

TRACE ANALYSIS FOR METALS BY TECHNIQUES OF
SPECTROFLUORIMETRY AND SPECTROPHOSPHORIMETRY

By

J.V. Thompson, M.Sc., (London), D.I.C., G.R.I.C.

A thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy of the
University of London

Department of Chemistry,
Imperial College of Science and Technology,
London, S.W.7.

September 1970.

ACKNOWLEDGEMENTS

The work described in this thesis is entirely original except where due reference has been made. No part of the work has previously been submitted for any other degree.

The work was carried out in the Department of Chemistry, Imperial College of Science and Technology between October 1968 and October 1970.

I wish to express my gratitude to my supervisors, Professor T.S. West and Dr. G.F. Kirkbright, for their invaluable assistance, guidance and encouragement throughout the course of this work, and my research colleagues both past and present for their helpful discussions.

I would also like to express my gratitude to the Science Research Council for the award of a research studentship and a grant to Professor T.S. West and Dr. G.F. Kirkbright for the purchase of the Garton Flash Tube and the T.R.W. nanosecond pulsed source.

CONTENTS

	Page
TITLE: Trace Analysis for Metals by Techniques of Spectrofluorimetry and Spectrophosphorimetry	1
ACKNOWLEDGEMENTS	2
CONTENTS	3
ABSTRACT	5
CHAPTER I: Introduction I	7
CHAPTER II: The Low Temperature Spectrofluorimetric Determination of Antimony(III) in Hydrobromic Acid	45
CHAPTER III: The Fluorimetric Determination of Trace Impurities of Lead in AnalaR Hydrochloric Acid	78
CHAPTER IV: Luminescence Investigations of the Concentrated Hydrofluoric Acid Medium	95
CHAPTER V: The Spectrophosphorimetric Determination of Microgram amounts of Niobium	103
CHAPTER VI: Introduction II	130

CHAPTER VII:	Lifetime Measurements of Inorganic Species in Hydrobromic and Hydrochloric Acid Media at Low Temperature	145
CHAPTER VIII:	Suggestions for Future Work	162
REFERENCES		165

ABSTRACT

The introduction gives a brief resumé of the general theory of fluorescence, phosphorescence and delayed fluorescence mechanisms together with the associated lifetimes of these processes. Factors effecting luminescence intensity are also discussed in some detail. Available apparatus and the specific instrumentation used for the work described in this thesis is also mentioned and finally observations on useful available literature are made.

Chapter II deals with the determination of antimony in hydrobromic acid and also discusses several observations made on related work concerning the interferences of iron(III) and copper(II) together with the low temperature absorption spectra of these two ions.

The third chapter deals with the determination of trace lead impurities in concentrated acid. This work was carried out after interest had been expressed by the manufacturers of the pure acids supplied concerning the suitability of this method as means of quality control.

In order to try to correlate a pattern to the results obtained previously for the hydrobromic and hydrochloric matrices the work described in Chapter IV shows the results obtained for the hydrofluoric acid matrix. However from the results obtained to date no definite conclusions could be drawn.

Chapter V describes the determination of niobium by a spectrophosphorimetric technique. This method shows that niobium can be determined in microgram quantities in the presence of large excesses of over 50 foreign ions. The fact that the interference of iron can be easily removed shows the potential that this method may have for the determination of niobium in steel samples.

A second introduction discusses the relevant theory and instrumentation required for the measurement of the lifetimes of several species, the results of which are to be found in the penultimate chapter. Finally, the implications of these results and suggestions for future work in this field are discussed in the last section.

CHAPTER I

INTRODUCTION

The general theoretical treatment of fluorescence and phosphorescence phenomena in solution has been reviewed by Bowen [1] [2], Pringsheim [3], Bartholomew [4], White [5], West [6], Hercules [7] and Parker [8] and will be outlined only briefly here.

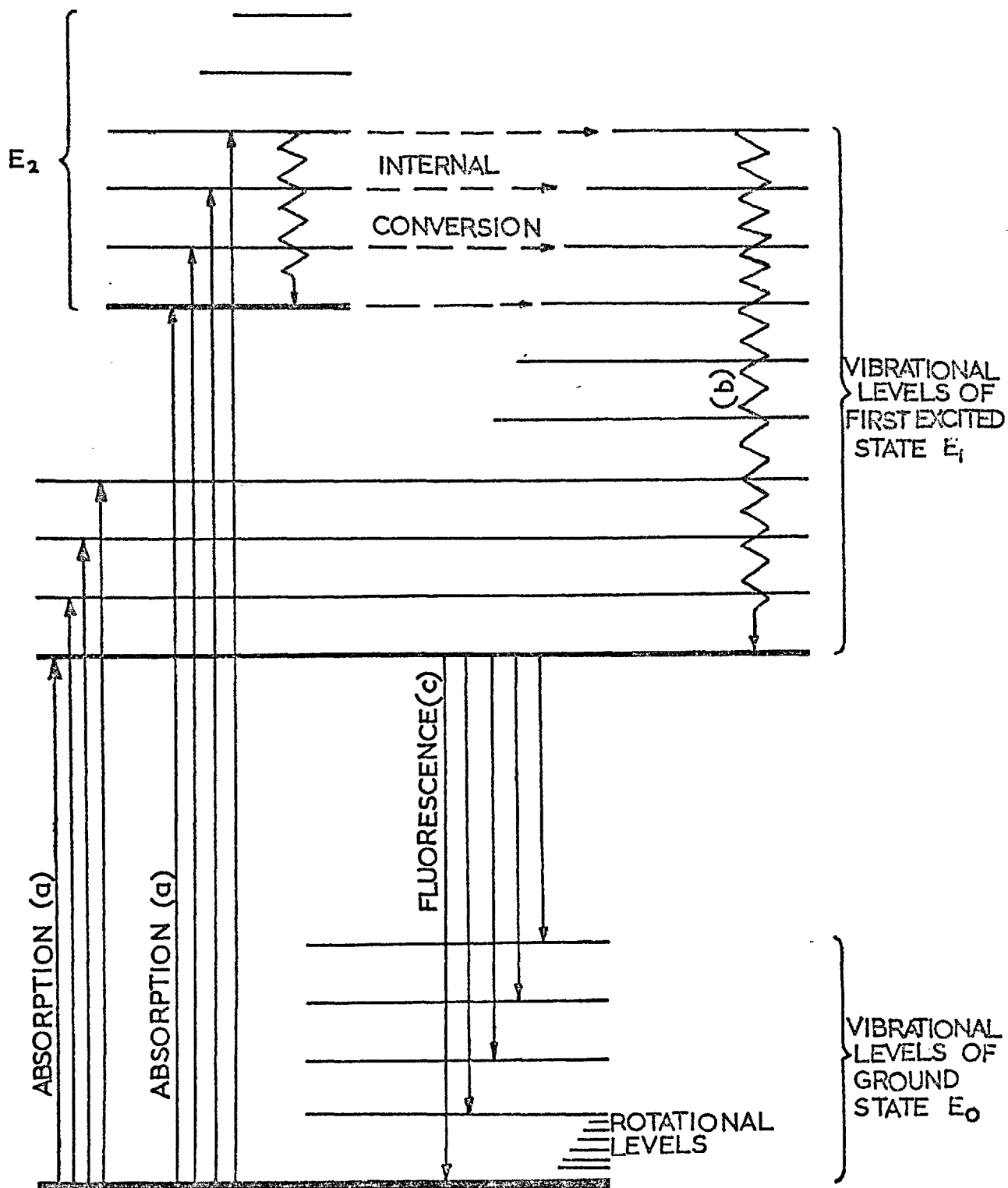
Fluorescence

Electronic transitions may be stimulated in molecules at room temperature by the absorption of light and usually take place from the lowest vibrational level of the ground state E_0 , to vibrational levels of higher electronic states E_1 , E_2 and E_3 . This is illustrated in the absorption spectra of simple molecules by the presence of several well defined maxima, each of which incorporates the corresponding rotational lines which are too close to be separated spectroscopically. However the vibrational levels of some molecules are so complex that transitions to the different vibrational levels of the first excited state give rise to one single broad band, sometimes together with a second band at higher frequency due to excitation to the second electronic excited level.

Once the molecule has been excited to the vibrational levels of the first excited state it rapidly loses its vibrational energy by collisions with neighbouring molecules. This is shown by transitions (b) in Figure 1.1. If the molecule has been excited to an even higher electronic excited state, E_2 and E_3 , then it may undergo radiationless transition known as internal conversion whereby transition to a high vibrational level of the first excited state, of the same energy as the low vibrational level of the higher electronic excited state just vacated, occurs. Collisional deactivation again causes loss of the resulting vibrational energy back to the E_1, V_0 state. From this level the molecule can return to any of the vibrational-rotational levels of the ground state by the emission of light of the corresponding frequency. These are transitions (c) in Figure 1.1. It is this emission process which is known as fluorescence.

If all the molecules which originally absorbed light underwent this complete mechanism then the solution would be said to have a quantum efficiency of unity. (The quantum efficiency is defined as the ratio of the number of quanta of energy emitted to the number of quanta absorbed). Other mechanisms, however, compete with the fluorescence process; these are internal conversion, collisional deactivation, conversion to lower triplet levels, and photochemical reactions

FIGURE 1.1.



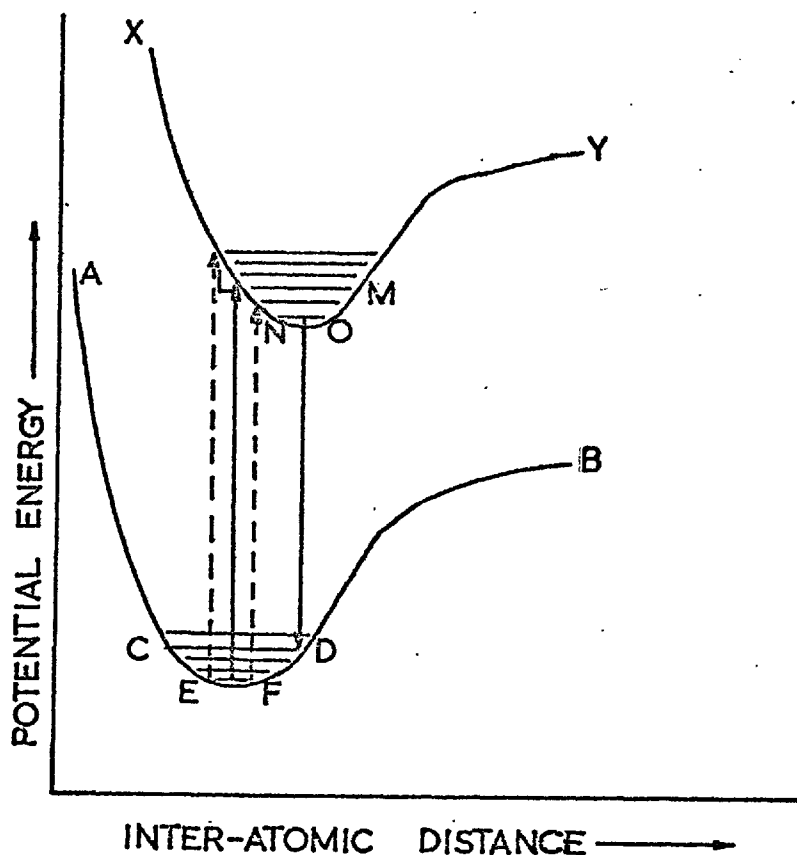
such as dissociation. These processes may reduce the fluorescence efficiency markedly.

Absorption bands of equal intensity and emission maxima of equal intensity would be expected if the position of the energy bands as indicated in Figure 1.1 was the only factor to be considered. In fact the intensities of the different absorption bands varies greatly, as do the fluorescence emission bands. In order to explain this the Frank-Condon Principle must be considered. This states that absorption, and hence excitation, takes place within 10^{-15} seconds. During this time the heavy nuclei of the atoms do not appreciably change their position or momentum, therefore, the nuclear configuration in the excited state is the same as that of the ground state prior to absorption. On the potential energy diagram Figure 1.2 the simple case of a diatomic molecule is considered.

The lower curve AB represents the potential energy of the ground state, and the upper curve XY the potential energy of the first electronic excited state. The small horizontal lines within each of these curves represent the vibrational levels of each of these electronic states.

As no nuclear positional or momentum change occurs the transition can be represented by a vertical line between the two electronic states. For molecules which possess no vibrational

FIGURE 1.2



energy the point from which transition is most likely to occur is the centre point of the line EF, or the line NO if emission is considered. Other transitions, however, can occur from other positions towards the ends of the line EF and from other vibrational levels, though the probability is much lower. Therefore one intense absorption band, together with several of lower intensity can be expected; this may be represented

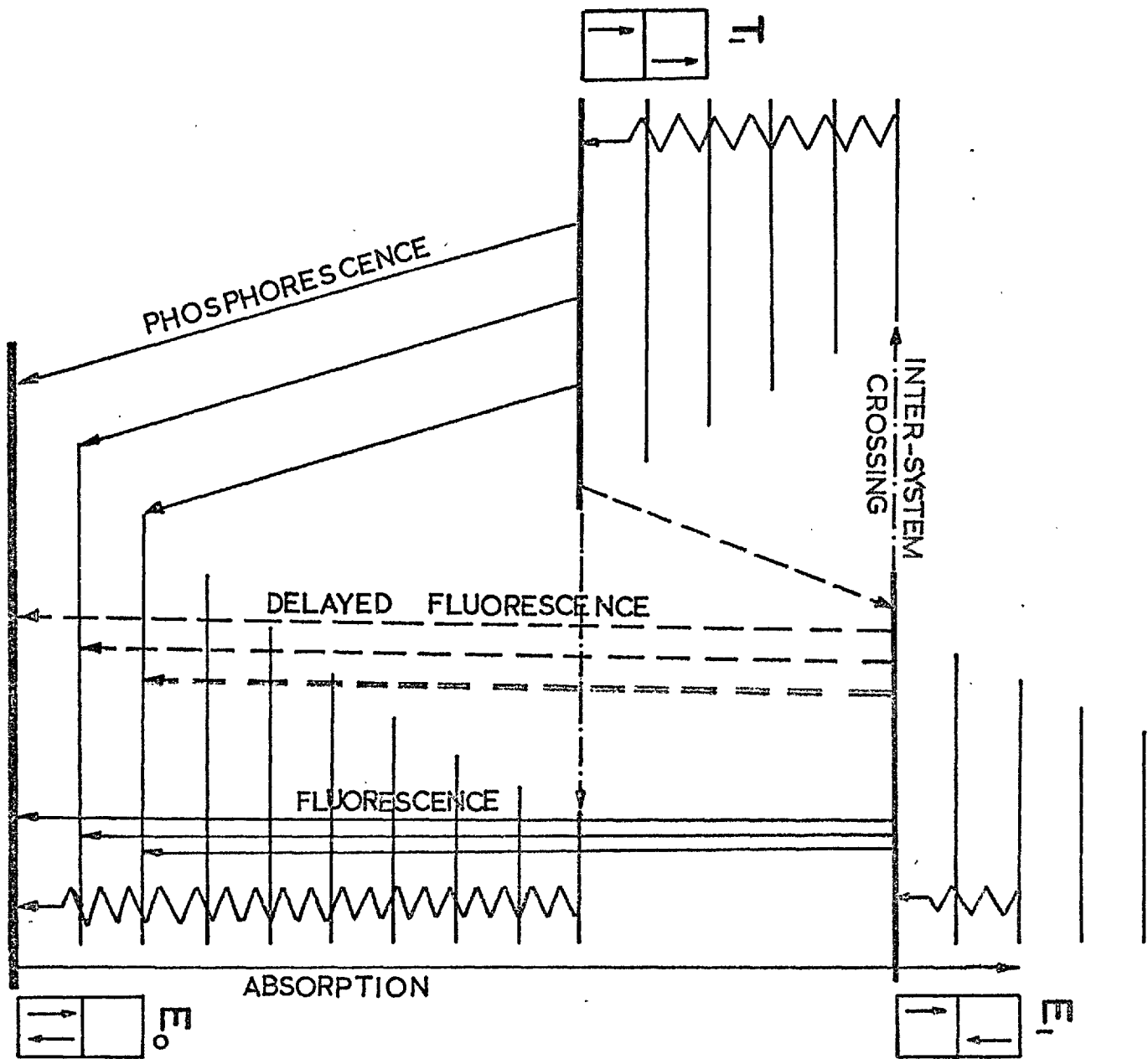
by the dotted lines drawn vertically from either end of the line EF. Following excitation and subsequent loss of vibrational energy the most probable transition will be from the mid-point of the line NO back to the ground state at D. This will be the most intense band though other weaker bands will be observed for transitions to other vibrational levels of the ground state. The molecule will finally lose its vibrational energy by collisions with other molecules in solution.

It should be noted that the emission spectra is frequently a mirror image of the primary absorption band. This is due to the fact that the distribution of vibrational levels in the first excited state, which determine the shape of the first absorption band, is approximately the same as those in the ground state which are responsible for the shape of the emission spectrum.

Phosphorescence

Electrons in atomic and molecular orbitals are spin coupled, E_0 and E_1 , Figure 1.3, representing the singlet states which correspond to these spin coupled states. Spin reversal of an electron may occur though according to the Pauli Exclusion Principle a new orbital must be formed for the uncoupled electron. This new configuration will show spectroscopically as a triplet because of the interaction of the spins and orbitals. Hund's Rule states that spin multiplicity favours the ground state, as

FIGURE 1.3

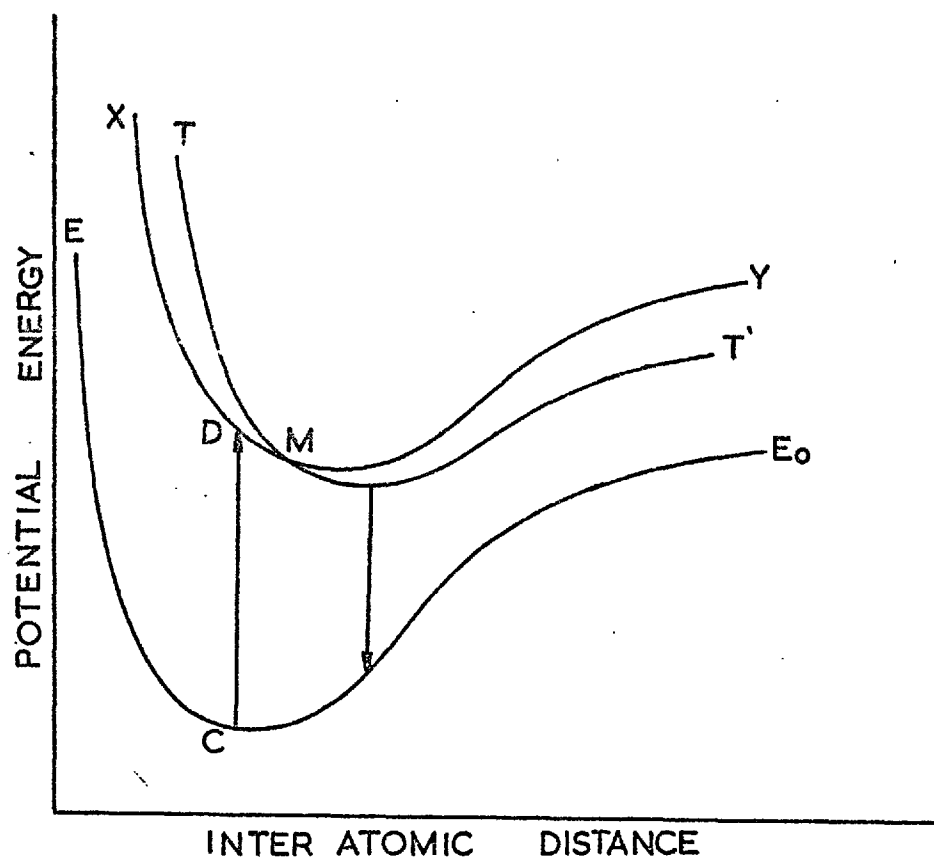


a result the excited triplet state T_1 is less energetic than the singlet E_1 from which it was derived. However, the energy difference separating the two states is normally small and exchange between the two can readily occur. This exchange process is known as inter-system crossing.

Processes in competition with normal fluorescence have similar rate constants, i.e. 10^{-8} seconds, one such process is inter-system crossing. The lowest vibrational level of the T_1 state is situated somewhere below the lowest excited singlet state but its higher vibrational levels reach the level of the lowest excited singlet state and transition between the two can occur. This mechanism is known as inter-system crossing where a molecule crosses over from the excited singlet to one of the upper vibrational levels of the lowest triplet state. From this point the molecule rapidly loses its vibrational energy and falls to the lowest vibrational level of the triplet state. Consideration of the process is clarified if a potential energy diagram is studied, Figure 1.4. This diagram refers only to a diatomic molecule, consideration of a polyatomic molecule, however, would involve the same principle.

Light absorption is represented by the vertical line CD. The molecule now in the excited singlet state rapidly loses its excess vibrational energy passing down the curve XY to the point M. At this point the positions and momenta of the atomic

Figure 1.4. Potential Energy Diagram Illustrating Inter-System Crossing



nuclei are identical to those corresponding to a molecule in the lowest triplet state, and at this point the molecule can transfer to the corresponding vibrational level of this triplet state. As a consequence the molecule adopts the relatively long lived triplet state during the lifetime of the E_1 state.

Normal fluorescence occurs when the electron returns to the ground state E_0 from E_1 , and the first excited state E_1 has a finite lifetime of $10^{-7} - 10^{-9}$ seconds. If the molecule possesses a triplet state T_1 below the E_1 state then phosphorescence may occur. The molecule passes from the E_1 state to T_1 and phosphorescence emission occurs when the electron returns to the ground state E_0 . Transitions between states of different multiplicity, however, are "forbidden" and consequently the direct promotion of an electron from E_0 to T_1 is "forbidden" as it would require simultaneous spin de-coupling. Once the triplet state has been achieved indirectly, re-radiation will be difficult as spin re-coupling must occur so the lifetime of the triplet state is relatively long - $10^{-4} - 10$ seconds.

The difference between fluorescence and phosphorescence is that whilst the former involves a singlet-singlet transition the latter involves a triplet-singlet mechanism. As a result fluorescence appears to be an instantaneous process (ca 10^{-8} seconds), whereas phosphorescence is a great deal slower (ca $10^{-4} - 10$ seconds). An important consequence of this time factor is seen when the process of collisional deactivation is considered. Though collisions between solute and solvent molecules can be an important factor in decreasing the intensity of fluorescence, phosphorescence has been noted only rarely at room temperature [9] where collisions occur readily, and most

samples have to be frozen to form a glass so that the collision rate is drastically reduced.

Phosphorescence emission occurs at a longer wavelength than the fluorescence emission for the same molecule because of the small loss in energy in the transition from the E_1 to T_1 state. It will, however, have a similar spectral shape to the fluorescence band because the same vibrational levels of the ground state are involved for both mechanisms.

Delayed fluorescence can occur by several mechanisms, the two most important of which will be discussed briefly here. Firstly, E-type or thermally assisted delayed fluorescence [10] [11]. This occurs by a mechanism similar to normal phosphorescence. However, when the triplet state has been attained, thermal energy excites the molecule back to the first excited singlet state from where its transition back to the ground state gives rise to fluorescence emission.

P-type delayed fluorescence is the second of the more common mechanisms, and this occurs by the collision of two excited triplet molecules, with the production of ground state molecule and one excited singlet molecule [12] [13]. The subsequent emission of delayed fluorescence occurs when the electron falls back from the excited singlet to the ground state.

Both these mechanisms give rise to emission of the same spectral characteristics as direct fluorescence though the

intensity is much lower, and the lifetime is characteristic of that of the triplet state.

For normal fluorescence the fluorescence intensity F is defined as the intensity of absorbed ^{radiation} measured in quanta per second multiplied by the quantum efficiency Φ_F .

$$\begin{aligned} \text{Therefore } F &= I_A \Phi_F \\ &= (I_0 - I_T) \Phi_F \end{aligned}$$

Beer Lambert's Law states however that

$$\frac{I_T}{I_0} = e^{-kc'l'}$$

where c' is the concentration of material (molecules/ml.) and k is the effective cross-sectional area of one molecule in sq.cm.

$$\text{Therefore } F = I_0(1 - e^{-kc'l'}) \Phi_F$$

Expansion of this equation gives :-

$$F = I_0 \left[kc'l - \frac{(kc'l)^2}{2} + \frac{(kc'l)^3}{6} - \dots - \frac{(kc'l)^n}{n!} \right] \Phi_F$$

Changing concentration to more practical units of moles/litre and calculating the molar extinction coefficient

$$F = I_0 [2.3 \epsilon cl] \left[1 - \frac{2.3 \epsilon cl}{2} + \frac{(2.3 \epsilon cl)^2}{6} - \dots \right] \Phi_F$$

Therefore for solutions which absorb only weakly (that is the value ϵcl is small), the above equation simplifies to :-

$$\underline{F = I_0 [2.3 \epsilon cl] \Phi_F}$$

Therefore the intensity of fluorescence is directly proportional to the concentration of the solute present, providing all other factors are kept constant. Also, for constant concentration, the fluorescence intensity varies directly with the incident radiation intensity. Therefore if a very high intensity source is used very low concentrations of fluorescent solute can be readily measured, and it is this point that illustrates the basic difference between molecular spectrofluorimetry and absorption spectrophotometry. In the latter technique the detection limit or sensitivity is governed by the minimum measurable difference between two signals of high intensity (I_0 and I_T) and the intensity of the source has no effect on the detection limit. In spectrofluorimetry, however, given a high intensity of exciting radiation, and a very sensitive and stable amplification and detection system, there should be, in theory, no limit to the concentrations detectable. In practice, this does not hold. The thermal noise of the photomultiplier tube and circuit can be significant, but the factor which most often limits the sensitivity is the magnitude and variation in the background (blank) fluorescence. This may arise in one of two ways, either the organic reagent used under the conditions of the determination may exhibit a large fluorescence signal or, from fluorescent impurities present in either the reagent or solvent. First or second order scattering of the incident light or Raman scattering by the

solvent may also be a limiting factor.

The possibility of Raman scattering has been fully discussed by Parker [14] who has thoroughly investigated the phenomena for several solvents. When light falls upon a substance, a proportion of it is scattered at the same wavelength, but a small percentage interacts with the vibrational and rotational modes of the solvent molecule and is re-emitted at a slightly longer wavelength. The difference in wavelength between the absorbed and emitted light corresponds to the energy absorbed during this interaction. Since the emission occurs at a longer wavelength than the incident radiation, it is possible that this Raman emission may cause serious interferences with a normal weak fluorescence signal if it is in the same wavelength region. Only the main Raman band need be considered as the others are of very low intensity. If water is the solvent then it will exhibit its main band at a frequency $0.3 \mu^{-1}$ lower than that of the exciting light. Other factors that contribute to the magnitude of the blank signal can be partially removed by the purification of reagents and solvents. Raman scattering cannot readily be overcome.

Quenching Processes

The quantum efficiency for any particular compound, Θ , should ideally have a value of unity, and in fact values of 0.97 for rhodamine B in ethanol, and 0.92 for fluoresceine in 0.1 M

sodium hydroxide solution have been reported [15]. Several factors however can cause a reduction in this value. These quenching effects can take several forms, (a) those which directly affect the quantum efficiency, and (b) those which interfere indirectly with the quantum efficiency, e.g., the inner filter effect.

1. Intermolecular Collisions

Deactivation of the excited state molecules caused by collisions with other molecules, in particular those of the solvent, is a very important factor when quenching processes are considered. As expected, an increase in the temperature will greatly effect this phenomena, and a negative temperature coefficient of between one and two percent per degree centigrade at room temperature is relatively common. This could therefore be a serious detracton from room temperature spectrofluorimetry; this is however not an appreciable effect for a technique generally used for trace analysis and an error of $\pm 5\%$ caused by this temperature change will give an absolute result insignificantly different to the actual amount present, if sub-microgram quantities are being considered. In phosphorescence the effect can be much more serious than in fluorescence due to the much longer lifetime of the triplet state [16] [17]. All these difficulties are, however, overcome by working at the

temperature of liquid nitrogen. The collision rate actually occurring is very small indeed because of the greatly increased viscosity of the medium, and the sample will also remain at a constant temperature of -196°C .

