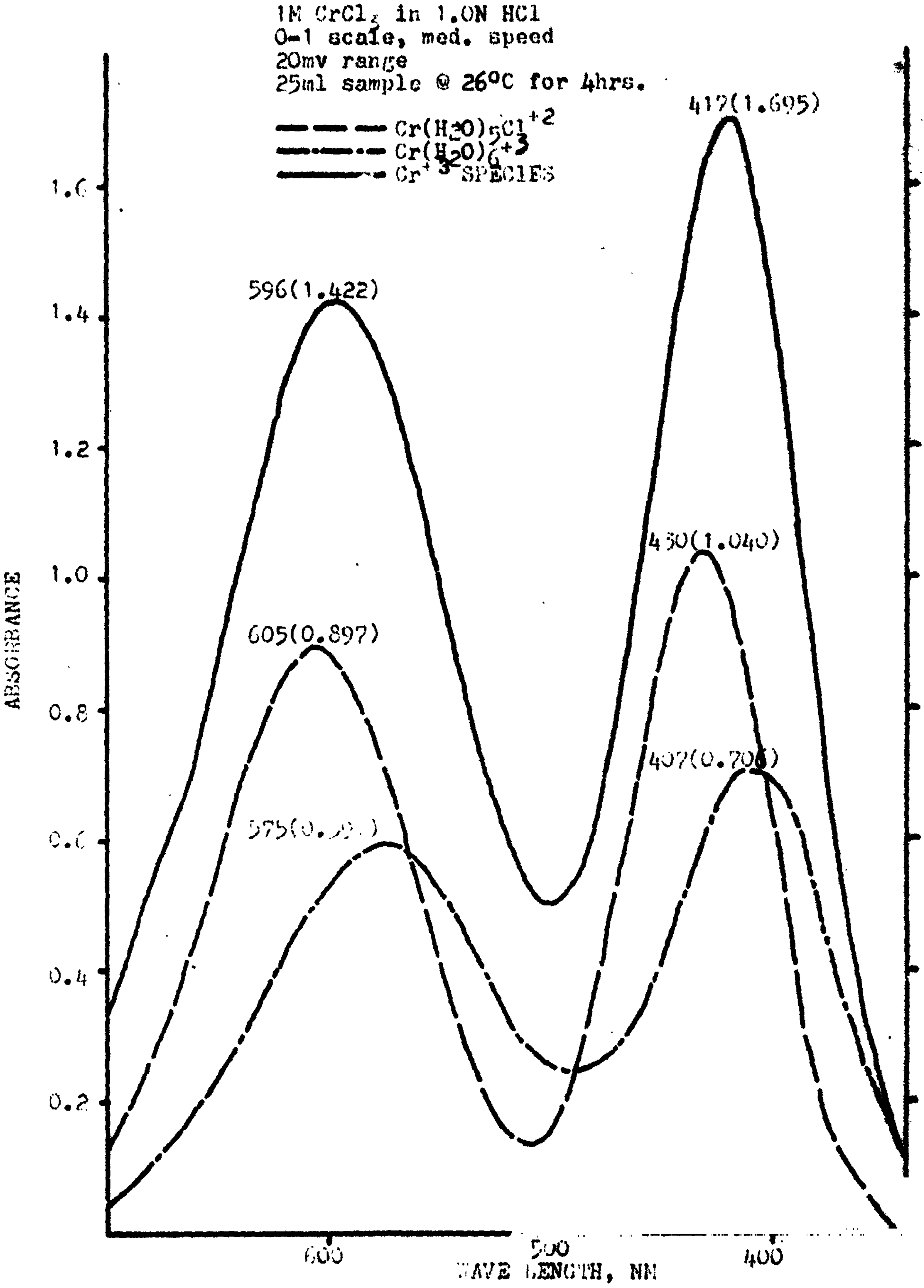
