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SPECTROPHOTOMETRIC ANALYSIS OF AQUEOUS MIXTURES OF SOME CHROMIUM (III) COMPLEXES

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Thesis
Submitted in Partial Fulfillment
for Honors in Chemistry
to the
Faculty of Spring Arbor College

by

Gregory Stevens

May, 1983

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SPECTROPHOTOMETRIC ANALYSIS OF AQUEOUS MIXTURES OF SOME CHROMIUM (III) COMPLEXES

I. INTRODUCTION

There is a great need for electrical storage development for remote power system applications that are supplied either by solar photovoltaic arrays or wind turbine generators.(1) Lead-acid batteries are currently used for this application but costs are high and the system level is difficult to maintain.(2) Over the past ten years, the NASA-Lewis Research Center has developed the NASA-Redox concept (3,4) to where small but complete Redox energy storage systems have been built. These inexpensive, relatively unsophisticated systems store energy during periods when ample power is being produced by solar or wind generators, and supplied to the various loads during low production periods.(5)

Another application for energy storage systems is in electric utility service where they would serve in a load leveling capacity.(6) These storage devices would be in the ten megawatt size range and would be used on a daily cycle.

The NASA-Redox Energy Storage system is an electrochemical storage device that utilizes the oxidation and reduction of two soluble redox couples for charging and discharging. The active solutions, seperated by a highly selective ion exchange membrane, are pumped through a stack of Redox flow cells where the electrochemical reactions take place at porous carbon felt electrodes. The redox couples currently in use are acidified solutions of chromium {Cr(III)/Cr(II)} and iron {Fe(III)/Fe(II)}.

A diagram showing the single Redox cell and the electrode reactions is

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shown in figure 1. The anion exchange membrane seperates the compartments and prevents the cross-mixing of the reactive cations. The electrode material is carbon felt, catalyzed by trace amounts of gold and lead on the chromium side. The need for the catalyst is evident because the rate of reduction of Cr(III) to Cr(II) is slow on most surfaces.(7,8) The catalyst must have a high overvoltage for hydrogen because, thermodynamically, hydrogen is evolved before chromium is reduced. The result of coevolution of hydrogen is a reduction in coulombic efficiency and a loss of balance electrochemically in the system after many cycles. Trace amounts of gold (12 to 25 ug/cm^2) and lead (100 to 200 ug/cm^2) deposited on the carbon felt meet the criteria for an effective catalyst. The gold produces a surface onto which lead deposits uniformly during a slow charging cycle. No catalyst is required on the iron electrode.

During a discharge cycle, chloride ions move from the cathode compartment to the anode compartment, and hydrogen ions move in the opposite direction. On charge all reactions are reversed.

The relatively inert inner-sphere complex ions $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_4Cl_2^{+}$ are present at equilibrium with $Cr(H_2O)_6^{+3}$ in aqueous solutions containing Cr(III) and chloride ion.(9) Both color changes and open-circuit voltage versus state-of-charge plots confirm the presence of these complex ions. Distinctive differences in the chromium solutions are observed at the same state of charge depending on whether the cell is in the charge or discharge mode, as seen in figure 2. At above 50 percent state-of-charge the charging rate drops off appreciably.

The two species, $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$, have been identified as present in Redox solutions by ion exchange chromatography and visible spectrophotometry. Spectral data indicates that the concentration of $Cr(H_2O)_5Cl^{+2}$ decreases much

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more rapidly with increasing state of charge than does the concentration of $Cr(H_2O)_6^{+3}$ indicating that $Cr(H_2O)_5Cl^{+2}$ is the predominant species being reduced during the charging cycle. There is a rapid rise in $Cr(H_2O)_5Cl^{+2}$ concentration as discharge takes place, and the concentration of $Cr(H_2O)_6^{+3}$ rises only after appreciable $Cr(H_2O)_5Cl^{+2}$ is produced. The main electroactive species, then, is pentaaquachromium chloride.(10)

$Cr(H_2O)_5Cl^{+2}$ is evidently reduced via an inner-sphere chloride bridged electrode reaction and the oxidation of $Cr(H_2O)_5Cl^{+}$ as an inner-sphere chloride bridged electrode reaction. A slowly attained equilibrium exists between $Cr(H_2O)_6^{+3}$ and $Cr(H_2O)_5Cl^{+2}$ that is catalyzed by Cr(II).(10)

From this information it is crucial that methods be developed to study and control the equilibrium between $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$. The ability to control this equilibrium would provide the means to increase the efficiency and capacity of the NASA Redox Energy Storage System.

Increased temperature of the system is believed to thermodynamically shift the equilibrium between the chromium complexes to favor the $Cr(H_2O)_5Cl^{+2}$ species--the main electroactive species. In order to study this temperature effect reliable methods of chromium analysis and determination are necessary.

This work describes and compares several methods of determining the relative concentrations of $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$. The three methods studied are curve resolving methods, used in evaluating spectrophotometric results, mixture studies, used in verifying curve resolving techniques, and chromium analysis.

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II. EXPERIMENTAL

All visible spectrophotometric work was done on a Perkin-Elmer Coleman 124 double beam spectrophotometer with a Sargent model SR recorder.

Preparation of $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$.

Ion exchange chromatography was used to obtain the pure $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$.(11) A solution of .07 M $Cr(H_2O)_4Cl_2^{+}$ was prepared by dissolving 4.663 g of $CrCl_2 \cdot 6H_2O$ in 250 ml of .002 M $HClO_4$. A 38cm x 11mm column was prepared using Dowex 50W-X8 (50-100 mesh) cation exchange resin. The .07 M $Cr(H_2O)_4Cl_2^{+}$ (63°C) was placed on the fresh column and eluted with .1 M $HClO_4$ (approximately 100 ml).

The most weakly held cation, $Cr(H_2O)_4Cl_2^{+}$, was liberated from the column as a result of the .1 M $HClO_4$ elution. Upon pouring 1.0 M $HClO_4$ onto the column $Cr(H_2O)_5Cl^{+2}$ was caused to move down the resin and was collected. Finally, 3.0 M $HClO_4$ was required to displace the very strongly bound $Cr(H_2O)_6^{+3}$ from the resin. Since we were interested only in the $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$ complexes, they were the only two complexes saved for this study.

The visible spectra of the complexes were in agreement with literature values.

Preparation of Standard Chromate solutions used in Chromium Analysis.