2. Solvent Effects

This effect on the fluorescence signal can be quite marked. Solvents which contain substituents such as bromo, iodo, nitro and azo groupings are generally unsuitable as the large magnetic fields which surround these bulky substituents tend to promote spin de-coupling of the electrons and hence triplet state formation. Whilst this effect will detract from the fluorescence signal it may help to induce phosphorescence [18] and this has been the subject of much discussion [19] [20]. Similarly molecules that exhibit strong van der Waals forces with the excited solute molecule will aid deactivation because of the prolonged collisional lifetime.

Polar solvents relative to non polar solvents also tend to inhibit fluorescence when considering metal chelate systems because of their strong solvation of the complex though the reverse may be true when truly aromatic systems are studied [19] [21].

3. Solvent Viscosity

An increase in the viscosity of the solvent medium will obviously decrease the intermolecular collision rate and may thus enhance the fluorescence signal. For this reason the very large increase in viscosity obtained by working at liquid nitrogen temperature is seen to be at least partly responsible for the correspondingly large increase in fluorescence sensitivity obtained [22].

4. Chemical Reaction

It has been previously well characterised that exposure to ultra-violet light can promote chemical reaction of the excited state molecules. In analytical spectrofluorimetry however any reagent exhibiting this property would not be considered as a practical proposition and would therefore be ignored. The only example of this met within the bounds of the experimental work covered here is the rapid decrease in the fluorescence of thallium (I) in concentrated hydrochloric acid, and this has been attributed to the rapid oxidation to thallium (III) caused by irradiation with ultra-violet light [23].

5. Dissolved Oxygen

Dissolved oxygen can have a pronounced effect on the magnitude of fluorescence for organic systems [2]; the effect does not appear to be so common, however, for metal chelate systems.

This certainly appears to be illustrated by work carried out in this laboratory which shows that no decrease in the signal is obtained for a sample that contains dissolved oxygen. However, dissolved gases may produce a large increase in the frequency of cracking when working at low temperature, and this frequency may be reduced by de-aerating the sample before cooling.

6. Cationic and Ionic Strength Effects

Transition metals which possess unfilled 'd' orbitals will quench fluorescence whereas diamagnetic ions when they are co-ordinated will tend to give fluorescent complexes. However, though paramagnetic ions will inhibit fluorescence they do enhance the intersystem crossing process and can therefore be expected to increase the phosphorescence phenomena if the work is carried out at low temperature [24].

7. Charge and Energy Transfer Processes

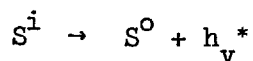
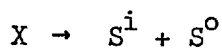
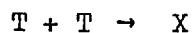
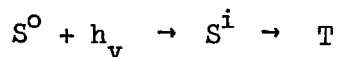
Charge transfer processes may also be responsible for the quenching of fluorescence. A mechanism for this has been proposed by Weller [25], who suggest that the excited fluorescent species M^* forms a charge transfer complex with the quenching species Y to produce an ion pair M^-Y^+ which will then dissociate to the ground states of M and Y , with the result that the energy is dissipated thermally; or that a triplet

state of M is formed together with the ground state of Y, on dissociation, and the excess energy dissipated in a similar manner.

Another mechanism which effectively quenches fluorescence is known as sensitized fluorescence. Where the energy from an excited species D^* is transferred to another species A which is the ground state to give A^* and D followed by the subsequent emission characteristic of the species A. Hence the fluorescence of the species D is effectively quenched. For singlet-singlet energy transfers of this form a theoretical suggestion as to the exact mechanism has been suggested by Perrin [26] [27] and this has been further developed by Förster [28] [29], but generally may be represented by the equation :-



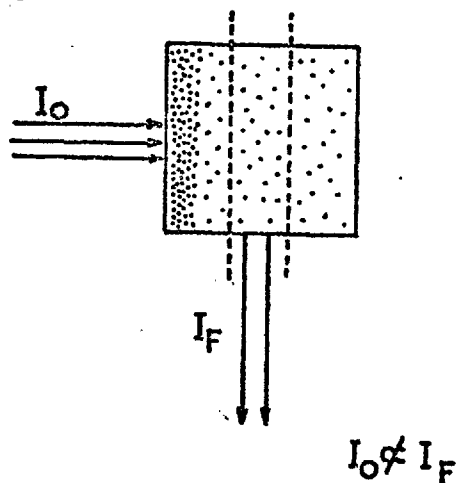
Triplet to singlet energy transfers have also been observed by several authors [30] [31] [32] [33] as have triplet to triplet energy transfers [34]. The latter is illustrated by the phenomena of P-type delayed fluorescence which assumes that an encounter between two triplet molecules gives rise to an intermediary species X which dissociates to give one excited singlet state and one ground state molecule. This mechanism is represented in the following way, the most important steps being :-



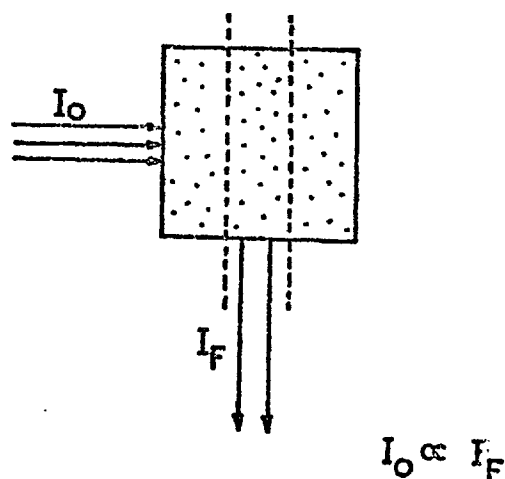
This was the mechanism suggested by Parker [35].

The other process by which the fluorescence signal may be reduced but does not affect the quantum efficiency value in any way is the inner filter effect. This phenomenon is common in fairly concentrated solutions where an absorbing concomitant molecule present will absorb either a proportion of the incident or emitted radiation and therefore reduce the analytical signal [36]. A fluorescent molecule can naturally act as its own inner filter and this phenomenon is clearly visible for concentrated aqueous solutions of fluorescein. This phenomenon is clarified if the sample cell geometry is considered, Figure 1.5.

A



B



In diagram A a large proportion of the incident radiation is absorbed in the first few fractions of a cm. of the solution, and as a result the fluorescence signal obtained at the photomultiplier detector is much lower than anticipated because the photomultiplier is observing the fluorescence emission from the centre portion of the cell. As a result the signal obtained is neither proportional to the incident radiation intensity or to the concentration of the fluorescent species.

The inner-filter effect can easily be overcome by dilution and diagram B shows that under ideal conditions no self-absorption occurs, and the fluorescence signal obtained will be directly proportional to both the incident radiation intensity and the concentration. Other factors which can cause a decrease in the fluorescence intensity are chemical reactions with foreign ions, oxidation and reduction, neutralisation, complexation and precipitation and though they are not strictly regarded as quenching actions they can definitely cause a serious interference effect if encountered.

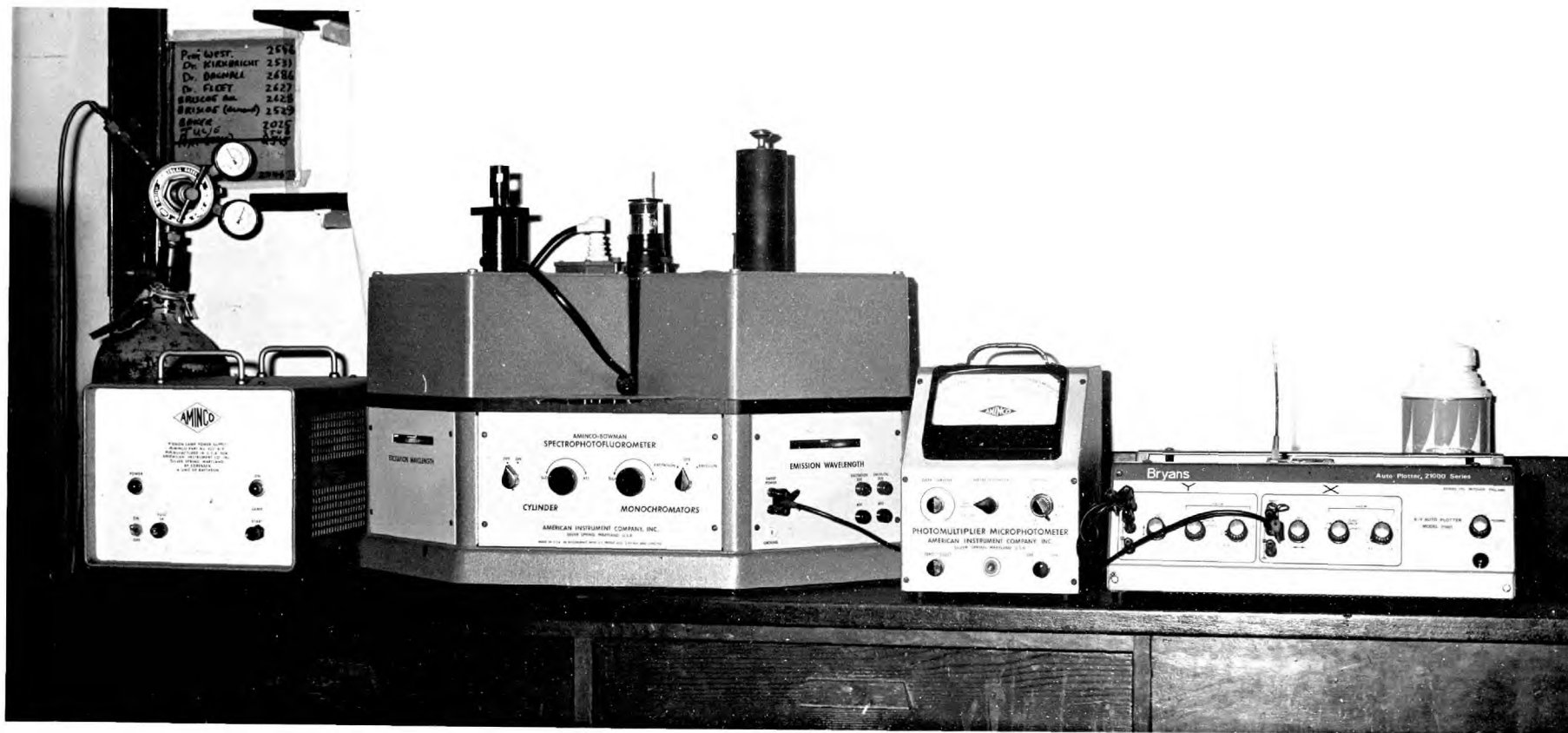
INSTRUMENTATION

Commercially available instruments for carrying out studies in the field of spectrofluorimetry and spectrophosphorimetry are generally rather similar in nature, and a description of

the Aminco-Bowman Spectrophotofluorometer, Figure 1.6, used by the author during the course of this work serves as an illustration of a typical instrumental assembly.

The general arrangement of the instrument is illustrated in Figure 1.7. The output from the photomultiplier passes directly to the photometer unit where after suitable amplification it is shown on the scale. A connection linking the microphotometer unit with an X-Y recorder also enables the photomultiplier output to be displayed on the Y-axis, the X-axis being directly linked to the wavelength drive mechanism of the optical unit, therefore enabling fluorescence excitation and emission spectra to be recorded. The D.C. power unit supplies the current for the 150 watt high pressure Xenon arc lamp which is mounted on the optical unit opposite the photomultiplier, a fan is fitted to the side of the Xenon lamp housing to prevent the arc from becoming too hot. A 115v/220v transformer is required to operate this American instrument in the United Kingdom.

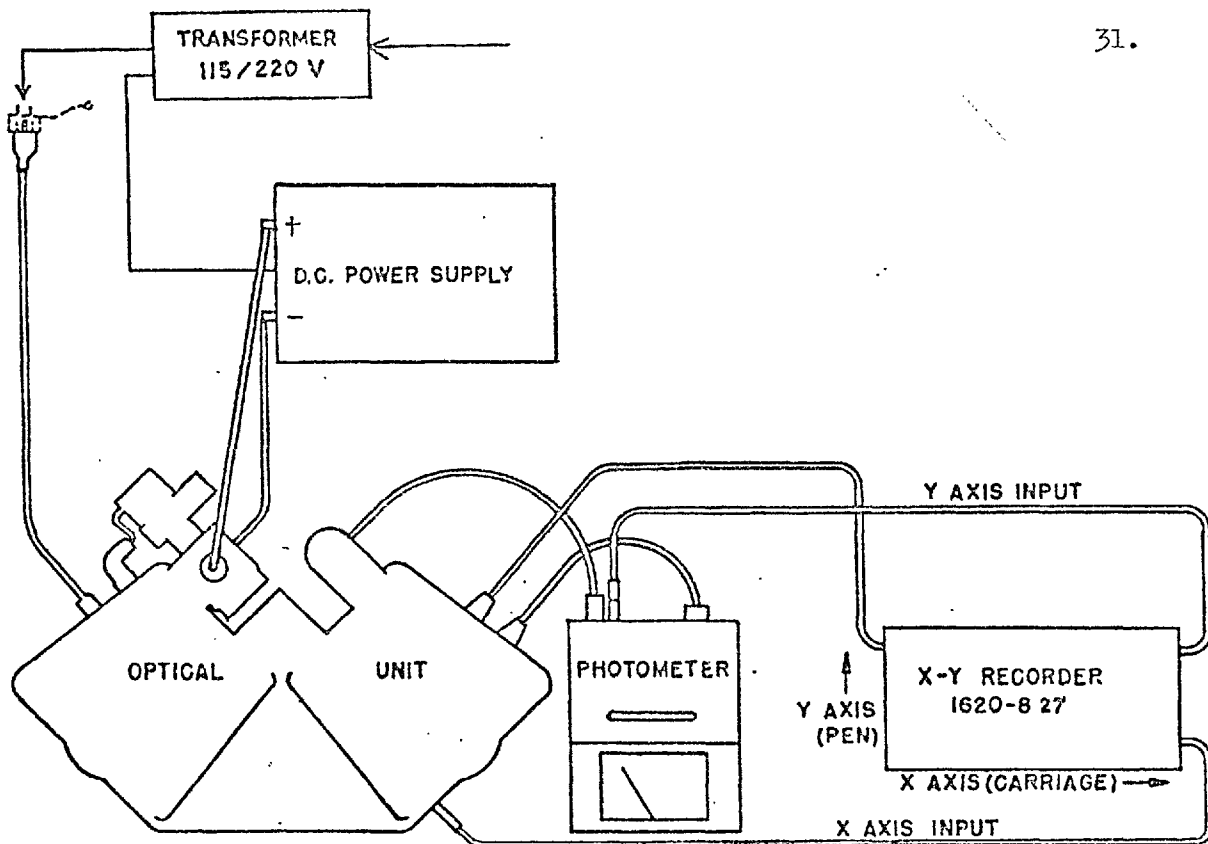
A more detailed picture of the optical unit is given in Figure 1.8. The light source used in all the experimental work reported here was a 150 watt high pressure Xenon arc lamp which gives a continuous spectrum from 220 nm to beyond the visible region and well into the infra-red. The power supply unit runs on an A.C. input but rectifies this to D.C. Initial switching on of the power supply produces 50 - 60 c.p.s. noise



which ceases after ignition of the lamp. The arc is struck by a momentary potential of approximately 25 K volts, however after this initial pulse the output voltage to the Xenon lamp drops to ca 19.8 volts D.C.

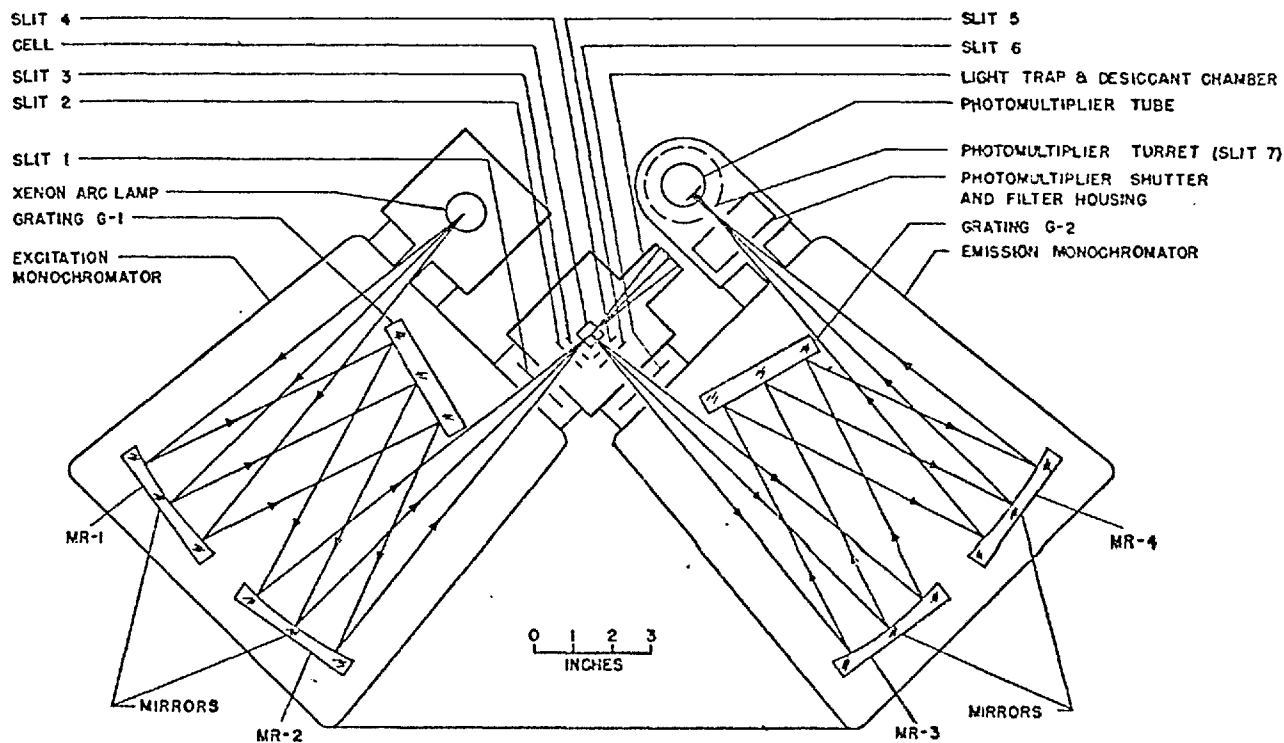
The output from the lamp passes through a plane quartz window into the sealed monochromator unit, initially passing through a set of baffles to a large front silvered concave mirror which collimates the light onto the grating monochromator. From the grating the monochromated first order radiation is passed to a second concave mirror which focusses this incident radiation onto the sample. The fluorescence radiation from the sample emitted at right angles to the incident beam, is dispersed by a second grating monochromator into monochromatic radiation incident on the photomultiplier. Each monochromator has a wavelength range from 200 nm to 800 nm, and are optically identical except for a difference in 'blaze' wavelength. The excitation grating is blazed at 300 nm (1st order) to strengthen the output from the Xenon lamp which decreases below 400 nm. The emission grating is blazed at 500 nm (1st order) to improve the response to fluorescence at wavelengths from 400 - 600 nm. Measurement of fluorescence signals at wavelengths above 700 nm requires the use of an R136 photomultiplier tube as both the IP21 and IP28 tubes possess very weak responses in this region. Additional scanning ranges of 300 to 900; 400 to 1000;

FIGURE 1.7.



31.

FIGURE 1.8.



500 to 1100 and 600 to 1200 nm can be achieved by realignment of the gratings. Scanning speeds for all wavelength ranges above can be varied between 75 and 270 seconds, with a dead time variation between 14 and 54 seconds. The metal slits provided from 0.1 mm to 5.0 mm, Figure 1.8, give equivalent half bandwidths of between 1.0 and 30 nm. Assessment of exactly which slit arrangement can be left largely to the operator, but as a general rule those giving a bandwidth of ≤ 5 nm are most suitable for characterisation and spectra plotting work and those providing a bandwidth of 30 nm are exceedingly useful for trace analysis work and phosphorescence measurements where scattered incident radiation problems are not apparent.

The sample compartment which is situated between the two monochromators can be adapted for room temperature fluorescence and low temperature fluorescence and phosphorescence. The two latter techniques are accommodated by removal of the normal 1 cm.² fused quartz cell used for room temperature measurements together with its holder, and replacing it with a special sample holder, which accommodates a quartz dewar flask into which the sample tube fits for low temperature techniques. The quartz dewar is 17.5 cm. in length and 4.25 cm. in diameter with a non silvered fused quartz base 1.6 cm. in diameter. This is accommodated in the sample holder so that

the base appears in the centre of the instrument light beam. The coolant, liquid nitrogen, in all studies mentioned here, is placed in the dewar to approximately one third depth. The sample tube containing sample is finally placed in this dewar so that it extends to the base of the non silvered portion. Sample cells provided with the instrument consisted of quartz tubes 20.0 cm. total length with an internal diameter of 5 mm. and 1 mm. wall thickness, the portion which actually holds the portion of the sample to be measured consisted of a narrower bore tube 1 mm. internal diameter and 1 mm. wall thickness. However, though these are suitable for studies involving organic solutions at low temperature, inorganic acid solutions when frozen frequently cause the sample tube to break, and therefore as the cost of the sample tubes provided with the instrument is high a cheaper and very satisfactory substitute was found in ordinary precision bore quartz or pyrex tubing 3 mm. internal diameter, 1 mm. wall thickness which had been sealed in the normal fashion at one end. Pyrex tubing appeared to be the most satisfactory because it cracked less frequently, it was considerably cheaper and the surface were much smoother, containing less imperfections. This tended to decrease the amount of bubbling within the nitrogen, and also the amount of scatter from the tube wall. However, due to the transmission properties pyrex glass could not be used below ca 320 nm and in these cases it was replaced by quartz.

The fluorescence signal passes from the sample through the "analysing" monochromator, and falls onto the photocathode of either an R.C.A. IP21 or IP28 photomultiplier tube.

Though completely interchangeable these two tubes vary in spectral response(S-4 and S-5 type respectively), current amplification and signal to noise ratio. A 9-stage IP28 was used for the antimony and niobium determinations and an IP21 for the remainder of the work. The photomultiplier power supply unit requires A.C. mains input and rectifies this to provide a stabilised 700 volts D.C. output, negative with respect to ground, to the photosensitive cathode.

The photomultiplier microphotometer unit consists of the associated circuitry for the photomultiplier tube, and an amplifier which responds to the small current produced by the photomultiplier tube and registers the amplified current on the meter. The unit also possesses circuitry for stabilising the dynode voltage to 0.1% for normal line voltage variations. This is required as the anode current of the photomultiplier tube is highly sensitive to variations in dynode voltage and therefore requires a stable power supply. This stabilisation is supplied by a 15 volt-amp line voltage stabiliser, and a 700 volt corona discharge tube. The line voltage stabiliser also provides stabilised power to the amplifier. A control for off-setting any photomultiplier dark current, caused either

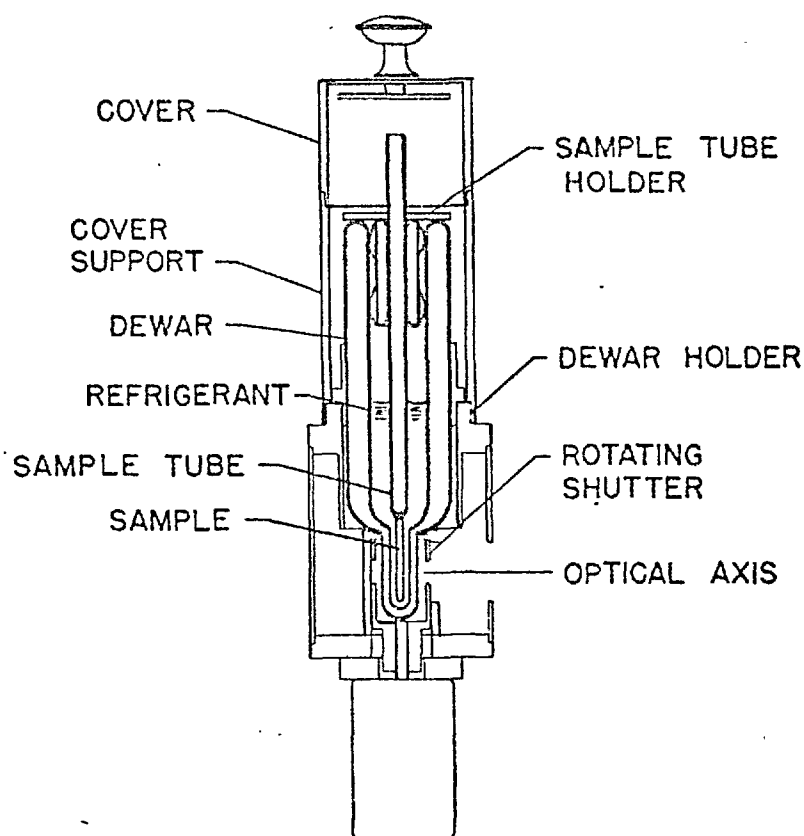
by thermionic emission or small light 'leaks' is placed on the microphotometer. The zero adjust control permits zeroing of the meter. The meter multiplier control allows the removal of high voltage from the photomultiplier tube, provides a zero reference voltage required for zeroing the meter and permits sensitivity variation in seven fixed steps: 1.0, 0.3, 0.1, 0.03, 0.01, 0.003 and 0.001 over a range of 1000 to 1 (relative intensity of signal on the meter is a product of the transmittance scale reading and the multiplying factor used). The sensitivity control provides continuous sensitivity variation over a range of 3.5 to 1. At the rear of the unit are outlets for a recorder and oscilloscope.

The recorder used for plotting all the spectra was a Bryans X-Y recorder Auto Plotter Series 21000 (Bryans Limited, Mitcham, England). This required 200 - 250 volts A.C. at 50 - 60 C/s, single phase and provided spectra 7 x 10 in. in area. As previously described the X-axis is directly linked to the wavelength scale of the optical unit, and the Y-axis to the rear of the microphotometer unit.

In order to measure phosphorescence spectra or phosphorescence lifetimes the Aminco-Keirs phosphoroscope (C26-62140) must be placed into the sample compartment of the optical unit which had been adapted using a B25-62140 cell holder, Figure 1.9. This consists of a motor driven can,

into which two openings are placed directly opposite each other so that they coincide with the light beam, around the base of the dewar. In this way illumination and measurement of the signal cannot take place simultaneously and therefore the problems of scatter are completely removed. Very wide slits can therefore be employed for trace phosphorescence analysis.

FIGURE 1.9. CELL ASSEMBLY WITH PHOSPHOROSCOPE ATTACHMENT



The Aminco-Bowman Spectrophotofluorometer being a single beam instrument, provides spectra that are characteristic of the Xenon arc output, the monochromators characteristics and the photomultiplier tube and amplifier response at the wavelength of fluorescence. Any fluorescence signal produced is therefore only a product of those parameters and therefore has little absolute significance. Parker and Rees [37] along with Chen [38] and other workers [39] [40] [41] [42] have described a method for the correction of the excitation and emission spectra in order to obtain the "true" spectra. The corrected excitation spectra is obtained by correction of the observed spectra for any variation in the Xenon arc lamp spectral distribution and the transmission characteristics of the excitation monochromator. The corrected fluorescence spectra produced by allowing for the transmission characteristics of the analysing monochromator and the variation with wavelength of the detector sensitivity. Such procedures, however, involve tedious point-by-point correction and unless a corrected spectra attachment is available [43] for rapid production of those spectra this procedure does not appear worthwhile for analytical requirements; though a certain amount of standardisation in this field of analysis would be of no little significance. Though it would obviously be of value to know the true position and intensity of the excitation

and emission maxima of any system, the apparent maxima are of a more practical significance, i.e., the maximum response on the operator's own instrument, and therefore providing reference is made the uncorrected spectra as obtained directly from the instrument are used in all work described here.

