

SPECTROFLUOROMETRIC STUDIES OF RARE  
EARTH CHELATES

By

ELIZABETH COLELLI STANLEY

Bachelor of Arts

Harpur College, State University of  
New York

Binghamton, New York

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# SPECTROFLUOROMETRIC STUDIES OF RARE EARTH CHELATES

Thesis Approved:

*Louis P. Varga*  
\_\_\_\_\_  
Thesis Adviser

*Glen E. Moore*  
\_\_\_\_\_

*J. H. Boyer*  
\_\_\_\_\_  
Dean of the Graduate College

621832

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## CHAPTER I

### INTRODUCTION

During recent years, rare earth chelate solutions have attracted considerable attention as potential liquid laser materials. Chelates of the rare earths, with such ligands as benzoylacetone (1-phenyl-1,3-butanedione) and dibenzoylmethane (1,3-diphenyl-1,3-propanedione), were first studied extensively by Crosby and Whan (20-25, 89). These workers described the energy transfer processes involved in the fluorescence and/or phosphorescence of the tris chelates of the rare earths. Since their reports, several groups (4, 5, 6, 10, 11, 12, 59) have completed further studies of the factors affecting line emission (observed as fluorescence) of these chelates. Several promising new ligands have been used, including thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione). Much of the recent work has involved the strongly fluorescing tetrakis rare earth chelates. Since potential laser materials have been of prime interest, attention has centered upon europium chelates, which emit more intensely than chelates of any of the other rare earths.

With this background in the literature, it seemed highly probable that the fluorescence emission of rare earth chelates might be useful in analytical procedures.

The present study was undertaken in order to determine the feasibility of a sensitive qualitative determination of the rare earths by spectrofluorometric methods. In addition, digital data processing methods, using available computer facilities, were tested to determine whether a general program could be devised which would be of use in the identification of the rare earths present in a complex mixture.

Several preliminary procedures were necessary before the actual fluorescence analysis could be studied. Initially, a method was developed for the reproducible preparation of rare earth chelates of known composition. Next, a Farrand spectrofluorometer was obtained and modified to provide increased sensitivity and flexibility. After the basic operating characteristics of the instrument had been determined, it was calibrated by standard methods (27, 63). During investigations with the three types of chelates mentioned above, appropriate conditions were chosen for the fluorescence procedures. The fluorescence spectra obtained for rare earth chelates, singly and in mixtures, were corrected and plotted with the aid of computer techniques. Computer methods were also used for the interpretation of the spectra of multi-component solutions.

The investigation reported here was confined to the qualitative analysis of the fluorescing rare earths. This preliminary study indicated that it should be possible to develop quantitative methods for rare earth analyses using the techniques which have been developed. However, additional equipment and further investigation will be required



to achieve the rapidity and accuracy desirable in a quantitative analysis.

### Spectrofluorometric Analysis

The fundamental principles relating to spectrofluorometric analysis have been reviewed by several authors (64, 66) and will be only briefly summarized here. It will be helpful to consider the electronic energy diagram of a typical rare earth chelate molecule (Figure 1) in order to describe the nature of its fluorescence and/or phosphorescence emission.

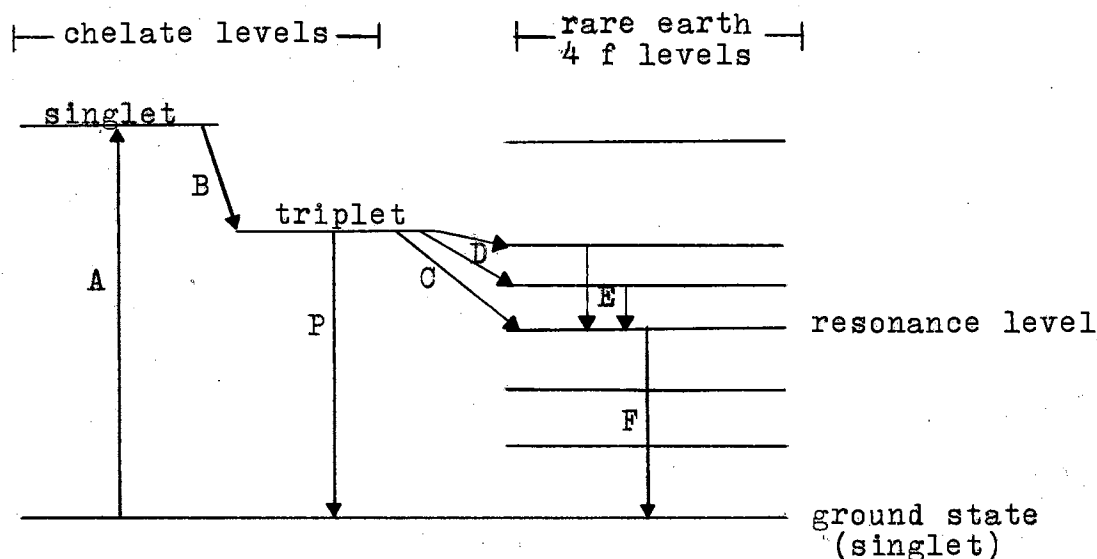


Figure 1. Energy Levels for a Rare Earth Chelate

As shown above, energy is absorbed by the molecule (step A), exciting a chelate singlet level. Conversion to a chelate triplet state then occurs by a radiationless transition (step B). The molecule may then undergo a further radiationless transition from the triplet state to an excited rare

earth ion state. If a resonance level (the state from which line emission characteristic of the ion can occur) of the ion is below the chelate triplet state, the energy is rapidly transferred to the resonance level. This radiationless transition may be direct (step C) or via other low-lying 4f levels (steps D and E). Fluorescence then occurs as a result of the transition from the rare earth's resonance level to the ground state (step F) or to a level slightly above the ground state which decays rapidly to the ground state. This latter behavior facilitates population inversion and laser action. However, if the ion's lowest resonance level is above the chelate triplet state, fluorescence line emission is not possible. In this case, broad phosphorescence bands, characteristic of the ligand, may be observed, due to a transition from the triplet state to the ground level (step P). When the two states are very close together, rapid intramolecular transfers may lead to very low yields of fluorescence and/or phosphorescence in competition with energy losses by radiationless transitions. It is therefore clear that fluorescence emission characteristic of the rare earth will occur only when the chelate employed has a triplet level above the ion's lowest resonance level. Therefore, selective excitation of the ions is made possible by suitable choices of ligands.

The quantum efficiency of fluorescence is unity if all of the excited molecules return to the ground state via step F; otherwise, if energy is lost by radiationless transitions or collision with other molecules (quenching) it is less than unity.

The equations describing the intensity of fluorescence may be derived directly from the Bouguer - Beer law. From the preceding discussion of the nature of fluorescence it is readily apparent that  $F$ , the total fluorescent intensity, is equal to the intensity of light absorbed multiplied by the quantum efficiency of fluorescence.

$$\begin{aligned}\log \frac{I}{I_0} &= -\epsilon cd \\ \text{or } I &= I_0(10^{-\epsilon cd}) \\ \text{or } I_0 - I &= I_0(1 - 10^{-\epsilon cd})\end{aligned}$$

where  $I_0$  = intensity of incident light  
 $I$  = intensity of transmitted light  
 $I_0 - I$  = intensity of absorbed light  
 $\epsilon$  = molar extinction coefficient  
 $c$  = concentration of absorbing specie  
 $d$  = optical depth

Therefore if  $\phi$  is the quantum efficiency of fluorescence

$$F = I_0(1 - 10^{-\epsilon cd})\phi$$

or for very dilute solutions

$$F = I_0(2.3\epsilon cd)\phi.$$

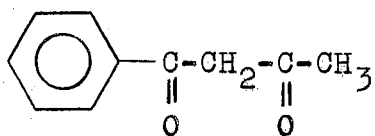
Therefore if  $I_0$  is constant, the fluorescent intensity is directly proportional to the concentration of the fluorescing species.

For these equations to be meaningful when applied to a particular case, it is necessary to obtain a "true" emission spectrum in which there is no dependence upon the character-

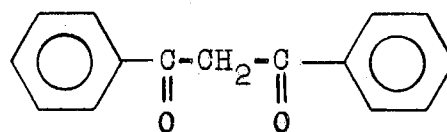
istics of the instrument used. Since a single beam spectrofluorometer was employed, correction factors had to be determined, expressing the spectral output of the source and the relative response of the detector as functions of frequency.

### Nomenclature

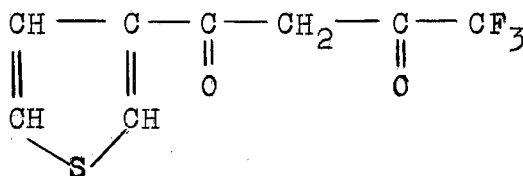
In the context of this thesis, the term "rare earths" will be considered to include the fourteen elements from cerium to lutetium, and a general rare earth metal will be represented as M. The ligands discussed will also be referred to in abbreviated form, with 1-phenyl-1,3-butanedione given as benzoylacetone or B, 1,3-diphenyl-1,3-propanedione as dibenzoylmethane or D, and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione as thenoyltrifluoroacetone or TTA. The structures of these three materials are shown below.



B



D



TTA

## CHAPTER II

### HISTORICAL

#### Preparation of Rare Earth Chelates

Several methods of preparation were reported during the early investigations of the spectroscopic properties of rare earth chelates. The chelate products obtained were of varying and often uncertain composition. Whan and Crosby (89) prepared hydrated rare earth trisbenzoyl-acetonates ( $MB_3 \cdot 2H_2O$ ) by reacting sodium benzoylacetate and a rare earth chloride in aqueous media. They also reported a preparation of rare earth trisdibenzoylmethides ( $MD_3$ ) in which an alcohol solution of the rare earth chloride was added to an alcohol solution of dibenzoylmethane and piperidine. With this method, prolonged vacuum drying was necessary to remove an extra mole of ligand. A third preparation of tris chelates, described by Sacconi and Ercoli (70), involved the combination of a rare earth chloride and a chelating agent (benzoylacetone) in ammonia-saturated ethanol.

When rare earth chelates began to attract wider interest as laser materials, several investigators (9, 73, 91), using the above methods or variations of them, reported preparations of europium chelates which seemed to be of unusual

composition. It was soon found that by using a modification of the piperidine method described above, and eliminating the drying step, a benzoylacetone chelate yielding laser emission could be obtained. This chelate was identified as an adduct of europium tris-benzoylacetate with an extra molecule of benzoylacetone and a piperidinium ion and may be written as  $MB_4 \cdot HP$ , where P represents piperidine (3, 9, 15, 71). Similar results were obtained for chelates with dibenzoylmethane (14, 15) and thenoyltrifluoroacetone (15, 76, 77), and later for octacoordinate chelates with a number of other ligands (3, 52). It has since been noted that the extra molecule of ligand, and a coordinated base, actually enhance fluorescence (9, 17, 55). This enhancement of emission may be attributed both to the minimization of quenching by the presence of an insulating sheath, and to an increase in the transition probability as the molecular symmetry is reduced.

#### Previous Studies on Rare Earth Chelates

The fluorescence of europium chelates was first reported by Weissman in 1942 (87), and the analytical aspects of rare earth chelate emission were investigated briefly in 1957 (88). However, the chelate systems were not studied extensively until the work of Crosby and co-workers (20-25, 89) demonstrated the potential of rare earth chelates as laser materials. Crosby and Whan investigated the fluorescence and phosphorescence of a number of tris rare earth chelates, and studied the intramolecular energy transfer

processes leading to emission. As noted earlier, fluorescence emission, characteristic of the rare earth ion, occurs after absorption by the chelate and radiationless transitions, via the chelate triplet state, to the ion's 4f electronic levels. Since a requirement of this mechanism is that the chelate triplet state lie near to, or above, the resonance energy level of the rare earth ion, it may be seen that excitation via energy transfer is a selective process. In this respect, it has been said that "the emission from an ion may be turned on or off by an appropriate choice of complexing agent" (25).

As a result of their observations, Crosby and Whan were able to assign energy levels for the ligands and the rare earth ions. They also proposed the use of rare earth chelates as optical masers (lasers), since they may be optically pumped, produce bright line emission, and have an upper state lifetime which allows the population inversion necessary for laser action.

After these investigations, several other groups initiated studies of rare earth chelates, specifically to evaluate their properties as laser materials. Europium chelates have been the most thoroughly studied, since the europium emission, primarily resulting from a  $5D_0 \rightarrow 7F_2$  transition, is sharper and more intense than that of the other rare earths. The preparation of the tetrakis chelates was described, as noted earlier, and subsequent investigations involved both tris and tetrakis  $\beta$ -diketone rare earth chelates, as solids, in solution and as frozen glasses. The

properties of their fluorescence emission, including decay times and temperature dependence, have been extensively discussed (4, 5, 6, 10, 11, 12, 59). The enhancement of fluorescence intensity, by an insulating sheath, Lewis bases, or deuterium substitution has also been observed by several groups, and the effects of ligand substituents have been investigated (3, 32, 36, 43, 44, 52).

Laser emission has been observed from europium chelates, and has been studied for several ligands, with varying chemical and physical conditions (9, 15, 47, 48, 49, 60, 71, 72, 73, 75, 76, 77, 91). Fluorescence and laser emission has been found in vinylic resin matrices as well as in more conventional media (31, 39, 51). Further related studies have been concerned with additional elucidation of coordination types and energy transfer processes (7, 8, 14), and with more extensive investigations of chelate systems (16, 17, 18, 35, 46, 55, 56, 61, 62).

#### Analysis of Rare Earths

Quantitative and qualitative analyses of the rare earths have been performed by a number of techniques, and general methods have been extensively discussed (86, 92). Prior to the development of instrumental methods of analysis, precipitation techniques were commonly employed for group analyses, but the separation of individual elements was difficult. Spectrophotometric methods led to improvements in analytical techniques, and, although sensitivity was low for rare earth ions, the formation of complexes was found to enhance sensi-



tivity for some elements. Emission spectroscopy has also been studied for rare earth analyses, and a number of excitation techniques have been successfully employed for both qualitative and quantitative analysis. X-ray absorption and emission, neutron activation, and isotopic tracer techniques have also been developed, but are not widely used.

Fluorescence methods, known to be selective and sensitive, appear to be well-suited to the analysis of rare earth ions, since sharp fluorescence bands may be observed for several elements, with ultraviolet excitation. However, the intensity of the fluorescence emission of aqueous solutions of rare earth salts is low, and analytical procedures have not been extensively developed. Methods have been described only for the determination of terbium (30) and for a number of rare earths in borate, oxalate and tungstate solutions (1). The fluorescence properties of the rare earths have been investigated in a number of solid matrices and, in some cases, analytical procedures have been studied (90).

As indicated earlier, studies on the fluorescence emission of rare earth chelates, carried out for theoretical purposes and for the investigation of potential laser materials, have shown that emission is strongly enhanced upon chelation. In addition, the choice of ligand influences the number of rare earths for which fluorescence is possible. These two properties of increased sensitivity and selectivity strongly indicate the usefulness of the fluorescence analysis of rare earth chelates. Several Soviet workers have reported

the spectrofluorometric determination of rare earths complexed with ortho-phenanthroline and salicylic acid (41, 65, 78) and, in a recent report, the determination of samarium and europium, after chelation with thenoyltrifluoroacetone, was discussed (42). The fluorescence of rare earth chelates has also been used in the zone location of rare earths on a paper chromatogram (45).

### Computer Techniques in Spectral Analysis

In recent years, computer techniques have been adapted to an increasing number of analytical applications, and they are known to greatly simplify data interpretation in a number of situations (74). In infrared analysis, computer storage and searching procedures are being employed to rapidly sort and match spectra (80). In both mass spectrometry and nuclear magnetic resonance spectroscopy, computer methods facilitate data reduction and lead to faster and more accurate analyses of complex mixtures (54). In many areas of spectral analysis, least squares calculations and curve-fitting procedures, performed rapidly by computer, allow the resolution of complex spectra and may ultimately permit a complete description of a spectrum in terms of band position, band intensity, band width, and a shape factor (13, 19, 79, 81). Computer applications in spectral analysis are presently being extended even further, as computer facilities become more readily available and as the potentialities of computer data processing are demonstrated.

In addition to the rather recent use of computers in

data interpretation and correlation, their application in simplifying routine calculations is well-known. In the field of fluorescence analysis, computer programs have been designed to perform the calculations necessary in the correction of experimental data (27, 28).

## CHAPTER III

### EXPERIMENTAL

#### Preparation of Rare Earth Chelates

##### Reagents

Rare earth oxides and metals (99%) were obtained from Lunex Company, Pleasant Valley, Iowa, and rare earth chlorides (99.9%) from K and K Laboratories, Inc., Plainview, New York. Dibenzoylmethane (1,3-diphenyl-1,3-propanedione, Eastman White Label) and benzoylacetone (1-phenyl-1,3-butanedione, Eastman White Label) were recrystallized from methanol. Thenoyltrifluoroacetone (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, Eastman White Label) was used without further purification. Piperidine (Matheson Coleman and Bell practical grade) was purified by distillation for some of the early preparations; it was later used successfully without purification. Absolute ethanol (U.S.I. reagent quality) was used directly.

##### Procedure

A number of chelate preparations were attempted during this investigation. The first synthesis of the benzoyl-acetonates (B) of gadolinium, dysprosium and samarium followed the procedure of Whan and Crosby (89). Rare earth chlorides ( $\text{MCl}_3 \cdot 6\text{H}_2\text{O}$ ) were prepared from the metals or oxides

by dissolving the samples in concentrated hydrochloric acid and slowly evaporating to dryness. In some cases, a small remaining amount of oxide was removed by filtration or centrifugation when the chloride was dissolved in water or alcohol. An aqueous rare earth chloride solution was added to an aqueous solution of sodium benzoylacetonate (prepared by refluxing sodium and benzoylacetone in a 1:1 ratio in dried xylene for eight hours). A flocculent white precipitate formed immediately. When dried, the product corresponded roughly to the formula  $MB_3 \cdot 2H_2O$ . However, the melting points of the three chelates prepared in this manner were inconsistent with those reported by Whan and Crosby. A second procedure, described by Sacconi and Ercoli (70), involved the combination of the rare earth chloride and benzoylacetone in ammonia-saturated ethanol. The results of this preparation were also inconclusive.

While the above procedures were being studied, early reports of success with a "piperidine method" for the preparation of rare earth chelates appeared in the literature (9, 15, 71). The preparation adopted followed the procedure of Bhaumik et. al. (9). A warm solution of 3 mmoles of the rare earth chloride in 15 ml absolute ethanol was added to a warm solution of 12 mmoles of the chelating agent and 12 mmoles of piperidine in 25 ml absolute ethanol. After initial stirring, the reaction mixture was allowed to cool to room temperature. Following slow crystallization (2-4 days), the product was filtered, washed with cold absolute ethanol, and dried for several days in a vacuum desiccator.

The chelates obtained by this procedure were shown to correspond to the empirical formula  $ML_4 \cdot HP$ , where M = rare earth ion, L = ligand, and P = piperidine. Impure products of uncertain composition were obtained when attempts were made to hasten the preparation by heating the reaction mixture or by oven-drying.

Rare earth analyses were carried out gravimetrically. A 60-100 mg sample of the chelate was ignited slowly in an open crucible to a black carbonaceous ash. It was then vigorously heated for approximately 45 minutes to form the white metal oxide. Although this procedure is not applicable to terbium and praseodymium, since they form mixed oxides, reproducible results were obtained for the remaining rare earths, which form trioxides.

Elemental analyses for C, H, N and S were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and F and M Scientific Corporation, Avondale, Pennsylvania.

Chelates of benzoylacetone (B), dibenzoylmethane (D), and thenoyltrifluoroacetone (TTA) were prepared and analyzed by the above methods. Their characteristics, and the analytical results, are shown in Table I. Due to the marked chemical similarity of the rare earths, and the similar properties of the chelates, elemental analysis of each compound was unnecessary.