A standardized 100 ppm chromium solution in the form of chromate was prepared by dissolving .2829 g Primary Standard $K_2Cr_2O_7$ in 1000.0 ml of standard .05 M KOH. Dilutions were made of this solution to 10 ppm, 7.5 ppm, 6.0 ppm, 3.5 ppm, 2.5 ppm, and 1.0 ppm chromium in the form of chromate ion. Absorbance was read for each diluted solution at 366 mu, using .05 M KOH as a reference. A graph was constructed plotting concentration (abscissa) vs. absorbance (ordinate).

Preparation of Chromium samples for analysis

In order for appropriate absorption readings to be taken, the chromium complexes must be converted to chromate ion and diluted such that their colors correspond to that of the standard chromate solutions. 2.0 ml of $Cr(H_2O)_5Cl^{+2}$ and 2.0 ml of $Cr(H_2O)_6^{+3}$ were seperately pipetted into a 100 ml volumetric flask. 50 ml of .05 M KOH was added to each flask followed by 8 drops 30% H_2O_2 and then more .05 M KOH to dilute each to 100 ml. The solutions were allowed to stand overnight. 10 ml of each chromate species was diluted to 1000 ml with .05 M KOH, making the total dilution factor from the original solution 1/5000. Absorbance at 366 mu was recorded for each diluted solution.

Mixture Studies

Mixtures of $Cr(H_2O)_5Cl^{+2}$ to $Cr(H_2O)_6^{+3}$ were made using the following ratios and volumes: 1:1 (2.0 ml:2.0 ml), 2:1 (4.0 ml:2.0 ml), and 1:2 (2.0 ml: 4.0 ml). 2.0 ml pipettes were used in this procedure. Absorption spectra were obtained for each of these mixtures. Mixtures of 1:1, 2:1, and 1:2 $Cr(H_2O)_5Cl^{+2}$ to 0.1 M $HClO_4$ and 1:1, 2:1, and 1:2 0.1 M $HClO_4$ to $Cr(H_2O)_6^{+3}$ were prepared and spectra were obtained using 0.1 M $HClO_4$ as reference.

Curve Resolving

The DuPont 310 Curve Resolver was used to study the absorption curves. It was used to add the component bands of the pure complexes, giving the

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composite band of the mixture.

The 310 Curve Resolver is a special purpose analog computer for the rapid resolution of overlapping peaks in experimental data. To accomplish this, the instrument generates a series of component peaks and synthesizes a sum curve matching the original data. The 310 was set to generate, on each of its function generator channels, peak shapes corresponding to Gaussian distributions. Individual peak parameters of height, width, and horizontal position were varied on each channel until each peak of the individual species spectra was represented by a seperate channel. The desired curves were then summed by switching on and off the appropriate channels to yield the composite curve structure similar to the spectra of the mixtures obtained from the mixture studies.

When working with mixtures in which one or both of the species is very concentrated the curve resolver will not be as accurate near the wavelength of maximum absorbance.

Computer Analysis

All computer work was done on a Radio Shack TRS-80 Level II computer utilizing disk basic.

III. DATA AND CALCULATIONS

Computer Analysis

The absorption spectra of $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$ and their mixtures are shown in figures 3 thru 5. Molar absorptivities (ε) at various wavelengths for the two species were calculated using these spectra and Beer's Law and were used in the computer analysis. They are listed in table 1.

A computer program was developed which computes the concentrations of two species using data from the absorption spectra of the mixture of the two species. The program, SPEC/BAS, is listed in the data section.

A sample run of the program is found in the data section. This program takes data from visible spectra as input and gives concentration of species, standard deviation and relative average deviation as output. It also incorporates a means of not including erroneous values in the calculation of the average concentration of the individual species.

When working with mixtures in which one or both of the species is very dilute (less than .1 M) the computer program SPEC/BAS must be edited to accomodate these values. There is an error factor in line 2040 (underlined in listing of program in data section) which must be increased to a value which will give acceptable output from the computer. The rationale behind this is that in the program there exists a subroutine (lines 2000-2180) which eliminates concentration values which are in error of the mean by a factor greater than the error factor. For very dilute solutions, which are already subject to spectrophotometric errors, a small error factor would cause most of the computed concentrations to be eliminated.

A listing of the solutions to the combinations of linear simultaneous equations is also contained in the output, as well as the total standard deviation and relative average deviation for all of these results, erroneous values included.

The program SPEC/BAS was used to analyze the absorption curves of the three mixtures of chromium complexes. The results are shown in table 2 in tabular form.

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Chromium Analysis

The plot of absorbance vs. concentration for chromium is shown in figure 6. The diluted $Cr(H_2O)_5Cl^{+2}$ had an absorbance reading of 0.342, which corresponds to a concentration of 3.80 ppm, according to the calibration curve. Knowing the dilution factor to be 1/5000, the original sample concentration is calculated to be 0.365 M $Cr(H_2O)_5Cl^{+2}$. The chromium complex $Cr(H_2O)_6^{+3}$ had an absorbance value of 0.760, corresponding to 0.813 M.

With this information, the concentrations of the chromium complexes used in the mixture studies can be calculated. The concentrations computed for this study are listed in table 2.

Curve Resolving

The summations of the individual component curves using the Curve Resolver are shown in figures 3 thru 5. The summation curve from the Curve Resolver accurately matches the absorption bands of the chromium complex mixture. The greatest error was found near the wavelength of maximum absorbance (λ_{max}), where the discrepancy between the mixture's absorbance and the Curve Resolver's results is as much as 5.0% for one peak. The mean discrepancy at λ_{max} was 1.7% for the peak whose maximum occurs near 585 mu and 2.3% for the peak whose maximum occurs near 415 mu.

λ_{max} Correlation

Figure 7 illustrates the plot of wavelength of maximum absorbance (abscissa) vs. concentration ratio (mole fraction) of $Cr(H_2O)_6^{+3}/(Cr(H_2O)_5Cl^{+2} + Cr(H_2O)_6^{+3})$ (ordinate). It is interesting to note that a linear relationship is found between absorbance and concentration ratio (mole fraction $Cr(H_2O)_6^{+3}$).

IV. DISCUSSION

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The computer program gave very good results for the determination of chromium complex ion concentrations from the analyzation of the chromium complex mixture's spectra data. Table 2 shows the percent errors of the mean values using the concentrations determined from the chromium analysis as the accurate standard values. The concentration values from the chromium analysis are within the expected error of the standard deviations for the computer analysis for the mixture ratios 1:1 and 2:1 $Cr(H_2O)_5Cl^{+2}$ to $Cr(H_2O)_6^{+3}$. This is not the case for the 1:2 mixture ratio, however. These errors are due, presumably, to a number of factors: molar absorptivity calculation errors, and absorbance errors due to a combination of wavelength errors in the spectrophotometer and large slopes of the absorption curves

The curve resolving proved to provide an accurate means of representing absorption curves using a Gaussian-type distribution. The summation curve errors occuring near the wavelength of maximum absorption were due to the extreme sensitivity of the Curve Resolver near the peaks of the curves. In addition, it must be taken into account that absorption curves are only similar to Gaussian-type distributions and can not be represented exactly by this type of a curve similation.