The main problem encountered with all single beam spectro-fluorimeters is the variation in the arc intensity both during the same day and from one day to the next; to the author's experience this variation can be as much as 200%. As the fluorescence signal is directly proportional to the incident light intensity any variation in the latter is immediately reflected in the analytical signal. In order to overcome this difficulty a standard must be constantly used. In all fluorescence studies made a 10^{-6} M solution of quinine bisulphate in 0.1 M sulphuric acid was employed repeatedly throughout any experiment [44] [45]. This solution has an excitation maximum at 350 nm and an emission maximum at 450 nm [6]. Though this does not allow for any variation in spectral distribution with time this was found to be negligible and was therefore not considered. Checking the instrument sensitivity before and after each experiment was found to be insufficient, and a system of measuring the standard between measurement of each unknown was used. For the phosphorimetric determination of niobium a 6.25×10^{-6} M niobium

solution was employed as the standard as the stability over a period of 5 hours appeared very good. The use of quinine bisulphate in this case was prevented due to its very short lifetime of approximately $2.0 \cdot 10^{-8}$ seconds.

The production of a dual beam instrument is seen by the author as a very important need if further work in the field of spectrofluorimetry and spectrophosphorimetry is to be made considerably easier; as the constant use of standard solutions certainly increases the time required for any analytical determination. Whether the system involves the direct monitoring of the Xenon arc or if it is produced on the lines of the classical spectrophotometer employing a second standard solution seems of less importance. But that there should be a rapid and accurate method of monitoring the intensity variations of the source is of paramount importance. Double beam spectrofluorimeters have been described by Hercules [7] though none are commercially available at the present time.

The advantages of a spectra correction attachment can be clearly seen in providing some sort of uniformity both to the information already available and to all future work. However the cost appears somewhat prohibitive at present, and the hoped for situation may therefore unfortunately never arise.

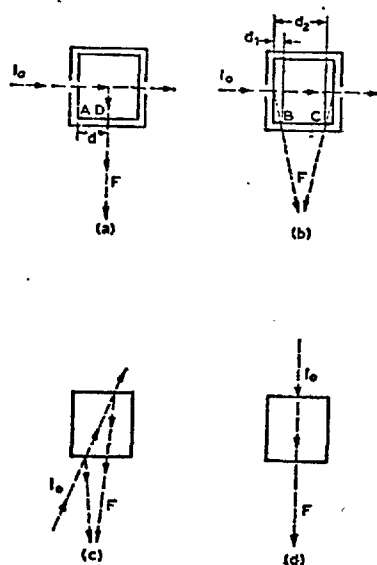
A further shortfall with the Aminco-Bowman instrument is the very low operating voltage (700 volts D.C.) of the

photomultiplier. If this is increased to 1100 volts D.C. using an AEI photomultiplier power unit type R1184 an increase of over 10 x in the sensitivity can readily be obtained without increasing the noise to an intolerable level.

Though the double monochromator instrument used for this work was very satisfactory, several other types are available and they may be more practical in certain cases. The use of an instrument for analytical trace work with a filter in place of the excitation monochromator appears very attractive because it allows much greater intensity and a wider spectrum of irradiation whilst a monochromator in the emission side allows more precise resolution of the fluorescence radiation. The light losses inside the grating monochromators used in the Aminco-Bowman are rather great, and therefore a large increase in sensitivity may be obtained by substituting a filter. However, fluorescence signals received from filter instruments invariably include spurious signals from light scatter, Raman emission, etc., which cannot be differentiated. Therefore the choice of instrument depends on the compromise required between sensitivity and selectivity, resolution and precision. In the case of the former a filter instrument is more suitable; however a double monochromator apparatus is desirable if selectivity, resolution and absolute precision are all required.

The reason for measuring the fluorescence at right angles to the incident beam is to cut down any scattering of the incident radiation which would otherwise augment the fluorescence signal and hence prevent accurate trace analysis. Even though most instruments possess efficient monochromators scattered radiation can still be a serious problem as the excitation and emission peaks overlap or are very close to one another. The interference from the cell walls caused by self-fluorescence [36], scatter or internal reflection is also minimised. Another important factor in deciding upon a suitable instrumental geometry is clarified when overall sensitivity is being considered, Figure 1.10.

Figure 1.10. METHODS FOR ILLUMINATION AND MEASUREMENT.



(a) and (b) right angle methods; (c) frontal illumination;
(d) in line method.

Instruments that measure the fluorescence signal at angles other than 90° to the incident radiation also have advantages. Frontal illumination for the study of solid samples and very strong solutions is required. A straight through system can be used for phosphorescence measurements and Parker and Rees [34] [37] have indicated certain advantages of this system when ordinary fluorescence systems are being studied.

Several workers have produced critical reviews of particular types and brands of commercially available instruments [6] [7] [46] [47] [48] [49] and before purchase of any apparatus is made it is advisable to consult these reviews.

REACTING CATION AND REAGENT CHARACTERISTICS

Though the actual mechanism for the fluorescence and phosphorescence of several elements in the strong acid media remains obscure it should be noted that no transition group element exhibits luminescence. Though several factors which have previously been indicated as inhibiting fluorescence do not seem to have been obeyed, e.g. ions which give rise to coloured complexes generally do not give rise to fluorescent compounds. (Their determination being carried out by measuring the extinction of fluorescence when they react with a fluorescent molecule. This is clearly shown by the reactions

of 8-hydroxyquinoline in forming fluorescent non coloured complexes with aluminium, beryllium and gallium and non fluorescent coloured complexes with copper and iron). This case of the acid glasses must therefore remain apart from general fluorescence theory until it has been more thoroughly examined (see Chapter VII).

In the case of the phosphorescence determination of niobium, a simple aromatic system, 8-hydroxyquinoline, which is itself phosphorescent, on reaction with the niobium forms a complex with slightly different spectral characteristics. The theory of the fluorescence mechanism has been the subject of previous discussion [50] [51] and will therefore be omitted from this text.

Several ions have previously been determined fluorimetrically using 8-hydroxyquinoline [52] and none (with the exception of lead) appear to possess phosphorescent properties. Therefore, not only does phosphorescence provide a selective method for niobium in the presence of all ions which react with 8-hydroxyquinoline, but also those which react to give fluorescent complexes. Taking this ideal example the advantage of the technique of spectroluminescence can clearly be seen when compared with absorption spectrophotometry, and a full comparison of these two techniques has been made by T.S. West in his review of chemical spectrophotometry [53].

Finally mention should be made of some of the more helpful literature available on the technique of spectro-luminescence. C.E. White [59] and more recently in conjunction with A. Weissler [55] have provided excellent coverage of the field with their biennial reviews. Several other texts [5] [53] [56] [57] [58] have provided great assistance during the course of this work and none less than the most recent texts by C.A. Parker [8] and D.M. Hercules [7], and a translation of an original Russian text by Konstantinova-Shlezinger [59] presents an excellent coverage of work carried out by Russian scientists.

CHAPTER II

THE LOW TEMPERATURE SPECTROFLUORIMETRIC DETERMINATION OF ANTIMONY(III) IN HYDROBROMIC ACID

Several spectrophotometric methods for the determination of trace quantities of antimony utilising the reagents thiourea [60], methyl violet [61], brilliant green [62] and rhodamine B [63] [64] are well known. A sensitive and selective method for the determination of antimony using the reagent bromopyrogallol red [65] has been reported by previous workers in this laboratory. A further method based on the absorption of light at 366 nm by the bromo-complex of antimony(V) in strong hydrobromic acid has been suggested [66], while a sensitive spot test for antimony using the reagent gallein has been proposed as a quantitative procedure [67].

Although all the above methods provide reasonably high sensitivity for the determination of antimony the attainable selectivity is poor, and separation of the antimony from other interfering species is usually necessary before the final determination. MacNulty and Wollard [64] achieved the separation of antimony by adopting the method that had been proposed by Blumenthal [68], viz. the coprecipitation of antimony with manganese dioxide, before determination of the element using the reagent rhodamine B. It is also necessary that antimony be present in the pentavalent oxidation state before the addition of the reagent.

No previous spectrofluorimetric procedure for the determination of antimony has been reported, but previous communications from this laboratory [69] [70] have described the spectral characteristics of the fluorescence of antimony in strong hydrochloric and hydrobromic acid glasses formed at liquid nitrogen temperature of -196°C . The sensitivity has been shown to be approximately 100 times greater in hydrobromic acid media than in hydrochloric acid. The same workers [71] have also reported an analytical method for the determination of trace amounts of tellurium in strong hydrochloric acid at -196°C .

This chapter describes the development of a method for the determination of traces of antimony by measuring the red fluorescence at 586 nm using an excitation wavelength of 360 nm. The optimum conditions for the determination have been established and study of the effects of a 50 fold molar excess of 55 foreign ions made.

EXPERIMENTAL

All fluorescence measurements were made using the Aminco-Bowman spectrophotofluorimeter together with the low temperature sample cell assembly as previously described. Pyrex tubes 20 cm. in length, internal diameter 4 mm. and 1 mm. wall thickness were employed as sample tubes in preference to the quartz tubing normally supplied; the frequency of sample

tube 'cracking' during freezing with these tubes was found to be greatly reduced. A sample volume of 0.5 ml. was sufficient to make accurate quantitative measurements in these tubes.

REAGENTS

Antimony(III) solution (10^{-2} M)

0.8124 g. of antimony potassium tartrate AnalaR grade, (B.D.H. Ltd.) was dissolved in 250 ml. of distilled water.

Hydrobromic acid

General purpose reagent grade (Hopkin and Williams) twice distilled in order to reduce the otherwise high reagent blank.

Diverse ions

10^{-2} or 10^{-3} M solutions of analytical reagent grade salts were used. All other reagents were analytical reagent grade.

CONSTRUCTION OF A CALIBRATION GRAPH

Between 0.2 and 5.0 ml. aliquots of 10^{-5} M antimony(III) solution (10^{-5} M $\equiv$ 1.218 $\mu\text{g}/\text{ml.}$) were transferred to 25 ml. volumetric flasks, 18 ml. of concentrated hydrobromic acid was added to each flask and finally diluted to volume with distilled water obtained from an all glass distillation apparatus. The fluorescence intensity of each sample was measured at -196°C

after an interval of 10 minutes, using an excitation wavelength of 360 nm, and measuring the fluorescence emission at 586 nm. The graph of fluorescence intensity against antimony(III) concentration (0.01 - 0.25 ppm), Figure 2.1, is a straight line, and passes slightly above the origin due to the fluorescence of the hydrobromic acid reagent blank.

SPECTRAL CHARACTERISTICS

Figure 2.2 shows the excitation and emission spectra of antimony(III) in hydrobromic acid at -196°C with the excitation maximum occurring at 360 nm and the emission maximum at 586 nm. These spectra are uncorrected for the characteristics of lamp emission, monochromator transmission and photomultiplier response. The relevant data for methods of correction to account for these factors are given elsewhere [38].

EFFECT OF HYDROBROMIC ACID CONCENTRATION

Neither the wavelength of maximum absorption nor the emission wavelength maximum were found to change in any way when the concentration of hydrobromic acid was varied. However the intensity of emission was found to be dependent on acid concentration, Figure 2.3. The optimum hydrobromic acid concentration being 6 M. Solutions of lower acid concentrations did not form a clear glass on freezing, and the fluorescence intensity was found to be lower in more concentrated

FIGURE 2.1.

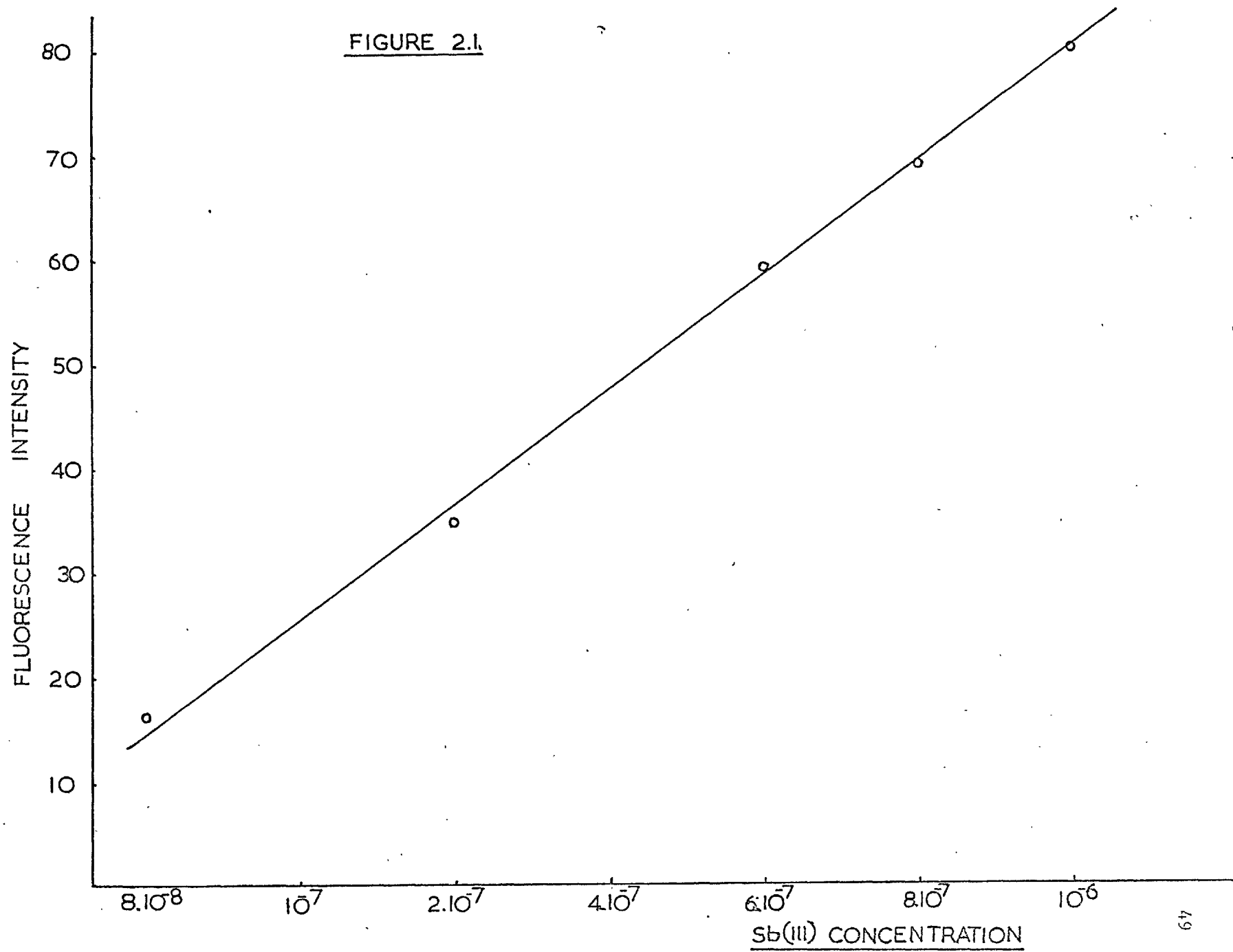
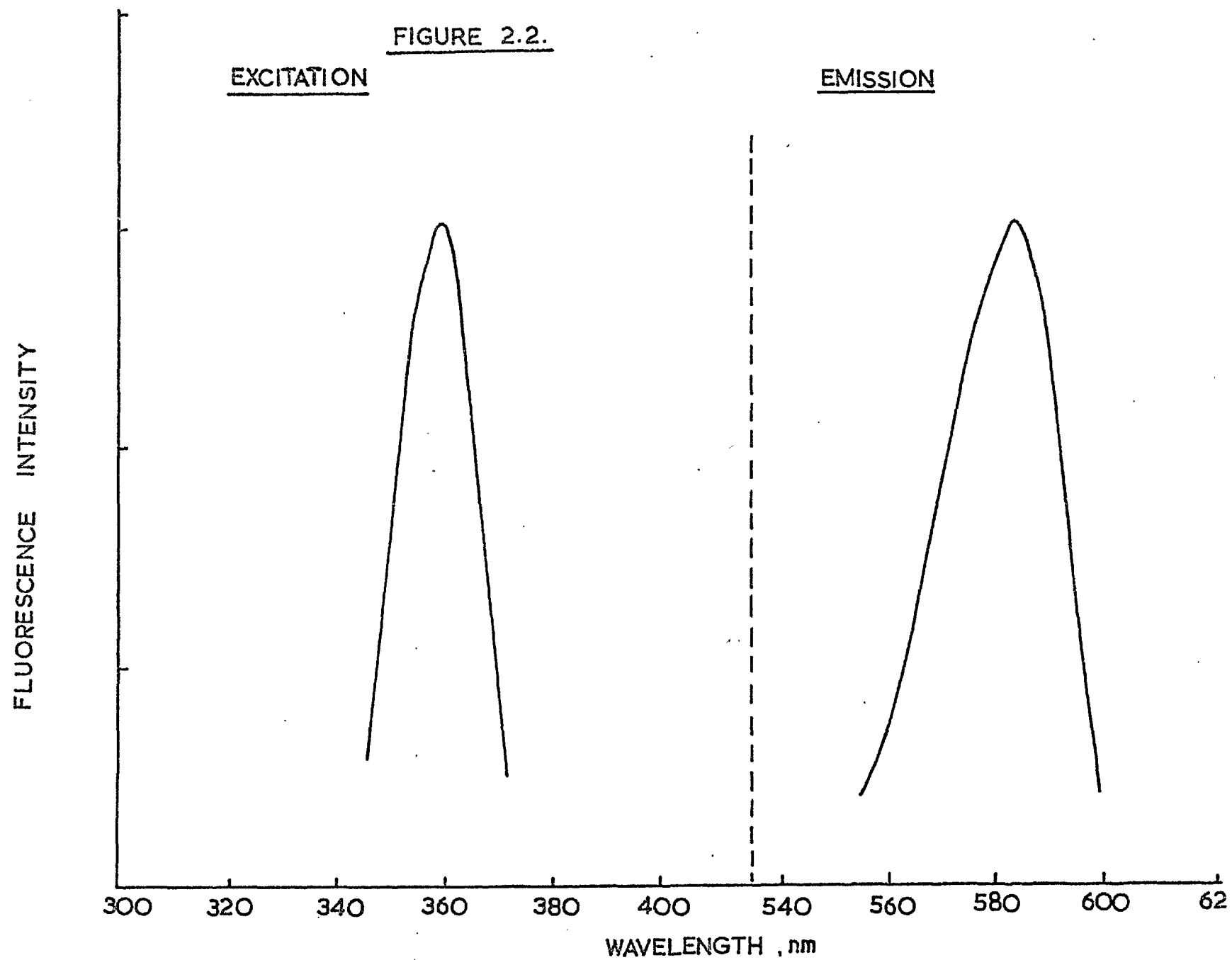
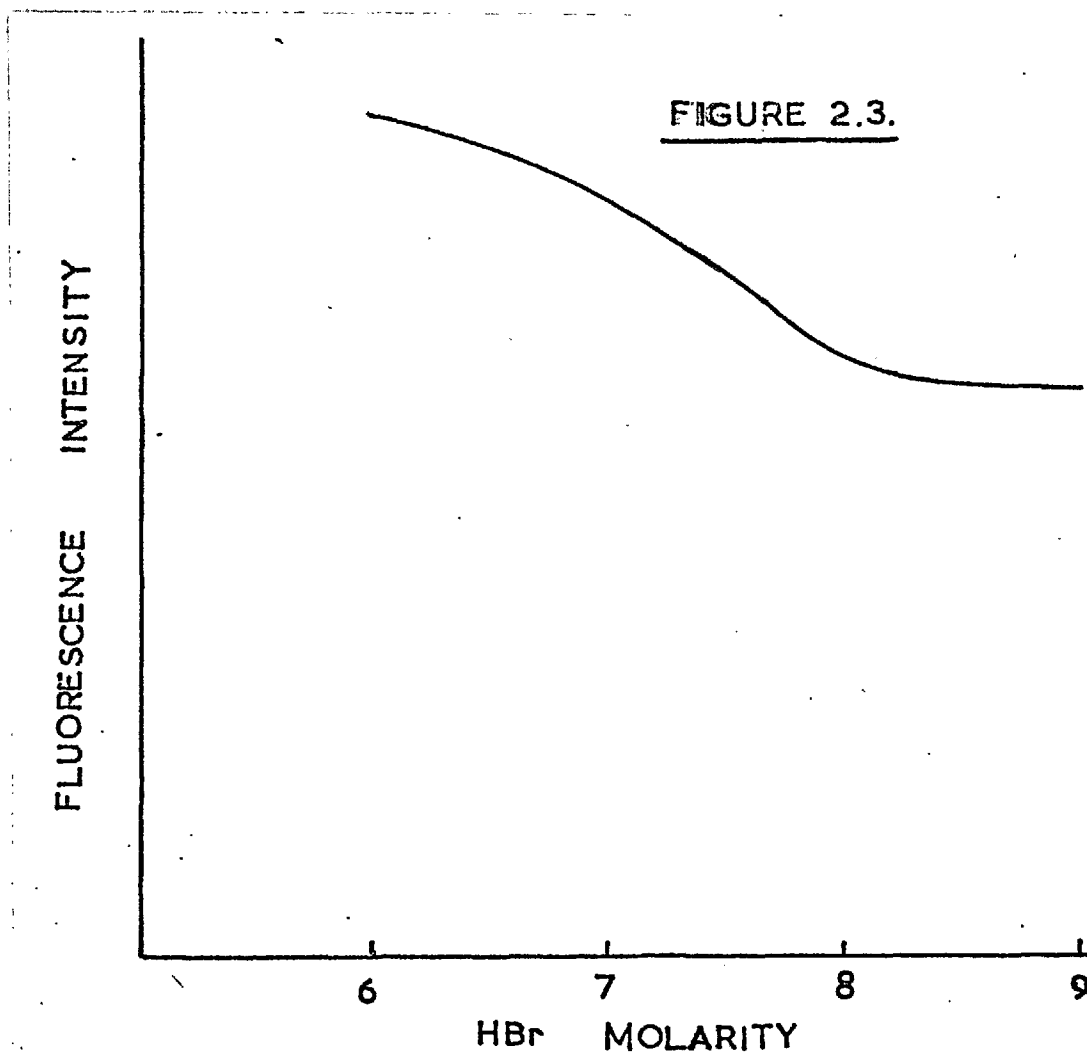


FIGURE 2.2.





solutions. A standard sample of 10^{-6} M quinine bisulphate in 0.1 N sulphuric acid at room temperature was used throughout to facilitate easy correction of readings due to the alteration in instrumental characteristics, in particular the intensity of the Xenon lamp source during the period of measurement.

EFFECT OF TIME ON FLUORESCENCE EMISSION

The effect of time on the fluorescence intensity was investigated under optimised conditions of excitation and emission wavelengths and acidity. It was found that a 10^{-6} M antimony(III) solution showed no measurable decrease in fluorescence intensity after standing for two hours; either in darkness or in normal laboratory fluorescent strip lighting. Continuous irradiation of a similar solution, at room temperature, in the spectrophotofluorimeter for 1 hour showed a reduction in fluorescence intensity of 4%. A standard sample of quinine bisulphate was again used to check that the instrumental characteristics remained constant.

EFFECT OF FOREIGN IONS

The effects of a 50-fold molar excess of 55 foreign ions on the determination of a 2.10^{-6} M antimony(III) solution (6 μ g of antimony in 25 ml.) were investigated. During the study of interferences a variation of $\leq 5\%$ in the fluorescence intensity from that of the standard solutions was considered to be acceptable. Under the standard conditions the results thus obtained are shown in Table 2.1.

TABLE 2.1

Effect of various ions on the determination of a
 2.10^{-6} M antimony(III) solution in 6M hydrobromic acid

<u>Ion</u>	<u>Interference</u>	<u>Ion</u>	<u>Interference</u>
Al	0	Mn(II)	+ 2.0
As	+ 1.2	Mn(VII)	+ 2.0
Ba	- 4.5	Hg(II)	+ 4.0
Be	- 3	Mo(VI)	- 3.6
Bi(III)	+ 2.3	Ni	+ 2.0
Cd	0	K	- 2.0
Ca	- 2	Sc	0
Ce(III)	- 1.8	Se	+ 1.0
Cr(III)	0	Ag	+ 1.9
Cr(VI)	- 1.0	Te(IV)	- 30
Co(II)	0	Tl(I)	- 2.0
Cu(II)	- 4.8	Sn(II)	+ 2.0
Ga	0	Sn(IV)	- 0.8
Ge(IV)	+ 1.8	Mg	+ 4.0
Hf	- 1.6	Ti(IV)	- 3
In	- 3.0	U(VI)	+ 5.2
Fe(II)	0	V(V)	- 4.2
Fe(III)	+ 2.0	Zn	- 0.8
La	- 0.6	Zr	0

Table 2.1 (contd/)

Ion	Interference	Ion	Interference
Acetate	- 2.0	Nitrate	- 0.9
Borate	+ 1.0	Oxalate	- 3.0
Chloride	0	Perchlorate	0
Citrate	+ 4.0	Phosphate	0
Cyanide	+ 2.0	Sulphate	0
Fluoride	0	Tartrate	+ 3.0
Iodide	- 2.0	Thiocyanate	- 4.0

Tellurium(IV), which gave a strong yellow coloured solution, gave rise as shown to a negative error of approximately 20%, due to the absorption of the incident radiation. However, the presence of a 20 fold molar excess of tellurium was found to give no negative interference. Table 2.II shows the absorption and fluorescence intensity readings obtained for a $2 \cdot 10^{-6}$ M antimony(III) solution containing varying concentrations of tellurium from 10^{-5} M to $5 \cdot 10^{-3}$ M and these results are plotted in Figure 2.4.