The effect of the well-known "lanthanide contraction" was noted in the tendency of the smaller (i.e. higher atomic number) rare earths, such as thulium, ytterbium and lutetium, to form crystalline chelates more rapidly than the larger

TABLE I

## Properties of Rare Earth Chelates

Chelate and color <sup>(1)</sup>	m.p. °C (uncorr.)	%C <sup>(2)</sup>		%H		%N		%S		%M	
		calc	found	calc	found	calc	found	calc	found	calc	found
PrB <sup>(3)</sup> y-g	132-133	61.8	61.9	5.5	5.6	1.6	1.7				
NdB y-v	132-133	61.7	61.5	5.5	5.5	1.6	1.7			16.5	17.1
SmB y	126-130										
EuB y-o	128-130										
GdB y	126-128	60.5	60.2	5.6	5.2	1.7	1.5			17.7	17.5
TbB y	119-121										
DyB y	125-127										
ErB p	109-110										
PrD <sup>(4)</sup> y-g	171-175	69.6	68.1	5.0	5.2	1.3	1.6				
NdD <sup>(4)</sup> g-v	190-195	69.4	68.4	5.0	5.2	1.3	1.7			12.8	12.3
SmD y	201-203										
EuD y	204-207										
GdD y	210-214	68.8	68.6	5.0	5.1	1.2	1.3			13.8	13.8
TbD y	216-218										
DyD y	230-233										
ErD p-o	247-249										

TABLE I (continued)

Chelate and color(1)	m.p. °C (uncorr.)	%C		%H		%N		%S		%M	
		calc <sup>(2)</sup>	found	calc	found	calc	found	calc	found	calc	found
PrTTA y-g	138-140										
NdTTA (v)	139-141										
SmTTA (y)	139-142	39.6	39.4	2.5	2.5	1.3	1.2	11.4	11.6	13.4	14.6
EuTTA y	140-143	39.5	39.2	2.6	2.4	1.3	1.2				
GdTTA y	141-143										
TbTTA y	141-143										
DyTTA y	143-145										
HoTTA y	144-146										
ErTTA p	145-147										
TmTTA (y-g)	147-149										
YbTTA y	145-148										
LuTTA c	149-151										

(1) y-yellow, g-green, r-red, v-violet, o-orange, p-pink, y-bright yellow, ( )-pale, c-colorless

(2) Calculated formulas are based on structures as  $ML_{2.4} \cdot H$  pip

(3) B = Benzoylacetone  
D = Dibenzoylmethide  
TTA = Thenoyltrifluoroacetone

(4) PrD and NdD were slightly wet when analyzed (contained approximately 1 mole  $H_2O$  per mole chelate)



ions. With bulky ligands such as dibenzoylmethane and thenoyltrifluoroacetone, the increase in the chelate's melting point with an increase in atomic number may also be an indication of the enhanced stability of the chelates with smaller ions.

Several Eastman White Label tris-thenoyltrifluoroacetate chelates (of Sm, Eu, Gd, Tb and Yb) were obtained for possible use as fluorescence standards. However, they proved unsatisfactory for the present study, due to the presence of impurities. The samarium chelate appeared to contain excess Sm (calc 18.4%, found 20.6%), apparently as  $\text{Sm}_2\text{O}_3$ , which was insoluble in the solvents used. The chelates of Gd, Tb and Yb were shown, by fluorescence studies, to contain traces of europium.

#### Description and Characteristics of Spectrofluorometer

The major equipment used in this investigation consisted of a Farrand spectrofluorometer and its attachments. This instrument, as shown in Figures 2 and 3, is a single-beam, dual monochromator spectrofluorometer, arranged for right-angle illumination. The basic instrument has been discussed in two recent publications (50, 58).

The light source is a Hanovia 150 watt D.C. high pressure xenon arc lamp, focused on the entrance slit by an off-axis ellipsoidal reflector. The lamp was focused during operation by the adjustment of screws controlling its vertical alignment. The lamp power supply is a standard Sola unit, providing a momentary potential between 25,000

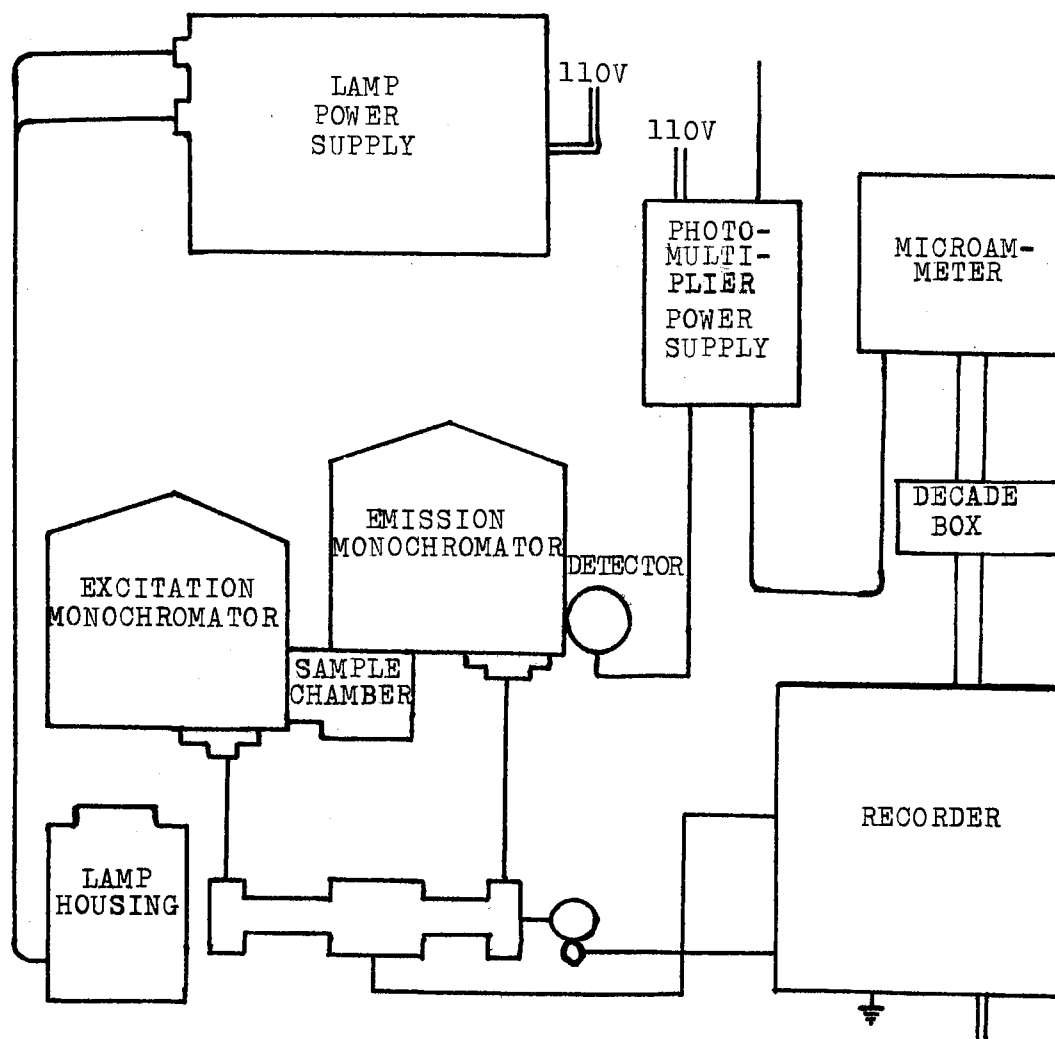


Figure 2. Block and Wiring Diagram for Spectrofluorometer (29)

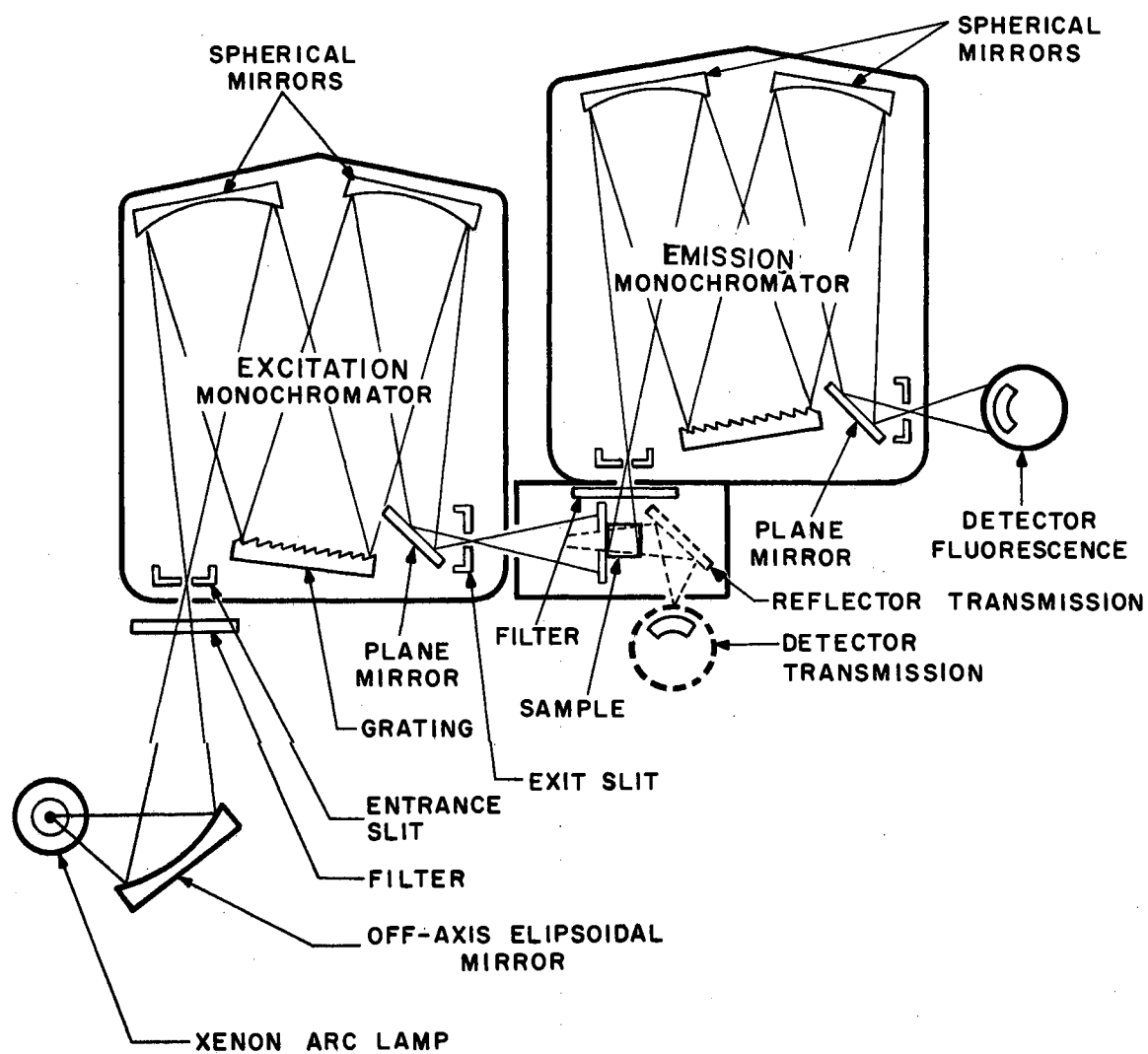


Figure 3. Optical Diagram for Spectrofluorometer (29)

and 40,000 volts to start the lamp, and operating normally at around 20 volts.

The replica gratings in both the excitation and the emission monochromators were taken from Farrand masters with 14,400 lines per inch. The monochromators operate at  $F/3.5$  and have a focal length of 160 mm and a dispersion of 11  $m\mu/mm$  in the first order. Both monochromators have a wavelength range of 220-700  $m\mu$ , read on linearly calibrated dials. Filters may be inserted at either monochromator entrance to block any undesired radiation.

Manually interchangeable slits are available with equivalent bandwidths of 1, 5, 10 and 20  $m\mu$  (widths approximately 0.1, 0.5, 1.0 and 2.0 mm). In general, doubling the width of any one slit doubles the signal observed. In order to obtain maximum resolution, the narrowest slits possible should be used. In the present work, 20  $m\mu$  slits were used in the excitation monochromator and 5  $m\mu$  slits in the emission monochromator, unless otherwise noted. This arrangement provides approximately the same signal as would four 10  $m\mu$  slits, but allows more precise observation of the emission spectrum. The use of smaller excitation slits is desirable, but not essential in the rare earth chelate systems, since the absorption bands are fairly broad.

The wavelength calibration of the monochromator dials was checked periodically with a General Electric G4T4-1 mercury lamp. When the lamp is placed in the sample compartment, with the xenon lamp off, the mercury line peaks may be observed. Since these peaks are extremely sharp, the emission monochrom-

ator dial may be set to correspond accurately with the expected peak wavelength. The excitation monochromator dial was then checked by comparison, using the xenon lamp. A cell filled with water provides a scattering peak, which should have its maximum when the wavelength settings are the same on both monochromators. Over the entire range of each monochromator, wavelength accuracy was maintained at  $\pm 1 \text{ m}\mu$  or better.

In normal fluorescence analysis, the excitation monochromator dial is set at the wavelength desired, and the emission monochromator is used to scan over the spectral range. If the excitation spectrum is desired, the reverse procedure is followed. The gear assembly shown in Figure 2 couples the recorder chart drive with the monochromator shafts, in a 1:3 gear ratio, to provide automatic scanning. The gear box includes a selector shaft which allows rotation of either grating, and microswitches connected to the chart drive which automatically stop the scan at the end of a spectrum. The entire spectrum,  $480 \text{ m}\mu$  or 11.2 inches on the chart, may be scanned at speeds varying from 0.75 inches per hour to 12 inches per minute. A scanning rate of 1.5 inches per minute was normally employed.

A constant temperature sample chamber was used, with cooling provided by water circulated from an ice-water bath to maintain an operating temperature of approximately  $0^{\circ}\text{C}$ . The sample, contained in a 1 cm fused silica cell, was placed in contact with an aluminum block through which the coolant circulates. A stream of nitrogen, dried by passage

through a tube of Linde type 4A, 1/16" molecular sieve, was employed to purge the sample compartment, thereby preventing fogging of the cell windows.

Manufacturer's data indicates that the photomultiplier tube (1P28) detector has maximum spectral response at 340 m $\mu$  and provides current amplification of  $1.25 \times 10^6$ . The photomultiplier power supply may be adjusted to furnish between 400 and 900 volts and was operated at 880 volts. Since a reproducible voltage level is essential when a calibrated phototube is used, connections were made to allow monitoring of the power supply output with a Heathkit Model EUW-24 VTVM. Operation of the photomultiplier tube at lower voltages (600-700 V) might serve to reduce noise levels.

Amplification of the low signals obtained was provided by a modified RCA Ultrasensitive DC Microammeter, connected to the photomultiplier power supply by shielded cable. Six ranges allow measurements of currents from 0.0002 to 1000 microamperes. Although values may be read directly from the meter, for automatic operation a Texas Instruments Model PWS ServoRiter recorder with a 10.0 mv scale and 0.5 sec. response time was employed. A Heathkit Model EUW-30 decade resistance box connected in parallel between the Microammeter and the recorder allowed additional selectivity in signal attenuation. The servo recorder provides a high signal-to-noise ratio, largely due to its enclosure in an electrostatic shield connected to a guard terminal. It was found that, with the circuit used, the best operation was attained, with lowest noise and interference levels, if the

guard and ground terminals were both connected to a direct earth ground. The photomultiplier power supply chassis and the shields on all cables were also connected to the earth ground.

As was mentioned above, the sensitivity of the spectrofluorometer could be varied by the microammeter range selector and/or the decade resistance box. Chart readings are then multiplied by the range selected (.01, .1, 1, 10, 100, 1000) and by the reciprocal of the resistance set on the decade box. Since this resistance is variable from zero to 100 K ohms, a wide range of sensitivity settings is available. However, at settings above 1000  $\Omega$  (when the range setting is 0.1) noise levels become excessively high. Since the meter reads 100  $\mu$ a full scale, and the recorder 10 mv, a setting of 100  $\Omega$  should lead to identical recorder and meter readings. In practice, a resistance of 94  $\Omega$  produced this equivalence. Consequently, the resistance settings used were between 94 and 940  $\Omega$ , taking even multiples for convenience in calculations. Using the mercury calibration lamp as a relatively stable source, it was found that as the sensitivity was varied, the response was within 1-3% of linearity.

Wavelength index marks could be inserted in the recorded spectrum by switching in a 15  $\Omega$  resistor across the recorder input. Although the wavelengths were determined visually from the rotating monochromator dial, precision and accuracy for the technique were quite acceptable. Marks at 10 mm intervals gave an average of  $(5.9 \pm 0.1)$  mm on the chart per

10 m $\mu$ . When the mercury lamp was used as a source and a mark was made at each peak wavelength, the average deviation between the mark and the peak was 0.6 m $\mu$ .

#### Instrumental Sensitivity

Quinine sulfate in dilute (0.1N) sulfuric acid is frequently used as a fluorescence standard. Its quantum efficiency of fluorescence has been determined (53) and its spectrum has been well-characterized. In addition, stable solutions may readily be prepared. The sensitivity of a spectrofluorometer may therefore be evaluated by determining either the concentration of quinine sulfate required to produce full-scale deflection, or the minimum detectable concentration (in  $\mu\text{g/ml}$  or ppm).

Sensitivity data is shown in Table II for the instrument described above. Quinine sulfate (Matheson Coleman and Bell) was used without further purification. The solvent (0.1N  $\text{H}_2\text{SO}_4$ ) was prepared by dilution of 2.00 N standard volumetric solution (W. H. Curtin and Company).

For the trials summarized in Table II, the slits were all 10 m $\mu$  in equivalent bandwidth, and a 3-73 filter was used to transmit only wavelengths above 400 m $\mu$ . Peak-to-peak noise was approximately 1 unit. The quinine sulfate samples were excited at 350 m $\mu$ .

Later trials, with fresh quinine sulfate solutions, 5 m $\mu$  slits, and no filter, confirmed that a concentration of  $10^{-7}$   $\mu\text{g/ml}$  was barely detectable and that a concentration of  $10^{-5}$   $\mu\text{g/ml}$  could readily be measured.



TABLE II  
Sensitivity of Spectrofluorometer

quinine sulfate conc. ( $\mu\text{g/ml}$ )	fluorescent intensity at 450 m $\mu$ above blank (arbitrary units on scale of 100)
$10^{-2}$	off scale
$10^{-3}$	24
$10^{-4}$	11
$10^{-5}$	7
$10^{-6}$	4
$10^{-7}$	2

This sensitivity compares very favorably with reported values of 0.005  $\mu\text{g/ml}$  (83), 0.01  $\mu\text{g/ml}$  (with 0.2 mm slits) (67), and  $10^{-4}$   $\mu\text{g/ml}$  (with a Farrand spectrofluorometer) (58).

#### Calibration of Spectrofluorometer

##### Theory

During recent years, as the methods of spectrofluorometric analysis have become more widely used, several writers (27, 63) have realized the need for standardization of published data. The spectrum obtained from a single-beam instrument, such as the Farrand unit, is actually only an "apparent" emission spectrum. It is dependent upon the particular optics used, the source output, and the response

characteristics of the detector. Although this spectrum may be very useful for routine analyses within a laboratory, it may bear very little resemblance to the "true" spectrum. Therefore, for any fundamental studies, or for the calculation of quantum efficiencies, it is necessary to correct the experimental data. Corrected results should be expressed in relative quanta per frequency (or wavelength) interval. The use of frequency units (reciprocal microns) is preferred in order to avoid the distortion of the fluorescence spectrum that occurs when wavelength units are employed. Intensities expressed in quanta, rather than energy, allow the calculation of quantum efficiencies from the integrated area under a peak. The spectral corrections, and the use of consistent units, allow the comparison of experimental results with published data, since the effects of varying experimental factors are virtually eliminated.

The calibration and correction procedure involves two major steps: (1) the determination of the response vs. frequency characteristics of the photomultiplier detector and (2) the subsequent measurement of the energy output of the source lamp as a function of frequency. The methods used also provide compensation for non-linear monochromator dispersion and light losses within the optical system.