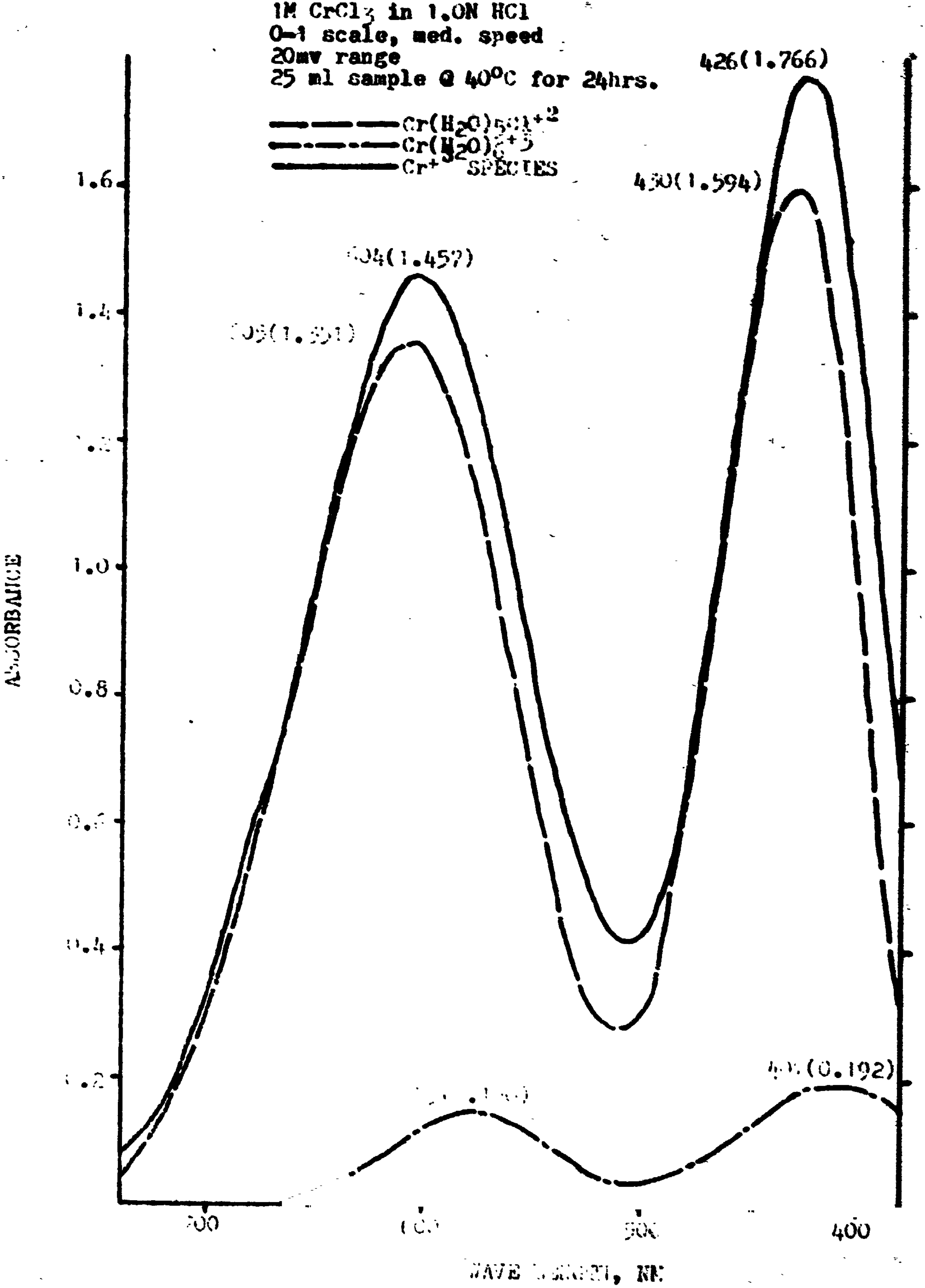