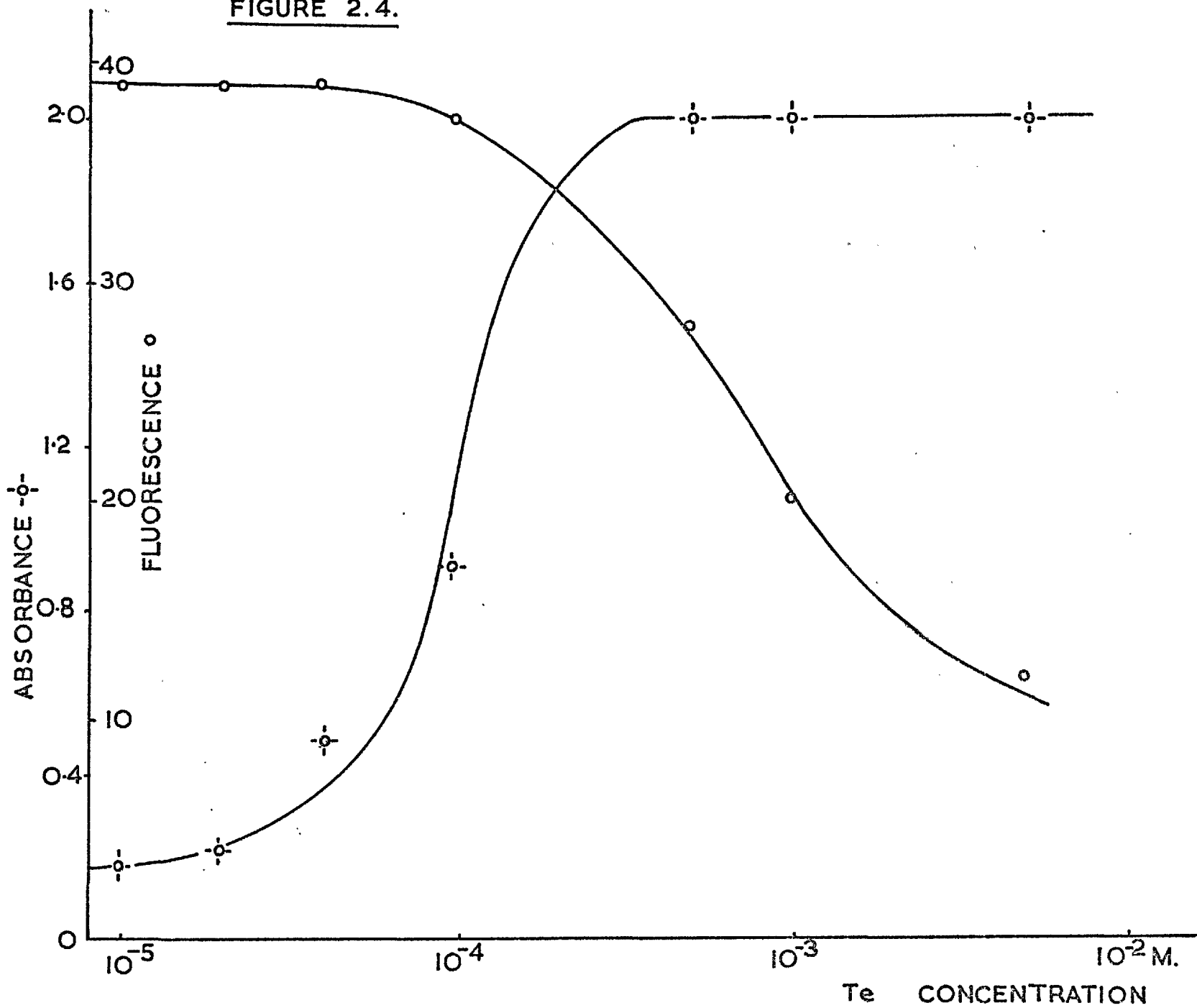
TABLE 2.II

The effect of excess tellurium on a $2 \cdot 10^{-6}$ M
antimony(III) solution

Solution	Tellurium Concentration	Fluorescence Reading	Absorption at 360 nm.
1	-	39,39	-
2	10^{-5} M	39,39	0.18
3	$2 \cdot 10^{-5}$	39,38	0.21
4	$4 \cdot 10^{-5}$	38,37	0.38
5	10^{-4}	33,34	0.90
6	$5 \cdot 10^{-4}$	28,28	2.0
7	10^{-3}	20,20	2.0
8	$5 \cdot 10^{-3}$	13,12	2.0

Evidence from observation of the absorption spectra at the wavelength of excitation for antimony(III) at 360 nm for the above solutions shows that the absorption noticeably increases between the tellurium concentrations of $4 \cdot 10^{-5}$ M and 10^{-4} M, and while it should be noticed that these measurements were made at room temperature (using 1 cm.² quartz cells and a Beckmann DB Spectrophotometer) absorption readings at low temperature will all be corresponding lower as the colour appeared to fade slightly on cooling to -196° C.

FIGURE 2.4.



From Figure 2.4 it can be seen that as the fluorescence decreases the absorption increases. It was found that the absorption at the emission maximum of 586 nm for antimony(III) for the above solutions was negligible even for the 5.10^{-3} M tellurium solution and therefore no portion of the negative error was caused by attenuation of the fluorescence emission signal.

Though the spectral characteristics of arsenic(III) are very similar to those of antimony(III) [70], because of the much lower sensitivity of the former, as much as a 1000 fold molar excess could be tolerated.

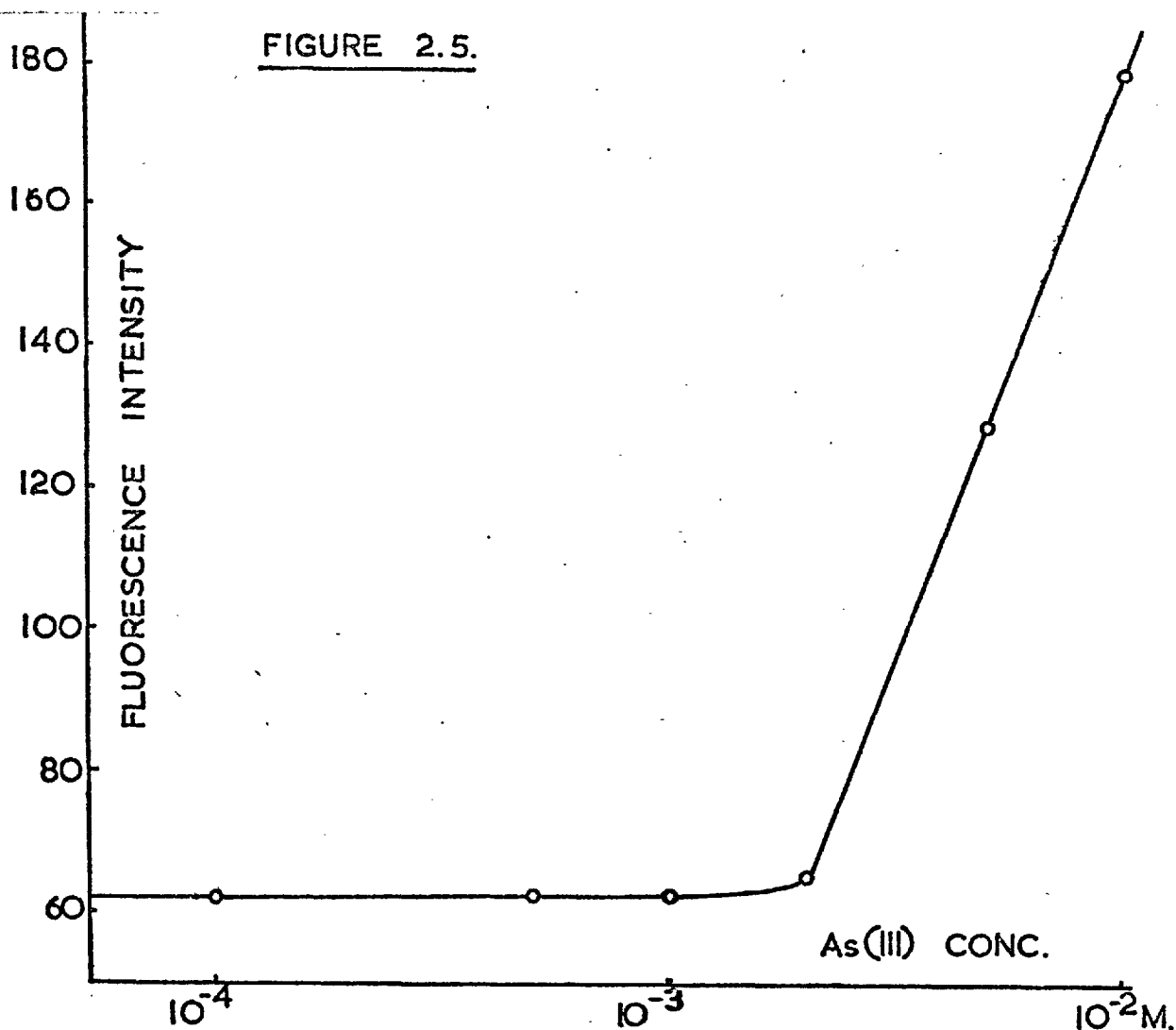
Figure 2.5 shows for a 2.10^{-6} M solution of antimony the effect of adding various concentrations of arsenic(III), and Table 2.III sets out the results obtained for this experiment :-

TABLE 2.III

The effects of varying concentrations of arsenic(III) on a 2.10^{-6} M solution of antimony(III) in 6M hydrobromic acid.

Solution	Arsenic(III) conc.	Fluorescence Reading	Scale
1	-	62,62	0.003
2	10^{-5}	62,62	0.003
3	10^{-4}	62,63	0.003
4	5.10^{-4}	61,62	0.003
5	10^{-3}	62,62	0.003
6	2.10^{-3}	65,64	0.003
7	5.10^{-3}	40,40	0.01
8	10^{-2}	54,55	0.01

Figure 2.5 indicating the change of fluorescence intensity with the above varying arsenic(III) concentrations for the standard 2.10^{-6} M antimony(III) solution.

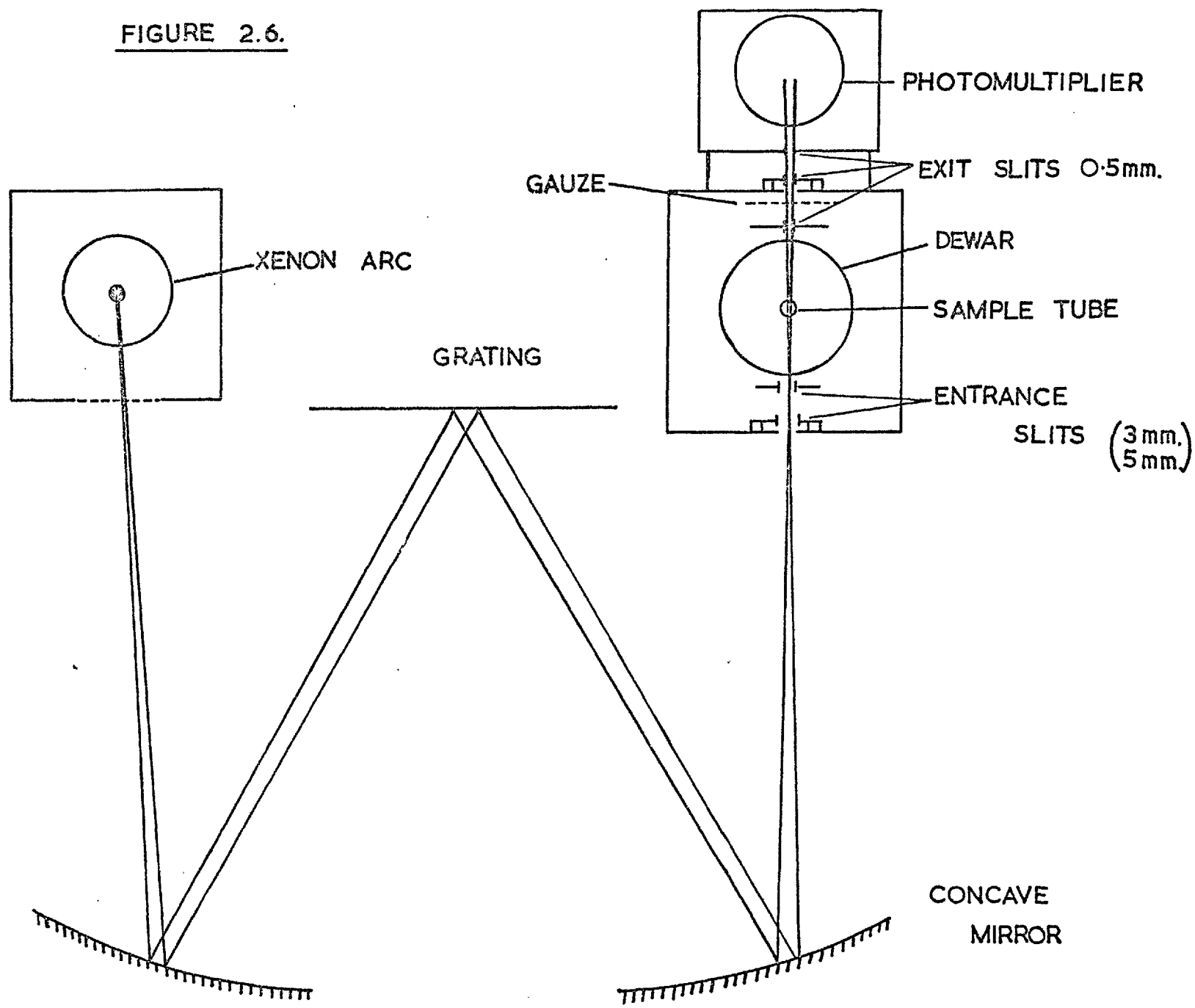


Iron(III) and copper(II) both gave coloured solutions, like tellurium(IV), in concentrated hydrobromic acid medium, iron(III) a yellow-brown colour, and copper(II) a red-purple colour. On cooling to -196°C however the yellow-brown colour

of the iron(III) faded considerably to give a pale yellow-straw colouration of approximately one-third of the original intensity, and the red-purple colour of copper(II) disappeared completely at -196°C . Hence any inner-filter effect caused by absorption of the incident radiation at 360 nm, that would have caused a serious negative error, was to a large extent eradicated; to the extent that a 50-fold molar excess of both could be tolerated.

A more detailed investigation of this phenomena following adaption of the instrument for low temperature absorption measurements, Figure 2.6, was thought to be valuable as both iron(III) and copper(II) are common interfering ions in room temperature fluorimetry due to the strong colouration of their complexes, and some idea of the potential use of working at low temperatures in order to decrease this method of interference obtained. The way in which the spectrum altered on cooling was also of value as to whether a general decrease in absorption throughout the spectrum is the cause, or whether a decrease in the width of, or shift of, the absorption band is responsible. A comprehensive picture therefore could possibly lead to the improvement in selectivity of all spectrofluorimetric methods by reducing the temperature, and obtaining a suitable alteration in the absorption spectra of any ion causing a serious interference by the inner-filter effect.

FIGURE 2.6.



Alteration of the instrument was achieved by placing the photomultiplier unit at the rear of the sample compartment of the Aminco-Bowman Spectrofluorimeter, thereby by-passing the second monochromator, Figure 2.6. Several pieces of copper gauze were required between the sample and the photomultiplier to act as a constant neutral density filter to attenuate the light to between 5 and 10% of its original intensity.

Wide slits of 5 mm. and 3 mm. were used in the incident beam, with 0.5 mm. slits between the sample and the photomultiplier. This was found to be the most satisfactory arrangement, though narrow incident slits would have been preferred in order to cut down the intensity of the incident beam. The sample tube position was found, however, to be very critical with this slit arrangement, and this was partially overcome by using the wider slits. This effect was now not so noticeable as before because of the divergent nature of the beam at this point; and therefore narrow slits could thus be employed after the sample in order to cut down the intensity.

A quartz sample tube of internal diameter 4 mm. and wall thickness 1 mm. was found to be the most suitable as it fitted firmly in the base of the measurement dewar, and therefore eliminated to a large extent errors caused by sample tube movement.

PROCEDURE FOR MEASURING LOW TEMPERATURE ABSORPTION SPECTRA

The spectra were measured in the following way. A solution blank of 6 M hydrobromic acid was placed in a quartz sample tube and frozen in liquid nitrogen in the sample dewar, and any excess liquid nitrogen poured off. (Measurement of the absorption spectra was found to be impossible with liquid nitrogen present because the bubbling constantly altered the position of the sample tube). The spectrum was measured immediately, before the glass melted, by slowly scanning the incident monochromator of the Aminco-Bowman instrument and passing the microphotometer output to the Bryans X-Y recorder. Leaving the sample tube in the instrument for 20 minutes to allow it to regain room temperature before re-measuring the spectrum. It was found that only a very slight difference in absorption occurred between the 'glass' at low temperature and the room temperature solution, though the former did show a slightly higher absorption. It was very important to prevent condensation forming on the base of the dewar flask during either period of measurement, and this was satisfactorily overcome by heating the outside of the dewar with a hot-air blower before the first measurement, and blowing a steady stream of dry air over the dewar for the 20 minutes it was placed in the sample compartment.

Removal of the sample tube after measuring the low temperature spectrum and heating it to room temperature before

replacing in the dewar in order to plot the second spectrum was impossible because of the critical positioning of the sample tube.

This whole procedure was repeated for both solutions of iron(III) and copper(II) and two spectra obtained for each, one at -196°C and the other at $+20^{\circ}\text{C}$. Figures 2.7 and 2.11.

All the spectra obtained were corrected by calculating the reading from the spectra of the sample solutions at -196°C and $+20^{\circ}\text{C}$ at every 10 nm as a percentage of the reading obtained at the same wavelength for the blank solution. This gives a direct reading of transmission and absorption results were calculated from these.

Correction of the spectra gave the curves 1 and 3 ($+20^{\circ}\text{C}$ and -196°C respectively), Figures 2.8 and 2.12. Curve 2 was obtained by measuring the absorption spectra using exactly the same strength solutions of the two ions as used in measuring the low temperature spectra, a Unicam SP800 absorption spectrophotometer, and quartz cells of 2 mm. path length, so that conditions were approximately the same as those for curve 1. The close agreement in the shape of these two spectra illustrates that little error was made in measurement, and correction in the manner proposed above. Unfortunately no check could be made on the curves obtained at -196°C , though this was attempted using a Hilger and Watts Ultrascan

Spectrophotometer. However, this met with little success owing to the very low intensity of the light beams and their attenuation when a dewar flask together with a sample tube was placed in the sample compartment. Unfortunately no other spectrophotometer with a sample compartment large enough to accommodate two dewar flasks side by side was available.

(a) Iron(III) in Hydrobromic Acid

A solution of $2 \cdot 10^{-3}$ M iron in 6 M hydrobromic acid was prepared by adding 0.5 ml. of a 10^{-1} M ferric chloride solution to 17 ml. of concentrated hydrobromic acid and diluting to 25 ml. with distilled water. The spectra of this solution at $+20^{\circ}\text{C}$ and -196°C were measured as previously described, Figure 2.7. Correction of these two spectra gave curves 1 and 3 respectively, Figure 2.8, and curve 2 was obtained using the Ultrascan Spectrophotometer.

The change in the spectra between $+20^{\circ}\text{C}$ and -196°C is quite marked. The absorption peak at 425 nm increases in intensity and becomes slightly narrower, while absorption at 360 nm the maximum of excitation of fluorescence of the antimony(III) under investigation is approximately 50% of the absorption at the same wavelength at room temperature. Further experimental work verified this approximate measurement. A quartz cell 2 mm. path length containing varying strengths of iron(III) solution in hydrobromic acid from 10^{-6} M to 10^{-3} M was placed

FIGURE 2.7.

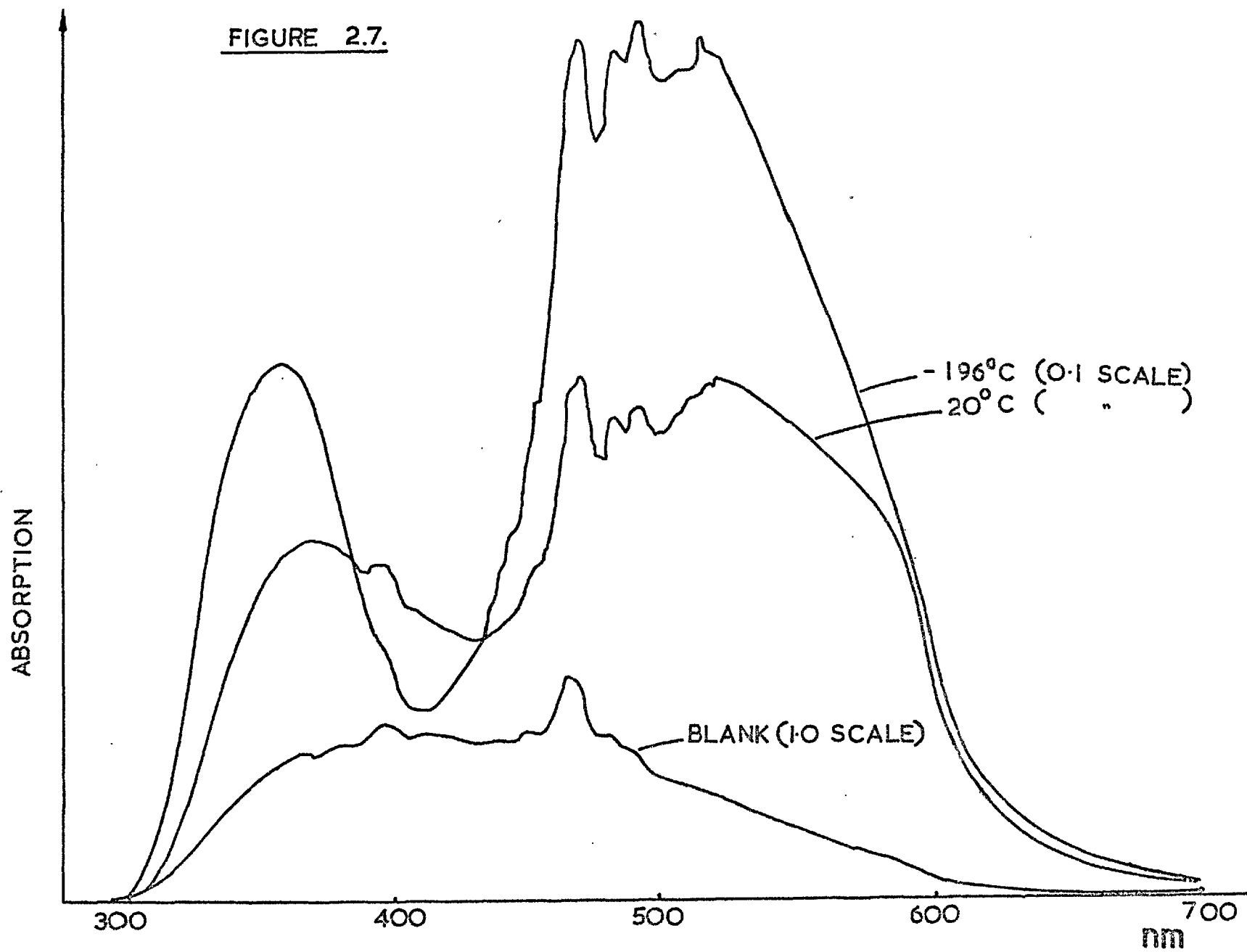
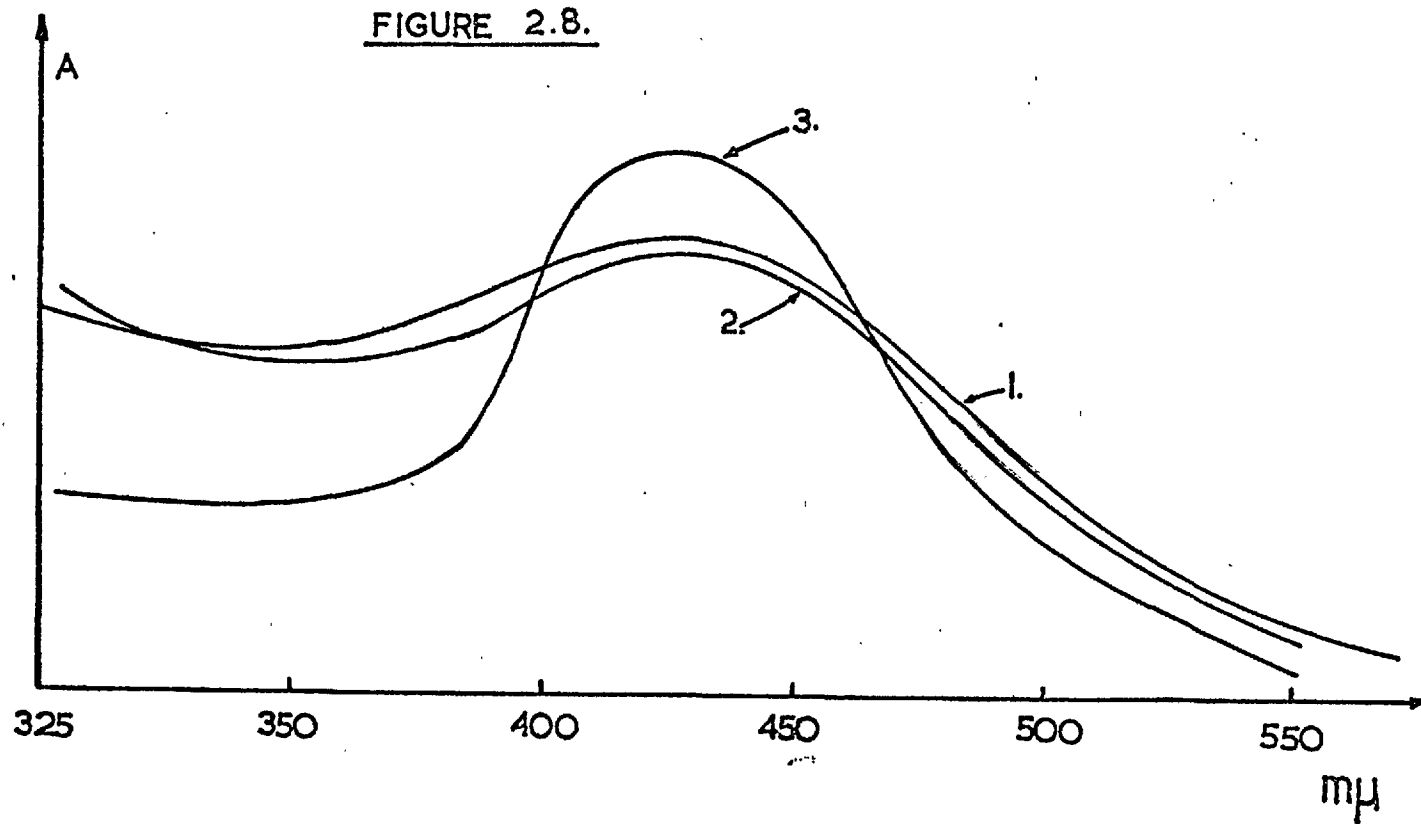
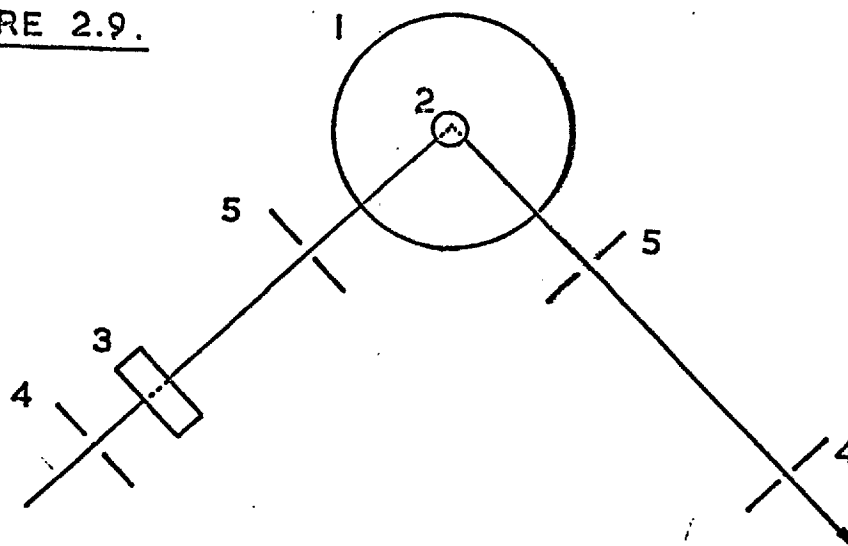


FIGURE 2.8.



in the sample compartment of the spectrofluorimeter, directly before the dewar flask which contained a sample of 2.10^{-6} M antimony solution in 6 M hydrobromic acid. Figure 2.9.

FIGURE 2.9.