In the first step, a lamp with a known spectral energy distribution is placed in the sample compartment, and the spectrum obtained is used to calculate a set of correction factors at selected frequency intervals. Several different light sources may be used, the choice depending on the

spectral region of interest. In the present work, a tungsten filament lamp was employed, and the spectral energy calculated as described below.

It is known that for a black-body source, the spectral radiance may be calculated by the Planck equation (38):

$$N_{\lambda}(T) = \frac{C_1 \lambda^{-5}}{e^{C_2/\lambda T} - 1}$$

where  $N_{\lambda}(T)$  = spectral radiance (watts/ $\mu^2/\mu$ )

$$C_1 = 3.7412 \times 10^{-4} \text{ w} - \mu^2$$

$$C_2 = 1.4385 \times 10^4 \mu - ^\circ\text{K}$$

$\lambda$  = wavelength ( $\mu$ )

$T$  = temperature ( $^\circ\text{K}$ )

For a non-black-body, (emissivity ( $\epsilon$ ) less than unity) contained in a lamp envelope with transmittivity ( $\tau$ ) less than unity, the equation is modified as follows (33):

$$N_{\lambda}(T) = \frac{\epsilon_{\lambda} \tau_{\lambda} C_1 \lambda^{-5}}{e^{C_2/\lambda T} - 1}$$

At temperatures less than  $3000^\circ \text{K}$ ,

$$e^{C_2/\lambda T} \gg 1$$

therefore

$$E = N_{\lambda}(T) = \frac{\epsilon_{\lambda} \tau_{\lambda} C_1 \lambda^{-5}}{e^{C_2/\lambda T}}$$

where  $E$  is then the energy flux per unit wavelength interval (in  $\text{w} - \mu^{-3}$  or energy  $\text{sec}^{-1} \text{ cm}^{-2} \text{ m}\mu^{-1}$ ).

In order to express the results in terms of quanta per unit frequency interval, the above expression must be multiplied by  $\lambda^3$  to give:

$$Q = \frac{\epsilon_{\lambda} \tau_{\lambda} C_1 \lambda^{-2}}{e C_2 / \lambda T} \quad \text{quanta sec}^{-1} \text{ cm}^{-2} (\mu^{-1})^{-1}.$$

When  $Q$  is known for the source and  $R$  is the observed (recorded) response at a given frequency, then the correction factor  $K$  may be found in quanta per unit frequency interval, since:

$$K = \frac{Q}{R}.$$

Observed spectra are then converted to "true" spectra by multiplying the recorded intensities at selected frequency intervals by the corresponding correction factors.

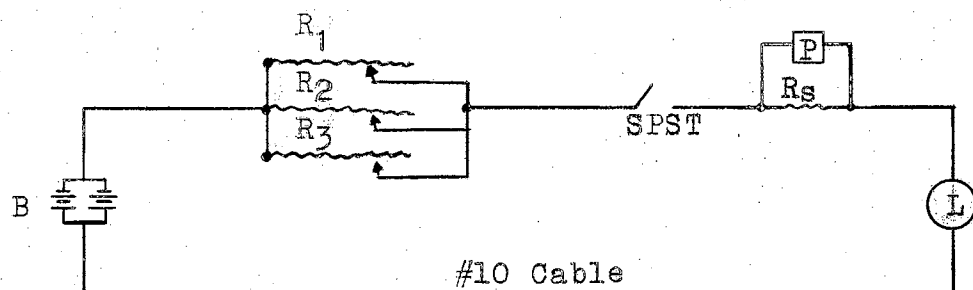
Since the instruments used in this investigation gave a spectrum linear in wavelength, data points were recorded, and correction factors determined, at even wavelength intervals. The values obtained were converted to units of frequency at a later stage in the calculations.

The second step, the determination of the output of the xenon source lamp, is necessary if varying excitation frequencies are to be used. To obtain relative values for the spectral output of the lamp, radiation from the source may be scattered or reflected by a neutral material and detected by the phototube. Multiplication of observed intensities by the correction factors obtained earlier provides

data for the emitted spectral energy distribution.

#### Procedure

For the calibration of the photomultiplier tube, a standard lamp was positioned directly in front of the entrance slit of the emission monochromator and was controlled by the circuit shown schematically in Figure 4.



$$R_1 = 7.5 \Omega, 8.5 \text{ amp}$$

$$R_2 = 6.2 \Omega, 8.2 \text{ amp}$$

$$R_3 = 2 \Omega, 13 \text{ amp}$$

Figure 4. Calibration Apparatus

The power source (B) was a Hampden Engineering, East Longmeadow, Mass., portable Ni-Cd battery bank, connected to supply 12 volts and enabling stable currents to be obtained. The slide wire resistors were adjusted to vary the current from 8 to 18 amperes. Currents were determined by measuring the potential drop across a Leeds and Northrup  $0.001 \Omega$ , 300 amp standard resistor ( $R_s$ ) with a Leeds and Northrup K3 potentiometer (P). The light source (L) was a General Electric ribbon filament lamp (6V-18A-T10), calibrated in terms of brightness temperature versus current.

The experimental procedures used for calibration of the detector differ from normal fluorescence procedures

only in the use of a standard lamp instead of a sample excited by a xenon lamp. Since the slits available were relatively large (5 mμ slits masked to provide an approximate 3 mμ bandwidth) the exact lamp position was not critical. It was placed with the center of the vertical strip filament in front of the slit, and adjusted slightly to yield maximum intensity. Attempts were made to avoid reflections from the lamp envelope.

When the lamp was initially turned on, a 30-40 minute warm-up period was allowed. Subsequently, times of approximately 10 minutes were allowed for stabilization when the current was changed. Several spectra were recorded from 250 to 700 mμ, for each of eight different current settings (between 14 and 18 amperes).

The neutral reflector required for calibration of the xenon lamp was prepared by igniting magnesium ribbon and depositing MgO on the diagonal face of an aluminum right triangular prism. With this reflector placed in the sample compartment, reflected radiation from the xenon lamp was observed at regular wavelength intervals.

#### Calculations and Results

The brightness temperature ( $T_B$ ) of the tungsten lamp was calculated from the measured current and the calibration data supplied by General Electric Company. The calibration data points have been plotted in Figure 5A. It may be noted that the calibration graph is a straight line above 14 amperes. Using the numerical calibration data, this line

was found to have a slope of  $80.2 \pm .6$  and an intercept of  $835 \pm 3$ .

The filament temperature ( $T$ ) was then determined from a modified form of the equation given earlier for spectral radiance. Since the brightness temperature,  $T_B$ , is defined as the temperature at which an ideal black body emits light of the same wavelength,  $\lambda$ , as the non-black body sample at temperature  $T$ , we may write:

$$\frac{C_1 \lambda^{-5}}{e^{C_2/\lambda T_B}} = \frac{\epsilon_{\lambda} \tau_{\lambda} C_1 \lambda^{-5}}{e^{C_2/\lambda T}}$$

where all terms are as previously defined.

Therefore,

$$T = \frac{C_2}{\lambda [\ln(\epsilon_{\lambda} \tau_{\lambda}) + \frac{C_2}{\lambda T_B}]}$$

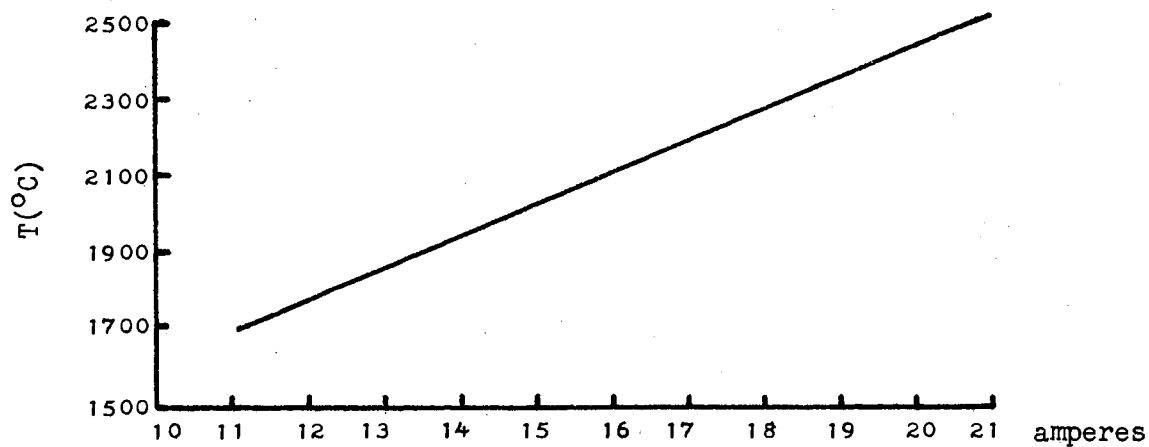
The wavelength ( $0.655\mu$ ) was that used in the lamp calibration.

The strip temperatures calculated from this equation were also checked against tabulated conversion data (40).

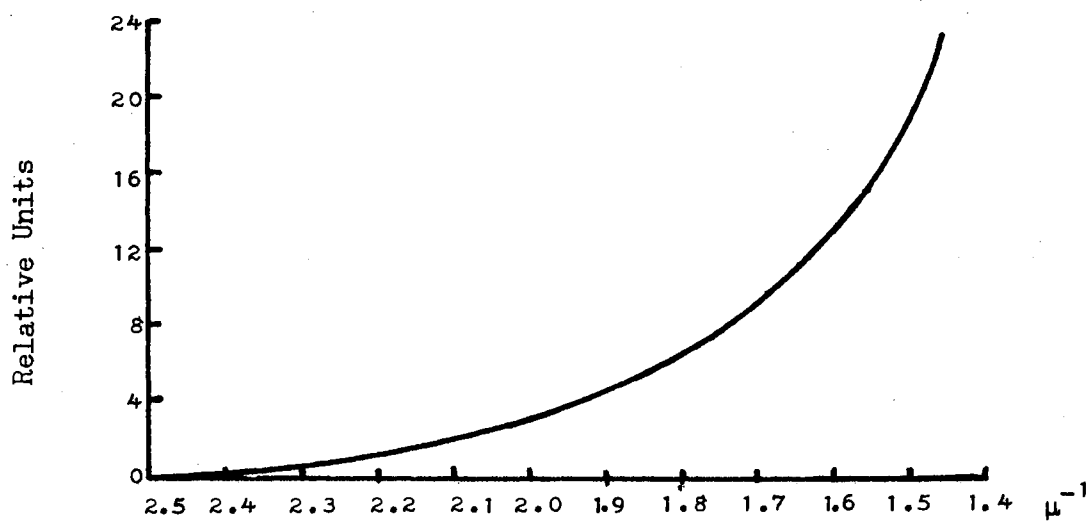
The spectral energy distribution of the lamp was then calculated by the equation shown earlier:

$$Q = \frac{\epsilon_{\lambda} \tau_{\lambda} C_1 \lambda^{-2}}{e^{C_2/\lambda T}}$$

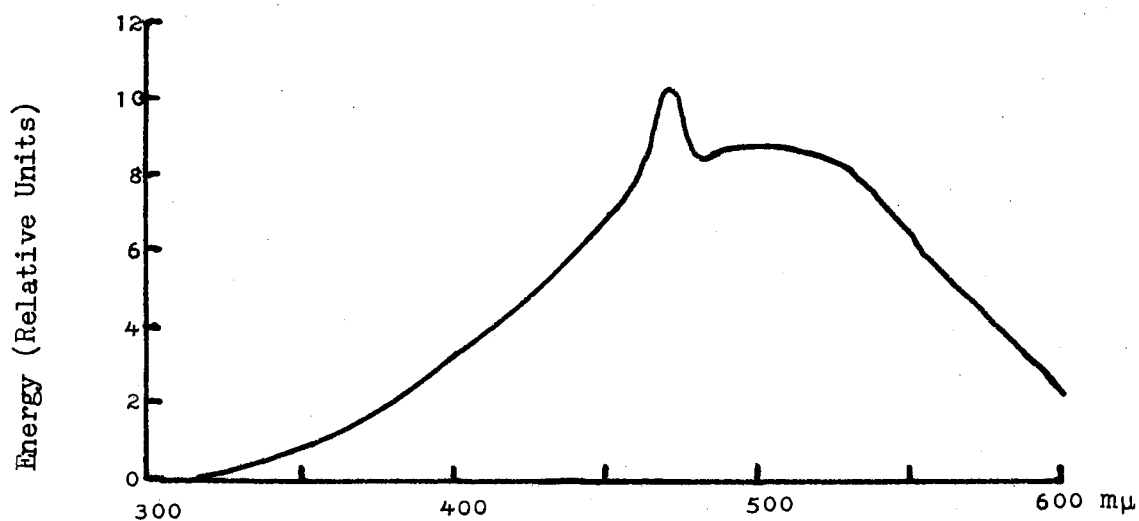
Literature values for the emissivity ( $\epsilon_{\lambda}$ ) of tungsten



A. Lamp Brightness Temperature versus Current



B. CFACT versus Frequency



C. Xenon Lamp Output versus Wavelength

Figure 5. Calibration and Results of Correction Procedures



were employed (26). Although the emissivity term is often neglected in this type of calculation, its value does change by more than 8% over the temperature range used ( $1800^{\circ}$  to  $2300^{\circ}\text{C}$ ), so that it appears to be a significant factor. The emissivity for a particular tungsten ribbon may deviate slightly from the reported values, but these small variations are negligible except in precise "absolute" measurements.

The transmittivity of the lamp envelope (two thickness) was measured with a Beckman DK-1 spectrophotometer, and the value for one thickness calculated from Beer's law. The results indicated a sharp drop in transmittivity near  $340\text{ m}\mu$ , corresponding to literature data for pyrex (2).

A computer program (Appendix I) was written for the calculation of T and Q for a total of fourteen sets of data (41 points per set) at eight different values of T. Six sets of data were later rejected; the first two because the lamp calibration graph was not linear in the region used, four later sets because wider slits of unknown size had been employed. The correction factor with respect to frequency (CFACT) was then calculated at  $10\text{ m}\mu$  intervals by dividing Q by the observed response (R). CFACT was found in relative units ( $\text{quanta sec}^{-1}\text{cm}^{-2}(\mu^{-1})^{-1}$ ). The factor expressed in energy with respect to wavelength (CORRL) is then  $\text{CFACT} \times \lambda^{-3}$  in relative units ( $\text{energy sec}^{-1}\text{cm}^{-2}\text{m}\mu^{-1}$ ). Multiplication by CFACT therefore converts the observed intensity to true relative quanta per unit frequency interval; multiplication by CORRL converts it to true relative energy per unit wavelength interval.

The correction factors used in treating later results are shown graphically in Figure 5B and are listed in Table III and Table IV. A sample calculation, for one temperature value, is listed in Appendix II. All terms are as defined in the correction program given in Appendix I. The points at even 10  $m\mu$  intervals are the average of eight sets of calculated values; the intermediate points were obtained by interpolation.

Values for the relative energy output (energy  $\text{sec}^{-1} \text{cm}^{-2} m\mu^{-1}$ ) of the xenon lamp were calculated by multiplying the intensities observed at 10  $m\mu$  intervals by the appropriate correction factors (CORRL). The results shown in the spectral energy distribution graph (Figure 5C) and in Table III were determined from the average of three separate trials.

### Fluorescence Studies

#### Solvent

The choice of an appropriate solvent is quite critical in an investigation of this nature, due to the sensitivity of the techniques used. The solvent may adversely affect the experimental results in two ways: (1) by interaction with the rare earth chelate and (2) by containing impurities which may produce interfering peaks. Alcoholic solvents have frequently been used in studies of the laser emission of rare earth chelates, but the emission intensity of the chelate peaks is relatively low. It has been postulated (77) that extensive dissociation of the chelate may occur in alcoholic

TABLE III

CORRECTION FACTORS FROM .300 TO .700 MICRONS

WAVELENGTH MICRONS	FREQUENCY 1/MICRONS	CFACT	CORRL	1/XE FACTOR
.300	3.333	0.005	0.017	0.021
.310	3.225	0.010	0.034	0.061
.320	3.125	0.019	0.057	0.135
.330	3.030	0.030	0.084	0.245
.340	2.941	0.045	0.116	0.415
.350	2.857	0.066	0.154	0.650
.360	2.777	0.094	0.201	0.951
.370	2.702	0.131	0.259	1.365
.380	2.631	0.278	0.324	1.863
.390	2.564	0.238	0.402	2.492
.400	2.500	0.312	0.488	3.235
.410	2.439	0.405	0.588	3.681
.420	2.380	0.515	0.695	4.365
.430	2.325	0.651	0.818	5.072
.440	2.272	0.808	0.949	5.912
.450	2.222	0.996	1.093	6.678
.460	2.173	1.209	1.242	7.663
.470	2.127	1.462	1.408	10.222
.480	2.083	1.749	1.582	8.400
.490	2.040	2.078	1.767	8.605
.500	2.000	2.450	1.960	8.722
.510	1.960	2.867	2.161	8.730
.520	1.923	3.332	2.369	8.694
.530	1.886	3.864	2.595	8.304
.540	1.851	4.466	2.836	7.430
.550	1.818	5.158	3.099	6.260
.560	1.785	5.935	3.379	5.575
.570	1.754	6.763	3.651	4.929
.580	1.724	7.661	3.926	4.162
.590	1.694	8.675	4.224	3.295
.600	1.666	9.866	4.569	2.056
.610	1.639	11.093	4.889	
.620	1.612	12.358	5.187	
.630	1.587	13.619	5.448	
.640	1.562	14.975	5.714	
.650	1.538	16.280	5.980	
.660	1.515	17.866	6.216	
.670	1.492	19.416	4.689	
.680	1.470	21.098	6.711	
.690	1.449	22.732	6.921	
.700	1.428	24.480	7.139	

TABLE IV

CORRECTION FACTORS FROM .4750 TO .6750 MICRONS

WAVELENGTH MICRONS	FREQUENCY 1/MICRONS	CFACT	WAVELENGTH MICRONS	FREQUENCY 1/MICRONS	CFACT
.4750	2.105	1.606	.5750	1.739	7.212
.4775	2.094	1.678	.5775	1.732	7.437
.4800	2.083	1.749	.5800	1.724	7.661
.4825	2.073	1.832	.5825	1.717	7.915
.4850	2.062	1.914	.5850	1.709	8.168
.4875	2.051	1.996	.5875	1.702	8.422
.4900	2.041	2.078	.5900	1.695	8.675
.4925	2.030	2.171	.5925	1.688	8.973
.4950	2.020	2.264	.5950	1.681	9.271
.4975	2.010	2.357	.5975	1.674	9.569
.5000	2.000	2.450	.6000	1.667	9.866
.5025	1.990	2.555	.6025	1.660	10.173
.5050	1.980	2.659	.6050	1.653	10.480
.5075	1.970	2.763	.6075	1.646	10.787
.5100	1.961	2.867	.6100	1.639	11.093
.5125	1.951	2.983	.6125	1.633	11.410
.5150	1.942	3.099	.6150	1.626	11.726
.5175	1.932	3.216	.6175	1.619	12.042
.5200	1.923	3.332	.6200	1.613	12.358
.5225	1.914	3.465	.6225	1.606	12.674
.5250	1.905	3.598	.6250	1.600	12.989
.5275	1.896	3.731	.6275	1.594	13.304
.5300	1.887	3.864	.6300	1.587	13.619
.5325	1.878	4.015	.6325	1.581	13.958
.5350	1.869	4.165	.6350	1.575	14.297
.5375	1.860	4.316	.6375	1.569	14.636
.5400	1.852	4.466	.6400	1.563	14.975
.5425	1.843	4.639	.6425	1.556	15.302
.5450	1.835	4.812	.6450	1.550	15.628
.5475	1.826	4.985	.6475	1.544	15.954
.5500	1.818	5.158	.6500	1.538	16.280
.5525	1.810	5.353	.6525	1.533	16.677
.5550	1.802	5.547	.6550	1.527	17.073
.5575	1.794	5.741	.6575	1.521	17.470
.5600	1.786	5.935	.6600	1.515	17.866
.5625	1.778	6.142	.6625	1.509	18.254
.5650	1.770	6.349	.6650	1.504	18.641
.5675	1.762	6.556	.6675	1.498	19.029
.5700	1.754	6.763	.6700	1.493	19.416
.5725	1.747	6.988	.6725	1.487	19.837
			.6750	1.481	20.257

media.