V. CONCLUSION

Several methods for determining the concentrations of $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$ in aqueous solutions containing Cr(III) and chloride ion were found to provide valuable results. Curve resolving was found to provide an excellent means of resolving spectra of mixtures of $Cr(H_2O)_5Cl^{+2}$ and $Cr(H_2O)_6^{+3}$

into their individual component absorption spectra. The chromium analysis studies proved to be very reliable and presented a method of evaluating the curve resolving and computer analysis.

Future applications for these methods of study can be seen in the area of temperature studies on the Cr(III) solution. Studies of this type would determine the potential of utiliqing the heat generated by the Redox Energy Storage System's pumps to increase the temperature of the electrolyte solutions. Increased temperature of the system is believed to have the effect of shifting the equilibrium between the chromium complexes to favor $Cr(H_2O)_5Cl^{+2}$ --the electroactive species. Should this effect occur. the electrical capacity and efficiency of the system would increase.

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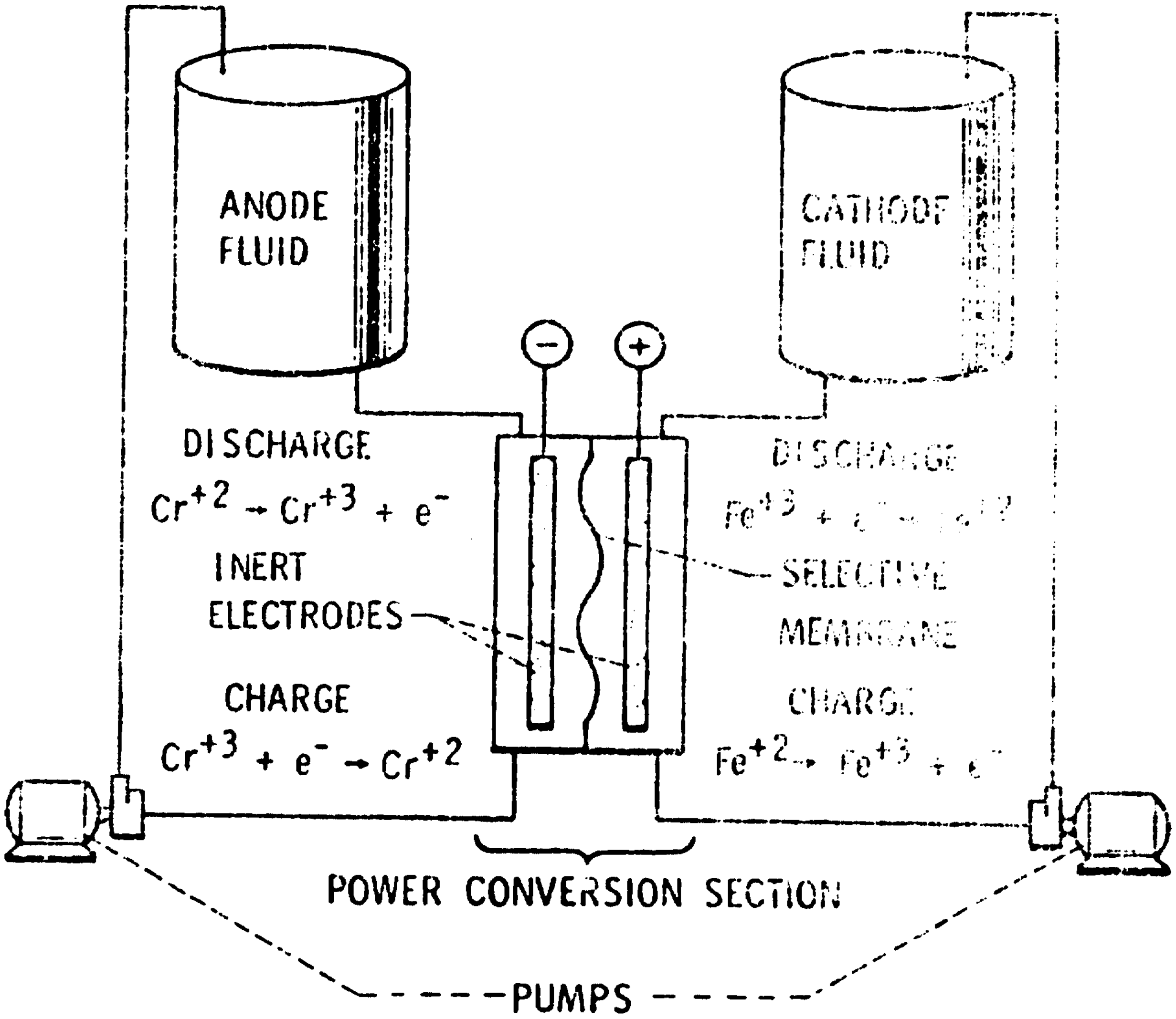
PRINCIPLE OF OPERATION OF NASA-REDOX CONCEPT