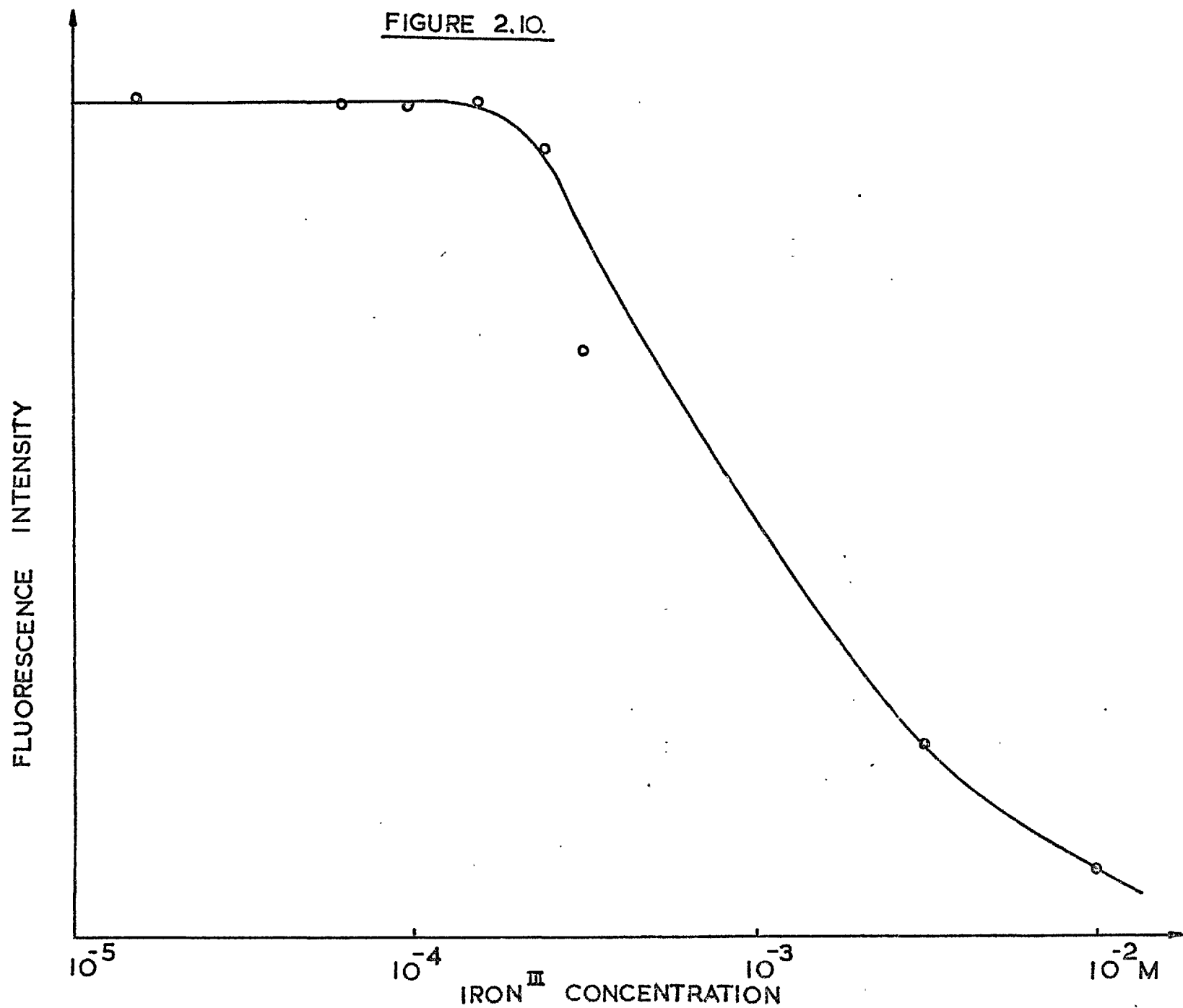


Legend to Figure 2.9.

1. Quartz dewar
2. Quartz sample tube containing antimony(III) sample.
3. 2 mm quartz cell containing iron(III) solution.
4. 3 mm slits.
5. 2 mm slits.

The fluorescence intensity for this sample was measured for each different iron(III) solution ^{and it} showed that a 20-fold molar excess with respect to the antimony(III) concentration

FIGURE 2.10.



could be tolerated before a serious negative error was incurred. Figure 2.10 shows these results together with the fact that as 50 fold molar excess that could be tolerated when the iron is present in the same solution as the antimony. This experiment showed that the inner-filter effect (absorption of the incident radiation) was the cause of the negative error present when antimony(III) is determined by this method in the presence of iron(III), and that by lowering the temperature to -196°C this effect can be reduced by about 50%. Attenuation of the emission radiation did not occur even for the strongest iron solutions as the absorption measured at 586 nm using a Beckmann DB Spectrophotometer was zero.

(b) Copper(II) in Hydrobromic Acid

A 2.10^{-3} M solution of copper(II) was prepared by adding 0.5 ml. of 10^{-1} M CuCl_2 solution to 17.0 ml. of hydrobromic acid and diluted to 25 ml. with distilled water. The uncorrected spectra, Figure 2.11, were plotted in exactly the same manner as previously described for the iron(III)/hydrobromic acid system. Correction of the room temperature and liquid nitrogen temperature spectra giving curves 1 and 3 respectively, Figure 2.12. Spectra 2 was obtained in the same way as above using the Unicam SP800 spectrophotometer, and again shows a very close similarity to curve 1, again showing that no serious error has been incurred during the measurement, and correction of the absorption spectra, with the single beam spectrofluorimeter.

FIGURE 2.11.

ABSORPTION

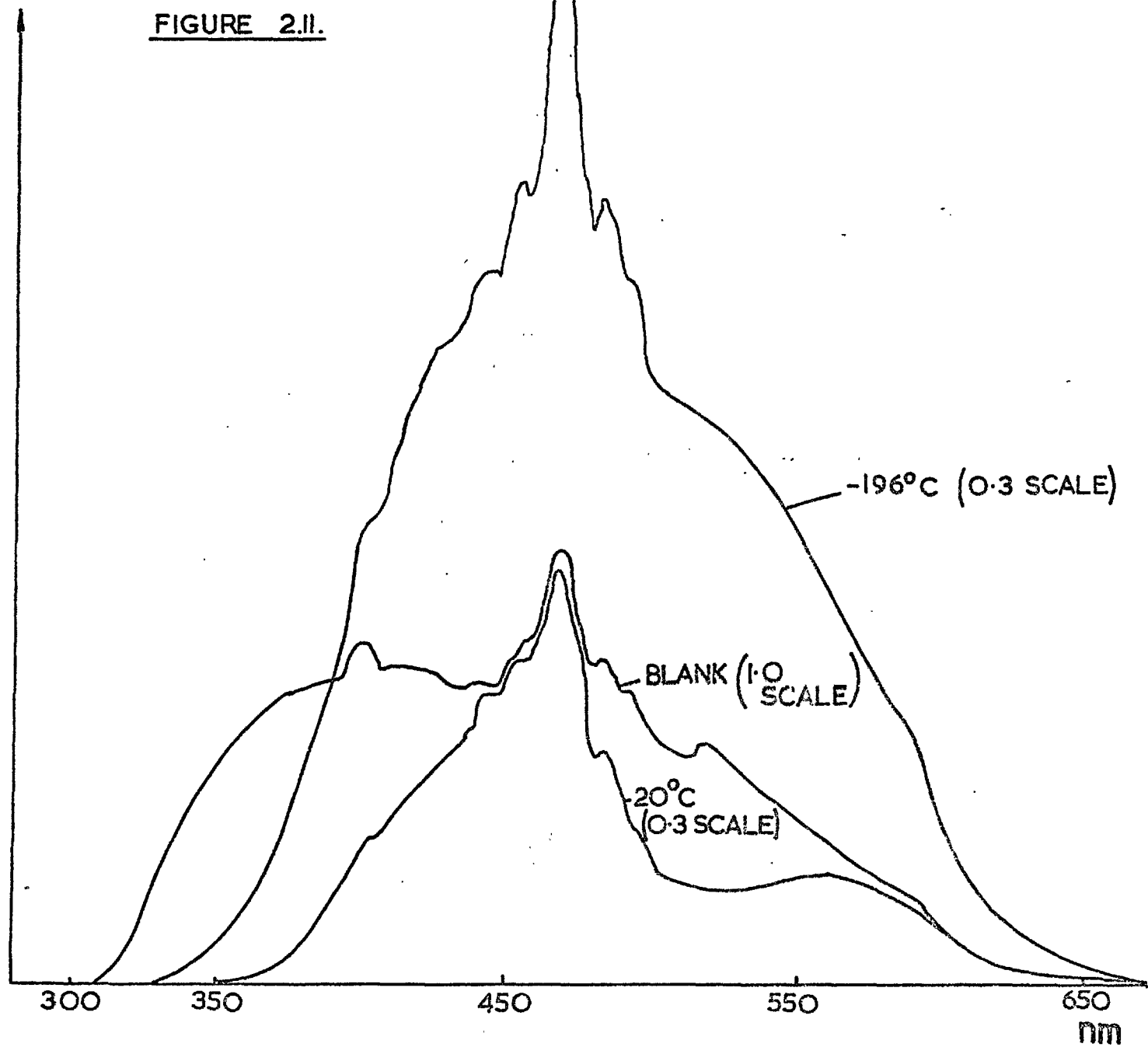
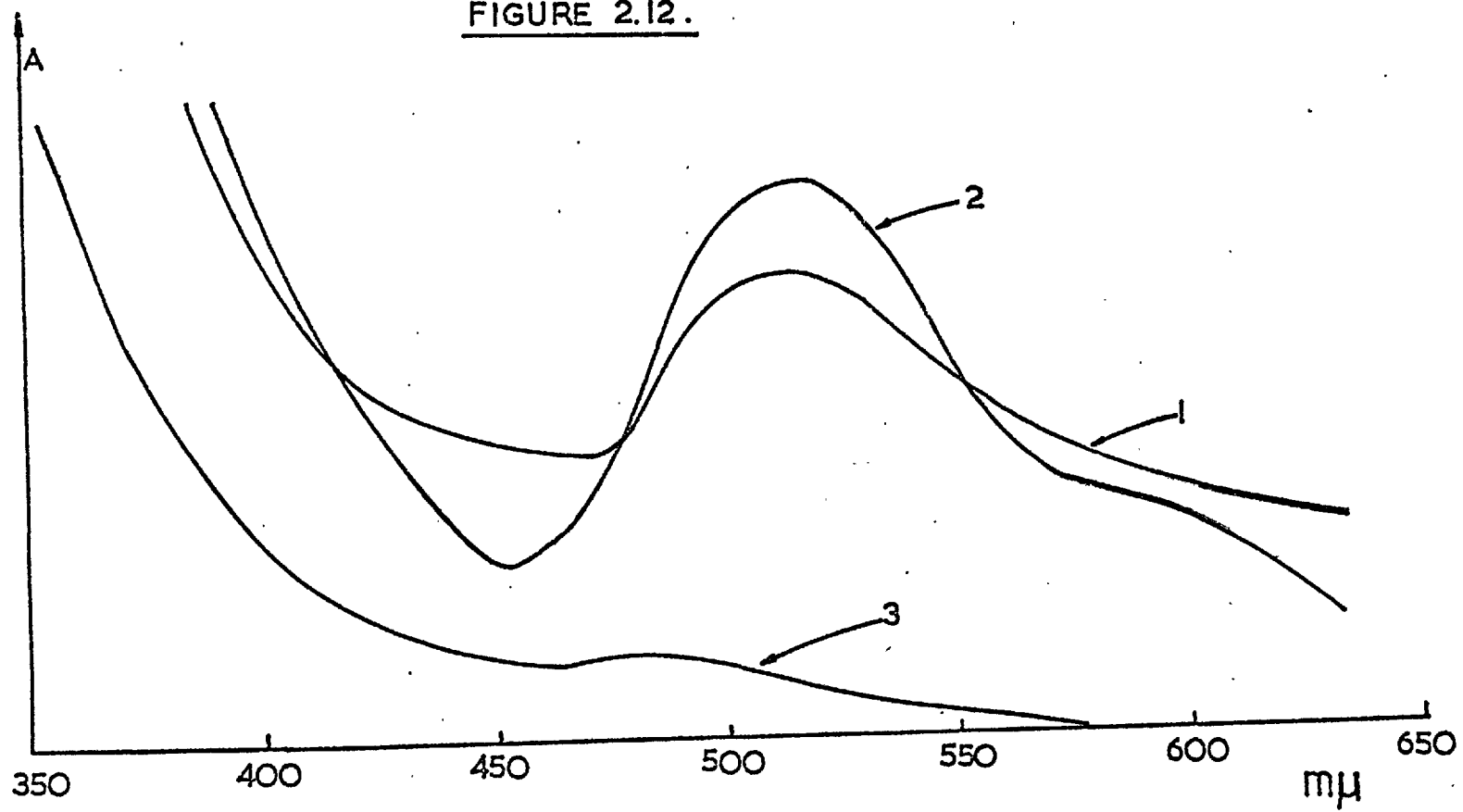


FIGURE 2.12.



The results obtained appear to agree with those obtained visually, the large absorption peak at room temperature which apparently gives rise to the intense purple-red colouration disappears almost completely when the temperature is lowered to -196°C to give a colourless glass. Again it is seen that the absorption at 360 nm and 586 nm is considerably lower at -196°C than at $+20^{\circ}\text{C}$ and therefore the inner filter effect will be much reduced at the lower temperature. This was checked by placing a 10^{-4} M copper(II) solution in 6 M hydrobromic acid solution in 2 mm quartz cells, one in the incident beam and a second cell in the emission beam, directly before and after the spectrofluorimeter cell which contained a 2.10^{-6} M antimony(III) solution in 6 M hydrobromic acid. Unlike the results obtained when the copper(II) was present in the same solution as the antimony(III) sample and no negative interference was observed; for the same strength copper(II) in the two 2mm. quartz cells - a negative interference of 45% was measured.

The general advantage of working at low temperature is therefore two fold; firstly the intensity of fluorescence is increased, normally by quite a significant factor, and secondly the inner filter effect interference from iron(III) and copper(II) can be markedly reduced. Though the first factor is well illustrated by antimony(III) which does not

fluoresce in hydrobromic acid at room temperature, the second factor may be extremely important when considering a method for thallium(I), lead(II), tin(II) and cerium(III) which all fluoresce in chloride media at room temperature [77] as well as at low temperature [69]: as a substantial reduction in the absorption intensity of iron(III) and copper(II) in chloride media is also obtained.

PRECISION

The precision of the method at its maximum sensitivity was tested by repetitive determination of several 2.10^{-6} M antimony(III) solutions, Table 2.IV. Each solution was measured three times.

TABLE 2.IV

Sample	Scale Reading	Net Antimony Response	Deviation	Total Variance
1.	51,50,52	49,48,50	0.26, -0.74, -1.74	3.64
2.	51,50,51	49,48,49	0.26, -0.74, 0.26	0.68
3.	50,49,51	48,47,49	-0.74, 1.26, 0.26	2.19
4.	48,50,49	46,48,47	-2.74, -0.74, -1.74	11.08
5.	49,50,50	47,48,48	-1.74, -0.74, -0.74	4.12
6.	52,53,51	50,51,49	1.26, 2.26, 0.26	6.76
7.	52,52,52	50,50,50	1.26, 1.26, 1.26	4.76
8.	50,50,51	48,48,49	-0.74, -0.74, 0.26	1.16

TABLE 2.IV (contd/)

Sample	Scale Reading	Net Antimony Response	Deviation	Total Variance
9.	51, 50, 51	49, 48, 49	0.26, -0.74, 0.26	0.68
10.	51, 52, 50	49, 50, 48	0.26, 1.26, -0.74	2.19
11.	51, 52, 53	49, 50, 51	0.26, 1.26, 2.26	6.76
12.	48, 49, 50	46, 47, 48	-2.74, -1.74, -0.74	11.08
13.	51, 52, 51, 50	49, 50, 49, 48	0.26, 1.26, 0.26, -0.74	2.27
Blank	2, 2, 2	-		
		Mean 48.74		57.37

$$\text{Standard Deviation} = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

$$= \underline{1.08}$$

$$\text{Standard Deviation (Percentage)} = \frac{S.D. \cdot 100}{\bar{x}} = \frac{1.08 \cdot 100}{57.37} = 2.2\%$$

ACCURACY

The data given in Table 2.V was obtained from the results of unknown antimony(III) solutions by the recommended procedure. A standard solution was prepared and measured simultaneously.

TABLE 2.V

Analysis of Antimony(III) solutions treated
as Unknown Samples

Sample	Antimony		Error %	Foreign Ions Present (ug)
	Present (μg)	Found (μg)		
1.	0.24	0.25	+ 4.2	Cu(II), 13 Pb, 42
2.	0.61	0.58	- 4.9	Ni, 14.5 Zn, 16
3.	2.4	2.4	0	Sn(II), 295 Cd, 225
4.	3.0	3.1	+ 3.3	Te(IV), 32 As(III), 190
5.	6.1	6.1	0	Se(IV), 200

CONCLUSION

In comparison with absorptiometric methods the determination of antimony by the method described is extremely sensitive. With the available instrumentation the absolute lower limit of detection of antimony, based on fluorescence signal to detector noise ratio of unity, is 4.10^{-8} M ($\approx 2.4 \cdot 10^{-3}$ μ g in the 0.5 ml. sample volume). The lower limit of determination, however, is somewhat higher (5.10^{-3} μ g). It is illustrative of the intensity of its emission at -196°C that the red fluorescence of antimony in HBr glass is clearly visible to the eye in 10^{-6} M solution on irradiation with a 150 W low pressure mercury vapour discharge lamp. The selectivity of the determination is very high. This may partly be attributed to the clear separation of the wavelengths of maximum excitation and emission from those of other cations which form fluorescent complexes in conc. HBr medium (e.g. bismuth(III), cerium(III), lead, tin(II) and uranium(VI)). No fluorescence is, therefore, stimulated from these cations at the optimum Sb(III) emission wavelength under the recommended conditions, and they do not interfere. The emission maximum wavelength of the antimony complex at 586 nm is long enough to ensure that few species can interfere by absorption of the emitted radiation.

In addition, we observe that several species which absorb strongly in the test solution at room temperature at 360 nm, give rise to glasses in hydrobromic acid which absorb less strongly or are virtually transparent at the same wavelength. In the range studied copper(II), whose CuBr_4^{2-} complex in 6M HBr is pink at room temperature, is colourless at -196°C . A second example of this effect, as mentioned above, is the appreciable reduction in absorbance at 360 nm which occurs when iron(III) solutions in 6M HBr are cooled to -196°C .

As a consequence of these effects the 'inner-filter' effect, whereby attenuation of the incident or emitted radiation occurs due to absorption by other species in the solution, is less serious at low temperature than at room temperature.

CHAPTER III

THE FLUORIMETRIC DETERMINATION OF TRACE IMPURITIES OF LEAD IN ANALAR HYDROBROMIC ACID

Previously reported methods for the determination of trace impurities in concentrated acid have generally been fairly lengthy procedures involving evaporation of the sample followed by analysis of the residues [72]. A chronovoltametric method for the determination of trace impurities of lead (0.0014 ppm) has also been reported by Kemula and Glodowski [73]. Several workers have also reported the fluorescence characteristics of several ions, including lead, in concentrated acids at low temperature [69] [70] [74]. A semi quantitative method for the detection of trace lead impurities by low temperature fluorimetric procedure has also been reported [75].

With this work in mind, and the obvious requirement for a sensitive, and rapid, technique for the accurate determination of the lead impurity in concentrated hydrochloric acid, the following work was initiated.

APPARATUS

An Aminco-Bowman Spectrophotofluorometer incorporating a 150 W Xenon arc (Hanovia), and an IP 21 photomultiplier tube was employed for all fluorescence measurements, together with a Bryans X-Y recorder for plotting the spectral characteristics.

The sample tubes were made from precision bore quartz tubing (Jencons Ltd.) 20 cm. long, 3 mm. internal diameter and 10 mm. wall thickness.

REAGENTS.

CONCENTRATED HYDROCHLORIC ACID. British Drug Houses Ltd., Aristar grade was used for the construction of the calibration graph. AnalaR grade hydrochloric acid (British Drug Houses Ltd, and Hopkin and Williams Ltd.) was used as received for the lead determination.

LEAD SOLUTION. A stock 10^{-3} M solution of lead nitrate was prepared by dissolving 0.3312 g. AnalaR grade (British Drug Houses Ltd.) in 1 litre of distilled water.

PROCEDURE

Exactly 5.5 ml. of Aristar grade concentrated hydrochloric acid was pipetted into a 10 ml. volumetric flask together with varying volumes of between 0 and 1.0 ml. of 10^{-5} M lead nitrate solution, and made up to the mark with distilled water. A 0.5 ml. aliquot of this solution was transferred to a quartz sample tube which was then placed in ^{the} Dewar flask containing liquid nitrogen until the acid solution had cooled to form a clear glass.

On the formation of a satisfactory glass the sample tube was rapidly transferred to the quartz measuring Dewar which was approximately one third full of liquid nitrogen. The fluorescence emission was measured at 390 nm using an excitation of 270 nm. This procedure was preferred rather than placing the sample tube directly in the quartz measuring Dewar as the frequency with which the sample tube and the glass cracked was found to be very much lower.

From the calibration graph obtained, Figure 3.1, the concentration of lead impurity in several samples of AnalaR acid treated in the same manner as above was determined.

A standard sample of 10^{-6} M quinine bisulphate in 0.1 M sulphuric acid was used constantly to check any variation in the Xenon arc intensity.

RESULTS

The precision of the method is very good, being in the region of $\pm 2.5\%$, Table 3.III.

Figure 3.2 shows the spectral characteristics for a typical sample of concentrated AnalaR acid, illustrating excitation maxima at 240 nm and 270 nm, and emission maxima at 390 nm.

CALIBRATION GRAPH: FIGURE 3.1.

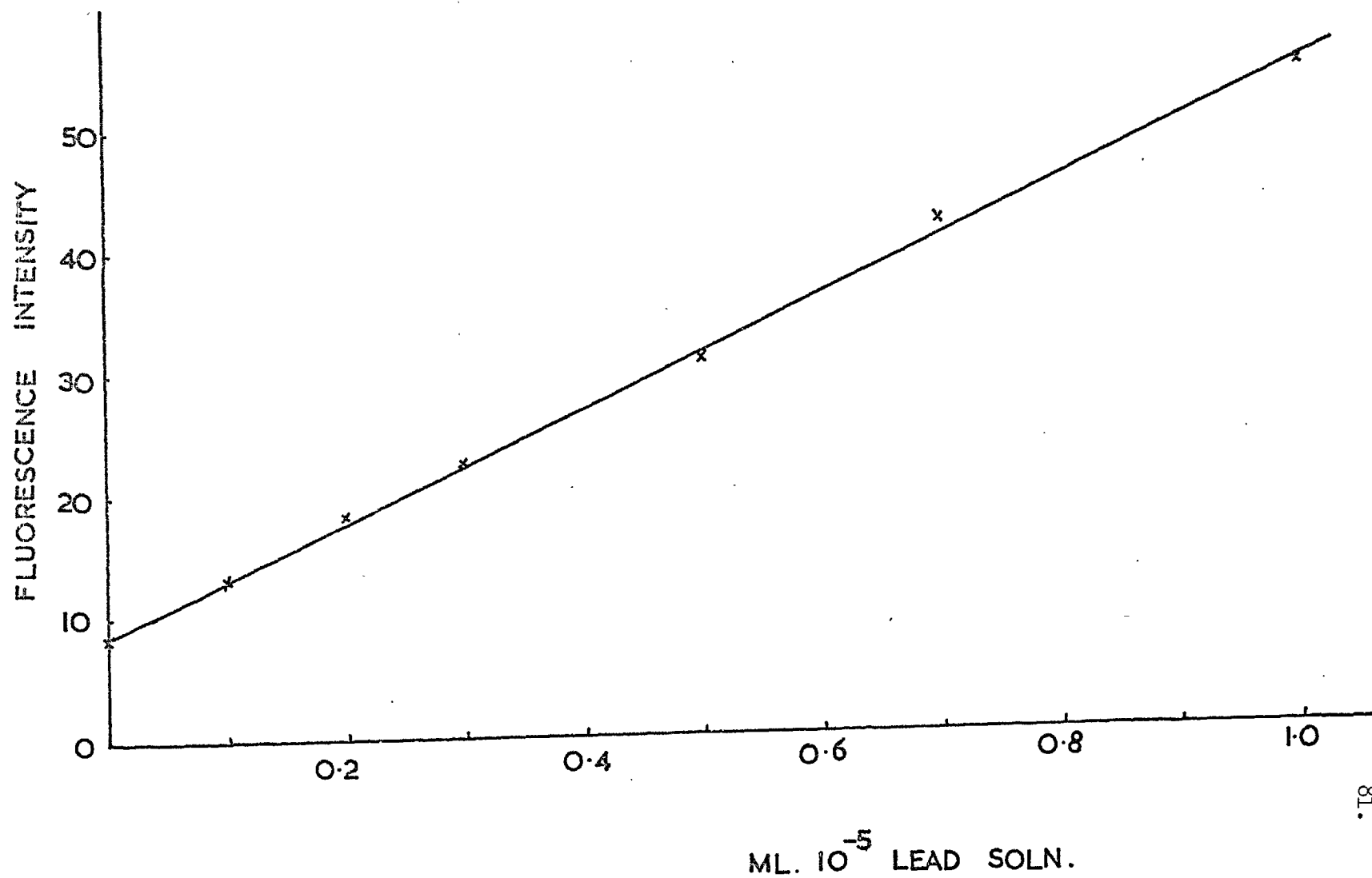
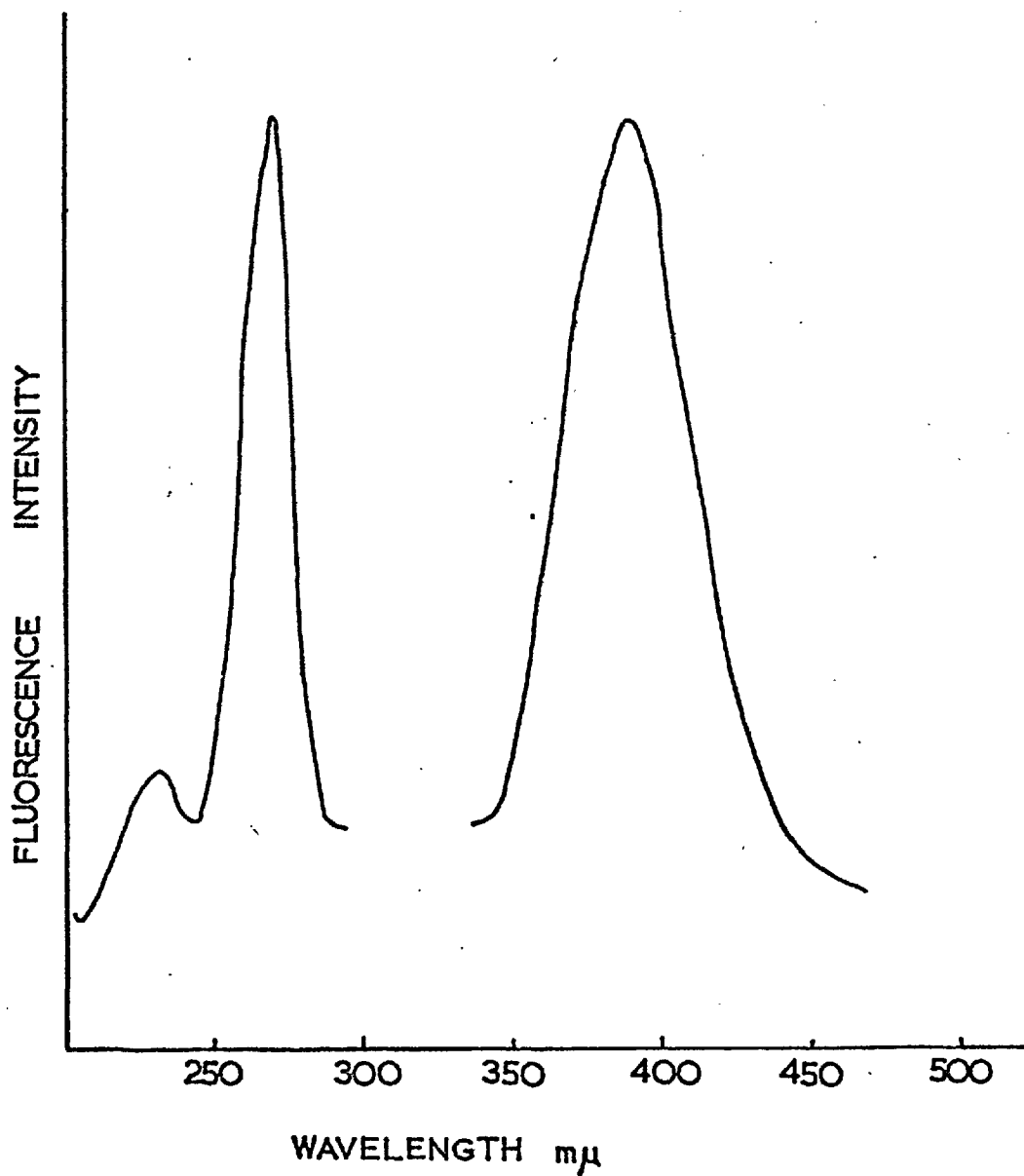


FIGURE 3.2.