It was observed during this investigation of rare earth chelates, and has been confirmed in the literature (14, 15, 77) that the highest fluorescence intensity, and the greatest stability, may be obtained with solvents such as acetonitrile or dimethylsulfoxide. Other solvents studied, with less satisfactory results, included absolute ethanol, reagent methanol, ethanol-methanol mixtures, acetone and toluene.

After acetonitrile was chosen as the solvent, considerable difficulty was experienced in attaining sufficient purity. The chelate solutions were to be excited near 400 mμ, and analyzed between 475 and 675 mμ. Even spectroquality solvent produced an interfering impurity (<.05 ppb) peak under these conditions. Initially, Baker Analyzed acetonitrile was distilled to yield a solvent with a reasonably level base line in the region of interest. However, it was later found that Mallinckrodt Nanograde (TM) acetonitrile (Lot PGXF) could be used without further purification. The commercially available solvent was therefore employed for all of the spectra reported.

#### Procedure

The solutions desired for spectral analysis were prepared by standard procedures immediately prior to use. Concentrations of all mixtures analyzed are shown in Table VI. All solutions were cooled in an ice-water bath before insertion in the cooled sample chamber.

The thenoyltrifluoroacetate chelate solutions appeared

to be stable, and the fluorescence spectra could be readily duplicated several days after solution preparation. With similar solutions of the benzoylacetate and dibenzoylmethide chelates, however, spectral changes, indicating dissociation of the chelate, were noted within a few hours.

After a satisfactory method had been developed for the fluorescence analyses, it was used consistently and gave reproducible results. This procedure is summarized in the steps indicated below:

- (1) The microammeter and the xenon lamp were turned on and given a 30 minute warm-up period. All other components (detector power supply, VTVM and recorder) were left on continuously during the period of this investigation.
- (2) The detector voltage was checked and set at 880 v.
- (3) The ice-bath was filled and the pump started, to cool the sample compartment. The flow of dry gas was started, to prevent condensation in the cell area.
- (4) The wavelength calibration of the monochromator dials was checked and any necessary adjustments were made.
- (5) The xenon lamp was adjusted to provide maximum illumination, using a cooled solution of 1  $\mu$ g/ml quinine sulfate in 0.1N  $\text{H}_2\text{SO}_4$  as a standard. A microammeter setting of  $\times 1$ , and a resistance of

- 94 ohms was used. The solution was excited at 350 m $\mu$ , and the intensity at 450 m $\mu$  was recorded for later use in the calculations.
- (6) After instrumental adjustments were completed, a "blank" spectrum was recorded with only the solvent present. The attenuation was chosen so as to approximate that to be used for later solutions.
  - (7) The cell was rinsed, first with solvent, then with solution, and filled with the precooled solution. The outside of the cell was carefully wiped to remove excess moisture. After the cell was placed in the sample chamber, a 10 minute equilibration period was allowed.
  - (8) By manual scanning, the excitation frequency giving maximum fluorescence intensity, and the appropriate attenuation were determined. Using these values, the spectrum was recorded from 450 to 700 m $\mu$ , with marks at 50 m $\mu$  intervals.
  - (9) A duplicate spectrum was obtained, if desired, after which steps (7) and (8) were repeated for fresh solutions. The peak intensity of a quinine sulfate solution was recorded periodically between trials in order to provide a standard in the calculations.

The observed spectra then had to be converted to the digital form necessary for computer analysis. Since a digital read-out system was not available, this conversion was

performed manually. Using a cross-hatched template and a lighted chart table, intensities above an interpolated base line were read at 2.5 m $\mu$  intervals from 475 to 675 m $\mu$ .

#### Determination of Spectra of Solutions

Preliminary investigations on the rare earth chelate solutions were directed toward establishing which chelates fluoresced with sufficient intensity to be useful in the study of mixtures. For this purpose,  $1 \times 10^{-3}$  M solutions of all of the available chelates were prepared. The excitation wavelength providing maximum fluorescence intensity was determined for each, and the relative fluorescence intensities compared. The peak positions, excitation wavelengths and approximate relative intensities for the chelates are shown in Tables VA and VB.

On the basis of the relative fluorescence intensities observed for the chelates, a systematic study of pure rare earths and mixtures was initiated. It was first noted that, although fluorescence could be observed for  $1 \times 10^{-3}$  M PrD, PrTTA, HoTTA and ErTTA solutions, and weak phosphorescence for LuTTA, the emission intensities for these chelates were too low for practical determinations with the present instrument. At higher concentrations, intensities for these chelates were still small, due to self-quenching effects. It therefore appeared that the presence of praseodymium, holmium, erbium or lutetium in a mixture would have little deleterious effect in qualitative analyses. Thus these four rare earths were not considered further in the present study.



TABLE VA  
Fluorescence Properties of Rare Earth Chelates  
Peak Positions (mμ) (1)

ligand	excitation wavelength (mμ)	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
D	405	594	nd	530(w)	580	nd	nd	nd	-	nd	-	-	-
		608(s)		563(s)	592								
				600	613(s)								
				604(w)									
				640(w)									
				648									
B	385	592	nd	532(w)	579	nd	490	nd	-	nd	-	-	-
		608(s)		564(s)	592		545(s)						
				600	614(s)		580(w)						
				605(w)									
				640(w)									
				648									
TTA	390	594	nd	533(w)	580(w)	phos.	490	nd	650	520(w)	nd	nd	phos.
		606(s)		562(s)	593	peak	545(s)			525(w)			peak
				598	613(s)	510	580(w)			535(w)			510
				604(w)						605(s)			
				645									

(1) s = strongest peak, w = weak peak; broad band or shoulder; wavelength approximate

TABLE VB  
Fluorescence Properties of Rare Earth Chelates  
Relative Intensities for Strongest Peaks (1)

ligand	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
D	0.02	-	0.3	30.	-	-	-	-	-	-	-	-
B	0.04	-	1.0	225	-	0.5	-	-	-	-	-	-
TTA	0.2	-	120.	2000.	0.75	1.2	-	0.004	0.05	-	-	0.02

(1) Intensity of SmB assigned as one

Other rare earths excluded, because no fluorescence was observed, included the chelates of neodymium and dysprosium, the benzoylacetate chelates of gadolinium, erbium and terbium, and the TTA chelates of thulium and ytterbium.

The emission observed for GdTTA and LuTTA is phosphorescence, rather than fluorescence. The exceptionally strong phosphorescence band is characteristic of chelates of Gd, La and Lu (with filled or half-filled 4f shells) and is most intense for gadolinium.

The remaining study has been concentrated on the following chelates: SmB and EuB; SmD, EuD and TbD; SmTTA, EuTTA, GdTTA and TbTTA. For these rare earths, the probable transition assignments have been given (using LS, or Russell-Saunders, notation) as follows:

Sm(34)	$^4F_{5/2} \rightarrow ^6H_{5/2}$	(560 mμ)
	$^4F_{5/2} \rightarrow ^6H_{7/2}$	(600 mμ)
	$^4F_{5/2} \rightarrow ^6H_{9/2}$	(650 mμ)
Eu(34,52)	$^5D_0 \rightarrow ^7F_0$	(580 mμ)
	$^5D_0 \rightarrow ^7F_1$	(592 mμ)
	$^5D_0 \rightarrow ^7F_2$	(613 mμ)
Tb(32,34)	$^5D_4 \rightarrow ^7F_6$	(490 mμ)
	$^5D_4 \rightarrow ^7F_5$	(545 mμ)
	$^5D_4 \rightarrow ^7F_4$	(580 mμ)
	$^5D_4 \rightarrow ^7F_3$	(620 mμ).

The final spectra of the chelates of interest were obtained by the methods described previously. From the data on  $1 \times 10^{-3}$  M solutions, concentrations were calculated which would provide nearly equal intensities (at the same attenuation) for each member of a set with a given ligand. The standard spectra for the pure rare earth chelates were recorded under carefully controlled conditions. Between three and six spectra were determined for each of the chelates. The digital values read from the recorded spectra were then averaged to be used as standards. The major source of error in the procedure was the difficulty in determining accurate numerical intensities at intervals of 2.5 m $\mu$  which led to an average deviation at each point of nearly 7%. The measured peak wavelengths, however, were reproducible within 1 m $\mu$ .

For each ligand, mixtures containing all possible combinations of fluorescing chelates were analyzed. Since this investigation did not include studies of varying concentration or quenching effects, the concentrations used were designed to give well-defined peaks for all components. Duplicate analyses were run for most of the mixtures, and the concentrations or the attenuation was varied slightly between trials for some of the mixtures. The spectra were converted to digital form for correction and analysis by the computer program.

## CHAPTER IV

### COMPUTER ANALYSIS AND RESULTS

Initial spectral examinations, performed visually, indicated that qualitative analyses should be feasible. As noted earlier, only four of the rare earths (Sm, Eu, Gd, and Tb) provided sufficiently intense emission spectra for use in the present study. It was found that the fluorescence bands of Sm, Eu and Tb were well-defined, and sufficiently well separated to allow definite identification of the element(s) present. In addition, the broad phosphorescence band of Gd could readily be distinguished in a mixture.

However, the spectra examined visually, obtained directly from the recorder, were actually "apparent" emission spectra. These spectra were distorted versions of the "true" spectra, due to the varying response characteristics of the detector. It was therefore desirable to correct the spectra, in order to examine the "true" version, for reasons discussed previously.

In order to perform the necessary corrections, the data were converted to digital form. The correction was readily accomplished via a simple computer calculation, eliminating much of the tedious and error-prone arithmetical data treatment.

After corrections, the data could then be re-plotted and examined visually for qualitative, and later quantitative, interpretation. However, it was apparent that, when the data were already in digital form, the analysis would be facilitated if computer techniques could also be used in the analysis of the spectral results.

#### Least-Squares Curve-Fitting Using Weighted Polynomials

It has been shown that, using least-squares linear regression techniques on high-speed computers, an approximation formula may be determined for any reasonable data set (68). Initially it was hoped that least-squares polynomial curve-fitting procedures might be applied, to find an approximation formula describing the corrected curves. If this were feasible, a curve made up of any number of data points might then be described by the coefficients of the polynomial fitting the curve. Since there would be fewer coefficients than data points, this method would have obvious advantages in the storage of data. Knowledge of an exact equation describing a curve would also facilitate procedures involving calculation of the area under a given curve. Any number of data points could also be regenerated for later examination and treatment.

The form of the equation used in the curve-fitting trials corresponded to a weighted polynomial, i.e.

$$Y = W (a_0 + a_1x + a_2x^2 + . . . . . + a_nx^n).$$

The weighting factor,  $W$ , is defined by

$$W = \frac{1}{y^2 p^2}$$

where  $p$  may be assigned arbitrarily as a constant or as a function of  $y$ . In the least-squares curve-fitting program employed, the coefficients of the weighted polynomial are found by a matrix inversion routine. Calculated values of  $y$  may then be compared with the corrected experimental values in order to evaluate the effectiveness of the fitting procedure. If a good fit is obtained, only the coefficients need be stored, and the curve may be regenerated from them.

If  $p$  represents the fractional deviation in a value of  $y$ , then the standard deviation,  $\sigma$ , is given by:

$$\sigma = py$$

and the weighting factor used is then:

$$W = \frac{1}{\sigma^2}.$$

It is also known that

$$\sigma^2 = \frac{\Sigma(y - \bar{y})^2}{k-1}$$

where

$y$  = experimental value

$\bar{y}$  = calculated value

$k$  = number of degrees of freedom.

For a good fit, the quantity  $\Sigma(y - \bar{y})^2$  should be minimized.

A "goodness-of-fit" parameter may then be defined as

$$\frac{\sum W(y-\bar{y})^2}{k-1}$$

If the fit is a good one, this quantity is nearly equal to one (69, 84), and it is known that the weights chosen provide a reasonable representation of the accuracy of the data. A value less than one usually indicates that the fit is good, but that the weighting factor could be larger (implying lower experimental error than expected).

The computer program used therefore was designed to calculate the best possible set of coefficients, the values of  $\bar{y}$ , the standard deviations and the goodness of fit parameter for each curve. The use of a program of this general type has been described in earlier work connected with solvent extraction studies (85).

In this investigation, the curve-fitting program was initially developed and tested with a fairly broad and symmetrical quinine sulfate emission peak. Good fits were obtained for this curve, with goodness-of-fit values near one for fifteen to twenty-one degree polynomials and a constant (.07) value for  $p$ . However, results with the rare-earth chelate fluorescence spectra were much less satisfactory. Figures 6 and 7 illustrate experimental curves for SmD and EuD (curves 1 and 5), and some of the results of the curve-fitting techniques. It may be noted that for the SmD curve, the use of a constant value of  $p$  (curve 2) resulted in extreme smoothing of the curve and elimination of the



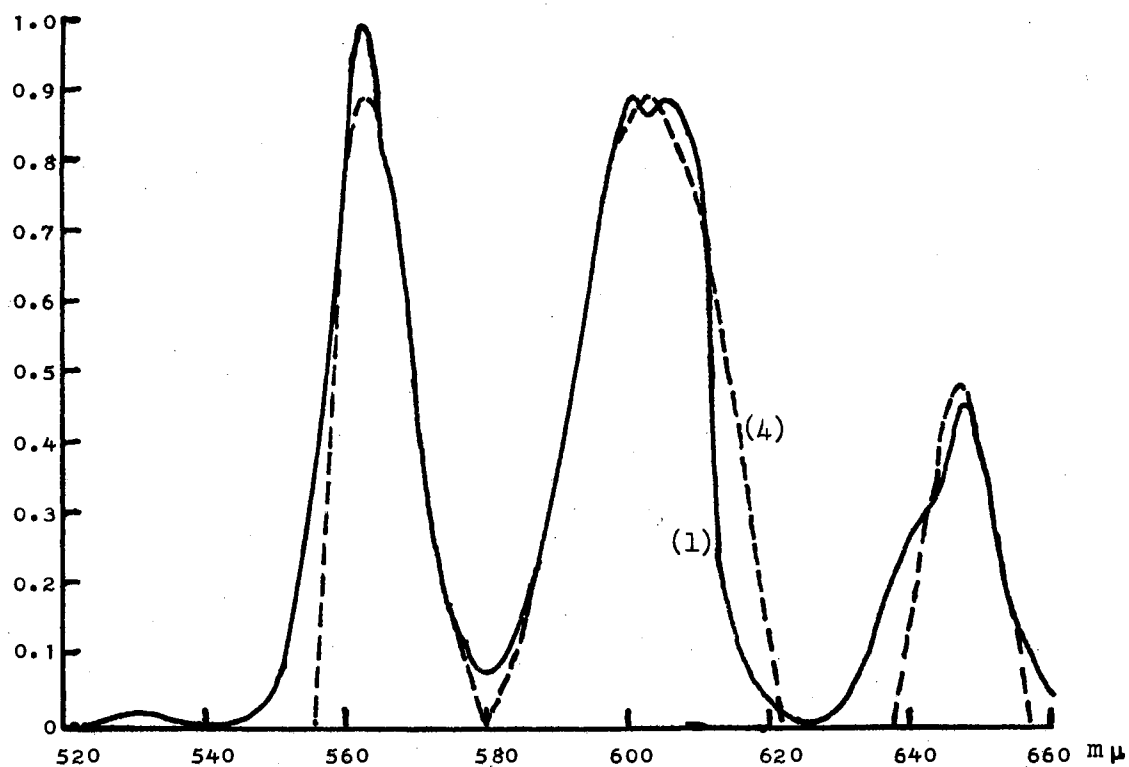
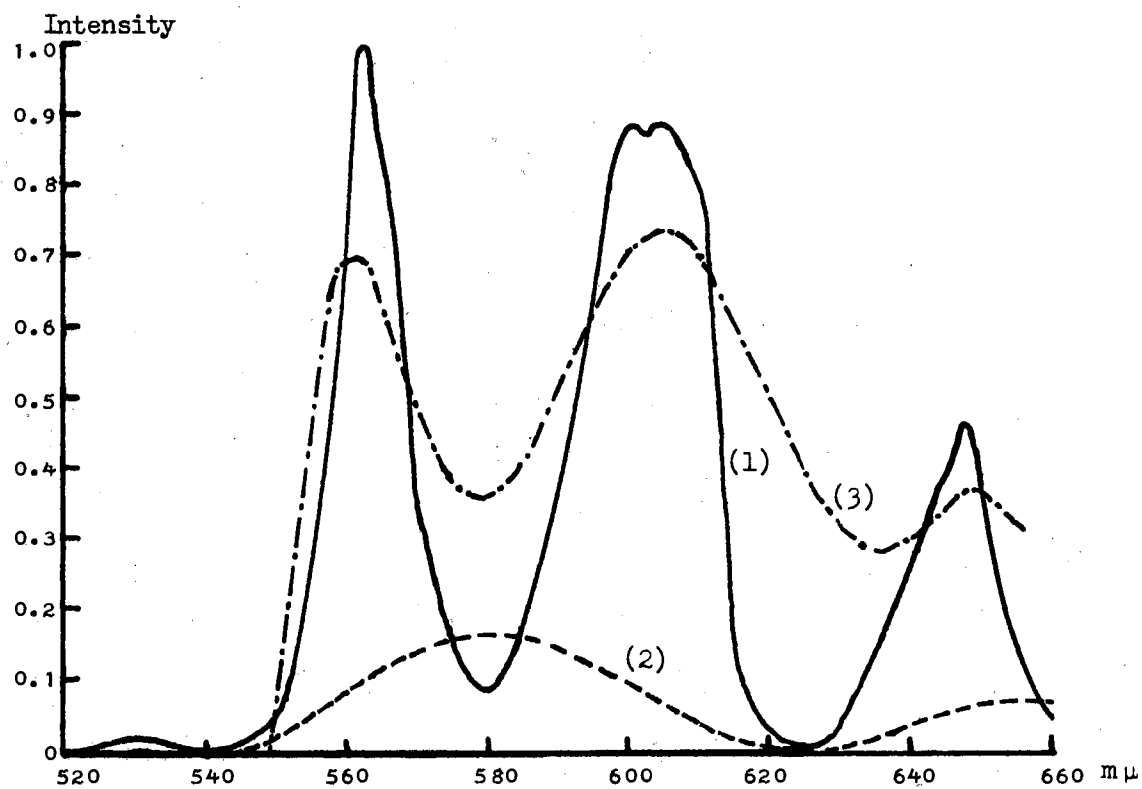


Figure 6. Polynomial Curve-Fitting (SmD)

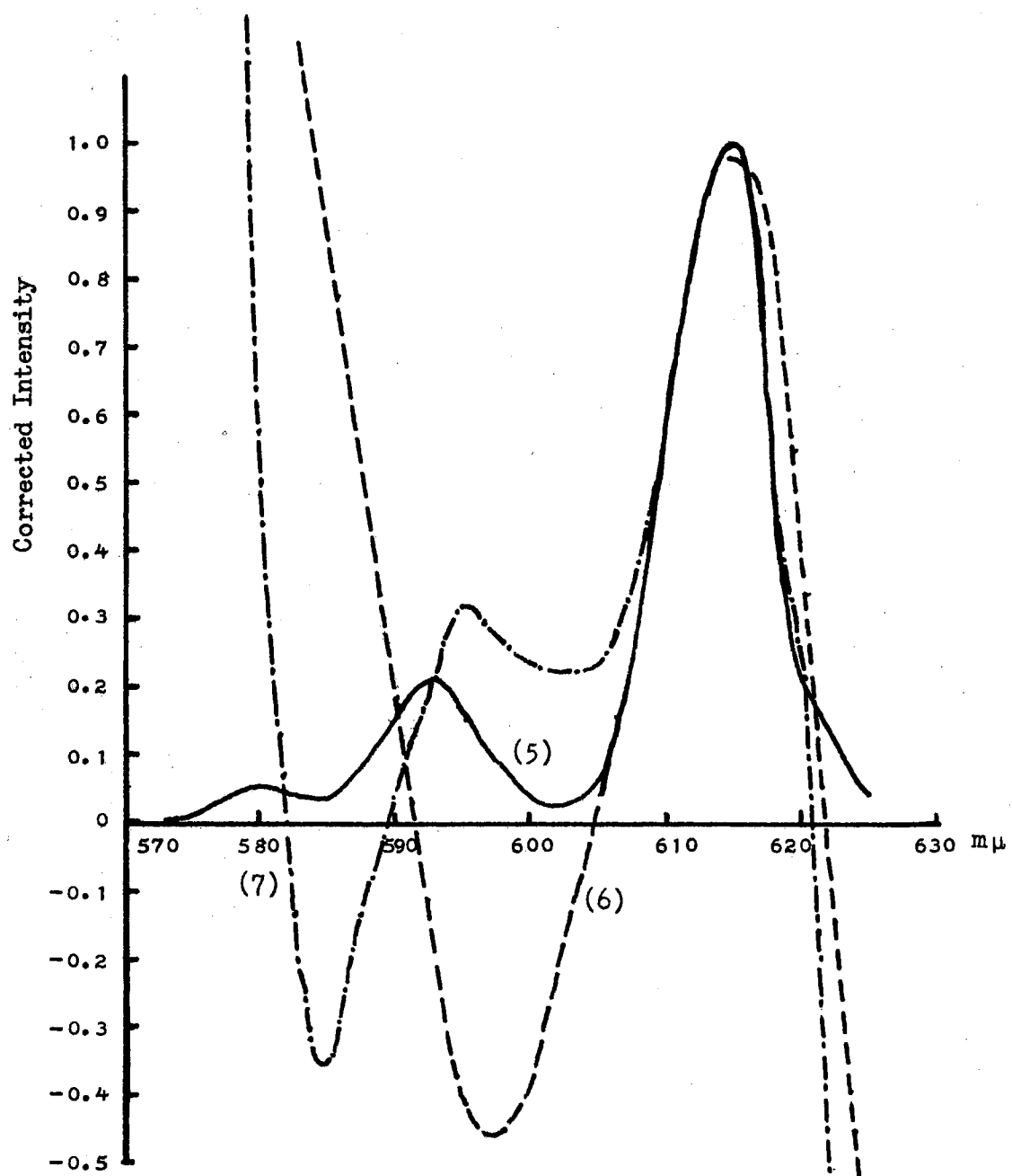


Figure 7. Polynomial Curve-Fitting (EuD)

characteristic peaks. When  $p$  was set equal to  $\frac{.01}{y^2}$ , (curve 3) the curve structure was approximated more closely, but was still not satisfactory. With  $p = \frac{.01}{y^3}$ , (curve 4) the peaks were fit quite well, but large fluctuations were present between peaks and at the ends of the spectrum. These fluctuations were even more pronounced if the zero points from .4750 to .5200  $\mu$  and from .6600 to .6750  $\mu$  were included. The results for EuD were even less satisfactory, since calculated curves (curves 6 and 7) could only approximate the major peak, with large fluctuations at all other points.