FIGURE. 9- SPECTRA #43



1M $CrCl_3$ in 1.0N HCl
0-1 scale, med. speed
20mv range
25 ml sample @ 40°C for 24hrs.

FIGURE. 10- SPECTRA #66

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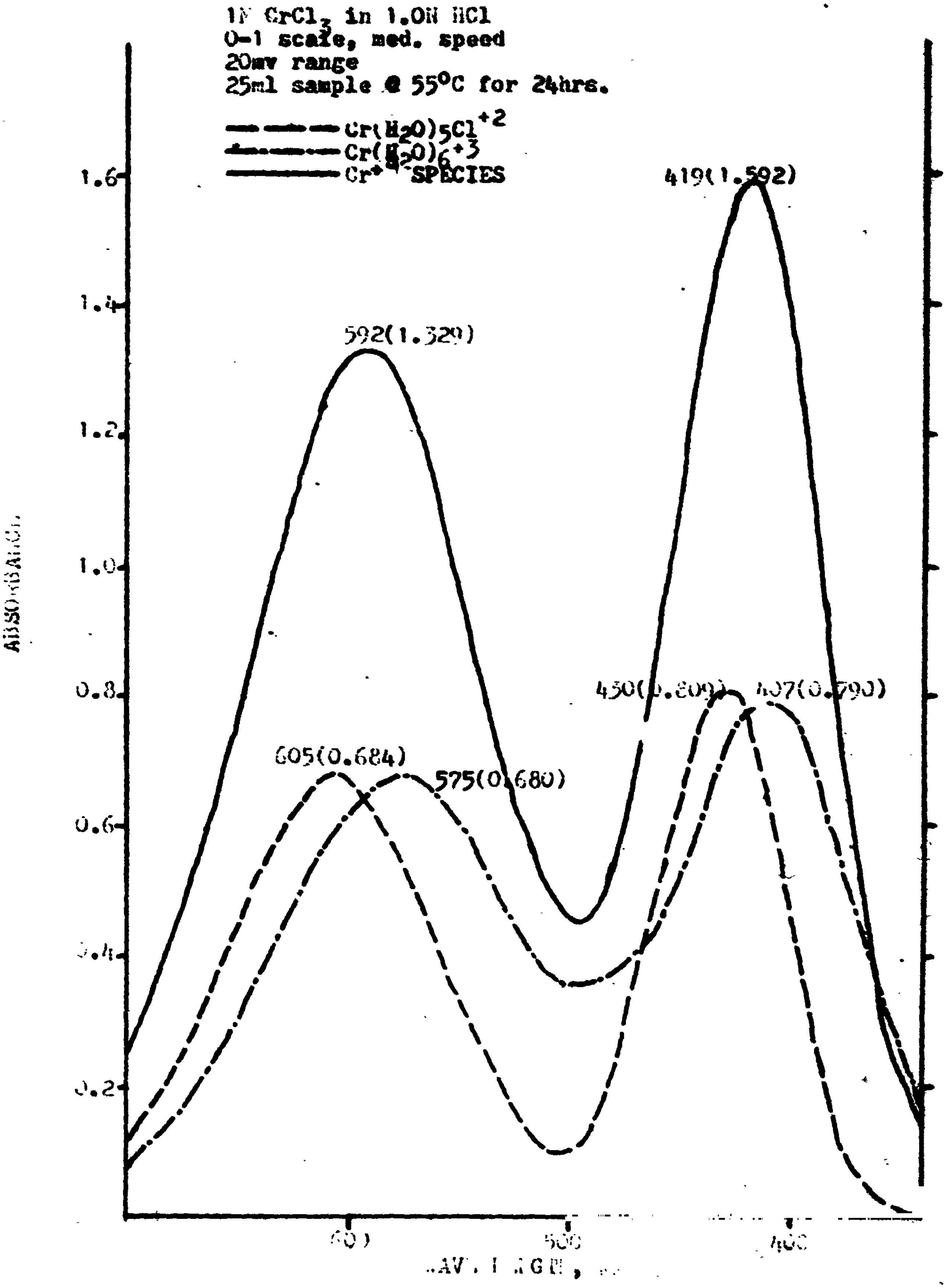


1M $CrCl_3$ in 1.0N HCl
0-1 scale, med. speed
20mv range
25ml sample @ 55°C for 24hrs.