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NASA REDOX

FIGURE 1

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OPEN-CIRCUIT VOLTAGE HYSTERESIS OF IRON/CHROMIUM REDOX CELL

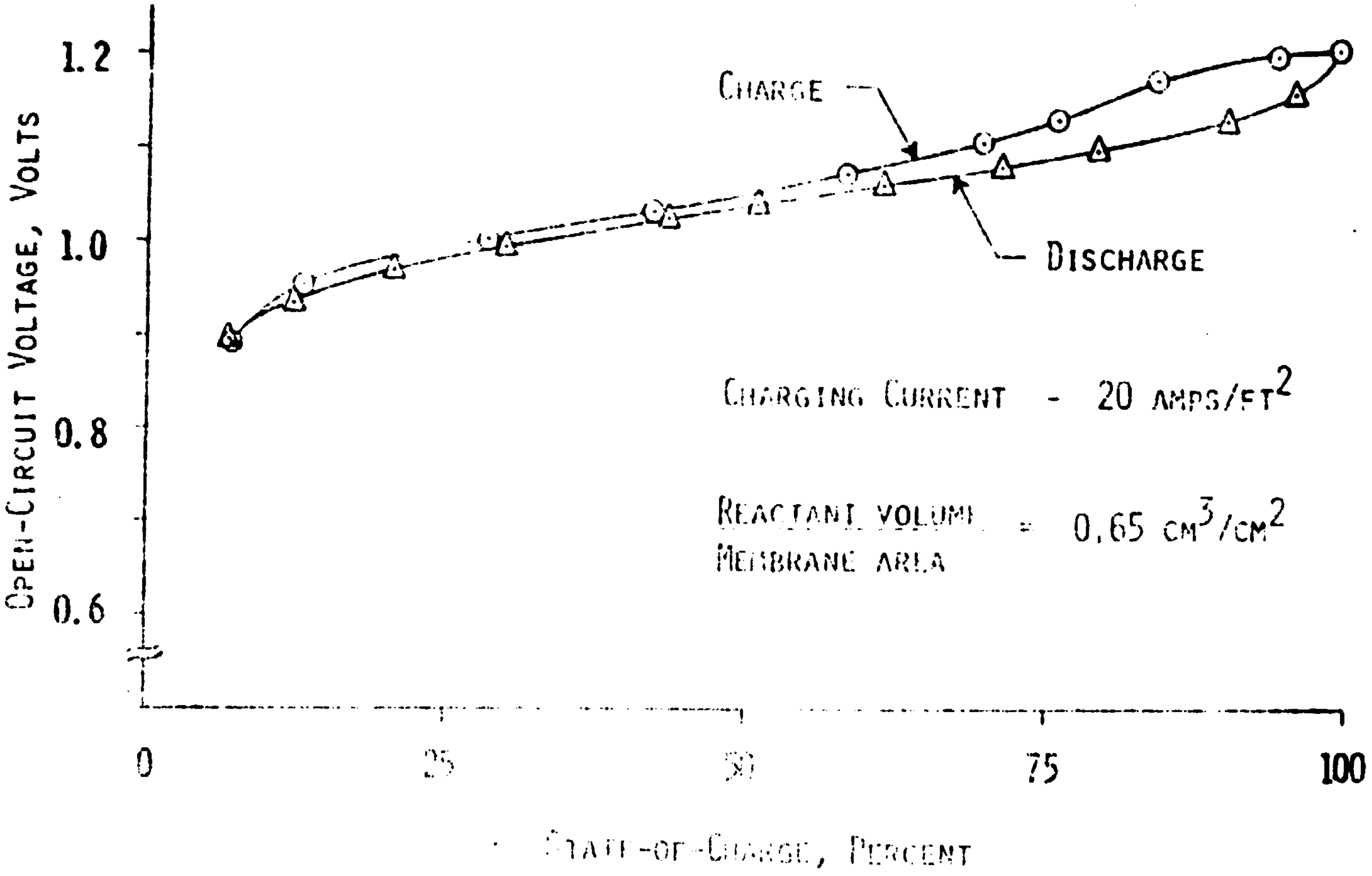

FIGURE 2