After a number of trials, under varied conditions, it became clear that a weighted polynomial of the form chosen was simply not flexible enough to fit the data available for the rare-earth chelates. In addition, the computer time required in the determination of the coefficients of a polynomial of the necessary high degree becomes prohibitive in routine analysis.

Consequently, the procedures adopted for computer interpretation of the fluorescence spectra involved only a comparison of corrected experimental emission intensity versus wavelength values, rather than a determination of an equation for the curve.

#### Direct Comparison of Corrected Emission Spectra

As noted earlier, the first necessary step in the treatment of the experimental data is a point-by-point multiplication by the correction factor in quanta per unit frequency interval. At the same time, the data points are multiplied

by the appropriate attenuation factors and by a factor expressing the output of the xenon lamp at the excitation frequency used. Also, since the lamp intensity is not constant, a reading was made of the quinine sulfate emission intensity prior to running each sample spectrum. Multiplication of the data points by this value divided by a reference value converts all of the data to the same level. The entire calculation is performed as indicated below:

$$Y_{\text{Corr}} = Y_{\text{exp}} \cdot \text{CFACT} \cdot \frac{\text{QS}}{\text{QSS}} \cdot \text{RANGE} \cdot \frac{1}{\text{RES}} \cdot \text{XE}$$

where QS = the measured quinine sulfate peak intensity  
 QSS = standard quinine sulfate peak intensity  
 RANGE = setting on microammeter  
 RES = setting on decade box  
 XE = xenon lamp factor

The corrected curve is then normalized by dividing all points by the largest value of y. It will be noted that, in the normalization procedure, the last four factors in the above equation will cancel out. They were included, however, to allow later conversion to quantitative analysis procedures without major programming changes at this stage.

It would obviously be very tedious and time consuming to perform these corrections upon the 81 points in each curve. Therefore a simple computer program (Appendix I) was written for the correction and normalization of the standard curves. The calculations for one curve then require only 0.4 minutes, and the corrected normalized

intensities are printed at 2.5 m $\mu$  intervals, in tabular form. The same corrections were also performed upon the spectra of mixtures, but were included in the interpretation program, which will be discussed later in this section.

In order to convert the corrected spectral data to graphical form, a plot subroutine (Appendix I), available in the Oklahoma State University Computer Center library, was modified to plot the fluorescence data and provide appropriate axis labels. In the standard plot program, the corrected intensities are read from cards punched as a part of the correction program. The ordinate scale, in wavelength, is printed at 2.5 m $\mu$  intervals. For any theoretical analysis, a Lagrangian interpolation program could be employed to calculate intensities on a scale linear in frequency, and corresponding to the correction factor used. However, the representations here, with both linear wavelength intervals and inverse frequency intervals labeled, suffice for the qualitative analysis of interest. The use of the correction factor with respect to frequency was retained to simplify later conversion to the appropriate scale.

Plots of four of the standards used in this investigation (SmTTA, EuTTA, GdTTA and TbTTA) are shown in reduced form, in Figures 8-11. It should be noted that these plots provide only the general shape of the spectra, since all values must be rounded off to fit on the closest available line of the IBM 1403 Printer. Even with this limitation, the computer plots are extremely valuable for qualitative

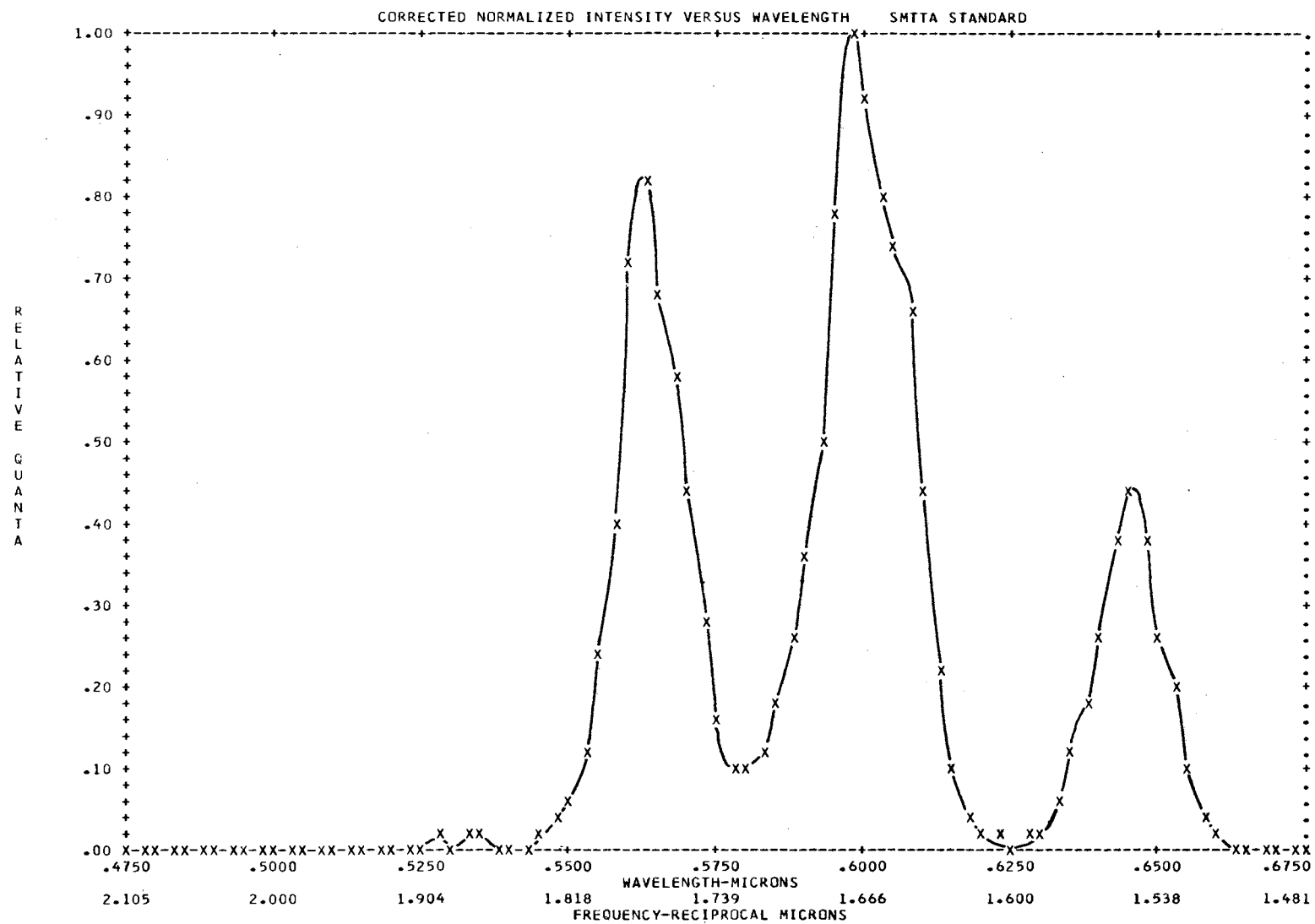


Figure 8. Fluorescence Spectrum of Samarium Thenoyltrifluoroacetate

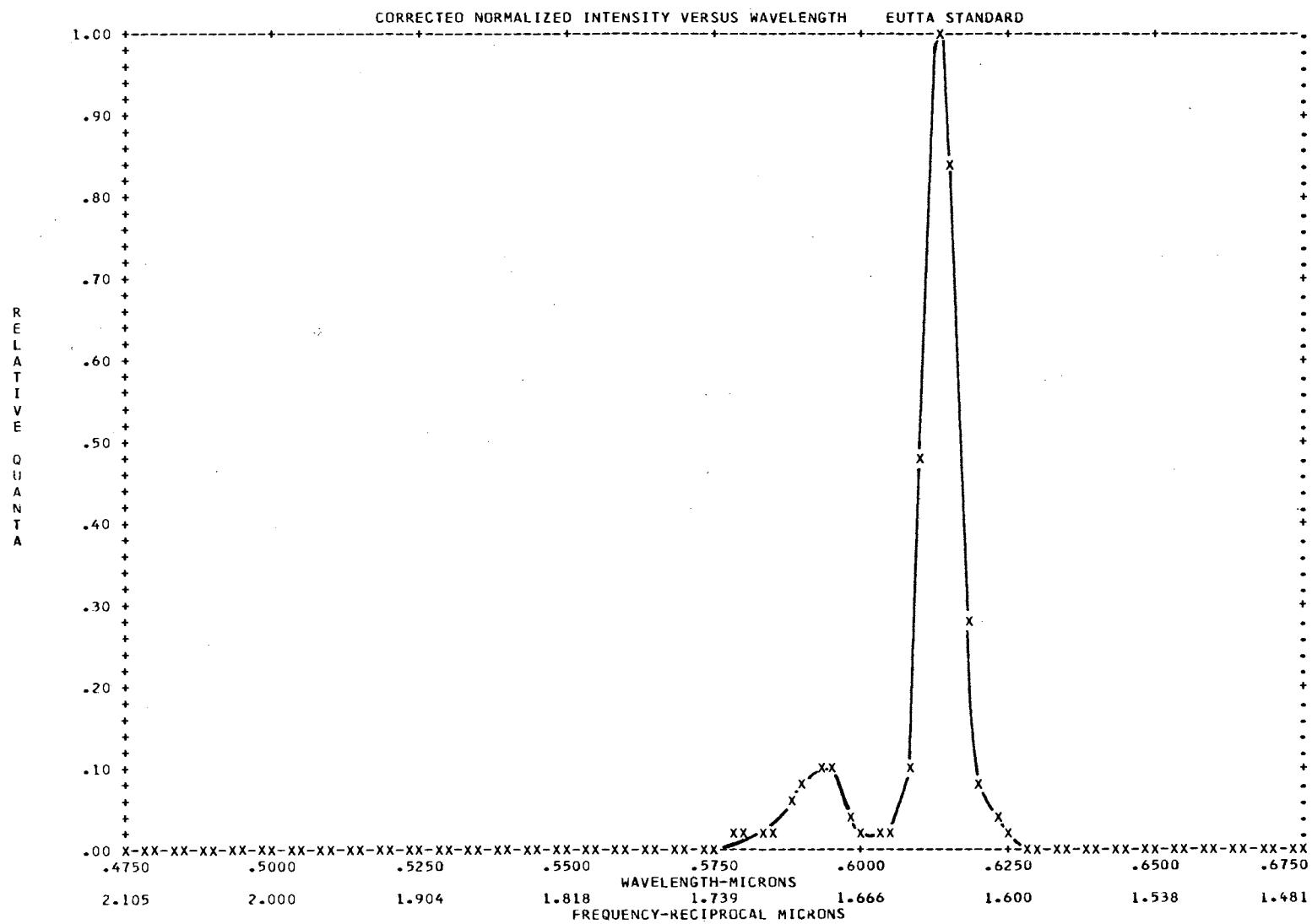


Figure 9. Fluorescence Spectrum of Europium Thenoyltrifluoroacetate

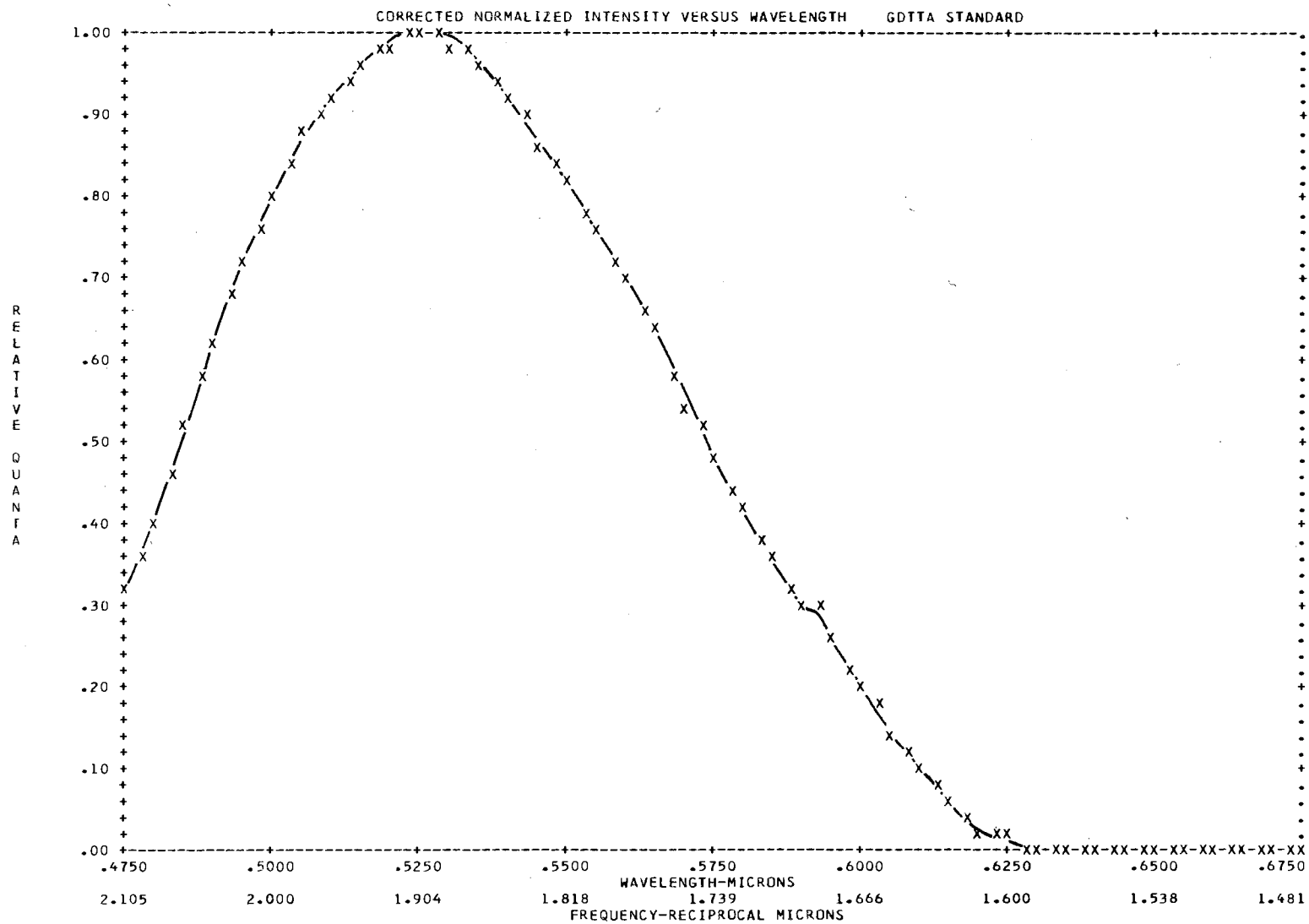


Figure 10. Fluorescence Spectrum of Gadolinium Thenoyltrifluoroacetate



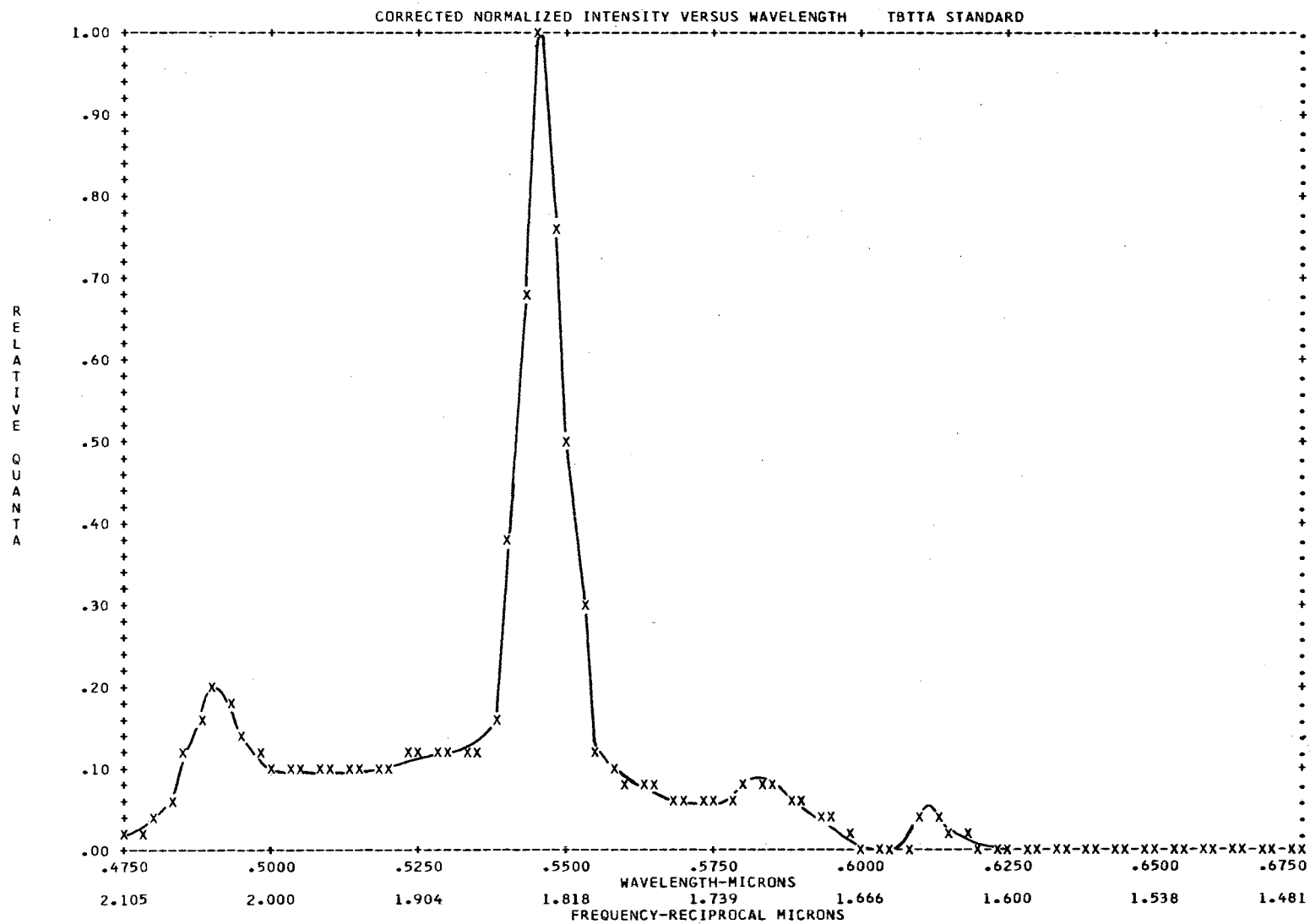


Figure 11. Fluorescence Spectrum of Terbium Thenoyltrifluoroacetate

work, since they eliminate virtually all hand-plotting procedures and require only about 0.8 minutes per curve (if an object deck is employed).