FIGURE 11. - SPECTRA #92

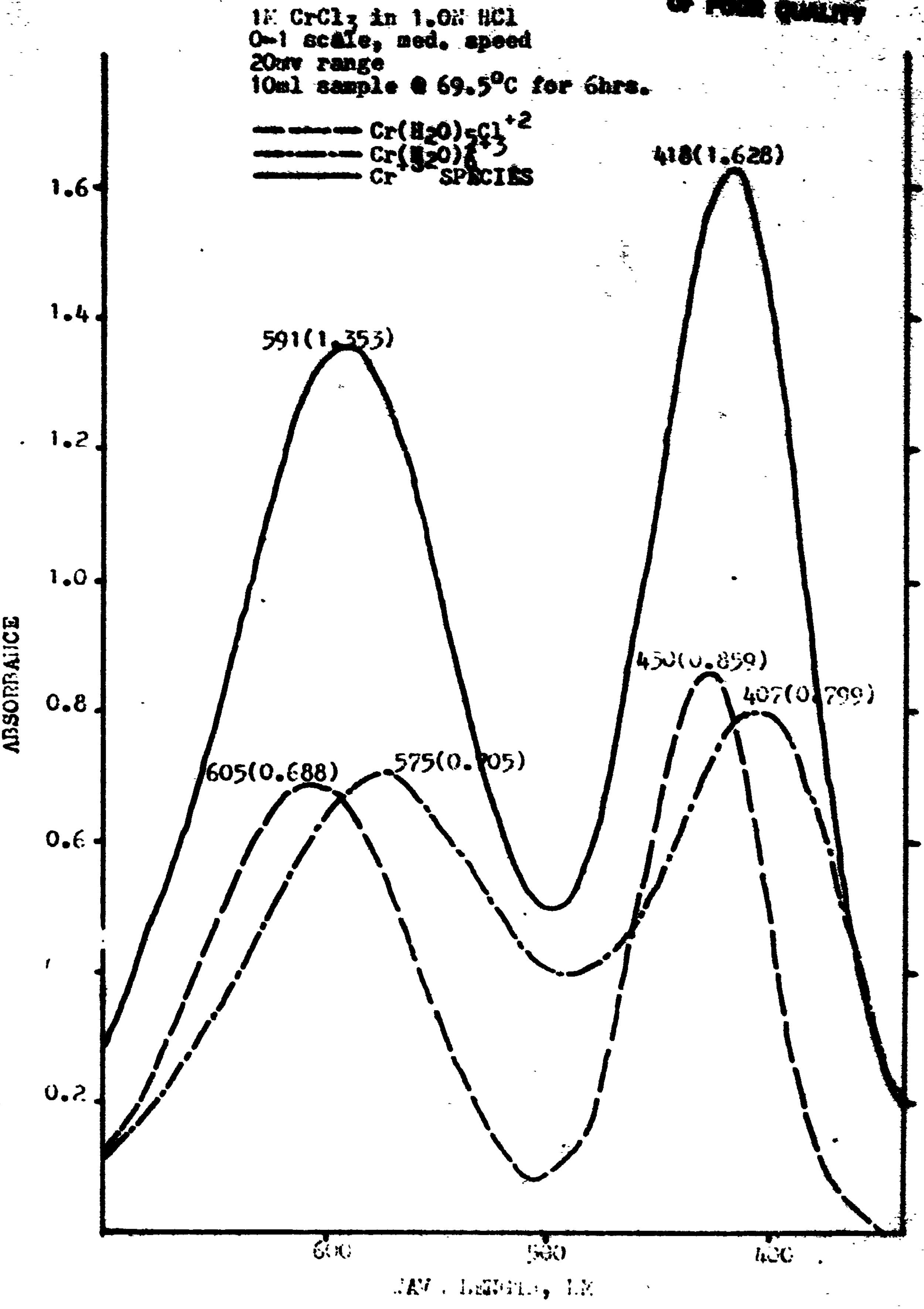


FIGURE. 12- SPECTRA #88