Several samples of AnalaR acid were investiaged, and the figures given in Table 3.I indicate the lead concentration found.

TABLE 3.1

Analysis of concentrated hydrochloric acid samples
as received.

Sample AnalaR Acid	Concentration Lead Found (ppm)
1 (H & W)	1.0 10^{-2}
2 (H & W)	8.5 10^{-2}
3 (H & W)	9.5 10^{-2}
4 (H & W)	6.1 10^{-2}
5 B.D.H.	2.8 10^{-2}
6 B.D.H.	2.8 10^{-2}
7 B.D.H. (Lead Free)	3 10^{-3}

The analysis of several 'unknown' samples containing a definite amount of lead added to Aristar grade hydrochloric acid gave the following results :

TABLE 3.II

Analysis of Unknown Samples for Lead
Concentration

Sample	Conc. Pb Added in 5.5 ml. (ppm)	Conc. Pb Found in 5.5 ml. (ppm)	Percent Error
1	0.057	0.057	-
2	0.075	0.074	-1.3
3	0.11	0.11	-
4	0.23	0.24	+4.1
5	0.30	0.31	+3.1

The effect of adding the following ions :-

Al, As, Co, Cu, Fe, Hg, Mn, Ni and Zn to give a 200-fold molar excess over the lead concentration of 0.1 ppm in the HCl sample was studied, and it was found that none of those ions gave rise to an error outside the statistical limit of $\pm 5\%$.

PRECISION MEASUREMENTS

Table 3.III

Nine identical solutions were employed, containing 5.5 ml. of concentrated AnalaR hydrochloric acid in 10 ml. of solution.

Sample	Reading	Deviation	Total Variance
1	58,58,57	-1, -1, -2,	6
2	58,58,59	-1, -1, 0,	2
3	60,60,61	1, 1, 2,	6
4	61,61,60	2, 2, 1,	9
5	59,59,60	0, 0, 1,	1
6	59,59,59	0, 0, 0,	0
7	58,58,59	-1, -1, 0,	2
8	57,57,57	-2, -2, -2,	12
9	62,61,59	3, 2, 0,	13
	$\bar{x} = 59.0$		<u>51</u>

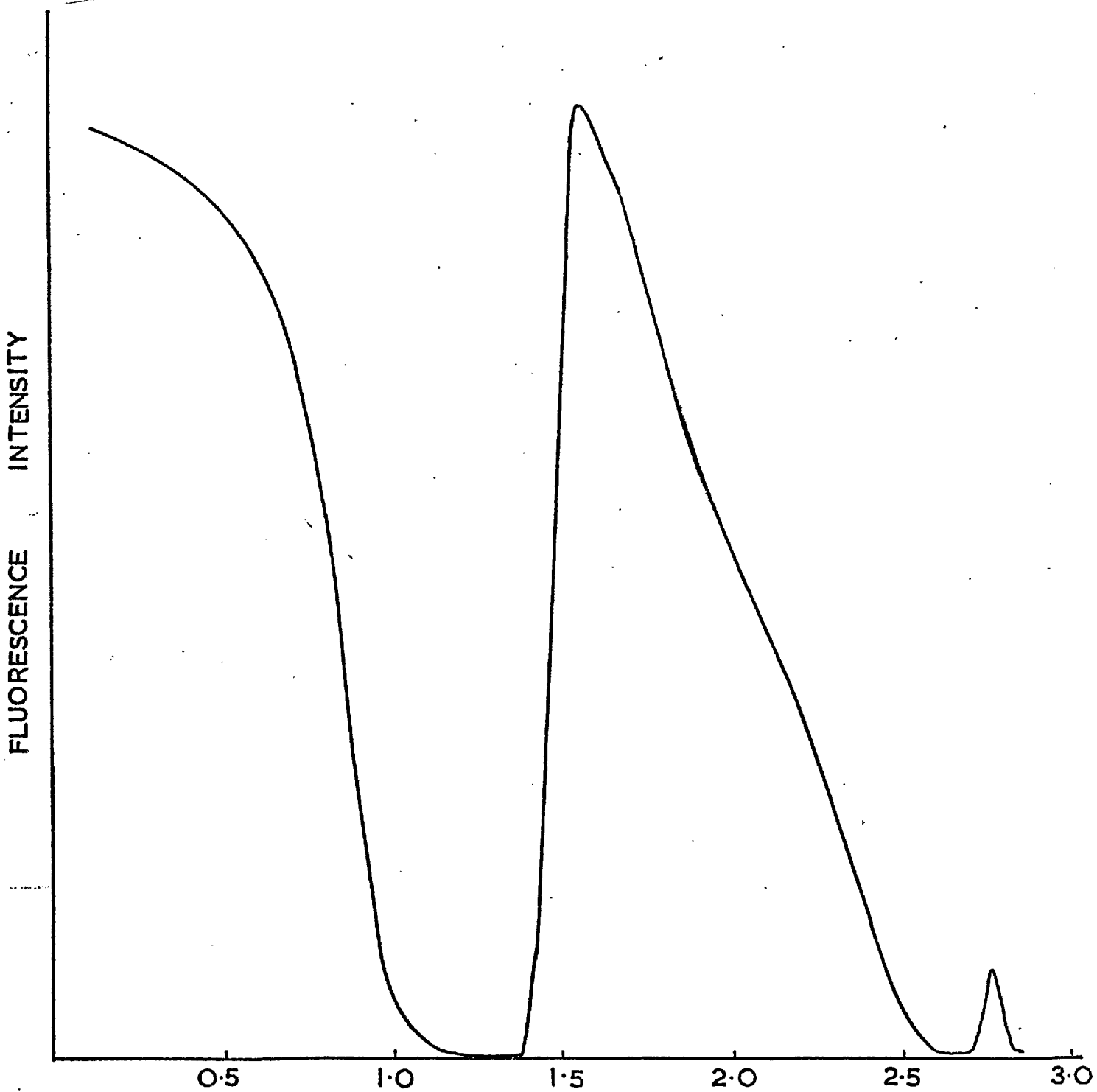
$$S.D. = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

$$= \sqrt{\frac{51}{26}} = 1.40$$

$$S.D.\% = \frac{1.4 \cdot 100}{59} = \underline{\underline{2.4}}$$

In all samples investigated the concentration of lead was considerably lower than that stated by either of the manufacturers, though the concentration of bismuth was found to be far greater than that of lead, such that bismuth could be determined in certain samples of Aristar acid.

It was noticed that when a lead solution in concentrated hydrochloric acid was left in the fluorimeter sample compartment and allowed to warm up the intensity of fluorescence steadily decreased until it completely disappeared. After an interval of between a half and one minute the fluorescence signal would re-appear to give a maximum of approximately the same magnitude as the original reading before decreasing again to zero at a slightly different rate than originally, Figure 3.3. A second much smaller peak was also noted shortly after the disappearance of the first peak. It was noticed that if the sample was removed during the period in which this first fluorescence peak occurred the concentrated hydrochloric acid had a 'snowy' crystalline appearance. It was proposed therefore that as the species which gives rise to the fluorescence is rigidly held in a low temperature glass, thus causing it to fluoresce, it will also be seriously restricted in a matrix of this form, with the result that rotational and vibrational energy will be reduced to a minimum and fluorescence again observed. The appearance of the second small peak, however, remained somewhat of a mystery as the time during which this occurred was very short, and no physical change of the matrix was visible. The fact that the first peak is caused by fluorescence, and not scatter, was verified. (Scatter would be expected to be much greater from a crystalline sample of this nature). As the excitation and emission maxima were found to be identical with those obtained

FIGURE 3.3.

from the clear glass at -196°C . Removal of the incident light was also carried out during this period of warming up, to discover if this peak was caused by re-emission of previously absorbed radiation [78] [79] [80] [81] and thus give some indication as to the mechanism of the fluorescence observed. However, no signal was observed, and therefore the possibility of an oxidation or free radical type mechanism was eliminated

DISCUSSION

This technique for the determination of trace amounts of lead in concentrated hydrochloric acid provided a very sensitive, selective and rapid procedure. It has the advantage over methods previously described that no neutralisation, extraction or evaporation procedure was required, thus enabling a far more convenient determination.

DETERMINATION OF LEAD IN CONCENTRATED HYDROBROMIC ACID

No specific method for the determination of lead impurities in concentrated hydrobromic acid has previously been reported. However, there seems no chemical reason to suppose that these methods previously reported for the determination of traces of lead in concentrated hydrochloric acid could not be applied [72] [73].

Previous work carried out in this laboratory [70] indicated the fluorescence obtained from lead in concentrated hydrobromic acid and an effort has been made here to determine if this method has any quantitative application.

REAGENTS

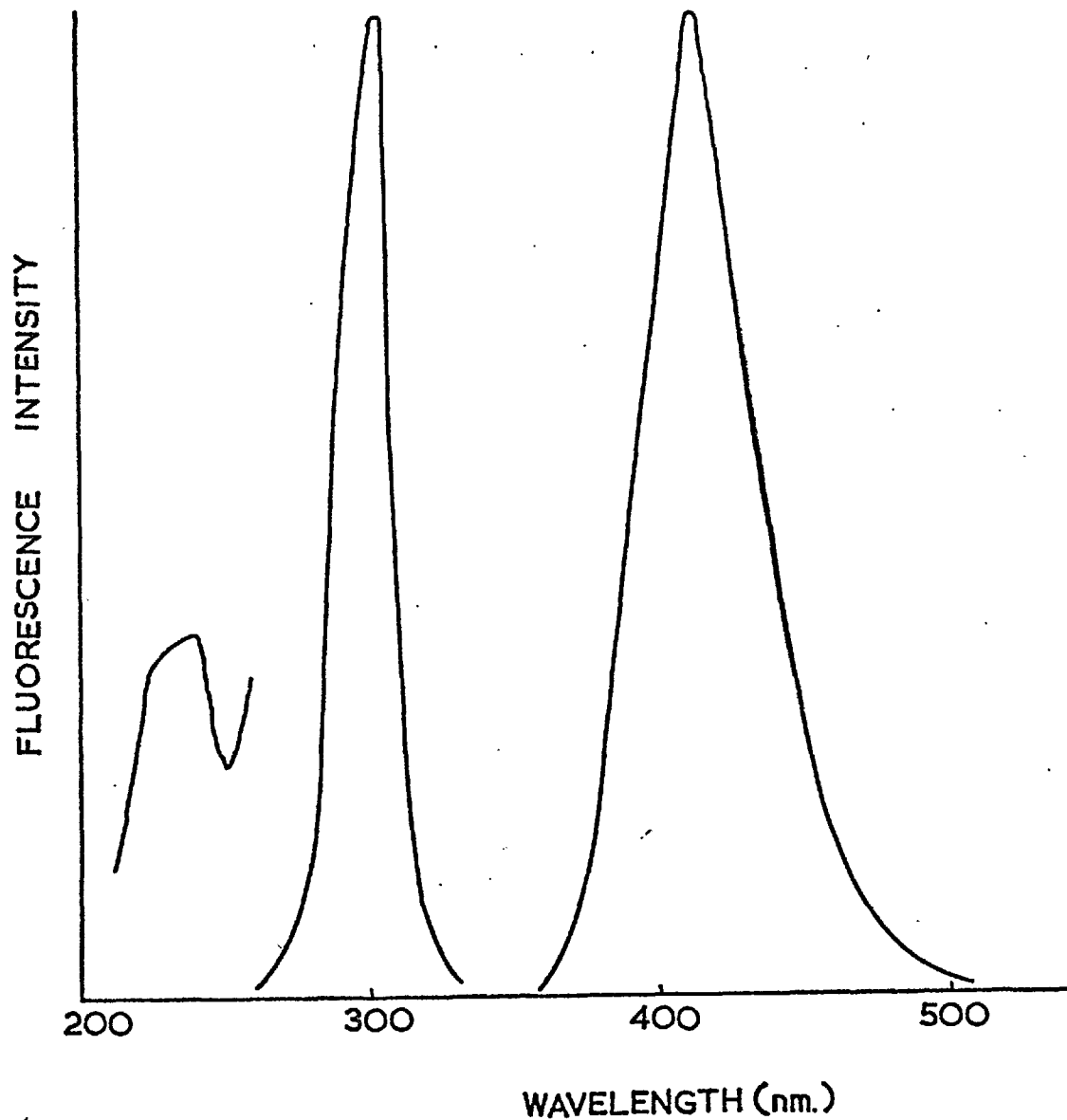
CONCENTRATED HYDROBROMIC ACID. British Drug Houses Ltd. Aristar grade was used for the construction of the calibration curve. General purpose reagent and AnalaR grade hydrobromic acid was used as received for the determination of the lead impurities.

A standard sample of 10^{-6} M quinine bisulphate in 0.1 M sulphuric acid was used constantly to monitor any alteration in the intensity of the Xenon arc lamp.

RESULTS

The precision of the method was found to be in the region of $\pm 2.0\%$. Figure 3.4 indicates the spectral characteristics for a typical sample of the concentrated general purpose reagent used, showing the excitation maximum at 304 nm and the emission maximum at 414 nm.

The results obtained from the analysis of several samples of AnalaR and general purpose reagent are given in Table 3.IV. (A) together with several 'unknown' samples (B) obtained by adding known quantities of lead to Aristar acid.



LEGEND FOR FIGURE 3.4. SPECTRAL CHARACTERISTICS OF A 10^{-3} M
 $\text{Pb}(\text{NO}_3)_2$ SOLUTION IN 6M HYDROBROMIC ACID AT -196°C .

1. Excitation spectrum; emission measured at 414 nm. (0.1 scale).
2. Emission spectra; excitation measured at 304 nm. (0.1 scale).
3. Excitation spectrum; emission measured at 414 nm. (0.003 scale).
4. Emission spectrum; excitation measured at 240 nm. (0.003 scale).

In all samples of hydrobromic acid investigated it was found that unlike hydrochloric acid samples used previously the concentration of lead was far greater than that of bismuth. Another difference from the hydrochloric acid media was noticed when the HBr system was allowed to warm in the sample compartment; no increase in fluorescence was noticed and this was attributed to the fact that no crystallisation occurred during the heating up process.

TABLE 3.IV

A.

Sample	Description	Lead Concentration (ppm)
1	G.P.R. Undistilled	8.6×10^{-2}
2	G.P.R. Undistilled	8.5×10^{-2}
3	G.P.R. Twice Distilled	3.8×10^{-2}
4	" " "	3.1×10^{-2}
5	" " "	2.9×10^{-2}
6	AnalaR	3.9×10^{-2}
7	AnalaR	2.7×10^{-2}
8	AnalaR	2.1×10^{-2}

B

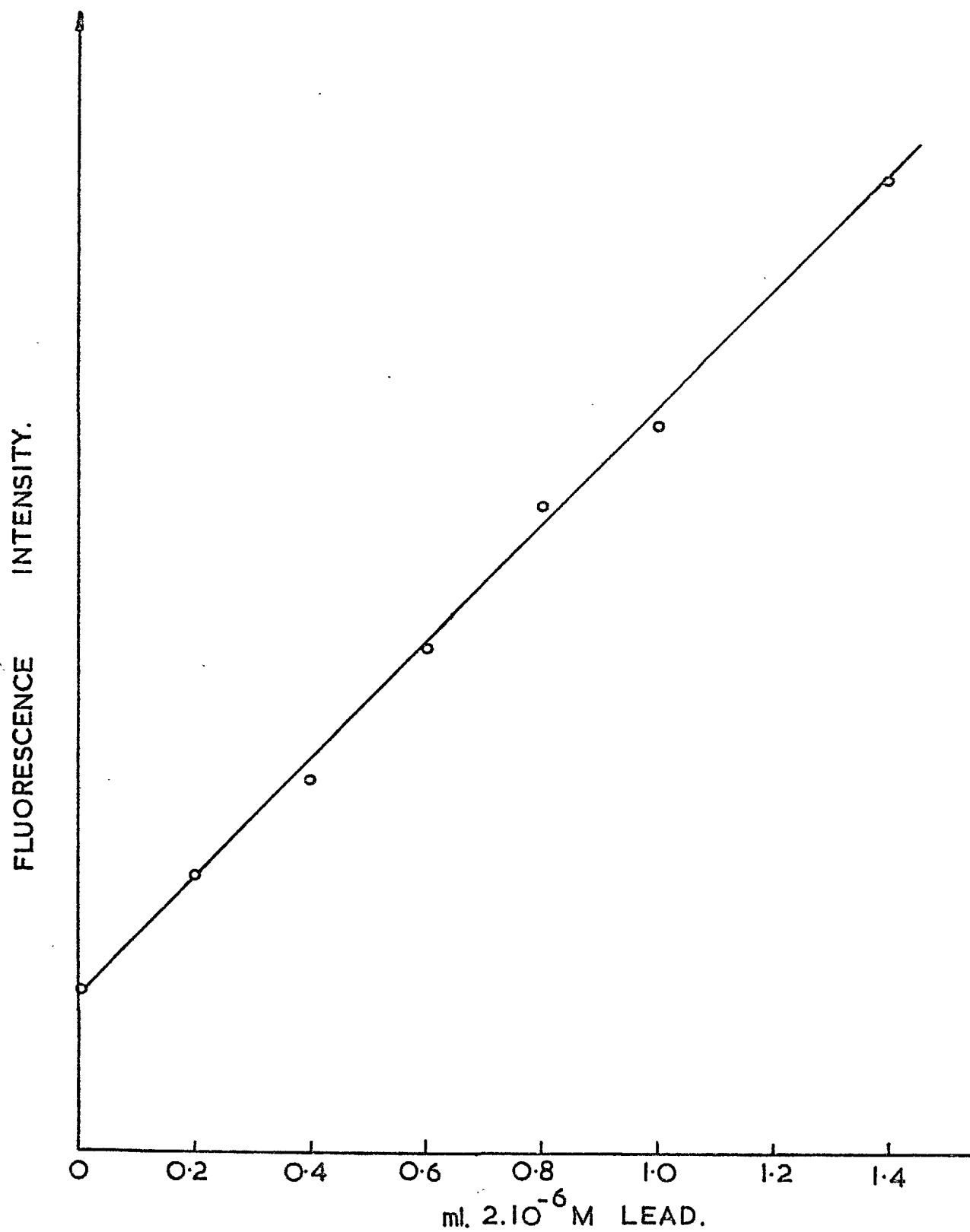
Sample	Lead Concentration (ppm)		Error %
	Added	Found	
1	$2.5 \cdot 10^{-2}$	$2.4 \cdot 10^{-2}$	-4
2	$4.2 \cdot 10^{-2}$	$4.2 \cdot 10^{-2}$	0
3	$5.6 \cdot 10^{-2}$	$5.4 \cdot 10^{-2}$	-3
4	$6.7 \cdot 10^{-2}$	$7.0 \cdot 10^{-2}$	+4
5	$7.8 \cdot 10^{-2}$	$8.0 \cdot 10^{-2}$	+3.5

LEAD SOLUTION. A stock solution of 10^{-3} M lead nitrate was prepared by dissolving 0.3312 g. of AnalaR grade (British Drug Houses Ltd.) in one litre of distilled water.

PROCEDURE FOR CONSTRUCTION OF THE CALIBRATION GRAPH

Exactly 7.5 ml. of Aristar grade hydrobromic acid was pipetted into a 10 ml. volumetric flask, between 0 and 1.4 ml. of $2 \cdot 10^{-6}$ M lead solution added and made up to the mark with distilled water from an all glass distillation unit. A 0.5 ml. aliquot of this solution was transferred to a pyrex sample tube which was placed directly in the measuring dewar. The fluorescence emission was measured at 414 nm using an excitation wavelength of 304 nm.

From the calibration thus obtained, Figure 3.5, the concentration of lead impurity in samples of AnalaR, ordinary

FIGURE 3.5.

general purpose reagent, and twice distilled general purpose reagent was measured.

DISCUSSION

The method described provides a rapid and selective method for the determination of lead traces and has the advantage that no treatment of the sample is first required.

It was found that the samples of general purpose reagent contained between 8.6 $\mu\text{g/ml}$. undistilled, and 3.8 $\mu\text{g/ml}$. twice distilled, and AnalaR grade acid samples between 2.1 $\mu\text{g/ml}$. and 3.9 $\mu\text{g/ml}$. The lead content of AristaR grade was too low to be measured by this procedure though this was only to be expected as the maximum content of lead was given as 5.10^{-7} %.

CHAPTER IV

LUMINESCENCE INVESTIGATIONS OF THE CONCENTRATED HYDROFLUORIC ACID MEDIUM

No previous study of the fluorescence of metal ions in hydrofluoric acid medium at low temperature has been reported though many reports of the fluorescence of metal ions in fluoride crystals have been published [82] [83]. Work on acid glasses formed by cooling concentrated hydrofluoric acid to liquid nitrogen temperatures has not been previously carried out due to the difficulty in preparation, handling and measurement of samples.

It was thought that a survey of the spectral characteristics and an approximate measure of the sensitivity was worthwhile in order to attempt a correlation of the fluorescence characteristics of certain metal ions with the halogen acid used (hydrofluoric, hydrochloric or hydrobromic acid), and also to investigate the analytical potential of the system.

RESULTS

In all cases examined between 6 M and 20 M hydrofluoric acid was found to give a clear glass but 'cracking' invariably occurred.

10^{-2} M solutions in 10 M acid were prepared by addition of 1.0 ml. of 10^{-1} M solutions of the appropriate ion to 4.5 ml. of concentrated hydrofluoric acid (AnalaR grade; Hopkin and Williams Ltd.) and distilled water added to a volume of 10 ml, in a 10 ml. polythene measuring cylinder. This gave a 10 M solution with respect to hydrofluoric acid concentration.

The above solutions were prepared using the following ions: antimony(III), arsenic(V), bismuth(III), cerium(III), copper(I), lead(II), tellurium(IV), tin(II), tin(IV) and uranium(VI).

A 0.5 ml. aliquot of each of these solutions was in turn placed in the quartz sample tube using a polythene dropper, and the sample tube rapidly frozen in a dewar flask of liquid nitrogen, to prevent the acid attacking the tube walls, before transferring to the quartz measuring dewar which was approximately one third full of liquid nitrogen. Having carried out this procedure the frozen sample in the dewar was observed under a mercury vapour discharge lamp. Under these conditions only bismuth(III) and uranium(VI) gave rise to any visible fluorescence. The dewar was then placed in the sample compartment of the Aminco-Bowman Spectrophotofluorometer and the fluorescence characteristics, if any, measured using the Bryans X-Y recorder.

The following ions were found to give rise to fluorescence: antimony(III), arsenic(V), bismuth(III), lead(II), and uranium(VI). Table 4.1 shows the maximum excitation and emission wavelengths for the fluorescing ions.

TABLE 4.1

Cation	Excitation Maxima	Emission Maxima	Comment
Antimony(III)	386,410,	586	Very weak, not visible
Arsenic(V)	250,284,318	538	Very weak, not visible
Bismuth(III)	235,324	410	Visible blue fluorescence. White precipitate formed.
Lead(II)	247	414	Very weak, slight precipitation
Uranium(VI)	266,320,404	500,520, 544,570, 600	Characteristic UO_2^{+} fluorescence

All the fluorescence measurements were carried out using one of the two most sensitive scales on the fluorimeter, with the exception of the bismuth(III) readings. This was measured using the 0.1 scale meter reading, and the sensitivity seemed comparable with that obtained in hydrochloric and hydrobromic acid despite the formation of a white precipitate on addition of the HF to the bismuth solution.

The spectra of the above mentioned ions are as shown in the diagrams, antimony(III), Figure 4.1; arsenic(V), Figure 4.2; bismuth(III), Figure 4.3; lead(II), Figure 4.4; and uranium(VI), Figure 4.5.

FIGURE 4.1.

98.

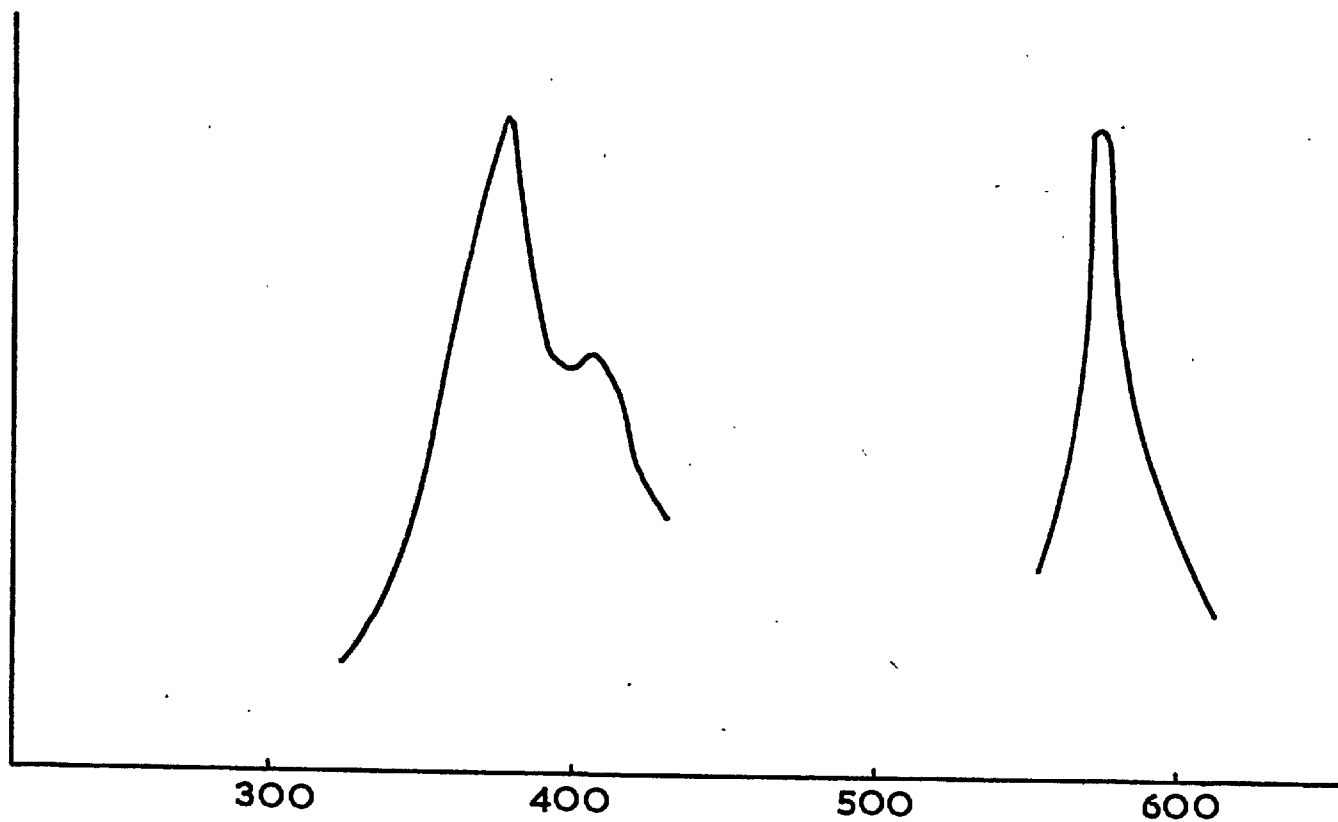


FIGURE 4.2.