Using the same plot subroutine, but a different main program for calculations (Appendix I) a plot comparing experimental and corrected intensities in a fluorescence spectrum of SmD was obtained (Figure 12). The program was written to read intensities from cards, normalize the experimental values, calculate wavelength intervals, and plot both curves on the same graph.

It may be noted, from Table V in Chapter III, that the spectra are characteristic of the rare earth ion present, and show only minor dependence upon the ligand used. Therefore chelates of Sm and Eu with B and D, and of TbD, are essentially the same as those shown for TTA. It may also be noted from the four spectra shown that the most intense peaks of Sm, Eu and Tb chelates, at .5975, .6125 and .5450 microns respectively, may readily be distinguished from each other. It is also obvious that the phosphorescence band of GdTTA is distinctive in its broadness.

Figure 13 illustrates the fluorescence spectrum of a mixture containing the same four chelates (SmTTA, EuTTA, GdTTA and TbTTA). It is apparent that simple visual examination of the plot will allow adequate qualitative results. However, in cases where one component was present in proportionately smaller amounts, its peak might not be as readily apparent. Also, in the analysis of a large number of mixtures, it could be undesirable to plot each curve. It

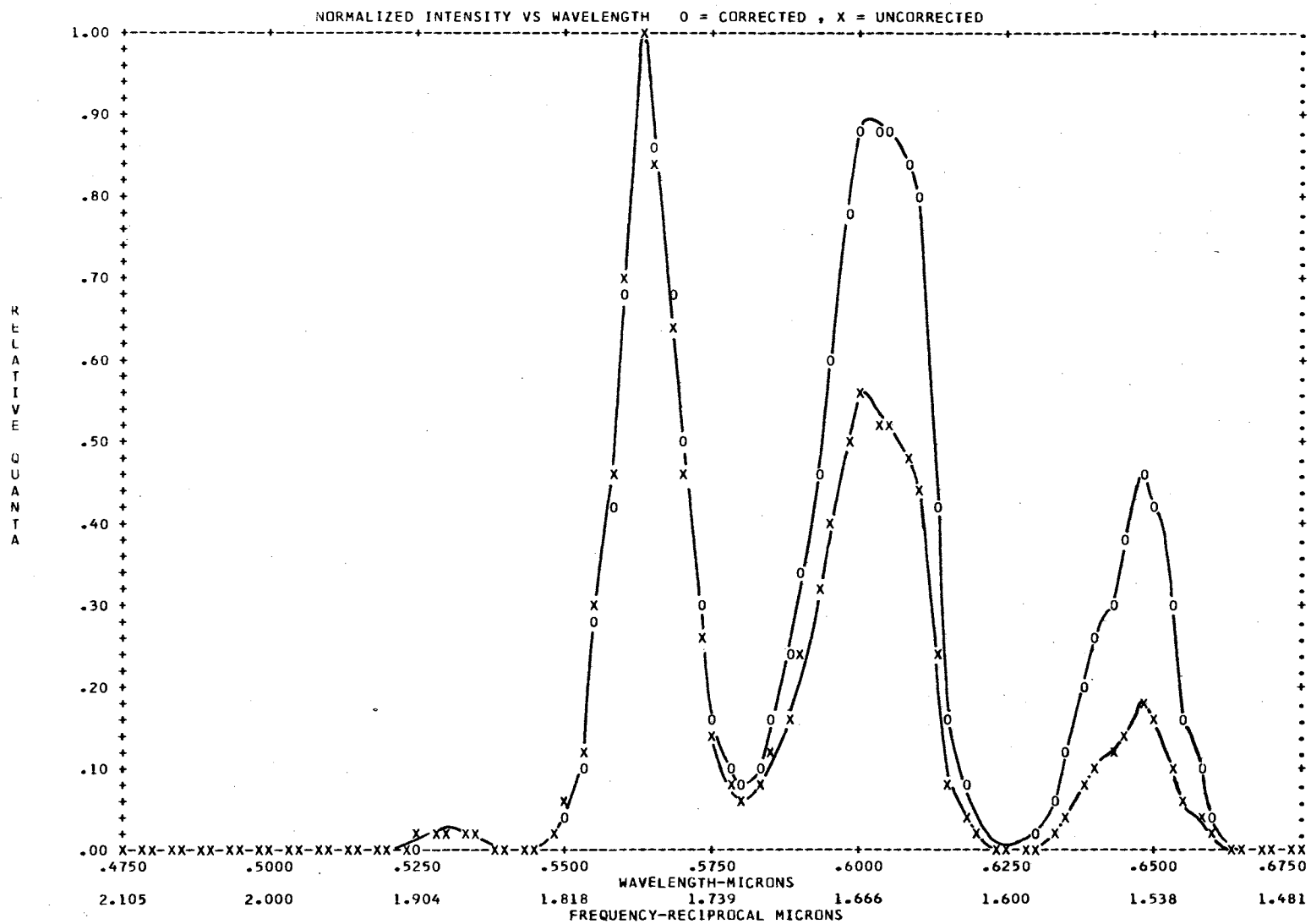


Figure 12. Comparison of Experimental and Corrected Fluorescence Spectra (SmD)

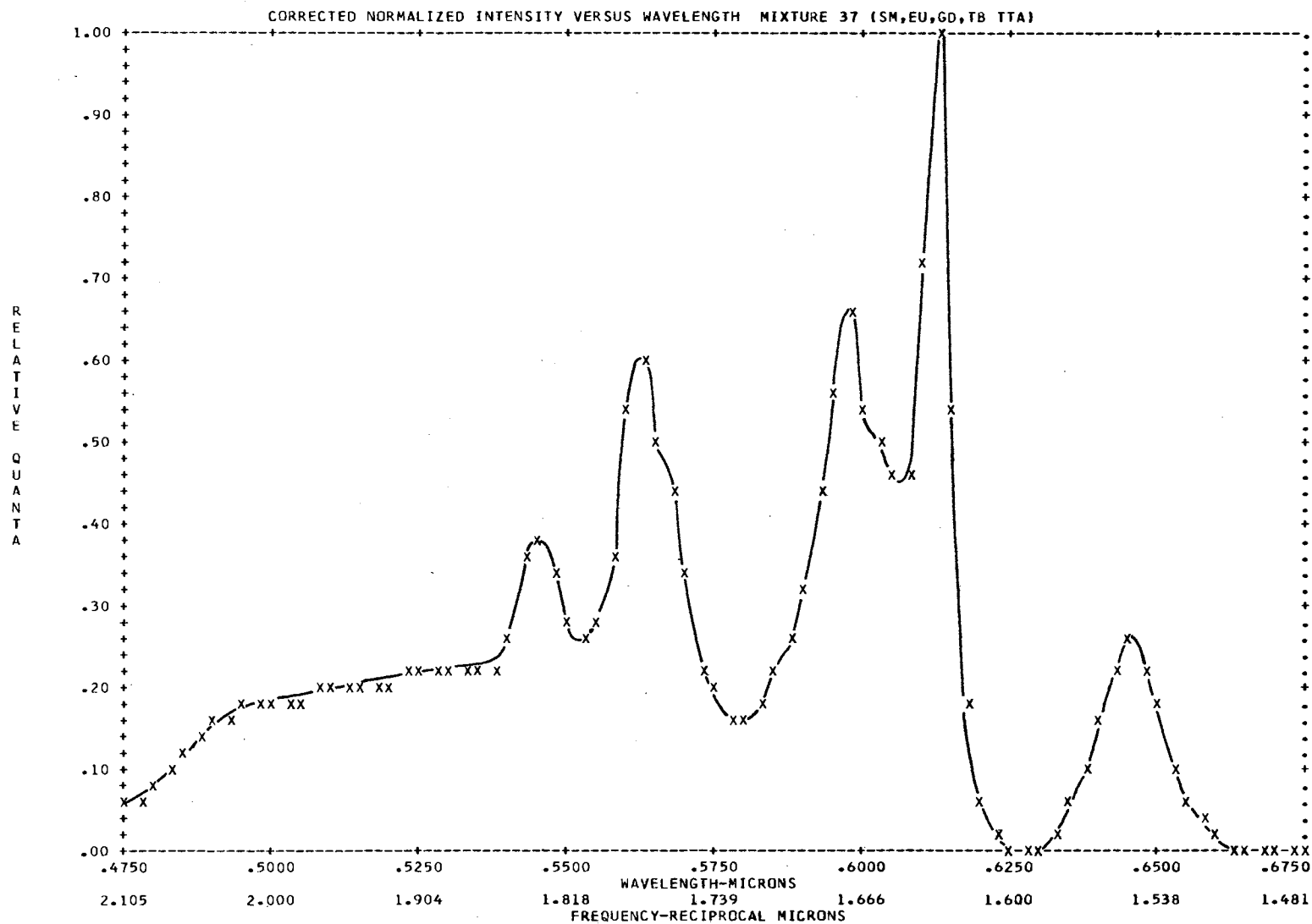


Figure 13. Fluorescence Spectrum of a Four-component Mixture

could frequently be sufficient to have a print-out only of the components actually present.

A computer program (Appendix I) was therefore devised to examine the fluorescence spectrum, and give numerical qualitative analysis results. It may be used alone, or in conjunction with a plot program. The standard spectra were assigned identification numbers listed below:

1 SmD	6 SmTTA
2 EuD	7 EuTTA
3 SmB	8 GdTTA
4 EuB	9 TbTTA
5 TbB	

The mixture analysis was then written in general form, so that mixtures of dibenzoylmethides, benzoylacetates, or thenoyltrifluoroacetates could be examined. The wavelength intervals are first calculated, as in previous programs. Then data cards are read which identify ITOTAL, the total number of mixtures to be analyzed, and MINN and MAXN, giving the range of standard numbers applicable (1-2 for D, 3-5 for B, 6-9 for TTA). The corrected normalized intensities of the standard curves, and XMAX (peak wavelength), are read from data cards punched as a part of the standard correction routine. Following this, the experimental Y values for the mixtures are read, corrected and normalized. The mixture is then analyzed by a basically simple and straightforward procedure. The peak wavelength (XMAX) for the mixture is compared to the peak wavelengths of the standards, and the

first component identified. Then the data points for the standard chosen are subtracted from those of the mixture. The remaining curve is normalized again, and a new peak wavelength is compared with the standards, identifying a second component. This procedure is repeated as many times as there are possible components. In order to allow for the inevitable experimental errors and provide maximum flexibility, it was necessary to allow a deviation in XMAX of  $\pm .0050$  microns. For example, TbTTA would be identified if XMAX for a mixture were .5400, .5425, .5450, .5475 or .5500. In order to accurately identify the broad GdTTA peak, this range was extended to  $\pm .0075$  microns. Further complications developed when it was noted that in some D and TTA mixtures, the first Sm peak (at .5625 microns) was larger than the second (at .5975 microns). Separate statements then had to be inserted in the program in order to insure identification of Sm by either peak wavelength.

The analysis data for each mixture were printed out in the form shown in Table VI. The table illustrates the results of analysis of the TTA mixture plotted in Figure 14. The printed NAME corresponds to the identification number assigned to the sample and the other terms are as defined previously. The first set of Y values is for the initial mixture, and the value for YMAX gives the normalization factor used. Its small value reflects the fact that, before normalization, the multiplication factors (QS, RANGE, RES, XE) affect the Y values. Noting that XMAX = .6125, component 7 (EuTTA) is identified. The data points for EuTTA

TABLE VI

## RESULTS OF ANALYSIS OF A FOUR COMPONENT MIXTURE

TOTAL NUMBER OF MIXTURES= 1

CONSIDER STANDARDS FROM 6 TO 9

NAME	XMAX	XXMAX
6	.5975	1.673
7	.6125	1.632
8	.5250	1.904
9	.5450	1.834

## WAVELENGTHS

.4750	.4775	.4800	.4825	.4850	.4875	.4900
.4925	.4950	.4975	.5000	.5025	.5050	.5075
.5100	.5125	.5150	.5175	.5200	.5225	.5250
.5275	.5300	.5325	.5350	.5375	.5400	.5425
.5450	.5475	.5500	.5525	.5550	.5575	.5600
.5625	.5650	.5675	.5700	.5725	.5750	.5775
.5800	.5825	.5850	.5875	.5900	.5925	.5950
.5975	.6000	.6025	.6050	.6075	.6100	.6125
.6150	.6175	.6200	.6225	.6250	.6275	.6300
.6325	.6350	.6375	.6400	.6425	.6450	.6475
.6500	.6525	.6550	.6575	.6600	.6625	.6650
.6675	.6700	.6725	.6750			

NAME	LEXIT	RES	QS	RANGE	XE
37	390	188.0	45.8	.01	1.685

## CORRECTED NORMALIZED Y VALUES

.0542	.0642	.0759	.0911	.1136	.1414	.1574
.1671	.1710	.1742	.1760	.1836	.1889	.1929
.1978	.2015	.2049	.2067	.2033	.2149	.2195
.2177	.2175	.2162	.2132	.2227	.2652	.3581
.3892	.3419	.2735	.2663	.2805	.3656	.5444
.5948	.5005	.4416	.3337	.2275	.1919	.1629
.1568	.1734	.2140	.2586	.3233	.4391	.5562
.6505	.5414	.4957	.4656	.4682	.7268	1.0000
.5474	.1726	.0556	.0155	.0053	.0027	.0083
.0257	.0614	.1018	.1533	.2193	.2656	.2221
.1733	.1092	.0699	.0357	.0109	.0037	.0000
.0000	.0000	.0000	.0000			

YMAX=.0003 XMAX=.6125

TABLE VI (CONTINUED)

MIXTURE CONTAINS COMPONENT 7

Y VALUES AFTER REMOVING THIS COMPONENT

.0542	.0642	.0759	.0911	.1136	.1414	.1574
.1671	.1710	.1742	.1760	.1836	.1889	.1929
.1978	.2015	.2049	.2067	.2033	.2149	.2195
.2177	.2175	.2162	.2132	.2227	.2652	.3581
.3892	.3419	.2735	.2663	.2805	.3656	.5444
.5948	.5005	.4416	.3337	.2260	.1873	.1517
.1420	.1581	.1876	.2005	.2353	.3346	.4622
.6092	.5244	.4804	.4385	.3751	.2383	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0025
.0227	.0614	.1018	.1533	.2193	.2656	.2221
.1733	.1092	.0699	.0357	.0109	.0037	.0000
.0000	.0000	.0000	.0000			

YMAX=.6092 XMAX=.5975

MIXTURE CONTAINS COMPONENT 6

Y VALUES AFTER REMOVING THIS COMPONENT

.0890	.1054	.1246	.1496	.1865	.2321	.2584
.2743	.2807	.2859	.2890	.3014	.3101	.3166
.3247	.3308	.3364	.3394	.3327	.3507	.3547
.3469	.3475	.3424	.3396	.3602	.4326	.5835
.6253	.5286	.3879	.3270	.2287	.2026	.1827
.1506	.1462	.1482	.1154	.0810	.1456	.1470
.1305	.1361	.1220	.0744	.0290	.0510	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0021	.0000
.0205	.0000	.0082	.0206	.0013	.0005	.0000
.0000	.0000	.0000	.0000			

YMAX=.6253 XMAX=.5450



TABLE VI (CONTINUED)

MIXTURE CONTAINS COMPONENT 9

Y VALUES AFTER REMOVING THIS COMPONENT

.1250	.1448	.1657	.1811	.1801	.2096	.2225
.2548	.2998	.3393	.3640	.3872	.4005	.4107
.4211	.4282	.4332	.4381	.4236	.4496	.4547
.4428	.4413	.4303	.4215	.4122	.3172	.2479
.0000	.0841	.1231	.2259	.2454	.2305	.2130
.1666	.1624	.1687	.1253	.0713	.1728	.1669
.1255	.1351	.1203	.0558	.0000	.0367	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0034	.0000
.0328	.0000	.0132	.0329	.0021	.0008	.0000
.0000	.0000	.0000	.0000			

YMAX=.4547 XMAX=.5250

MIXTURE CONTAINS COMPONENT 8

Y VALUES AFTER REMOVING THIS COMPONENT

.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0057	.0030	.0000
.0043	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0000	.0000
.0000	.0000	.0000	.0000	.0000	.0076	.0000
.0722	.0000	.0290	.0725	.0046	.0018	.0000
.0000	.0000	.0000	.0000			

YMAX=.0725 XMAX=.6575

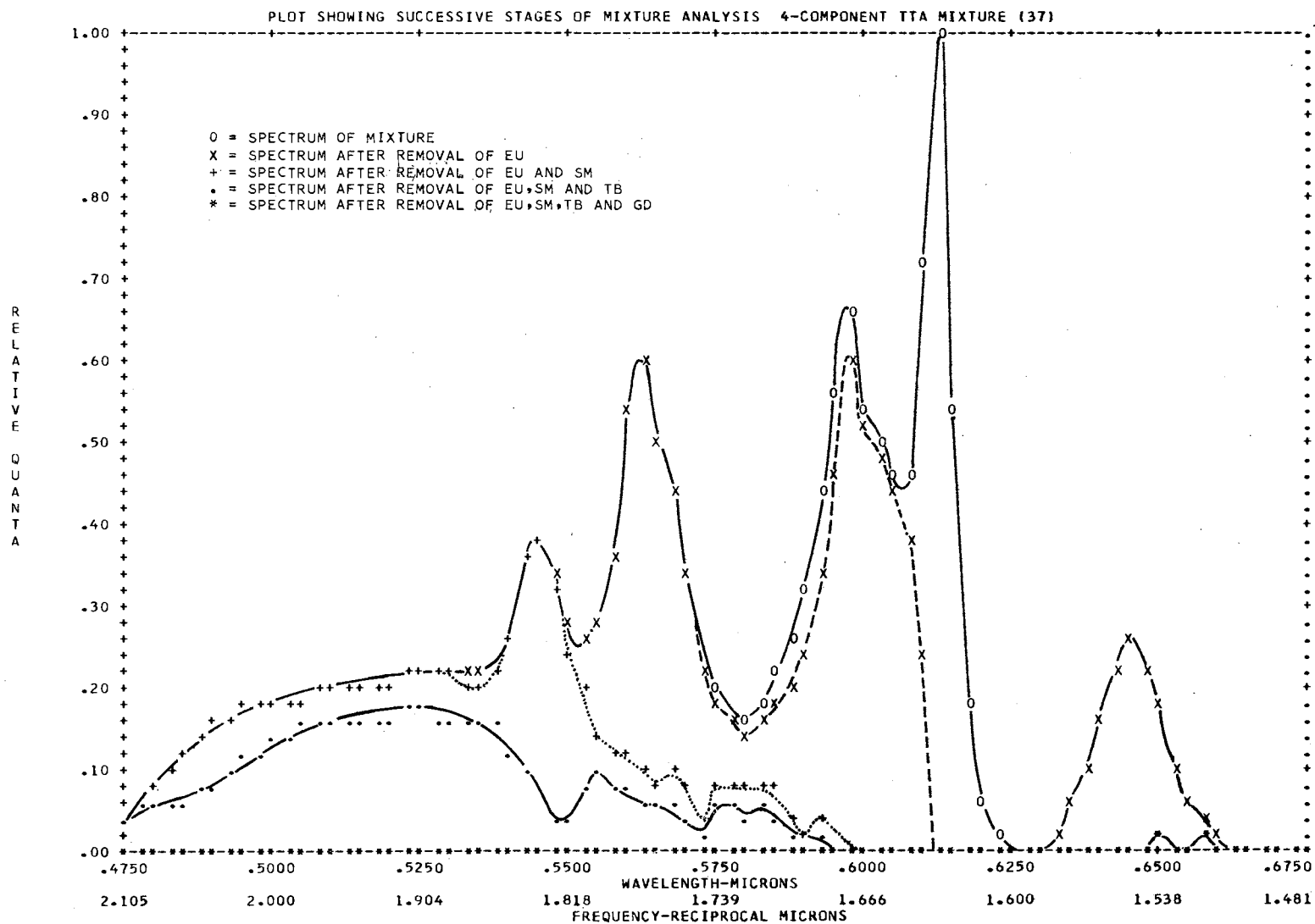


Figure 14. Successive Stages of a Mixture Analysis

are then subtracted, leaving a curve with  $X_{MAX} = .5975$ . In succeeding steps, components 6, 9 and 8 (Sm, Tb and Gd) are then identified.