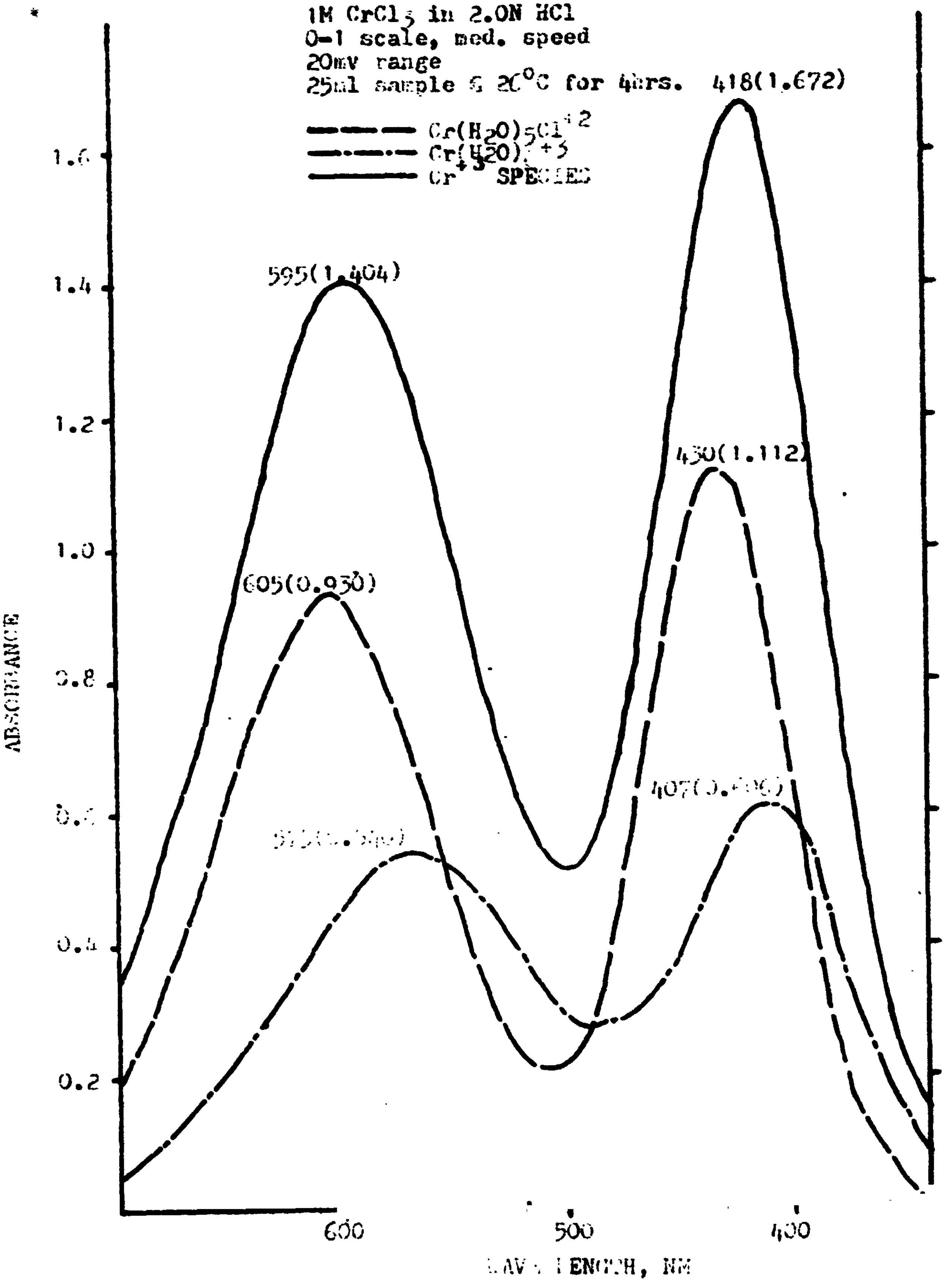


FIGURE. 13- SPECTRA # 36