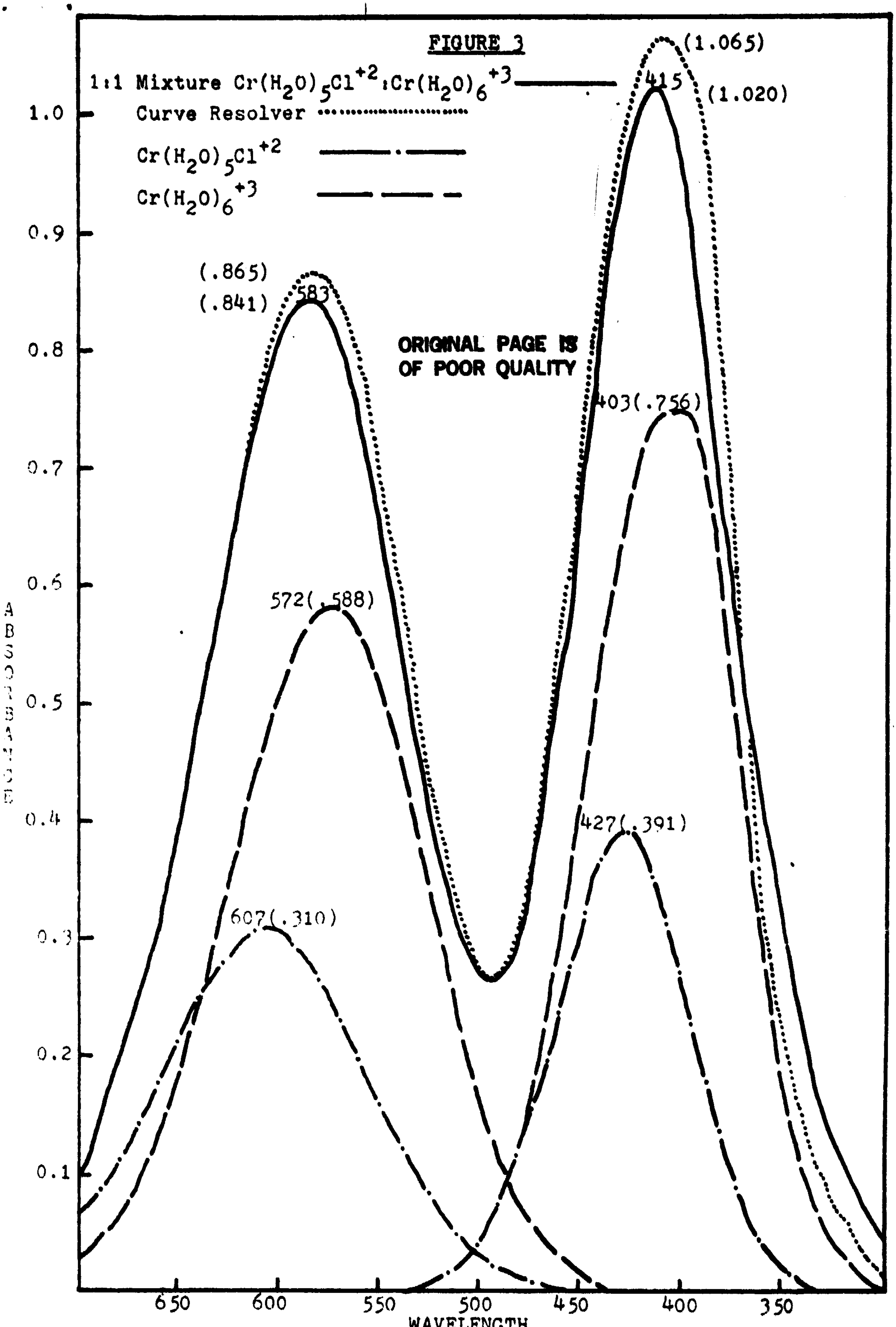

FIGURE 3

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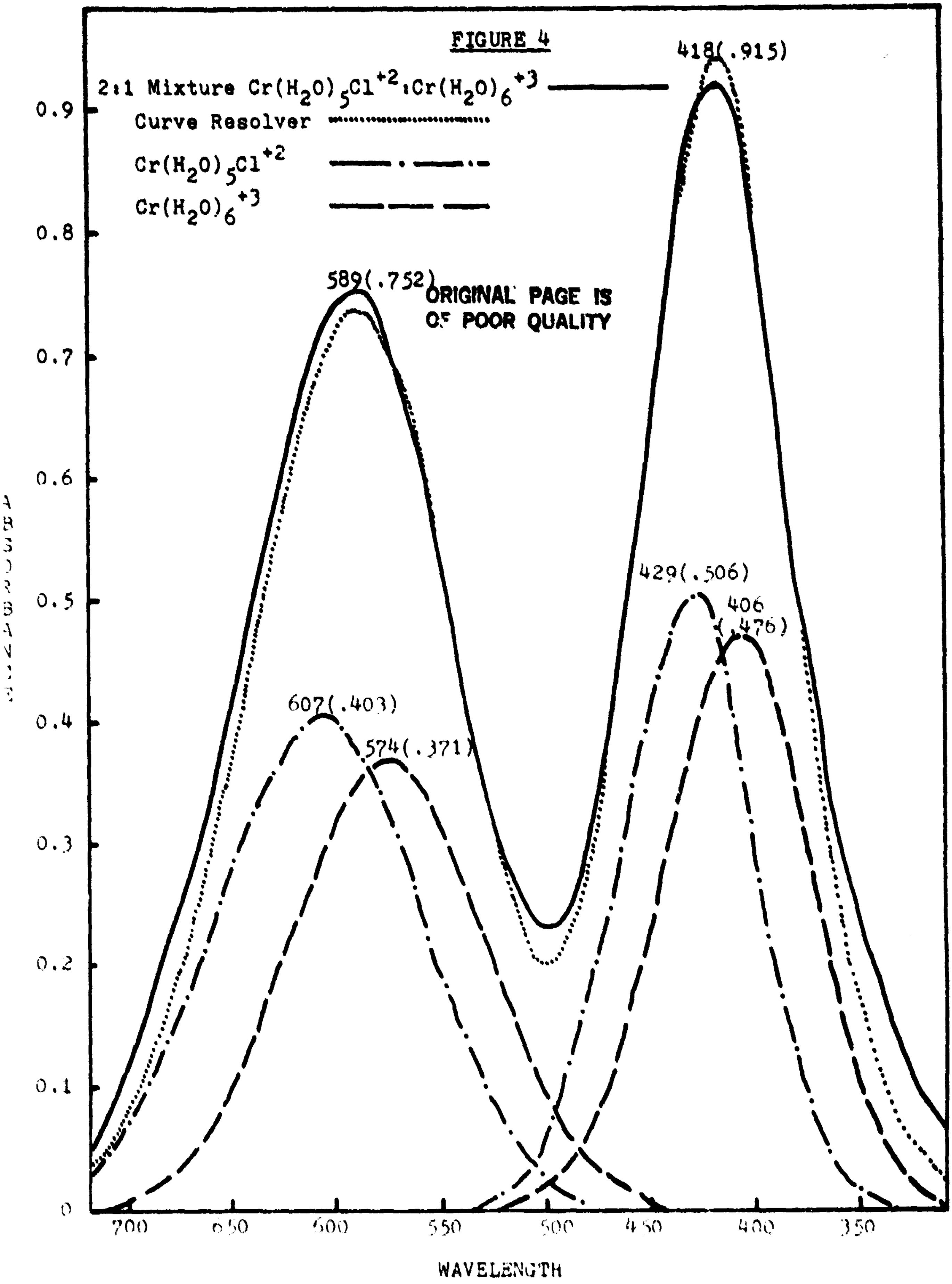

FIGURE 4

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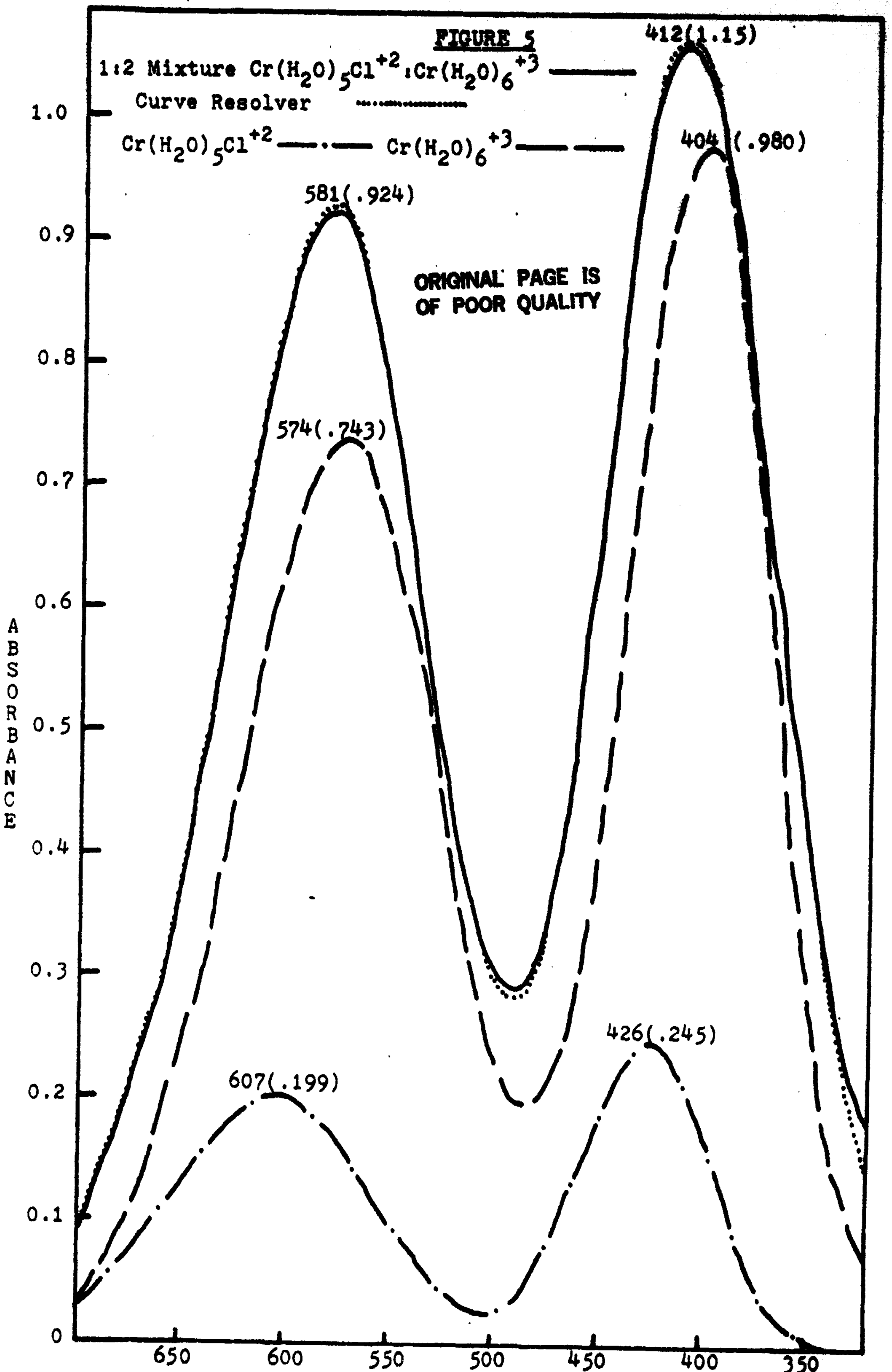