In order to graphically observe the successive steps in a mixture analysis a further calculation is necessary, since the data have been normalized in each step. Therefore, a final plot calculation program (Appendix I) was written, to be used in conjunction with the plot subroutine. The Y values after each step in the mixture analysis were read from data cards, and the normalization factors used in each step ( $Y_{MAX1}$ ,  $Y_{MAX2}$ , etc.) were defined. The original curve for the mixture, and the curve after subtracting the first component were correct as read. However, in order to maintain the same scale for the entire plot, the data points after normalization and subtraction of the second component had to be multiplied by  $Y_{MAX1}$ . The next set was multiplied by both  $Y_{MAX1}$  and  $Y_{MAX2}$ , and the procedure continued. As a result of these calculations, a plot showing the curve after subtraction of each component (Figure 14) was obtained, with all curves on the same scale. It is significant that the points after removal of all components lie very close to zero. Negative fluctuations were not possible, since any negative values in the analysis procedure were set equal to zero. The remaining deviations from a perfect base line are due to experimental errors, errors in conversion to digital data, and to the effects of one chelate upon the others present.

A wide variety of mixtures was analyzed by this method,

with all of the results as expected. The mixtures analyzed with the components identified, are shown in Table VII. In several cases, the same component is identified more than once. This is again a result of experimental errors and of the slight spectral changes that occur due to interaction between mixture components. It is probable that much of this repetition could be avoided if a direct digital read-out spectrofluorometer were used to provide accurate numerical readings at closely spaced (1 m $\mu$  or less) intervals.

The results obtained, however, were entirely satisfactory for the procedure and equipment employed. Mixture number 27 represented the only case in which an "extra" component was identified. In this spectrum, it had been observed earlier that europium was present as a trace impurity and this observation was therefore confirmed.

TABLE VII  
Mixtures Analyzed and Results

Identification number(s)	Components	Found
10,12	$2 \times 10^{-3} \text{ M SmD}$	SmD
	$1 \times 10^{-5} \text{ M EuD}$	EuD
11	$1 \times 10^{-3} \text{ M SmD}$	SmD
	$5 \times 10^{-6} \text{ M EuD}$	EuD
13	$1 \times 10^{-3} \text{ M SmB}$	SmB
	$5 \times 10^{-6} \text{ M EuB}$	EuB
14,15	$1 \times 10^{-3} \text{ M SmB}$	SmB
	$1 \times 10^{-5} \text{ M EuB}$	EuB
16,17	$4 \times 10^{-4} \text{ M SmB}$	SmB
	$1.6 \times 10^{-3} \text{ TbB}$	TbB
18	$4 \times 10^{-6} \text{ M EuB}$	EuB
	$2 \times 10^{-3} \text{ M TbB}$	TbB
19,20	$2 \times 10^{-4} \text{ M SmB}$	SmB
	$2 \times 10^{-6} \text{ M EuB}$	EuB
	$2 \times 10^{-3} \text{ M TbB}$	TbB
21	$1 \times 10^{-4} \text{ M SmTTA}$	SmTTA
	$4 \times 10^{-7} \text{ M EuTTA}$	EuTTA
22	$1 \times 10^{-4} \text{ M SmTTA}$	SmTTA
	$6 \times 10^{-7} \text{ M EuTTA}$	EuTTA
23	$1.2 \times 10^{-5} \text{ M SmTTA}$	SmTTA
	$5 \times 10^{-3} \text{ M GdTTA}$	GdTTA
24	$2 \times 10^{-5} \text{ M SmTTA}$	SmTTA
	$1 \times 10^{-3} \text{ M TbTTA}$	TbTTA

TABLE VII (continued)

Identification number(s)	Components	Found
25	$3 \times 10^{-7} \text{M}$ EuTTA $5 \times 10^{-3} \text{M}$ GdTTA	EuTTA GdTTA
26	$8 \times 10^{-7} \text{M}$ EuTTA $5 \times 10^{-3} \text{M}$ TbTTA	EuTTA TbTTA
27	$5 \times 10^{-3} \text{M}$ GdTTA $1 \times 10^{-3} \text{M}$ TbTTA	GdTTA TbTTA EuTTA
28, 29, 30	$2 \times 10^{-5} \text{M}$ SmTTA $6 \times 10^{-3} \text{M}$ GdTTA $1 \times 10^{-3} \text{M}$ TbTTA	SmTTA GdTTA TbTTA
31, 32	$2 \times 10^{-5} \text{M}$ SmTTA $5 \times 10^{-7} \text{M}$ EuTTA $5 \times 10^{-3} \text{M}$ GdTTA	SmTTA EuTTA GdTTA
33, 34	$5 \times 10^{-7} \text{M}$ EuTTA $6 \times 10^{-3} \text{M}$ GdTTA $1 \times 10^{-3} \text{M}$ TbTTA	EuTTA GdTTA TbTTA
35, 36	$1.5 \times 10^{-5} \text{M}$ SmTTA $5 \times 10^{-7} \text{M}$ EuTTA $1 \times 10^{-3} \text{M}$ TbTTA	SmTTA EuTTA TbTTA
37, 38	$1.5 \times 10^{-5} \text{M}$ SmTTA $5 \times 10^{-7} \text{M}$ EuTTA $6 \times 10^{-3} \text{M}$ GdTTA $1 \times 10^{-3} \text{M}$ TbTTA	SmTTA EuTTA GdTTA TbTTA

## CHAPTER V

### SUMMARY AND CONCLUSIONS

In summarizing the results of this investigation, it is again helpful to divide the study into several classifications. The development of preparative methods for the rare earth chelates, and the calibration of a sensitive spectrofluorometer were necessary prerequisites to the actual spectrofluorometric analysis and data-processing procedures. The progress made in each of these areas will greatly facilitate further studies with this system. The methods established for the preparation of the tetrakis chelates of the rare earths with benzoylacetone, dibenzoylmethane or thenoyltrifluoroacetone are direct, and require very little time in actual manipulation. Most significantly, the products have consistently conformed to the expected results and have been of high purity. The Farrand spectrofluorometer, with the modifications described earlier, has been shown to provide excellent sensitivity and reproducibility. The completion of all necessary calibration steps concerned with the spectrofluorometer, and the use of a computer program to perform the correction procedures permits the observation of "true" emission spectra. Furthermore, the calibration procedures employed could be duplicated fairly readily in the case of major instrumental

modifications.

The development of methods for the actual fluorescence analyses and the results obtained in this preliminary study should also enhance the feasibility of more general investigations of this type. The fluorescence analysis of the rare earths and the computer data-processing techniques were shown to be quite promising for the qualitative analysis of a rare earth mixture.

It should be emphasized, however, that this has been a preliminary investigation only. Many more facets of the methods used should be studied before extensive usefulness is claimed. For the rare earths in particular, different chelate systems may be shown to offer more advantages than those employed in the present study. It would be of especial interest to extend the scope of the fluorescence analysis procedures to the weakly fluorescing rare earths, including praseodymium, holmium and erbium. This might be accomplished by the use of a more efficient chelate system or by the development of increased instrumental sensitivity. In order to simplify the method for general routine analysis, direct solution studies, with the crystallization step eliminated, warrant investigation.

The fluorescence procedure will undoubtedly be most useful if it may be extended to the quantitative analysis of the rare earths. Before this achieved, detailed studies of quenching and interference effects will be necessary.

It may be clear that, at present, the most time-consuming



and error-prone step in the procedure is the conversion of data from graphical to digital form. If a method such as this one, involving point by point correction and computer analysis, is to be feasible in routine analysis, it is imperative that direct digital readout systems be employed. Such systems coupled directly to a card punch, should allow the use of rapid and accurate computer data-processing techniques. Automated methods of spectral interpretation should then facilitate many fluorescence analyses.

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## APPENDIX I

### COMPUTER PROGRAMS

All of the major computer programs written for the purposes of this investigation are included, in their final form. The programs were written in Fortran IV and are designed for use with an IBM 1410 data processing system.

Although the programs have been discussed earlier, short explanations and the necessary definitions are included on comment cards. It should be noted that, for printing purposes, long statements have been continued on the following line. In actual use, these statements were written on one line, or continuation cards were used. The three plot programs all call for the plot subroutine given as the last program.

During this investigation, cards were punched for the experimental data used in the correction and normalization programs. These programs included card outputs to provide the corrected data for the plot and mixture analysis programs. For the most efficient use of this method of analysis, some of the programs (i.e. correction and plot of standards, analysis and plot of mixtures) should be combined. Present core storage facilities did not permit this, but such a combination will be feasible when an IBM 7040 system becomes available.



It may be estimated that after the spectral data have been converted to digital form and the cards punched, and when standard data are available, the correction, analysis and plot of the spectrum of a mixture requires approximately one minute. This time will probably be less when the programs are combined and when an object deck (rather than a Fortran deck) is used.

```

C      CALCULATION OF CORRECTION FACTORS
C      C1 AND C2 = RADIATION CONSTANTS
C      LAMBDA = WAVELENGTH IN MICRONS
C      TRANS= TRANSMITTIVITY OF LAMP ENVELOPE
C      EMISS = EMISSIVITY OF TUNGSTEN
C      AT 0.655 MICRONS , E = EMISS AND 0.808 = TRANS
C      TB = BRIGHTNESS TEMPERATURE , T = STRIP TEMPERATURE
C      FREQ = FREQUENCY IN RECIPROCAL MICRONS
C      RESP = RECORDED SIGNAL, IN ARBITRARY UNITS
C      CFACT=CORRECTION FACTOR IN RELATIVE QUANTA PER UNIT
C           FREQUENCY INTERVAL
C      CORRL=CORRECTION FACTOR IN RELATIVE ENERGY PER UNIT
C           WAVELENGTH INTERVAL
C      REAL LAMBDA
C      DIMENSION LAMBDA(41),TRANS(41),TB(8),T(8),E(8),
C           EMISS(41),RESP(41)
1  FORMAT(2F6.3)
2  FORMAT(F8.2,F6.3)
4  FORMAT(1H1,2X,2HTB,7X,1HT/2F8.2)
5  FORMAT(/16X,6HLAMBDA,1X,5HEMISS,1X,5HTRANS,2X,4HFREQ
C           3X,4HRESP,4X,6HENERGY,7X,5HCORRL,8X,5HCFACT/)
6  FORMAT(16X,3F6.3,2F7.3,3E12.4)
7  FORMAT(I3)
8  FORMAT(12F6.3)
C      C1=3.7412E-04
C      C2=14385
C      DO11M=1,41
11 READ(1,1)(LAMBDA(M),TRANS(M))
C      DO12N=1,8
12 READ(1,2)(TB(N),E(N))
C      CALCULATION OF STRIP TEMPERATURE
C      DO 30 I=1,8
C      PROD=0.808*E(I)
C      T(I)=C2/(0.655*(ALOG(PROD)+C2/(0.655*TB(I))))
C      WRITE(3,4)TB(I),T(I)
C      READ(1,8) (EMISS(J),J=1,41)
10 WRITE(3,5)
C      READ(1,8) (RESP(K),K=1,41)
C      CALCULATION OF CORRECTION FACTORS
C      DO 20 L=1,41
C      TERM=C2/(LAMBDA(L)*T(I))
C      ENERGY=(EMISS(L)*TRANS(L)*C1)/(LAMBDA(L)*LAMBDA(L)*
C           EXP(TERM))
C      CFACT = ENERGY/RESP(L)
C      FREQ=1./LAMBDA(L)
C      CORRL=CFACT/(LAMBDA(L)*LAMBDA(L)*LAMBDA(L))
20 WRITE(3,6)LAMBDA(L),EMISS(L),TRANS(L),FREQ,RESP(L),
C           ENERGY,CORRL,CFACT
C      READ(1,7)JJ
C      IF(JJ.EQ.1)GO TO 10
C      DATA CARD(0 OR 1)PERMITS MULTIPLE CALCULATIONS OF
C      CFACT AT ONE TEMPERATURE VALUE
30 CONTINUE
END

```

```

C      CORRECTION AND NORMALIZATION OF STANDARD CURVES 1-9
C
C      Y = INTENSITY IN RELATIVE UNITS
C      X = WAVELENGTH IN MICRONS
C      XX = FREQUENCY IN RECIPROCAL MICRONS
C      CFACT = CORRECTION FACTOR IN RELATIVE QUANTA PER
C              UNIT FREQUENCY INTERVAL
C      QSS = STANDARD QUININE SULFATE REFERENCE PEAK HEIGHT
C      QS = OBSERVED QUININE SULFATE PEAK HEIGHT
C      RES = RESISTANCE ON DECADE BOX
C      RANGE = RANGE OF MICROAMMETER
C      XE = CORRECTION FACTOR FOR XENON LAMP FOR EXCITATION
C              WAVELENGTH USED
C      LEXIT = EXCITATION WAVELENGTH
C      NAME = IDENTIFICATION NUMBER - 1=SMD, 2=EUD, 3=SMB,
C              4=EUB, 5=TBB, 6=SMTTA, 7=EUTTA, 8=GDTTA, 9=TBTTA
C      XMAX = WAVELENGTH AT WHICH MAXIMUM INTENSITY OCCURS
C      DIMENSIONX(81),XX(81),Y(81,9),CFACT(81),NAME(9),
C              XMAX(9),XXMAX(9),YMAX(9)
1  FORMAT(9F8.4)
2  FORMAT(2I4,2F6.1,2F6.3)
3  FORMAT(12F6.4)
4  FORMAT(2I4)
5  FORMAT(11F10.4)
6  FORMAT(/48X,32HCORRECTED NORMALIZED INTENSITIES/)
7  FORMAT(7X,1HX,8X,2HXX,9(9X,I1))
8  FORMAT(I4,F8.4)
9  FORMAT(1H1,5X,4HNAME,2X,5HLEXIT,4X,2HXE,4X,2HQS,4X,
3HRES,3X,5HRANGE,4X,4HXMAX,4X,5HXXMAX,3X,4HYMAX/)
10 FORMAT(5X,I3,I7,F8.3,F6.1,F7.1,F7.2,F8.4,F9.4,F8.4)
C      CALCULATION OF WAVELENGTHS
      X(1)=.4750
      XX(1)=2.1053
      DO 20 I=2,81
      X(I)=X(I-1)+.0025
20  XX(I)=1./X(I)
C      CORRECTION OF DATA
      QSS=60.0
      READ(1,4)MINN,MAXN
      READ(1,1)(CFACT(K),K=1,81)
      WRITE(3,9)
      DO 100 N=MINN,MAXN
      READ(1,2)NAME(N),LEXIT,RES,QS,RANGE,XE
      READ(1,3)(Y(K,N),K=1,81)
      DO 21 K=1,81
21  Y(K,N)=Y(K,N)*CFACT(K)*(QS/QSS)*RANGE*(1./RES)*XE
C      NORMALIZATION OF DATA
      M=1
      YMAX(N)=Y(1,N)
      DO22 J=2,81
      IF(YMAX(N).GT.Y(J,N))GOTO22
      M=J
      YMAX(N)=Y(J,N)
22  CONTINUE

```

```
C      CORRECTION AND NORMALIZATION (CONTINUED)
C
      XMAX(N)=X(M)
      XXMAX(N)=XX(M)
      WRITE(3,10)NAME(N),LEXIT,XE,QS,RES,RANGE,XMAX(N),
           XXMAX(N),YMAX(N)
      WRITE(2,8)NAME(N),XMAX(N)
      DO 30 K=1,81
30  Y(K,N)=Y(K,N)/YMAX(N)
100 WRITE(2,1)(Y(K,N),K=1,81)
      WRITE(3,6)
      WRITE(3,7)(NAME(N),N=1,9)
      DO 200 K=1,81
200 WRITE(3,5)X(K),XX(K),(Y(K,N),N=1,9)
      END
```

```

C      ANALYSIS OF MIXTURE
C
C      ITOTAL = NUMBER OF MIXTURES, MINN AND MAXN = IDENTIFI-
C      CATION NUMBERS OF FIRST AND LAST APPLICABLE
C      STANDARDS AND YY = INTENSITY IN RELATIVE UNITS
      DIMENSION YY(81,10),CFACT(81),X(81),XX(81),YMAX(10),
      XMAX(10),XXMAX(10),NAME(10),XMAXP(10),XMAXM(10),
      XMAXPP(10),XMAXMM(10)
      1 FORMAT(9F8.4)
      2 FORMAT(I4,2F8.4)
      3 FORMAT(2I4,2F6.1,2F6.3)
      4 FORMAT(12F6.4)
      5 FORMAT(1H1,25HTOTAL NUMBER OF MIXTURES=,I3)
      6 FORMAT(/1X,23HCONSIDER STANDARDS FROM,I3,3H TO,I3)
      7 FORMAT(/10X,4HNAME,2X,4HXXMAX,4X,5HXXMAX/)
      8 FORMAT(10X,I3,3X,F5.4,3X,F5.3)
      9 FORMAT(1H1,4HNAME,3X,5HLEXIT,2X,3HRES,4X,2HQS,5X,
      5H RANGE,3X,2HXE/)
     10 FORMAT(1X,I3,5X,I3,2X,F5.1,2X,F4.1,F9.2,F7.3)
     11 FORMAT(I4)
     12 FORMAT(/15X,29HCORRECTED NORMALIZED Y VALUES/)
     13 FORMAT(2X,7F8.4)
     14 FORMAT(/19X,5HYMAX=,F5.4,1X,5HXXMAX=,F5.4)
     15 FORMAT(/2X,26HMIXTURE CONTAINS COMPONENT,I3//)
     16 FORMAT(/2X,45HMIXTURE CONTAINS NO OTHER STANDARD
      COMPONENTS)
     17 FORMAT(11X,38HY VALUES AFTER REMOVING THIS COMPONENT/)
     18 FORMAT(/25X,11HWAVELENGTHS/)
C      CALCULATION OF WAVELENGTHS
      X(1)=.4750
      XX(1)=2.1053
      DO 20 I=2,81
      X(I)=X(I-1)+.0025
     20 XX(I)=1./X(I)
      QSS=60.0
      READ(1,3)ITOTAL
      READ(1,3)MINN,MAXN
      READ(1,1)(CFACT(K),K=1,81)
      WRITE(3,5)ITOTAL
      WRITE(3,6)MINN,MAXN
      WRITE(3,7)
C      READ IN DATA FOR STANDARDS
      DO 50 N=MINN,MAXN
      READ(1,2)NAME(N),XMAX(N),XXMAX(N)
      WRITE(3,8)NAME(N),XMAX(N),XXMAX(N)
     50 READ(1,1)(YY(K,N),K=1,81)
      WRITE(3,18)
      WRITE(3,13)(X(K),K=1,81)
      DO200 II=1,ITOTAL
      N=10
C      READ IN DATA FOR MIXTURE
      READ(1,3)NAME(N),LEXIT,RES,QS,RANGE,XE
      WRITE(3,9)
      WRITE(3,10)NAME(N),LEXIT,RES,QS,RANGE,XE