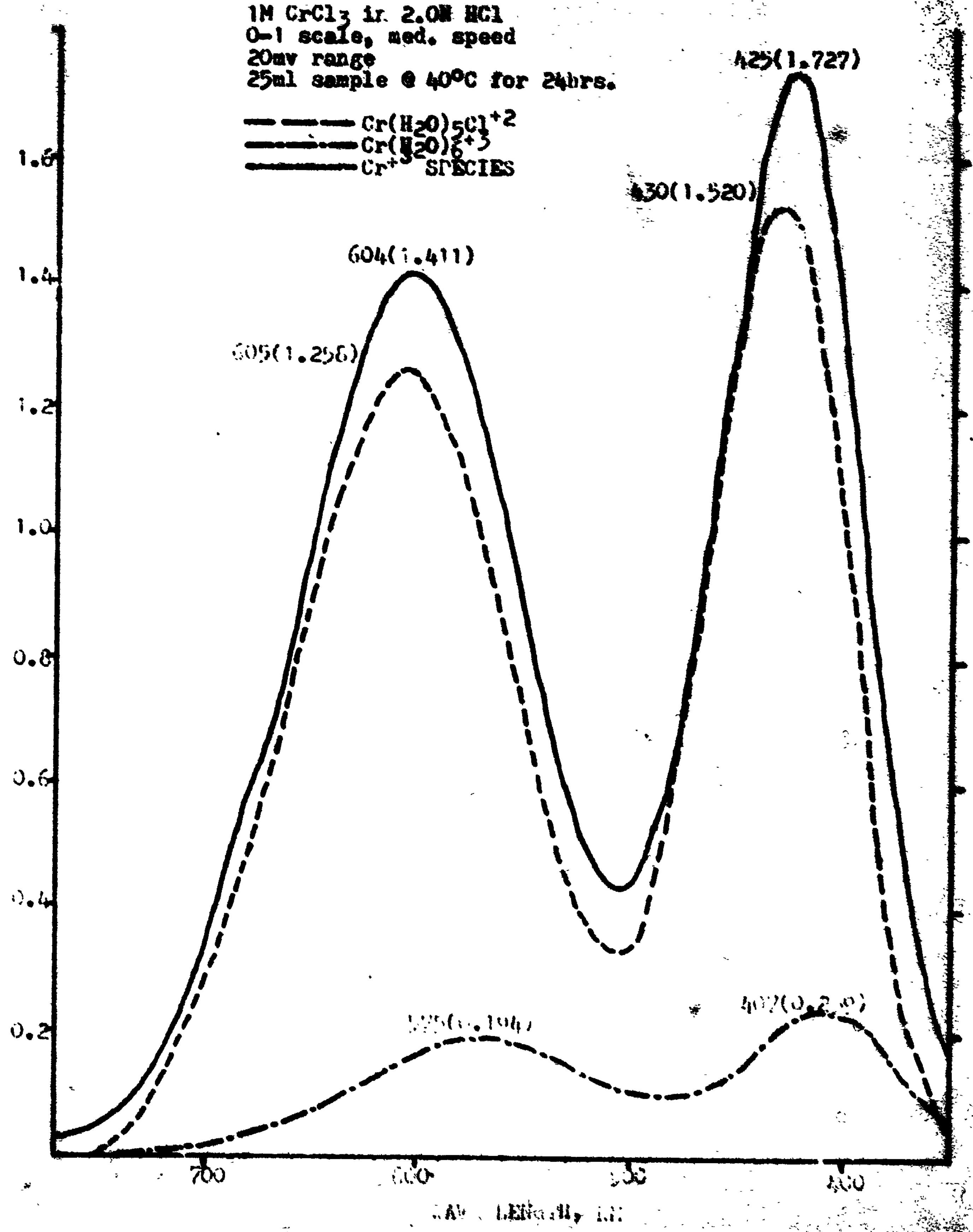
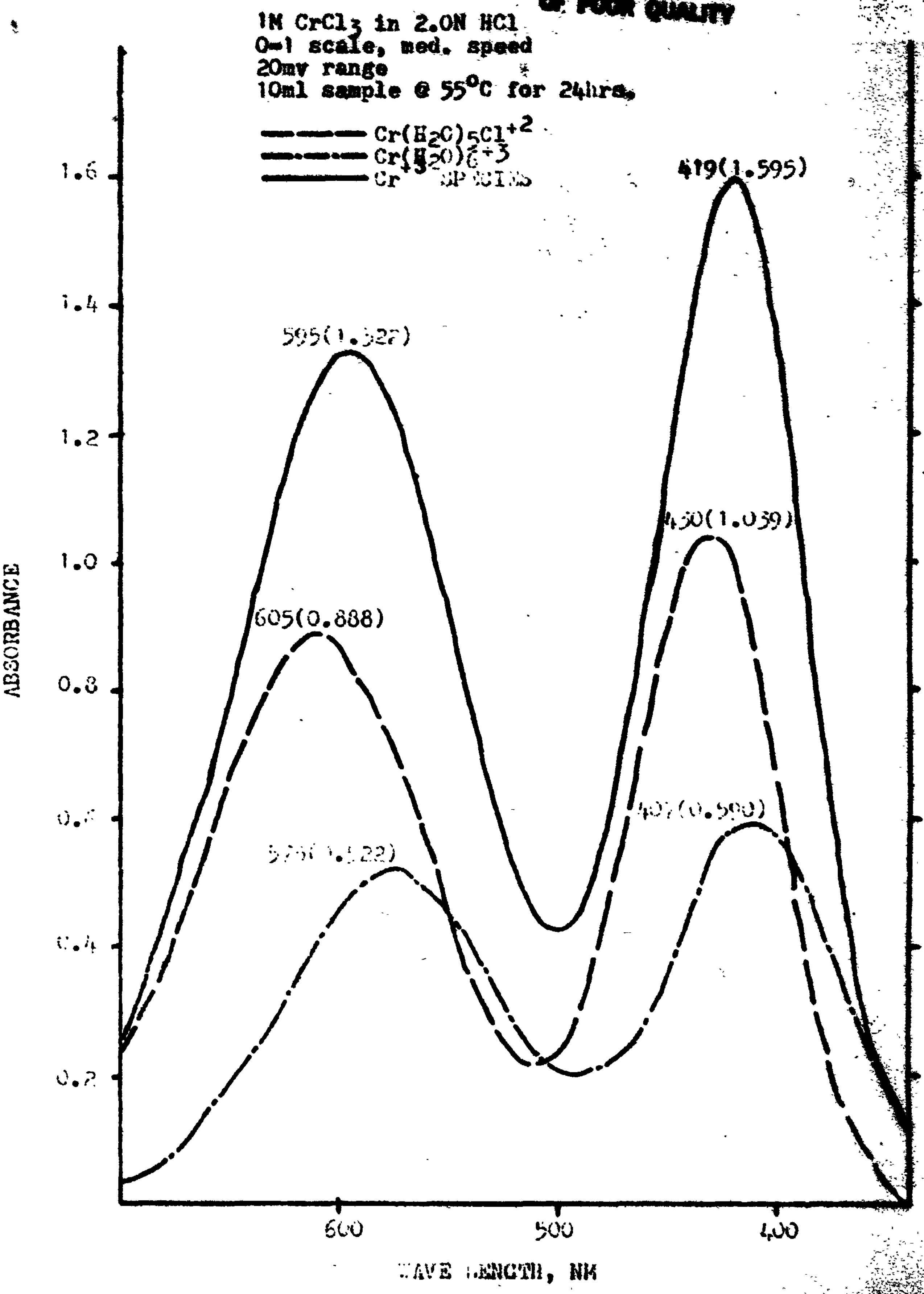