FIGURE 5

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TABLE 1

Wavelength	ϵ $Cr(H_2O)_5Cl^{+2}$	ϵ $Cr(H_2O)_6^{+3}$
652	11.15	3.76
628	15.05	7.30
592	15.66	13.06
556	8.93	12.81
532	5.04	8.96
460	13.21	6.28
442	18.91	10.58
418	19.62	16.93
388	7.78	16.16
370	2.58	11.93

TABLE 2

Mixture Ratio		Concentration (M) from SPEC/BAS	Concentration (M) from Cr Analysis	% Error
1:1	$Cr(H_2O)_5Cl^{+2}$	0.200 ±.019	0.183	8.5
	$Cr(H_2O)_6^{+3}$	0.399 ±.026	0.407	2.0
2:1	$Cr(H_2O)_5Cl^{+2}$	0.255 ±.020	0.243	4.7
	$Cr(H_2O)_6^{+3}$	0.272 ±.022	0.271	0.4
1:2	$Cr(H_2O)_5Cl^{+2}$	0.145 ±.013	0.122	15.8
	$Cr(H_2O)_6^{+3}$	0.517 ±.020	0.542	4.8

FIGURE 6

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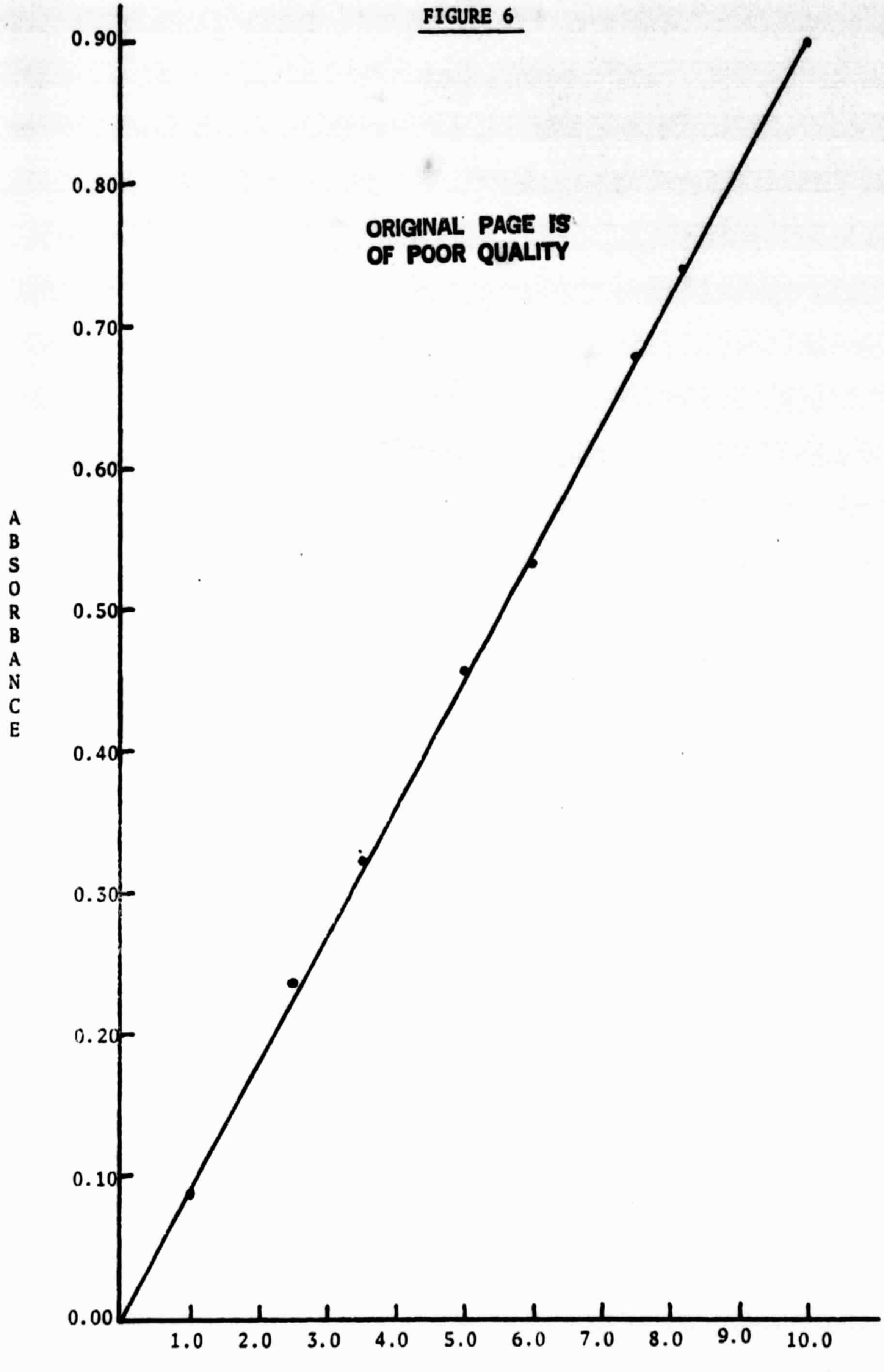