```

```

C     ANALYSIS OF MIXTURE (CONTINUED)
C
      WRITE(2,11)NAME(N)
      READ(1,4)(YY(K,N),K=1,81)
C     CORRECT DATA FOR MIXTURE
      DO 21 K=1,81
21    YY(K,N)=YY(K,N)*CFACT(K)*(QS/QSS)*RANGE*(1./RES)*XE
C     NORMALIZE DATA FOR MIXTURE
      M=1
      YMAX(N)=YY(1,N)
      DO 22 J=2,81
      IF(YMAX(N).GT.YY(J,N))GOTO22
      M=J
      YMAX(N)=YY(J,N)
22    CONTINUE
      XMAX(N)=X(M)
      XXMAX(N)=XX(M)
      WRITE(3,12)
      DO 23 K=1,81
23    YY(K,N)=YY(K,N)/YMAX(N)
      WRITE(3,13)(YY(K,N),K=1,81)
      WRITE(2,1)(YY(K,N),K=1,81)
      WRITE(3,14)YMAX(N),XMAX(N)
      WRITE(2,14)YMAX(N),XMAX(N)
C     IDENTIFY MIXTURE COMPONENTS BY MATCHING PEAK
C     WAVELENGTHS WITH STANDARDS
      DO 100 JJ=MINN,MAXN
      XMAXP(N)=XMAX(N)+.0025
      XMAXM(N)=XMAX(N)-.0025
      XMAXPP(N)=XMAX(N)+.0050
      XMAXMM(N)=XMAX(N)-.0050
      M=0
      DO 70 I=MINN,MAXN
      IF(XMAX(N).EQ.XMAX(I))M=I
      IF(XMAXP(N).EQ.XMAX(I))M=I
      IF(XMAXM(N).EQ.XMAX(I))M=I
      IF(XMAXPP(N).EQ.XMAX(I))M=I
      IF(XMAXMM(N).EQ.XMAX(I))M=I
70    CONTINUE
      IF(MINN.EQ.1)GOTO 73
      IF(MINN.EQ.3)GOTO 71
      IF(MINN.EQ.6)GOTO 72
71    IF(XMAX(N).EQ.0.5625)M=3
      GOTO73
72    IF(XMAX(N).EQ.0.5625)M=6
      XMAXGP=XMAX(N)+.0075
      XMAXGM=XMAX(N)-.0075
      IF(XMAXGP.EQ.XMAX(8))M=8
      IF(XMAXGM.EQ.XMAX(8))M=8
73    IF(M.NE.0)WRITE(3,15)M
      IF(M.EQ.0)WRITE(3,16)
      IF(M.EQ.0)GOTO200
C     SUBTRACT POINTS FOR COMPONENT IDENTIFIED
      DO 80 K=1,81

```

```
C    ANALYSIS OF MIXTURE (CONTINUED)
C
  YY(K,N)=YY(K,N)-YY(K,M)
80  IF(YY(K,N).LT.0.0)YY(K,N)=0.0
    WRITE(3,17)
    WRITE(3,13)(YY(K,N),K=1,81)
    WRITE(2,1)(YY(K,N),K=1,81)
C    NORMALIZE NEW CURVE
    L=1
    YMAX(N)=YY(1,N)
    DO 90 J=2,81
      IF(YMAX(N).GT.YY(J,N))GOTO90
      L=J
      YMAX(N)=YY(J,N)
90  CONTINUE
    XMAX(N)=X(L)
    XXMAX(N)=XX(L)
    WRITE(3,14)YMAX(N),XMAX(N)
    WRITE(2,14)YMAX(N),XMAX(N)
    DO 91 K=1,81
81  YY(K,N)=YY(K,N)/YMAX(N)
C    REPEAT TO IDENTIFY REMAINING COMPONENTS
100 CONTINUE
200 CONTINUE
END
```

```

C      PLOT OF CORRECTED NORMALIZED INTENSITY VERSUS
C      WAVELENGTH OR FREQUENCY
C
      DIMENSION X(81),Y(81)
1  FORMAT(9F8.4)
      DO 50 J=1,18
C      READ IN Y VALUES FROM CORRECTION PROGRAM
      READ(1,1)(Y(K),K=1,81)
C      CALCULATE WAVELENGTH INTERVALS
      X(1)=.4750
      DO20 I=2,81
20  X(I)=X(I-1)+.0025
      CALL PLOT(X,.4750,.6750,0,Y,.0,1.0,0,0,.0,.0,0,81,1,
               1,3,2)
50  CONTINUE
      STOP
      END

C      PLOT COMPARING EXPERIMENTAL AND CORRECTED VALUES FOR
C      SMD
C
      DIMENSION X(162),Y(162)
1  FORMAT(12F6.4)
2  FORMAT(9F8.4)
C      CALCULATE WAVELENGTH INTERVALS
      X(1)=.4750
      DO 20 I=2,81
20  X(I)=X(I-1)+.0025
      X(82)=.4750
      DO40 I=83,162
40  X(I)=X(I-1)+.0025
C      READ EXPERIMENTAL AND CORRECTED Y VALUES
      READ(1,2)(Y(K),K=1,81)
      READ(1,1)(Y(K),K=82,162)
C      NORMALIZE EXPERIMENTAL Y VALUES
      YMAX=Y(82)
      DO21 J=83,162
      IF(YMAX.GT.Y(J))GOTO21
      YMAX=Y(J)
21  CONTINUE
      DO22K=82,162
22  Y(K)=Y(K)/YMAX
      WRITE(3,2)(Y(K),K=1,162)
      CALL PLOT(X,.4750,.6750,0,Y,.0,1.0,0,0,.0,.0,0,162,2,
               1,3,2)
      STOP
      END

```



```

C      CALCULATIONS FOR SUCCESSIVE PLOT OF MIXTURE ANALYSIS
C
      DIMENSION X(405),Y(405)
1  FORMAT(9F8.4)
C      CALCULATE WAVELENGTH INTERVALS
      X(1)=.4750
      DO20 I=2,81
20  X(I)=X(I-1)+.0025
      X(82)=.4750
      DO 21 I=83,162
21  X(I)=X(I-1)+.0025
      X(163)=.4750
      DO 22 I=164,243
22  X(I)=X(I-1)+.0025
      X(244)=.4750
      DO 23 I=245,324
23  X(I)=X(I-1)+.0025
      X(325)=.4750
      DO 24 I=326,405
24  X(I)=X(I-1)+.0025
C      READ CORRECTED Y VALUES FOR MIXTURE, Y VALUES AFTER
C      SUBTRACTING FIRST COMPONENT AND Y VALUES
C      AFTER NORMALIZING AND SUBTRACTING
C      SECOND COMPONENT ( CALCULATED IN MIXTURE
C      ANALYSIS) ETCETERA
      READ(1,1)(Y(K),K=1,405)
C      YMAX IS THE NORMALIZATION FACTOR USED IN THE MIXTURE
C      ANALYSIS
      YMAX1 =.6092
      YMAX2=.6253
      YMAX3=.4547
C      MULTIPLY FINAL Y VALUES BY YMAX TO CONVERT TO
C      ORIGINAL SCALE
      DO 30 I=163,243
30  Y(I)=Y(I)*YMAX1
      DO 31 I=244,324
31  Y(I)=Y(I)*YMAX1*YMAX2
      DO 32 I=325,405
32  Y(I)=Y(I)*YMAX1*YMAX2*YMAX3
      WRITE(3,1)(Y(I),I=1,405)
      WRITE(2,1)(X(I),I=1,405)
      WRITE(2,1)(Y(I),I=1,405)
      END

C      PLOT SHOWING SUCCESSIVE STAGES IN A MIXTURE ANALYSIS
C
      DIMENSION X(405),Y(405)
1  FORMAT(9F8.4)
      READ(1,1)(X(I),I=1,405)
      READ(1,1)(Y(I),I=1,405)
      CALL PLOT(X,.4750,.6750,0,Y,.0,1.0,0,0,.0,.0,.0,405,5,
                2,3,2)
      STOP
      END

```

```

C          PLOT SUBROUTINE
C
C          GENERAL PLOTTING SUBROUTINE DEVELOPED BY E.J. KOBETICH
C          (KANSAS STATE UNIVERSITY) AND ADAPTED BY R.W.
C          WHITNEY AND C.F. CROMWELL (OKLAHOMA STATE
C          UNIVERSITY)
C          FURTHER MODIFICATIONS WERE MADE FOR THE PURPOSES OF
C          THIS INVESTIGATION
C          SUBROUTINE PLOT(X,XMIN,XMAX,LX,Y,YMIN,YMAX,LY,Z,ZMIN,
C          ZMAX,LZ,NPT,NPLOT,NCOPY,NCD,NDIM)
C          DIMENSION X(1),Y(1),Z(1),SX(9),TITLE(8),L(134),NCH(41),
C          MOP(18),SXI(9)
1  FORMAT(8A10)
2  FORMAT(58A1,2A9,4A1)
3  FORMAT(1H1,26X,8A10)
4  FORMAT(1H ,A1,5X,F4.2,122A1)
5  FORMAT(133A1)
6  FORMAT(10X,F5.4,7(10X,F5.4),8X,F5.4)
7  FORMAT(1PE17.2,E116.2)
8  FORMAT(1PE17.2,E61.2,E55.2)
9  FORMAT(1PE17.2,2E40.2,E36.2)
10 FORMAT(1PE17.2,3E30.2,E26.2)
11 FORMAT(1PE17.2,4E24.2,E20.2)
12 FORMAT(63X,2A9)
112 FORMAT(1HA,57X,28HFREQUENCY-RECIPROCAL MICRONS)
106 FORMAT(10X,F5.3,7(10X,F5.3),8X,F5.3)
      SLOG(F)=ALOG(F)/2.302585
      LLX=LX+1
      NDD=NCD+1
      GOTO(15,13,14,13),NDD
13  READ(1,1)(TITLE(I),I=1,8)
14  IF(NDD.GE.3)READ(1,2)(MOP(I),I=1,18),(NCH(I),I=1,40),
      TAB1,TAB2,ND,NP,NM,NB
15  NCH(41)=NB
      NPN=NPT/NPLOT
      IF(LX.GT.0)GOTO17
      CX=120./(XMAX-XMIN)
      SX(1)=XMIN
      SX(9)=XMAX
      SXI(1)=1./XMIN
      SXI(9)=1./XMAX
      U=XMIN
      DO16 K=2,8
      U=(XMAX-XMIN)/8.+U
      SX(K)=U
16  SXI(K)=1./SX(K)
      GOTO19
17  XLX=LX
      CX=120./XLX
      NX=SLOG(XMIN)
      DO18K=1,LLX
18  SX(K)=10.** (NX+K-1)
19  CALLPOT(X,XMIN,LX,NPT,0,120.,CX)
      IF(LY.GT.0)GOTO20

```

```

C      PLOT SUBROUTINE (CONTINUED)
C
      CY=50./(YMAX-YMIN)
      GOTO21
20  YLY=LY
      CY=50./YLY
      KY=CY
      NY=SLOG(YMIN)
21  CALLPOT(Y,YMIN,LY,NPT,1,50.,CY)
      IF(NDIM.LT.3)GOTO24
      IF(LZ.GT.0)GOTO22
      CZ=40./(ZMAX-ZMIN)
      GOTO23
22  ZLZ=LZ
      CZ=40./ZLZ
23  CALLPOT(Z,ZMIN,LZ,NPT,0,40.,CZ)
24  DO50NN=1,NCOPY
      M1=1
      T1=33.
      LYY=LY
      TT=50.
      WRITE(3,3)(TITLE(I),I=1,8)
      DO43KK=1,51
      N=1
      NNN=NPN
      JED=1
      T=51-KK
      DO25J=1,133
25  L(J)=NB
      L(133)=ND
      IF(LY.GT.0)GOTO26
      L(13)=NP
      IF(T.GT.TT)GOTO30
      SCALE=T/CY+YMIN
      L(133)=NP
      N=0
      TT=TT-5.
      IF(T.LE.0.)SCALE=YMIN
      GOTO30
26  GOTO(27,27,28,28,27,28),LY
27  SS=KY*LYY
      GOTO29
28  SS=KY*LYY+1
29  L(13)=ND
      IF(T.GT.SS)GOTO30
      SCALE=10.**(NY+LYY)
      N=0
      LYY=LYY-1
      L(13)=NP
      L(133)=NP
30  IF(50..EQ.T)GOTO31
      IF(0..NE.T)GOTO37
31  DO32J=14,133
32  L(J)=NM

```

```

C      PLOT SUBROUTINE (CONTINUED)
C
      IF(LX.GT.0)GOTO34
      DO33J=13,133,15
33  L(J)=NP
      GOTO36
34  KX=120/LX
      DO35J=13,133,KX
35  L(J)=NP
36  IF(50..EQ.T)L(133)=ND
37  DO40LM=1,NPLOT
      DO39I=JED,NNN
      IF(Y(I).NE.T)GOTO39
      J=X(I)
      IF(NDIM.NE.3)GOTO38
      IZ=Z(I)
      L(J+13)=NCH(IZ+1)
      GOTO39
38  L(J+13)=NCH(LM)
39  CONTINUE
      JED=NNN+1
      NNN=NNN+NPN
40  CONTINUE
      IF(T1.NE.T)GOTO41
      IF(15..GE.T)GOTO41
      L(2)=MOP(M1)
      M1=M1+1
      T1=T1-1.
41  IF(N.EQ.1)GOTO42
      WRITE(3,4)L(2),SCALE,(L(J),J=12,133)
      GOTO43
42  WRITE(3,5)(L(J),J=1,133)
43  CONTINUE
      GOTO(44,45,46,47,48,49,44),LLX
44  WRITE(3,6)(SX(K),K=1,9)
      GOTO50
45  WRITE(3,7)(SX(K),K=1,LLX)
      GOTO50
46  WRITE(3,8)(SX(K),K=1,LLX)
      GOTO50
47  WRITE(3,9)(SX(K),K=1,LLX)
      GOTO50
48  WRITE(3,10)(SX(K),K=1,LLX)
      GOTO50
49  WRITE(3,11)(SX(K),K=1,LLX)
50  WRITE(3,12)TAB1,TAB2
      WRITE(3,106)(SXI(K),K=1,9)
      WRITE(3,112)
      RETURN
      END

      SUBROUTINEPOT(V,VMIN,LV,NP,J,VC,C)
      DIMENSIONV(1)
      IF(LV.GT.0)GOTO2

```

C PLOT SUBROUTINE (CONTINUED)

C

```
DO1I=1,NP
1 V(I)=FLOAT(IFIX(C*(V(I)-VMIN)+.5))
  GOTO4
2 DO3I=1,NP
3 V(I)=FLOAT(IFIX(C*(ALOG(V(I)/VMIN)/2.302585)+.5))
4 IF(J.GT.0)GOTO7
  DO6I=1,NP
  IF(V(I).LT.0.)GOTO5
  IF(V(I).LE.VC)GOTO6
5 V(I)=VC+1.
6 CONTINUE
7 RETURN
END
```

# APPENDIX II

## SAMPLE CALCULATION OF CORRECTION FACTORS

TB T  
2475.00 2813.95

LAMBDA	EMISS	TRANS	FREQ	RESP	ENERGY	CORRL	CFACT
.300	.456	.424	3.333	6.560	.3196E-10	.1804E-09	.4872E-11
.310	.456	.592	3.225	6.600	.7242E-10	.3683E-09	.1097E-10
.320	.457	.696	3.125	6.630	.1340E-09	.6171E-09	.2022E-10
.330	.458	.735	3.030	6.680	.2165E-09	.9019E-09	.3241E-10
.340	.459	.746	2.941	6.680	.3272E-09	.1246E-08	.4898E-10
.350	.461	.748	2.857	6.690	.4778E-09	.1665E-08	.7142E-10
.360	.462	.752	2.777	6.700	.6827E-09	.2184E-08	.1019E-09
.370	.463	.756	2.702	6.740	.9558E-09	.2799E-08	.1418E-09
.380	.463	.758	2.631	6.780	.1306E-08	.3513E-08	.1927E-09
.390	.462	.764	2.564	6.800	.1761E-08	.4368E-08	.2591E-09
.400	.461	.767	2.500	6.870	.2328E-08	.5295E-08	.3389E-09
.410	.460	.771	2.439	6.900	.3036E-08	.6384E-08	.4400E-09
.420	.458	.777	2.380	6.990	.3906E-08	.7543E-08	.5588E-09
.430	.457	.781	2.325	7.010	.4960E-08	.8901E-08	.7077E-09
.440	.455	.786	2.272	7.100	.6220E-08	.1028E-07	.8760E-09
.450	.454	.791	2.222	7.150	.7730E-08	.1186E-07	.1081E-08
.460	.452	.794	2.173	7.230	.9464E-08	.1344E-07	.1309E-08
.470	.451	.797	2.127	7.260	.1150E-07	.1526E-07	.1584E-08
.480	.450	.798	2.083	7.290	.1381E-07	.1714E-07	.1895E-08
.490	.449	.802	2.040	7.340	.1652E-07	.1913E-07	.2251E-08
.500	.448	.804	2.000	7.360	.1955E-07	.2126E-07	.2657E-08
.510	.447	.806	1.960	7.400	.2297E-07	.2340E-07	.3105E-08
.520	.446	.807	1.923	7.420	.2677E-07	.2566E-07	.3608E-08
.530	.445	.807	1.886	7.400	.3095E-07	.2810E-07	.4183E-08
.540	.444	.807	1.851	7.380	.3557E-07	.3061E-07	.4820E-08
.550	.443	.809	1.818	7.310	.4074E-07	.3350E-07	.5573E-08
.560	.442	.810	1.785	7.230	.4634E-07	.3650E-07	.6410E-08
.570	.440	.811	1.754	7.180	.5233E-07	.3935E-07	.7288E-08
.580	.438	.811	1.724	7.120	.5872E-07	.4227E-07	.8248E-08
.590	.436	.811	1.694	7.020	.6559E-07	.4549E-07	.9344E-08
.600	.434	.811	1.666	6.870	.7294E-07	.4915E-07	.1061E-07
.610	.433	.811	1.639	6.800	.8096E-07	.5245E-07	.1190E-07
.620	.431	.811	1.612	6.700	.8930E-07	.5592E-07	.1332E-07
.630	.429	.810	1.587	6.690	.9800E-07	.5858E-07	.1465E-07
.640	.428	.810	1.562	6.680	.1075E-06	.6142E-07	.1610E-07
.650	.427	.810	1.538	6.670	.1176E-06	.6421E-07	.1763E-07
.660	.426	.807	1.515	6.660	.1277E-06	.6672E-07	.1918E-07
.670	.424	.807	1.492	6.650	.1385E-06	.6925E-07	.2082E-07
.680	.422	.807	1.470	6.640	.1497E-06	.7171E-07	.2254E-07
.690	.421	.806	1.449	6.630	.1615E-06	.7418E-07	.2436E-07
.700	.419	.806	1.428	6.620	.1736E-06	.7649E-07	.2623E-07

VITA

Elizabeth Colelli Stanley  
Candidate for the Degree of  
Master of Science

Thesis: SPECTROFLUOROMETRIC STUDIES OF RARE EARTH CHELATES

Major Field: Chemistry

Biographical:

The author was born in Johnson City, New York, on March 21, 1942. She graduated from Binghamton North High School in 1959. She received a B.A., with a major in Chemistry, in 1963 from Harpur College, State University of New York at Binghamton. The author worked as a chemist for I.B.M., Vestal, New York, from June 1963 until September 1963. She is a member of the American Chemical Society and of Phi Kappa Phi, National Honor Society.