FIGURE. 14- SPECTRA #52



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  DETERMINATION OF CONCENTRATIONS OF TWO SPECIES
    IN SOLUTION USING UV-VIS SPECTROSCOPY DATA

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SPECTRA #52 NASA REDOX TEMP STUDY-RETAINING VALUE=0.10

WAVELENGTH       ABSORBANCE       MOLAR ABSORPTIVITIES               REL. [illegible]

    652            0.775            11.18           7.7[illegible]         2[illegible]
    628            1.099            15.05           7.30           2.1
    591            1.313            15.06          13.06           2.1
    556            1.005             9.[illegible]          12.81           2.1
    531            [illegible]             5.04           8.9[illegible]           2.1
    492            0.942            13.21           6.28           [illegible]
    442            1.237            18.91          10.58           2.1
    418            1.[illegible]            19.62          12.93           2.1
    398            0.990             7.78          16.16           2.1
    378            3.[illegible]             2.58          11.93           2.1

THE CONCENTRATION OF THE FIRST SPECIES IS .5606 MOLAR

THE CONCENTRATION OF THE SECOND SPECIES IS .3483 MOLAR


FIRST SPECIES STANDARD DEVIATION IS 0.088
SECOND SPECIES STANDARD DEVIATION IS 0.085

FIRST SPECIES RELATIVE AVERAGE DEVIATION IS  11.53%
SECOND SPECIES RELATIVE AVERAGE DEVIATION IS 11.[illegible]%


                  DATA

CONCENTRATION #1                      CONCENTRATION #2

 .613678             1 , 2            .119671
 .59791              1 , 3            .259811
 .564326             1 , 4            .389751
 .55455              1 , 5            .424673
 .668222             1 , 6            .111884
 .483662             1 , 7            .0417382
 .623852             1 , 8            .219124
 .586345             1 , 9            .338327
 .601721             1 , 10           .284791
 .57093              2 , 3            .328426
 .528339             2 , 4            .416231
 .512874             2 , 5            .448115
-.130857             2 , 6           1.77535
 .951393             2 , 7           -.311635
 .624881             2 , 8            .219909
 .565024             2 , 9            .243621
 .590965             2   10           .287117
 .455154             3 , 4            .46722
 .43421              3 , 5            .452384
 .536447             3 , 6            .367775
 .426187             3 , 7            .50221
1.7641               3 , 8          -1.10229
 [illegible]              3 , 9            .344[illegible]
 .609581             3 , 10           .283714
 .75[illegible]180               5            .536[illegible]
 .5[illegible]2715               6            .4[illegible]271
 .478185             4   7            .478157
 .341128             4 , 8            .54657
 .757[illegible]15             4   9            .115041
 .768867             4 , 10           .248687
 .495397             5 , 6            .457951
 .430342             5 , 7            .43454
 .344556             5 , 8            .542775
1.52944              5 , 9           -.122708
 .92909              5 , 10           .213994
 .74737              6 , 7           -.0728946
 .590596             6 , 9            .287679
 .547862             6 , 9            .349247
 .574955             6 , 10           .29858
 .511726             7 , 8            .349083
 .49857              7 , 9            .372595
 .548258             7 , 10           .293093
 .486367             8 , 9            .37647
 .557281             8 , 10           .293965
 .745561             9   10           .253684

THERE WERE 34 SIMULTANEOUS EQUATIONS USED FOR THE CONCENTRATION DETERMINATION

TOTAL STANDARD DEVIATION FOR FIRST SPECIES IS 0.240
TOTAL STANDARD DEVIATION FOR SECOND SPECIES IS 0.[illegible]

TOTAL RELATIVE AVERAGE DEVIATION FOR FIRST SPECIES IS 4[illegible]%
TOTAL RELATIVE AVERAGE DEVIATION FOR SECOND SPECIES IS [illegible]
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  DETERMINATION OF CONCENTRATIONS OF TWO SPECIES
    IN SOLUTION [illegible]

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SPECTRA #51 NASA RED [illegible]

[illegible]

      652          0.779          11.15         3.7[illegible]       [illegible]
      626          1.099          15.08         7.[illegible]        0.[illegible]
      591          1.3[illegible]  15.6[illegible] 17.0[illegible]   0.[illegible]
      556          1.005           8.93         1[illegible]         0.[illegible]
      531          0.660          15.0[illegible] 5.94               0.[illegible]
      460          0.941          13.21         6.25                 0.[illegible]
      442          1.337          19.91        10.56                 0.[illegible]
      418          1.595          19.62        16.93                 0.[illegible]
      388          0.990           7.79        16.16                 0.[illegible]
      370          0.495           2.55        11.93                 0.[illegible]