FIGURE 7

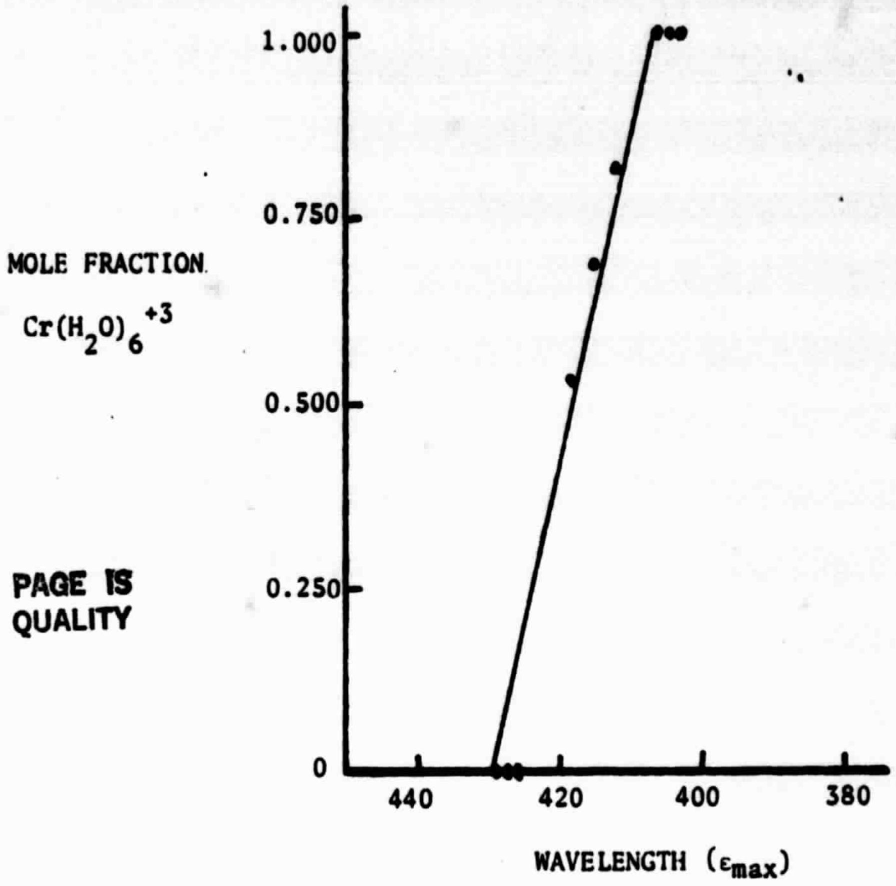

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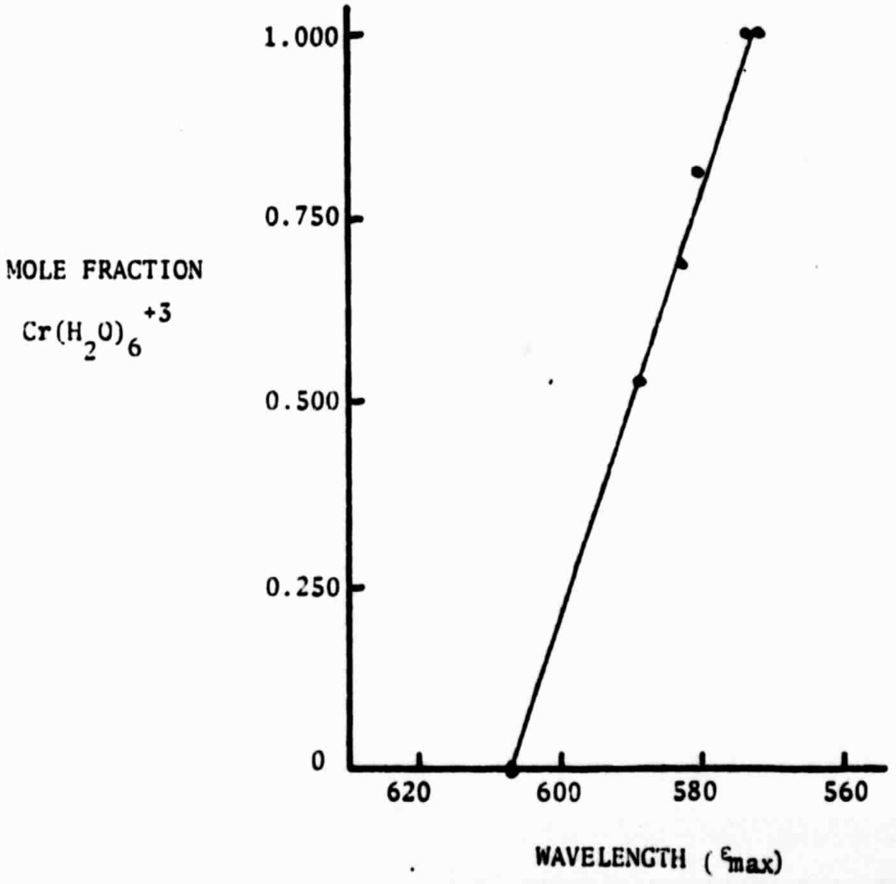
FIGURE 8



SAMPLE RUN OF THE COMPUTER PROGRAM "SPEC/BAS"

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```
******************************************  **  *****

  DETERMINATION OF CONCENTRATIONS OF TWO [illegible]
    IN SOLUTION USING UV-VIS SPECTROSCOPY [illegible]

*******************************  *************  *****  **  *****


1 TO 1 MIXTURE OF [illegible] TO [illegible] COMPLEX .

WAVELENGTH      ABSORBANCE      [illegible] ABSORPTIVITY 1 2          CELL WIDTH

    652            0.377          11.[illegible]      [illegible].73         0.1
    628            0.528          15.0[illegible]     7.7[illegible]         0.1
    58[illegible]  0.[illegible]  15.[illegible]      13.06                  0.1
    556            0.[illegible]  [illegible]         12.81                  0.1
    512            0.41[illegible] 7.01               8.9[illegible]         0.1
    460            0.518          12.21               [illegible]            0.1
    [illegible]    0.[illegible]1 1[illegible].91     10.5[illegible]        0.1
    418            1.0[illegible] 1[illegible]        1[illegible]           [illegible]
    38[illegible]  0.[illegible]  [illegible]         [illegible]1           0.1
    370            [illegible]    [illegible]         12.[illegible]         0.1


[illegible]


THE CONCENTRATION OF THE [illegible]


[illegible]
[illegible]