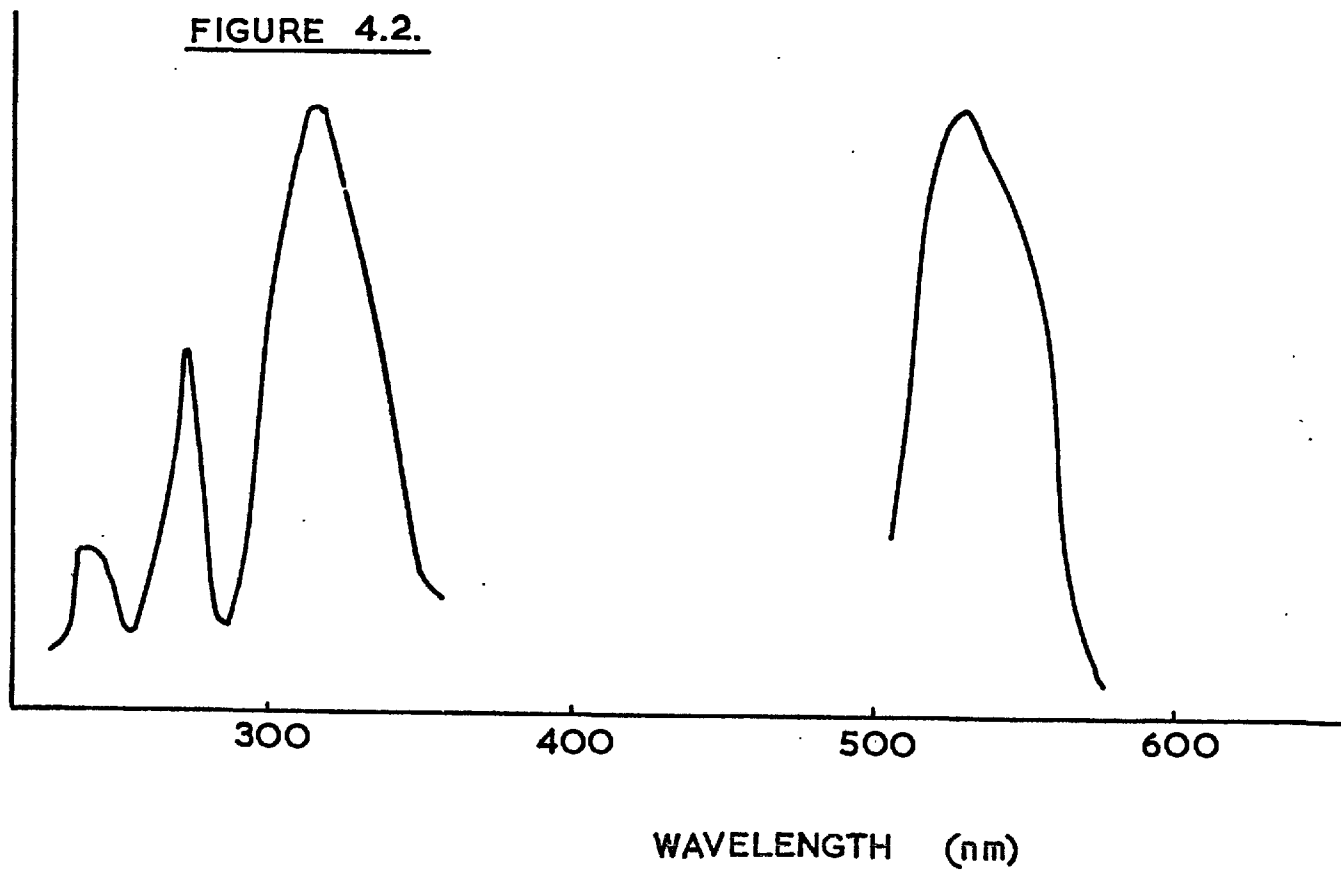


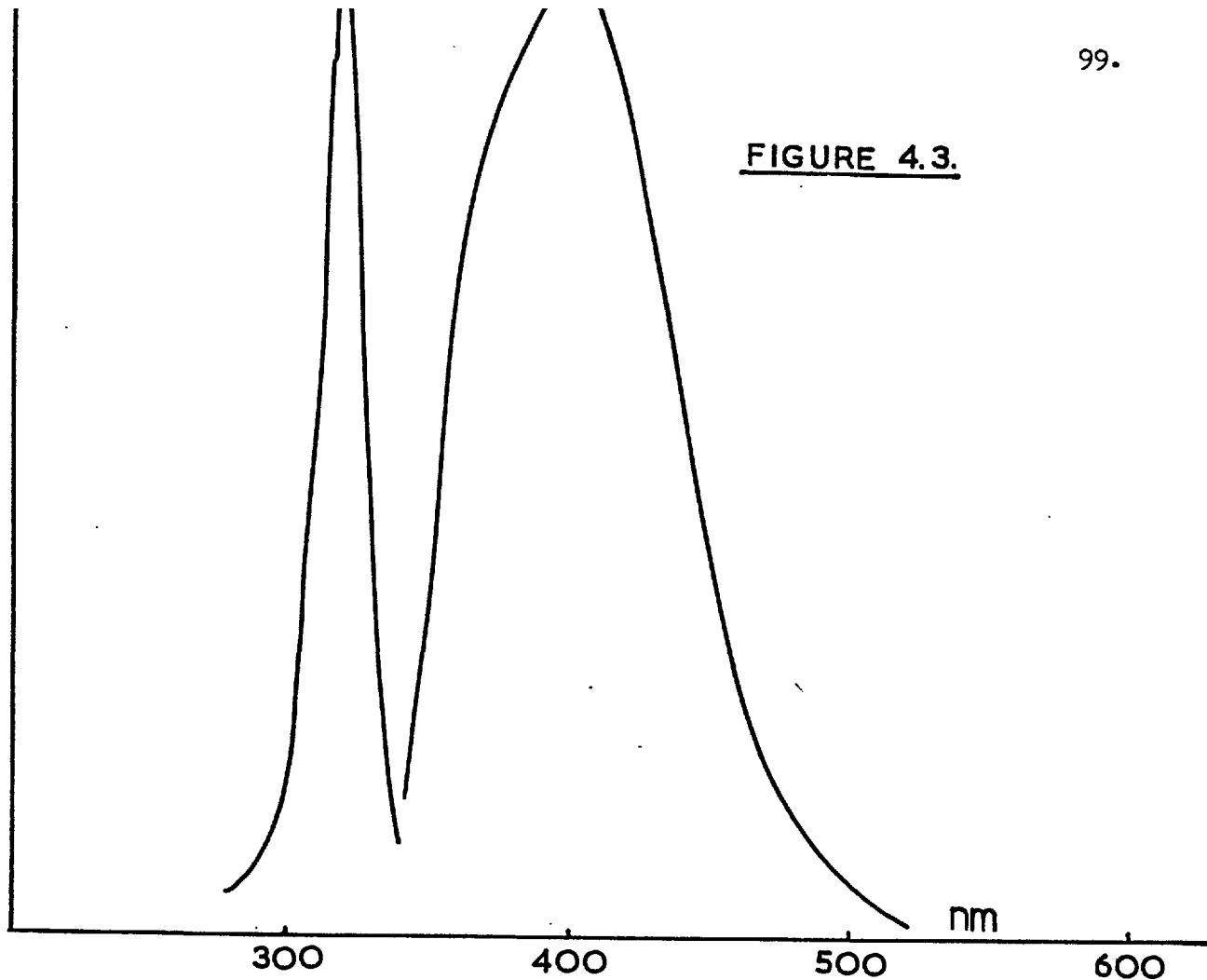
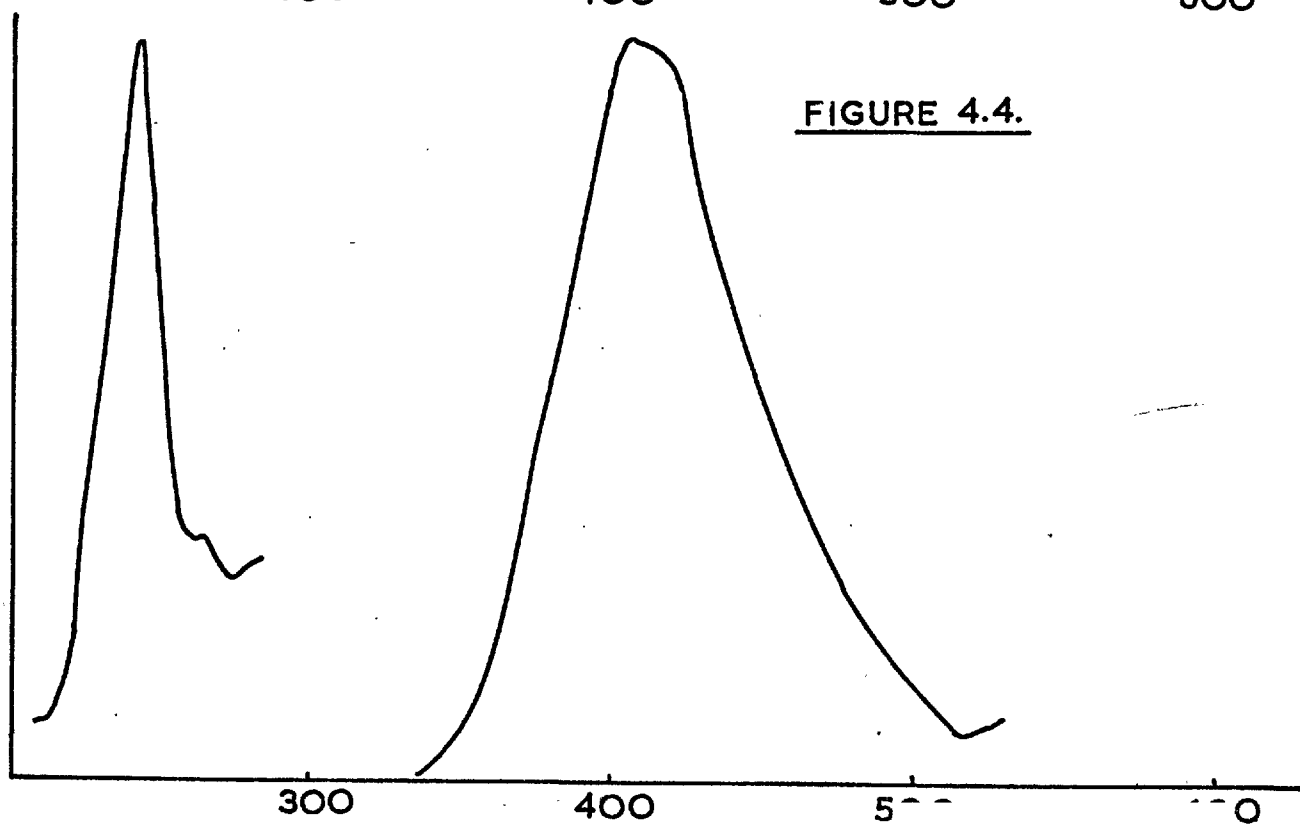
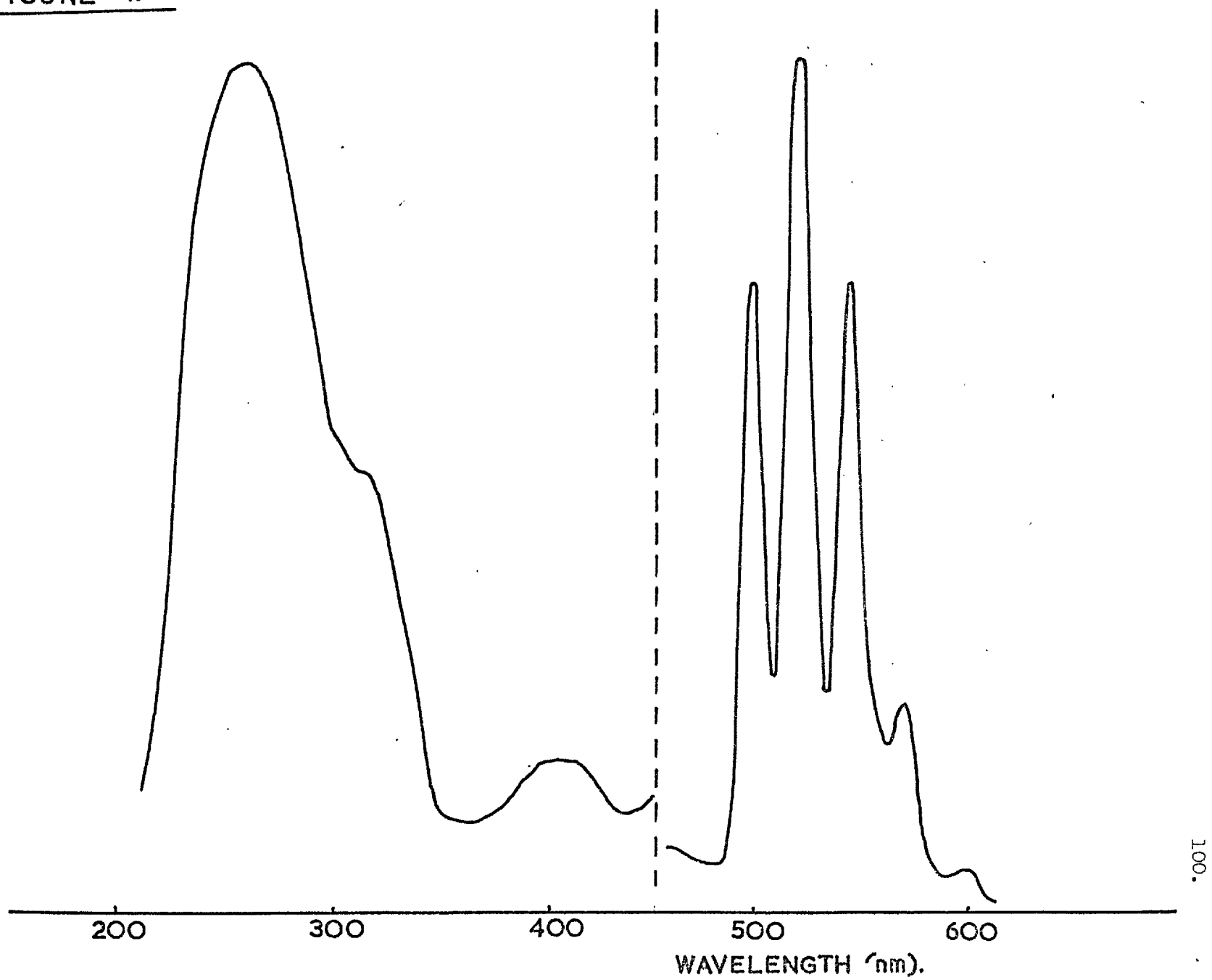
FIGURE 4.3.FIGURE 4.4.

FIGURE 4.5.



DISCUSSION

The results obtained from this experiment were generally disappointing in that no pattern with respect to results obtained for hydrochloric and hydrobromic acids could be discerned.

The antimony(III) fluorescence was very weak, with approximately the same excitation and emission maxima as in hydrochloric acid (390 - 580 nm) and hydrobromic acid (360 - 586 nm). The arsenic(V) spectra had both lower excitation and emission wavelengths, 318 nm and 538 nm respectively compared with hydrobromic acid at 356 nm and 584 nm. The spectra obtained for bismuth(III) was almost identical to that obtained in chloride media, 330 nm and 410 nm, (and this may indicate that the fluorescence obtained is some property of the bismuth alone rather than its surrounding matrix). The white precipitate found at this and lower concentrations was probably BiF_3 .

The spectra for lead in hydrofluoric acid shows that though the emission maximum is similar to that obtained for the chloride and bromide media (390 nm and 414 nm respectively) the excitation maxima at 247 nm is lower than that for chloride at 276 nm which in turn is lower than that for the bromide system at 304 nm, i.e. an increase in excitation wavelength occurs as the matrix changes from fluoride to chloride and finally to bromide (247, 276 and 304 nm). The white precipitate which

was observed on addition of the hydrofluoric acid to the lead solution is probably PbF_2 .

A similar pattern can be seen with uranium(VI) where the wavelength of maximum excitation alters from 266 nm in fluoride to 302 nm in chloride, and finally to 327 nm on bromide.

CONCLUSION

As an analytical procedure therefore the use of the hydrofluoric acid matrix is of little value. The only possible advantage being that only bismuth(III) fluoresces at concentrations desirable for trace analytical chemistry, and though precipitation occurs at higher concentrations it is probable that at the concentrations being considered (in the region of 10^{-7} M) that this phenomena is not significant. A selective method for bismuth determination may therefore be obtainable.

Not only because of the low sensitivity of the remaining ions but also the difficulty in preparing, handling and measuring samples in the quartz tubes the analytical applications of this system appear seriously limited.

CHAPTER V

THE SPECTROPHOSPHORIMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF NIOBIUM

INTRODUCTION

Several spectrophotometric methods are available for the determination of niobium. Some of the most sensitive methods are those based on the use of the reagents Bromopyrogallol Red [84] [85] [86] and 4-(2-pyridylazo)-resorcinol [87] [88] [89] [90] [91]. Selectivity in these methods is controlled by the use of masking agents and/or a preliminary separation of the interferences from the niobium to be determined. A spectrofluorimetric method for the determination of niobium, which utilises the reagent Lumogallion, has been described by Klimov and Didkovskaya [92]. Niobium may be determined spectrophotometrically with 8-hydroxyquinoline after extraction of niobium oxinate into chloroform, although the method is rather insensitive ($E_{385\text{nm}} = 11,000$). Kassner, Garcia-Porrata and Grove [93] have used this method for the determination of niobium in steels after preliminary precipitation of the niobium as niobic acid. During the course of an investigation of the low temperature fluorescence and phosphorescence characteristics of the metal complexes of 8-hydroxyquinoline we have observed intense phosphorescence from niobium(V) oxinate in the rigid clear glass

formed from a mixture of diethyl ether, isopentane, alcohol and chloroform at -196°C . Measurement of this phosphorescence permits the sensitive detection of niobium without the problems from the fluorescence of the reagent blank or oxinates of other elements present which may be encountered if the total low temperature luminescence (fluorescence + phosphorescence) intensity is measured. With an intense radiation source and wide excitation monochromator band-pass the determination may be much more sensitive than the corresponding spectrophotometric procedure. This chapter reports the sensitive method which has been developed for the determination of niobium by extraction of niobium oxinate into chloroform from aqueous citrate medium at pH 9.4, dilution of the chloroform with EPA (diethyl ether: isopentane: ethanol), and measurement of the phosphorescence intensity at 580 nm of the clear glass formed from this solution at liquid nitrogen temperature.

EXPERIMENTAL

Apparatus. Phosphorescence measurements were made with the Aminco-Bowman Spectrofluorometer (American Instrument Co.) fitted with a 150 W Xenon arc lamp and RCA IP28 photomultiplier tube, and equipped with a Bryans X-Y recorder. The Aminco rotating 'can' phosphorescope was used and the low temperature housing and dewar flask with fused silica base supplied for phosphorimetry were used to hold the sample tubes. Precision

bore pyrex tubes of length 200 mm, bore 3 mm. and 1 mm. wall thickness sealed at one end were employed as sample tubes. A sample volume of 0.5 ml. is enough to fill these tubes sufficiently for work with the Aminco-Bowman Spectrofluorometer.

In order to obtain maximum sensitivity compatible with good definition of maxima, 5 mm. slits (Aminco slit arrangement No. 5.) corresponding to a 50 nm band-pass were used in the excitation and analysing monochromators.

REAGENTS

NIOBIUM SOLUTION (2×10^{-2} M). A stock niobium solution was prepared by fusing 0.6645 g. of Nb_2O_5 (Specpure grade, Johnson and Matthey, London) in 2.5 g. of fused potassium bisulphate. The melt was cooled, a few drops of concentrated sulphuric acid were added, and the melt was re-heated until completely clear. The melt was then dissolved in 100 ml. of 10% citric acid and the solution was diluted to 250 ml. with distilled water.

8-HYDROXYQUINOLINE. 1% 8-hydroxyquinoline (AnalaR grade) in chloroform.

DIVERSE IONS. A 2×10^{-2} M tantalum solution was prepared from Ta_2O_5 (Specpure grade, Johnson and Matthey, London) in the same way as described for the niobium solution. However

in order to prevent the tantalum re-precipitating as Ta_2O_5 the hot melt should be added slowly, in order to prevent spluttering, to the citric acid solution, which should be heated to just below boiling point and rapidly stirred. If this procedure is not rigorously obeyed Ta_2O_5 will re-precipitate. 10^{-2} M solutions of other ions were prepared from analytical reagent grade salts.

EPA MIXTURE. The EPA solvent for phosphorimetry was prepared by mixing AnalaR grades of diethyl ether, isopentane and absolute ethanol in the volume ratio 5:5:2.

pH 9.4 SOLUTION. 17.5 ml. of concentrated ammonia solution (AnalaR grade, specific gravity 0.88) were diluted to 250 ml. with distilled water. 10 g. of citric acid (AnalaR grade) was dissolved in 250 ml. distilled water to give a 4% w/v solution. The niobium sample solutions to be analysed are 4% with respect to citric acid, and compensation should be made for this citric acid when the buffered solution is prepared for the extraction procedure. Thus for 'x' ml. of sample add $3 - x$ ml. of 4% citric acid and 3 ml. of dilute ammonia solution. A satisfactory buffered pH 9.4 solution is thus obtained.

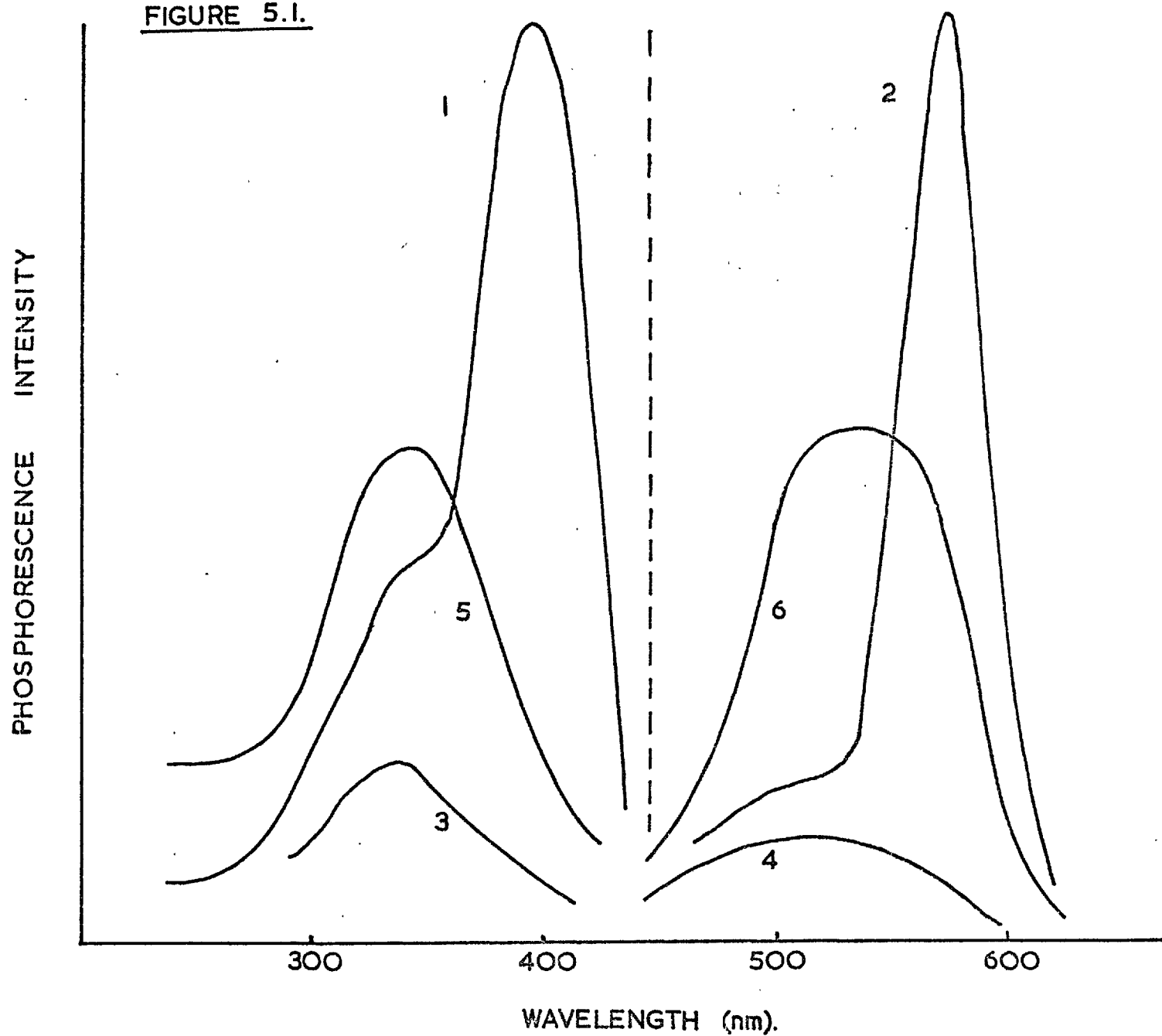
CALIBRATION GRAPH FOR NIOBIUM

Transfer accurately aliquots of the diluted niobium stock solution (between 0.2 ml. of 8×10^{-5} M and 1.0 ml. of 2×10^{-4} M solution, x ml.) to a series of 10 ml. volumetric flasks which contain 3 ml. of dilute ammonia solution and 3-x ml. of 4% citric acid solution. To each flask add 2 ml. of 1% 8-hydroxyquinoline in chloroform. Dilute to volume with distilled water. Shake the solutions for 5 minutes, extract 1 ml. aliquots of the chloroform phase from each flask using a syringe, and dilute these to exactly 10 ml with EPA mixture. Transfer each of these solutions in turn to a pyrex sample tube and cool the tube in liquid nitrogen in the measurement dewar. Measure the phosphorescence intensity at 580 nm of each solution using an excitation wavelength of 398 nm. The graph of phosphorescence intensity vs. niobium concentration (0.18 to 2.30 ppm Nb in the original 8 ml. of aqueous solution before extraction) is linear and, after subtraction of the reagent blank prepared simultaneously, passes through the origin.

RESULTS AND DISCUSSION

Spectral Characteristics. Figure 5.1 shows the phosphorescence excitation and emission spectra for the reagent blank and the niobium oxinate complex in EPA respectively.

FIGURE 5.1.



LEGEND TO FIGURE 5.1

- Spectra
1. Excitation spectrum for niobium oxinate.
Emission measured at 580 nm.
 2. Emission spectrum for niobium oxinate.
Excitation measured at 398 nm.
 3. Reagent blank excitation spectrum. Emission
measured at 580 nm.
 4. Reagent blank emission spectrum.
Excitation wavelength set at 398 nm.
 5. Reagent blank excitation spectrum. Emission
measured at 536 nm.
 6. Reagent blank emission spectrum. Excitation
wavelength set at 338 nm.

These spectra are uncorrected for variation in emission characteristics of the Xenon arc lamp and the response characteristics of the photomultiplier. The relevant correction data has appeared elsewhere [38]. The niobium oxinate complex exhibits its excitation maximum at 398 nm and its phosphorescence emission maximum at 580 nm. The blank solution prepared by omitting the niobium solution in the recommended procedure (but retaining an equivalent amount of KHSO_4) shows weak phosphorescence with an excitation maximum

at 338 nm and emission at 536 nm. A blank prepared in the same way, but whose excitation and emission spectra were recorded at the wavelengths of maximum excitation and emission for the niobium complex shows similar but less intense phosphorescence.

EFFECT OF pH

The results of experiments conducted to determine the effect of the pH of the initial aqueous medium on the extraction of niobium oxinate confirm the observations made by other workers that efficient extraction may be obtained over the pH range 4.5 to 9.75 [94].