THE CONCENTRATION OF THE FIRST SPECIES IS .5562 MOLAR

THE CONCENTRATION OF THE SECOND SPECIES IS .3537 MOLAR

FIRST SPECIES STANDARD DEVIATION IS 0.119
SECOND SPECIES STANDARD DEVIATION IS 0.105

FIRST SPECIES RELATIVE AVERAGE DEVIATION IS 1[illegible]
SECOND SPECIES RELATIVE AVERAGE DEVIATION IS 2[illegible].79%

                  DATA

CONCENTRATION #1                    CONCENTRATION #2

 .[illegible]          1 . 2          .219675
 .59792                1 . 3          .296263
 .556326               1 . 4          .399751
 .55453                1 . 5          .424673
 .660325               1 . 6          .111004
 .693684               1 . 7          .0417302
 .623965               1 . 8          .219124
 .596365               1 . 9          .330327
 .601721               1 . 10         .284791
 .57093                2 . 3          .329426
 .529339               2 . 4          .416221
 .511974               2 . 5          .445110
-.130997               2 . 6          .[illegible]
 .881393               2 . 7         -.211637
 .624051               2 . 8          .219909
 .565014               2 . 9          .340601
 .599996               2 . 10         .287117
 .455154               3 . 4          .46725
 .43421                3 . 5          .492364
 .538447               3 . 6          .367375
 .426157               3 . 7          .50201
1.7641                 3 . 8         -1.10228
 .557916               3 . 9          .34[illegible]
 .600552               3 . 10         .265714
 .356105               4 . 5          .5[illegible]
 .505715               4 . 6          .42[illegible]
 .439505               4 . 7          .4[illegible]
 .341225               4 . 8          .546[illegible]
 .757119               4 . 9          .22[illegible]
 .768587               4 . 10         .246693
 .495357               5 . 6          .457951
 .430342               5 . 7          .49454
 .344586               5 . 8          .542779
1.52944                5 . 9         -.123709
 .92909                5 . 10         .217954
 .74737                6 . 7         -.0720945
 .590556               6 . 8          .257275
 .547065               6 . 9          .349247
 .574955               6 . 10         .29955
 .511724               7 . 8          .349003
 .40957                7 . 9          .[illegible]
 .540255               7 . 10         .299017
 .[illegible]          8 . 9          .[illegible]
 .55[illegible]        8 . 10         .[illegible]
 .[illegible]          9 . 10         .[illegible]

THERE WERE [illegible]

TOTAL STANDARD DEVIATION FOR FIRST [illegible]
TOTAL STANDARD DEVIATION FOR SECOND [illegible]

TOTAL RELATIVE AVERAGE DEVIATION [illegible]
TOTAL RELATIVE AVERAGE DEVIATION [illegible]
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  DETERMINATION [illegible]
   IN SOLUTION USING [illegible]

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SPECTRA [illegible] VALUE=0.25

   [illegible]        [illegible]        [illegible]                    [illegible]

   6[illegible]        0.775        [illegible]      3.7[illegible]        0.[illegible]
   6[illegible]        1.055         5.27      7.30        0.1
   59[illegible]       1.31[illegible]        15.66     13.05        0.1
   55[illegible]       1.005         5.57     11.81        0.
   531        0.660         5.04      8.96        0.1
   452        0.941        13.21      5.28        0.1
   44[illegible]       1.337        19.6[illegible]     10.55        0.1
   41[illegible]       1.55[illegible]        19.11     18.73        0.1
   383        0.990         7.78     16.16        0.1
   370        0.495         2.95     11.93        0.1

THE CONCENTRATION OF THE FIRST SPECIES IS .5607 MOLAR

THE CONCENTRATION OF THE SECOND SPECIES IS .3245 MOLAR

FIRST SPECIES STANDARD DEVIATION IS 0.035
SECOND SPECIES STANDARD DEVIATION IS 0.035

FIRST SPECIES RELATIVE AVERAGE DEVIATION IS   5.16%
SECOND SPECIES RELATIVE AVERAGE DEVIATION IS   [illegible]

                 DATA

CONCENTRATION A               CONCENTRATION B

 .[illegible]              1 . 2        .21[illegible]
 .5[illegible]              1 . 3        .29602[illegible]
 .5[illegible]              1 . 4        .28979.
 .5[illegible]              1 . 5        .424673
 .660321              1 . 6        .111804
 .633659              1 . 7        .0417301
 .627965              1 . 8        .219124
 .566365              1 . 9        .338327
 .601[illegible]              1 . 10       .284791
 .57092               2 . 3        .328426
 .526379              2 . 4        .416231
 .5[illegible]              2 . 5        .448115
-.[illegible]              2 . 6        1.[illegible]
 .85.343              2 . 7       -.311635
 .[illegible]              2 . 8        .219909
 .5650[illegible]              2 . 9        .340601
 .5905[illegible]              2 . 10       .287117
 .455154              3 . 4        .45729
 .434[illegible]              3 . 5        .45226[illegible]
 .539447              3 . 6        .367375
 .416157              3 . 7        .50201
1.7641               3 . 8       -1.10228
 .557926              3 . 9        .344015
 .509551              3 . 10       .25331[illegible]
 .256106              4 . 5        .536[illegible]
 .505713              4 . 6        .4[illegible]
 .439537              4 . 7        .470157
 .741226              4 . 8        .54667
 .707115              4 . 9        .229862
 .76[illegible]              4 . 10       .246687
 .495357              5 . 6        .457951
 .42034[illegible]              5 . 7        .46454
 .344598              5 . 8        .542775
1.51944               5 . 9       -.123725
 .92929               5 . 10       .213954
 .74737               6 . 7       -.0720945
 .959594              6 . 8        .257679
 .547055              6 . 9        .349247
 .574955              6 . 10       .29058
 .51[illegible]              7 . 8        .349093
 .4585[illegible]              7 . 9        .372985
 .540135              7 . 10       .299097
 .[illegible]              8 . 9        .3764[illegible]
 .[illegible]              8 . 10       .[illegible]
 .[illegible]              9 . 10       .[illegible]

[illegible]

[illegible]
[illegible]

[illegible]
[illegible]
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