[illegible]
[illegible]
```

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```
                 DATA

CONCENTRATION #1                      CONCENTRATION #2

   200015              1 , 2            .4006[illegible]
  .205681              1 , 3            .392[illegible]
  .198026              1 , 4            .4154[illegible]
  .19618[illegible]              1 , 5            .420898
  .206305              1 , 6            .390873
   216471              1 , 7            .3607[illegible]1
   214324              1 , 8            .367098
  .207342              1 , 9            .387602
   202507              1 , 10           .40214
  .200475              2 , 3            .389[illegible]8
  .194722              2 , 4            .417731
   192062              2 , 5            .423215
   1[illegible]5261              2 , 6            54926
  .260814              2 , 7            .38147[illegible]
   225046              2 , 8            35597[illegible]
   200817              2 , 9            38661
   [illegible]              2 , 10           402194
   171092                , 4            [illegible]
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   134071              [illegible]            [illegible]
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   2114[illegible]              [illegible]            [illegible]
   [illegible]              [illegible]            [illegible]
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   [illegible]              [illegible]            [illegible]
   [illegible]              [illegible]            [illegible]
   114267              4 , 8            [illegible]
   200512              4 , 9            [illegible]
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   22164[illegible]              [illegible]            [illegible]6616
   [illegible]              [illegible]            [illegible]
   [illegible]              6 , 10           [illegible]
  .[illegible]10249              [illegible]            .371752
   199107              [illegible]            [illegible]
  .19[illegible]              , 10           464[illegible]
   188724              [illegible]            [illegible]
   [illegible]              [illegible]            [illegible]
   [illegible]                 1[illegible]           [illegible]

TOTAL [illegible] CONCENTRATION

TOTAL STANDARD DEVIATION [illegible]
TOTAL STANDARD DEVIATION [illegible]

TOTAL RELATIVE STANDARD DEVIATION [illegible]
TOTAL RELATIVE STANDARD DEVIATION [illegible]
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```
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$="" THEN 80 ELSE 90
90 CLS
100 LPRINT"**************************************************"
110 LPRINT" "
120 LPRINT"  DETERMINATION OF CONCENTRATIONS OF TWO SPECIES"
130 LPRINT"     IN SOLUTION USING UV-VIS SPECTROSCOPY DATA"
140 LPRINT" "
150 LPRINT"**************************************************"
160 LPRINT" ":LPRINT" "
165 GOTO 3000
170 REM     INPUT DATA
175 CLS
180 PRINT "ENTER THE NUMBER OF WAVELENGTHS FROM WHICH"
190 PRINT "DATA IS TAKEN"
200 INPUT D
210 IF D<2 THEN 220 ELSE 235
220 PRINT"YOU MUST ENTER AT LEAST 2 WAVELENGTHS."
230 GOTO 180
235 CLS
240 GOSUB 6000
245 CLS
250 E=D-1
260 DIM W(D),A(D),M(D,2),B(D),C(D,D,2),SD(2,2),RAD(2,2),F(2),G(2)
270 FOR I=1 TO D
280 PRINT"ENTER WAVELENGTH #";I
290 INPUT W(I)
300 PRINT""
310 PRINT"ENTER ABSORBANCE AT WAVELENGTH";W(I)
320 INPUT A(I)
330 PRINT""
340 PRINT"ENTER MOLAR ABSORPTIVITY OF FIRST"
350 PRINT"COMPONENT AT WAVELENGTH";W(I)
360 INPUT M(I,1)
370 PRINT""
380 PRINT"ENTER MOLAR ABSORPTIVITY OF SECOND"
390 PRINT"COMPONENT AT WAVELENGTH";W(I)
400 INPUT M(I,2)
410 PRINT""
420 PRINT"ENTER THE CELL WITH USED (IN CM)"
430 INPUT B(I)
440 CLS
445 PRINT"PLEASE WAIT"
450 NEXT I
460 REM      PRINTED OUTPUT OF DATA
470 LPRINT"WAVELENGTH","ABSORBANCE","MOLAR ABSORPTIVITY 1,2",
480 LPRINT"CELL WIDTH"
490 LPRINT" "
500 F$="#.###"
510 G$="##.##"
520 H$="#.#"
530 FOR I=1 TO D
540 LPRINT TAB(4) W(I);
550 LPRINT TAB(19);LPRINT USING F$;A(I);
560 LPRINT TAB(35);LPRINT USING G$;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 K=2:E=D-1
640 FORI=1 TO E
650 FORJ=K TO D
```

COMPUTER PROGRAM "SPEC/BAS"

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660 C(I,J,1)=(A(I)*M(J,2)-A(J)*M(I,2))/(B(I)*(M(I,1)*M(J,2)-M(I,2)*M(J,1)))
670 C(I,J,2)=(A(J)*M(I,1)-A(I)*M(J,1))/(B(I)*(M(I,1)*M(J,2)-M(I,2)*M(J,1)))
680 S(1)=S(1)+C(I,J,1)
690 S(2)=S(2)+C(I,J,2)
700 N=N+1
710 NEXT J
720 K=K+1
730 IF K=(D+1) THEN 790
740 NEXT I
750 X=S(1)/N
760 Y=S(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=2
1020 FOR I=1 TO D
1030 FOR J=K TO D
1040 LPRINT C(I,J,1);I;",";J,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 COMPARISONS"
1245 N2=N
1250 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 DETERMINATION"
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)";I$
1410 IF I$="YES" THEN LPRINT CHR$(12):GOTO5
1415 CLS
1420 FOR I=46TO66:SET(I,10):NEXT
1430 FOR I=10TO15:SET(66,I):NEXT
1440 FOR I=66TO46 STEP -1:SET(I,15):NEXT
1450 FOR I=15TO10 STEP -1:SET(46,I):NEXT I
1460 IF I$="NO" PRINT@280,"THANK YOU": ELSE PRINT@280,"TRY AGAIN":
1470 PRINT@900," "
1480 FOR I=1TO3000:NEXT
1490 IFI$="NO" THEN 9000 ELSE 1400
```

```
2000 REM   LINES 2000-2100 ELIMINATE ERRONEOUS CONCENTRATION VALUES
2005 L=0
2010 K=2:N=0:S1=0:S2=0
2020 FOR I=1 TO E
2030 FOR J=K TO D
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--652,628,592,556,532,460,442,418,"
6020 INPUT"388, AND 370";K$
6030 IF K$="YES" THEN 6040 ELSE RETURN
6040 CLS
6050 FOR I=1TOD
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,.1,628,15.05,7.3,.1,592,15.66,13.06,.1
8901 DATA 556,6.93,12.01,.1,532,5.04,6.96,.1,460,13.21,6.28,.1
8902 DATA 442,16.91,10.58,.1,418,19.62,16.93,.1,388,7.78,16.16
8903 DATA .1,370,2.58,11.93,.1
9000 END
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