The experiment was carried out using solutions containing 0.25 ml. of 10^{-3} M niobium and varying amounts of ammonium hydroxide and citric acid solutions, such that the pH range from 3.10 to 10.7 is studied and the results thus obtained are given in Table 5.1 and Figure 5.2.

FIGURE 5.2.

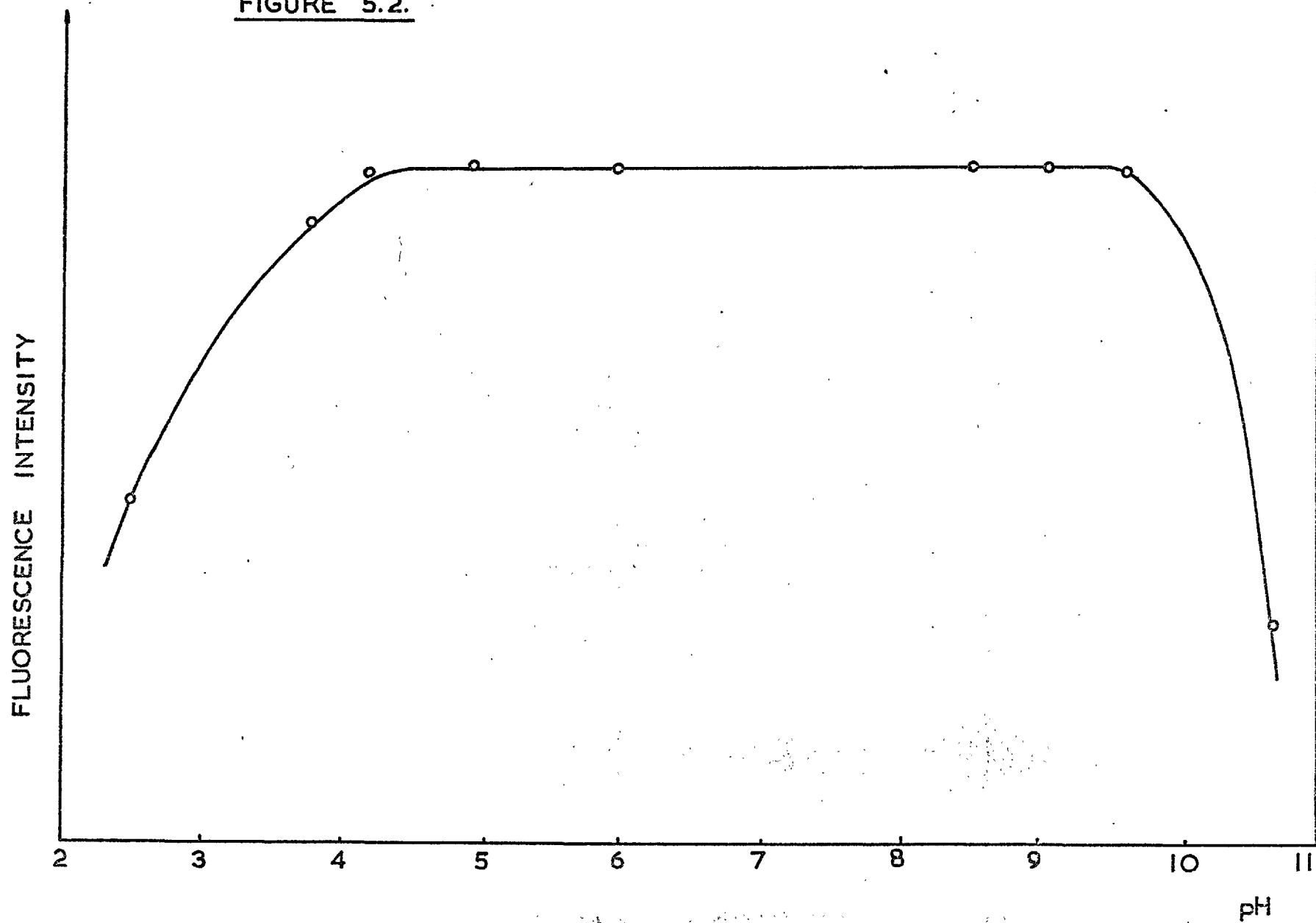


TABLE 5.1Effect of pH on the Extraction of Niobium

Solution	ml. NH_4OH	ml. Citric Acid	pH	Fluorescence Reading
1	-	7.5	3.10	19,19
2	1.0	7.5	4.10	34,34
3	2.0	7.5	4.30	37,36
4	3.0	7.5	5.04	37,37
5	4.0	7.5	5.83	36,37
6	5.0	7.5	8.48	37,37
7	6.0	7.5	9.10	36,37
8	7.5	7.5	9.5	36,37
9	7.5	0.25	10.7	13,12

The pH was measured using a Beckman pH meter together with a glass electrode (Pye-Unicam Ltd.) and a standard calomel electrode. All pH measurements were taken on the aqueous phase after the extraction had been effected. A fluorescence reading of 36,37 corresponded to 100% extraction. This was verified by carrying out a second extraction and measuring the fluorescence intensity of the resulting organic phase; a reading of zero corresponding to complete extraction.

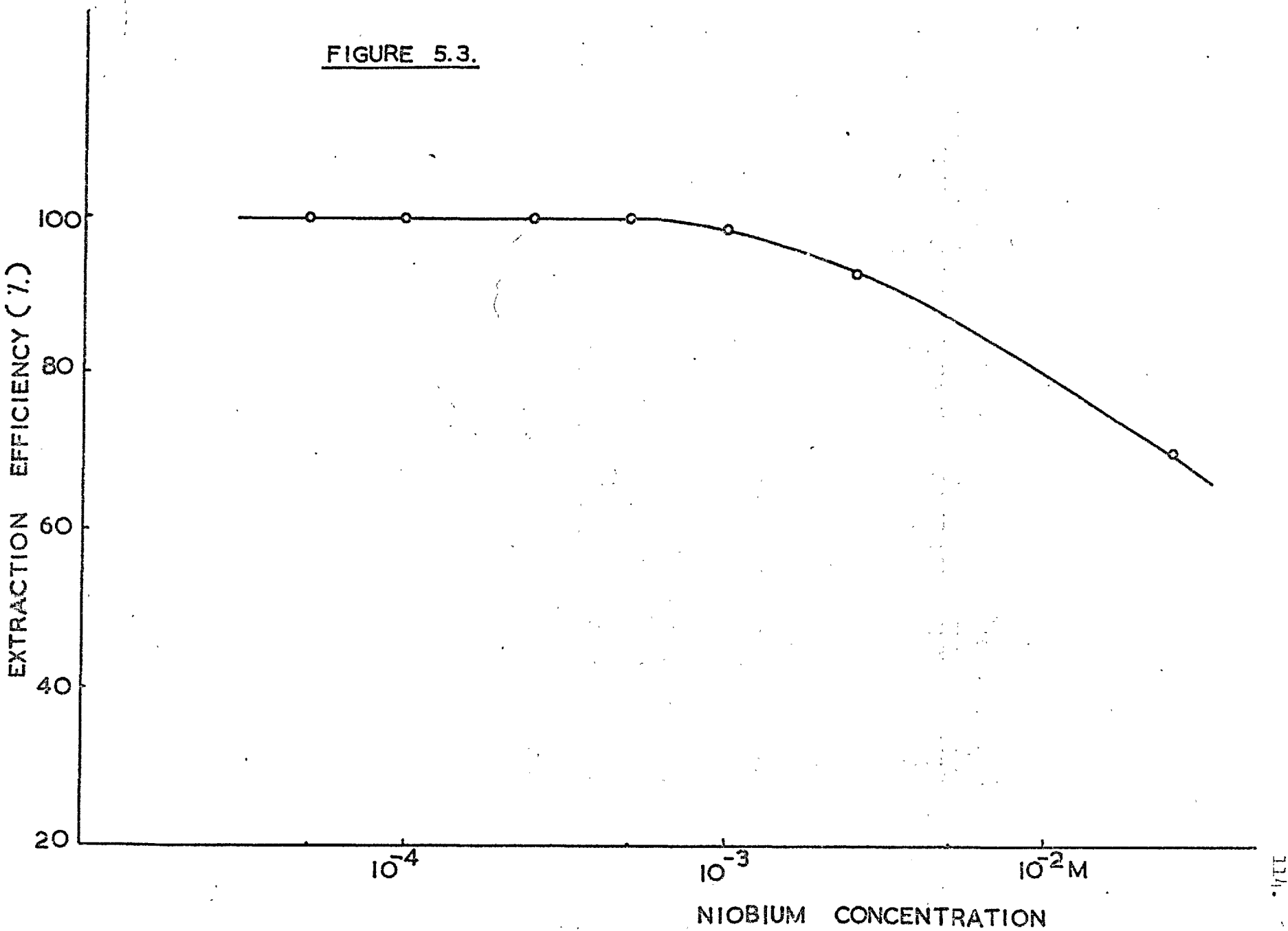
The conditions employed by Kassner, Garcia-Porrata and Grove [93] for the determination of niobium in steels and extraction of the niobium from the ammoniacal citrate medium at pH 9.4 were adopted. The results of repetitive extraction experiments for concentrations studied indicated that niobium was virtually quantitatively extracted at this pH when the optimum 8-hydroxyquinoline concentration was employed.

EFFECT OF REAGENT CONCENTRATION

The 8-hydroxyquinoline reagent concentration employed must be high enough for the efficient extraction of niobium. With a spectrophosphorimetric procedure of this type, however, the use of very great excesses of reagent may lead to the extensive cracking and/or precipitation in the glass formed when the solution diluted with EPA is cooled to liquid nitrogen temperature. This was found to limit the usable upper limit of the oxine concentration in the chloroform used for extraction to 1%. This in turn limited the amount of niobium extractable to ca 1 ml. of 2×10^{-3} M solution. This is still in excess of the amounts determined in the recommended procedure.

Figure 5.3 illustrates the effect of using 2 ml. of a 1% 8-hydroxyquinoline in chloroform solution to extract varying amounts of niobium (between 0.5 ml. of 10^{-4} M and 2.0 ml. of 10^{-2} M) in the 8 ml. of buffered aqueous solution. All

FIGURE 5.3.



these solutions were made up as previously described using 10 ml. volumetric flasks such that the aqueous phase is buffered at pH 9.4, the pH for maximum extraction efficiency. If greater than 1.0 ml. of 2.10^{-3} M niobium solution is added to this aqueous phase ($\approx 23.2 \mu\text{g/ml}$ in the 8 ml.) then the extraction efficiency decreases.

The extraction efficiency was obtained by measuring the fluorescence readings for the first extraction, carrying out a second, and third extraction, using in each case a further 20 ml. aliquot of chloroform 8-hydroxyquinoline solution and following dilution with EPA measurement of the fluorescence of these organic solutions. For 100% extraction efficiency from one extraction no fluorescence signal should be obtained for either of the two remaining extracts.

If a more concentrated oxine solution was used, i.e. 4% then this limit can be extended slightly higher to $40 \mu\text{g/ml}$. in the aqueous phase, but 'cracking' of the glass formed on cooling of the organic phase after dilution with EPA was found to be far more frequent due to the precipitation of excess 8-hydroxyquinoline on cooling, and this method was therefore not employed.

The use of a 4% 8-hydroxyquinoline in chloroform solution also seriously affected the detection limit as blank readings obtained were significantly higher than those for a 1% solution.

Solutions of intermediary strength also gave rise to 'cracking' and higher blanks and therefore a 1% solution was found to be the most satisfactory.

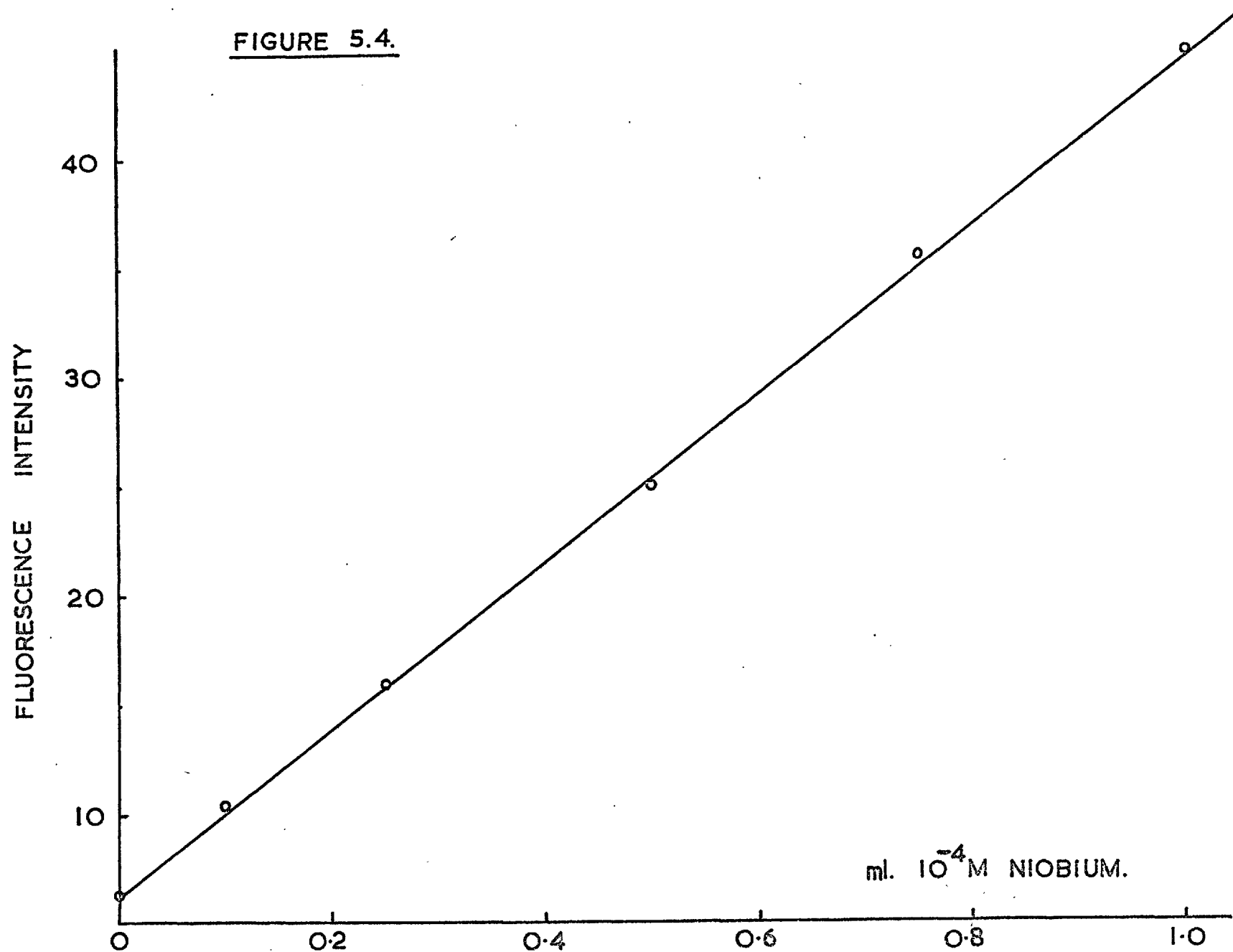
Some of the available excess when 2 ml. of a 1% solution of reagent is chloroform is employed may be depleted by consumption by small amounts of foreign ions to form extractable or non-extractable oxinates without affecting the niobium extraction efficiency.

CALIBRATION RANGE AND PRECISION.

Linear calibration graphs were obtained over the range 1.46 to 18.4 $\mu\text{g.}$ of niobium in the original 8 ml. of the aqueous solution before extraction. Figure 5.4. The determination of larger amounts of niobium was not investigated. The lower determination limit is set not only by instrumental noise and reagent blanks, but also by the need to dilute the chloroform extract extensively with EPA in order to form a satisfactory glass without cracking or snow formation.

In order to extend the lower limit of detection for the method, 25 ml. volumetric flasks were employed and 5 ml. of 1% 8-hydroxyquinoline in chloroform employed. Having extracted the niobium into the 5 ml. chloroform phase, the chloroform was removed and evaporated down over a steam bath to 0.5 ml. and the residue then diluted to 5.0 ml. with EPA before freezing.

FIGURE 5.4.



This should have improved the detection limit by a factor of 20. However, the problem incurred was one of constant cracking of the glass, and this additional step had therefore to be omitted.

If only the entrance slits to the sample compartment were completely removed an increase in detection limit of approximately 15% was obtained. Removal of all the slits in the spectrofluorimeter, however, gave rise to a much higher blank reading and no increase in detection limit could be achieved.

The standard deviation, determined by measurement of the phosphorescence intensity of 10 separate solutions each prepared by extraction of 9.2 $\mu\text{g.}$ of niobium was found to be equivalent to 2.0% of the response due to the niobium complex after subtraction of the reagent blank.

The results obtained are shown in Table 5.II.

TABLE 5.II

Precision Measurements for 10 Solutions Each
Containing 9.2 μg . Niobium

Solution	Reading	Deviation	Total Variance
1	37,37,36	0.57, 0.57,-0.43	0.84
2	35,37,37	-1.43, 0.57, 0.57	2.69
3	36,35,37	-0.43,-1.43, 0.57	2.55
4	37,37,36	0.57, 0.57,-0.43	0.84
5	37,37,36	0.57, 0.57,-0.43	0.84
6	36,36,37	-0.43,-0.43, 0.57	0.70
7	36,37,37	-0.43, 0.57, 0.57	0.84
8	36,36,36	-0.43,-0.43,-0.43	0.56
9	36,35,36	-0.43,-1.43,-0.43	2.41
10	37,37,38	0.57, 0.57, 1.57	3.12
	Average $\bar{x}$ = 36.43		<u>15.39</u>

Three samples were taken from each solution, to give a total of thirty readings.

$$\begin{aligned}
 \text{Standard Deviation} &= \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \\
 &= \sqrt{\frac{15.39}{29}}
 \end{aligned}$$

Standard Deviation = 0.73

$$\begin{aligned}\text{Standard Deviation (Percentage)} &= \frac{\text{S.D.} \cdot 100}{\bar{x}} = \frac{0.73 \cdot 100}{36.43} \\ &= \underline{2.0\%}\end{aligned}$$

INFLUENCE OF TIME

No detectable deterioration in phosphorescence intensity was observed when prepared solutions after extraction were allowed to stand for five hours at room temperature under normal laboratory lighting (fluorescent strip-lighting) before measurement.

EFFECT OF FOREIGN IONS

The effect of 40 foreign ions on the niobium determination was investigated. The effect of 50-fold molar excesses of the ions on the phosphorescence intensity produced by 9.2 µg. of niobium in the recommended procedure was studied. An ion was considered to interfere when it produced at this concentration level an error of greater than twice the standard deviation of the determination in pure aqueous solution, i.e. $\geq 4\%$. The species found not to interfere under these conditions were Be, Bi, Ca, Cr(VI), Ga, In, K, Mg, Mo(VI), Na, NH_4 , Sb(V), Th, W(VI), Zr, Br^- , Cl^- , ClO_4^- , CN^- , CO_3^{2-} , F^- , HSO_4^- , I^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , oxalate and tartrate

The presence of these ions illustrated in Table 5.III at the 50-fold molar excess level caused the errors shown.

TABLE 5.III.

Interferences caused by several ions when present in a 50-fold molar excess above the niobium concentration of 9.2 μg .

Ion	Percentage Interference	Ion	Percentage Interference
Al(III)	-35	Mn(II)	-90
Cd(II)	-25	Ni(II)	-75
Co(II)	-75	Pb(II)	+35
Cr(III)	-70	Ti(IV)	-26
Cu(II)	-30	V(V)	-50
Fe(III)	-62	Zn(II)	-50
Hg(II)	-50	U(VI)	-85

All the following ions appear to be extracted and to give strongly coloured solutions in the organic phase thus giving rise to serious negative interference due to attenuation of the incident and emission radiation. Cobalt gives rise to a yellow brown chloroform layer; copper a yellow-green; iron(III), dark green; manganese(II), yellow; nickel, blue; titanium, vanadium and uranium all bright yellow.

In order to remove these interferences the following masking agents, Table 5.IV, were added to the aqueous phase to prevent their extraction by 8-hydroxyquinoline.

TABLE 5.IV.

Masking agents for ions causing errors
in the determination of niobium,

Ion	Masking Agents Used	Suitable Reagent	Percent Interference after adding Reagent
Al	F ⁻ , Nitrilotriacetic Acid, Triethanolamine.	Triethanolamine	-
Cd	CN ⁻ (1 ml. 1% soln.).	CN ⁻	-
Co	CN ⁻ (1 ml. 1% soln.).	CN ⁻	-
Cr(III)	Triethanolamine, EDTA, Ascorbic Acid.	-	-70
Cu	CN ⁻ , (1 ml. 1% soln.).		-
Fe(III)	F ⁻ , PO ₄ ³⁻ , SCN ⁻ , CN ⁻ , 2- E.D.T.A., N.T.A., C ₂ O ₄ ²⁻ , Citrate, Tartrate, Tiron, Thiourea, Peroxide(H ₂ O ₂).	-	-62
Hg(II)	CN ⁻ (1 ml. 1% soln.).	CN ⁻	-
Mn(II)	CN ⁻ , E.D.T.A.	E.D.T.A.	-
Ni(II)	CN ⁻ , (1 ml. 1% soln.).	CN ⁻	-
Pb	E.D.T.A., CN ⁻ (1 ml. 1% soln.).	CN ⁻	-

Table 5.IV (contd).

Ion	Masking Agents Used	Suitable Reagent	Percent Interference
Ti(IV)	E.D.T.A., H_2O_2 , Triethanolamine.	Triethanolamine	-
V(V)	CN^- (1/2 ml. 1% soln.).	CN^-	-
U(VI)	F^- , CO_3^{2-} , E.D.T.A. Oxalate	F^-	-8
Zn	CN^- (1 ml. 1% soln.).	CN^-	-

The interferences of Cd, Co, Cu, Hg, Mn(II), Ni, Pb, V and Zn were removed completely at this level by the addition of 1 ml. of a 1% solution of E.D.T.A. and potassium cyanide to the solution to be analysed. The interference of a 50-fold molar excess of either Al or Ti(IV) was removed by the addition of 0.2 ml. of triethanolamine to the sample solution before extraction.

Tantalum does not interfere in the recommended procedure when present at the 100-fold molar excess level over niobium.

The strong interference of iron(III) could not be suppressed by any of the masking agents shown in Table 5.IV. Only Tiron and peroxide successfully masked the iron but they both also masked the niobium. Reduction with ascorbic acid was also tried but on addition of the organic phase the dark green colour of iron oxinate re-appeared, and therefore as masking and

reduction techniques had proved unsuccessful prior removal of the iron(III) before determination of niobium was required.

Iron(III) can be quantitatively extracted between pH 2.0 and 10.0 [136] using 8-hydroxyquinoline-chloroform, whereas niobium is extracted between pH 4.2 and 9.6, and therefore separation of the two elements ought to be possible in the range pH 2.0 to 4.2.

This was attempted by bringing the niobium, iron, citric acid solution to pH 2.5 using dilute hydrochloric acid (measuring the pH with a Beckman pH meter), the iron was then extracted using a 10 ml. aliquot of 1% 8-hydroxyquinoline in chloroform, the extraction repeated to ensure complete separation, and the aqueous phase finally washed with 10 ml. of pure chloroform. The aqueous phase was separated and adjusted to pH 9 using dilute ammonia solution. However on alteration of the pH chloroform, oxine and iron oxinate, which presumably had dissolved in the chloroform, which was itself partially soluble with the aqueous phase at the lower pH value, re-appeared thus preventing the determination of niobium due to the strong green colouration of the organic phase.

In order to remove all the oxine and iron oxinate at pH 2.5. several other solvents were unsuccessfully tried. Those used were diethyl ether, n-butanol, iso-butylmethylketone, methyl n-propylketone, cyclohexanone and iso-butyl acetate.

Up to six extractions with each of these solvents were attempted but the iron-oxinate colour still persisted. A hydrochloric acid:potassium hydrogen phthalate buffer to give a pH of 3.2 was also tried, and though most of the iron was removed so also was the niobium.

Finally a successful method was evolved by adding 5.0 ml. of 4% citric acid to the x ml. of niobium/iron sample solution, this gave a measured pH of 2.5. The iron oxinate was quantitatively separated from the niobium by two extractions using 2.0 ml. of 1% 8-hydroxyquinoline in chloroform solution, and the aqueous phase was finally washed using 5.0 ml. of pure chloroform. The pH was then adjusted to exactly 9.4 by the addition of 5+ x ml. of the ammonia solution previously described, and at this point the niobium is quantitatively extracted and determined. At least 1000-fold excess of iron could be satisfactorily removed in this way to give no interference whatsoever, however, a blank and standard should be subjected to the same procedure simultaneously when high precision is required.

Chromium(III) gave rise to a negative interference of ~70% due to the formation of the hydroxide on adjustment of the pH to 9.4 with the ammonia solution, and hence possible adsorption of the niobium and reagent onto the precipitate. Prior removal of the chromium would seem the best method as all previous attempts

to use masking reagents had proved unsuccessful. This may be possible using the reagent acetylacetone [137] which will remove all the chromium(III) at values below pH 1. The niobium not being extracted at this pH in the presence of a large excess of citrate.

Vanadium interference was satisfactorily removed by the addition of 0.5 ml. of a 1% solution of potassium cyanide solution and vigorous shaking for 10 minutes with the organic phase in order to extract all the niobium, and the uranium interference was largely removed by addition of 1.0 ml. of a 1% solution of sodium fluoride. A rapid extraction of the niobium was required as a brown colour develops slowly on standing and if separation of the two layers and measurement is left for as long as 20 minutes a negative error of 85% was incurred.

ACCURACY

Table 5.V shows the results of the analysis of solutions for niobium by the recommended procedure.

TABLE 5.V

Analysis of niobium solutions treated
as unknown solutions.

Sample	Niobium $\mu\text{g.}$		Error, %	Foreign Ions Present ($\mu\text{g.}$)
	Present	Found		
1	3.34	3.48	+4.0	-
2	4.84	4.84	-	-
3	5.96	6.02	+1.0	-
4	8.92	8.70	-2.5	-
5	9.68	9.80	+1.5	-
6	11.90	12.00	+1.0	-
7	1.86	1.90	+2.0	Ta(360)
8	2.98	2.86	-4.0	Pb(1040) EDTA + CN^-
9	5.20	4.98	-4.5	Co(270), Ni(445) EDTA + CN^-
10	7.44	7.48	+0.6	Cu(510) EDTA + CN^-
11	7.44	7.66	+2.8	Ca(400), Mg(70)
12	9.28	9.06	-2.4	Fe(780) prior extraction
13	11.90	11.54	-3.0	Al(140) + triethanolamine

PHOSPHORESCENCE LIFE-TIME.

The phosphorescence life-time of niobium oxinate in EPA:chloroform at -196°C was measured by presentation of the photomultiplier output of the spectrofluorometer directly at an oscilloscope and observation of the decay curve of the phosphorescence, i.e. the Aminco photomultiplier microphotometer unit was not used due to the long time constant of the measuring circuit incorporated (approximately 0.5 second). Repetitive experiments gave a value for the phosphorescence lifetime, τ , of 7.5 ± 0.8 milliseconds.

CONCLUSION.

The method described here for the determination of traces of niobium, based on our observation of the phosphorescence of its complex with 8-hydroxyquinoline in EPA at -196°C , is more sensitive than the corresponding absorptiometric method with 8-hydroxyquinoline and most other absorptiometric methods which employ organic reagents. The determination can be made very selective when cyanide and EDTA, fluoride, or triethanolamine are used as masking agents. Unlike spectrofluorometry, in the spectrophosphorimetric method employed here a wide band-pass may be employed for the excitation and no problems are encountered with scattered radiation from the Dewar flask, sample tube or small amounts of particulate material in the solution. The

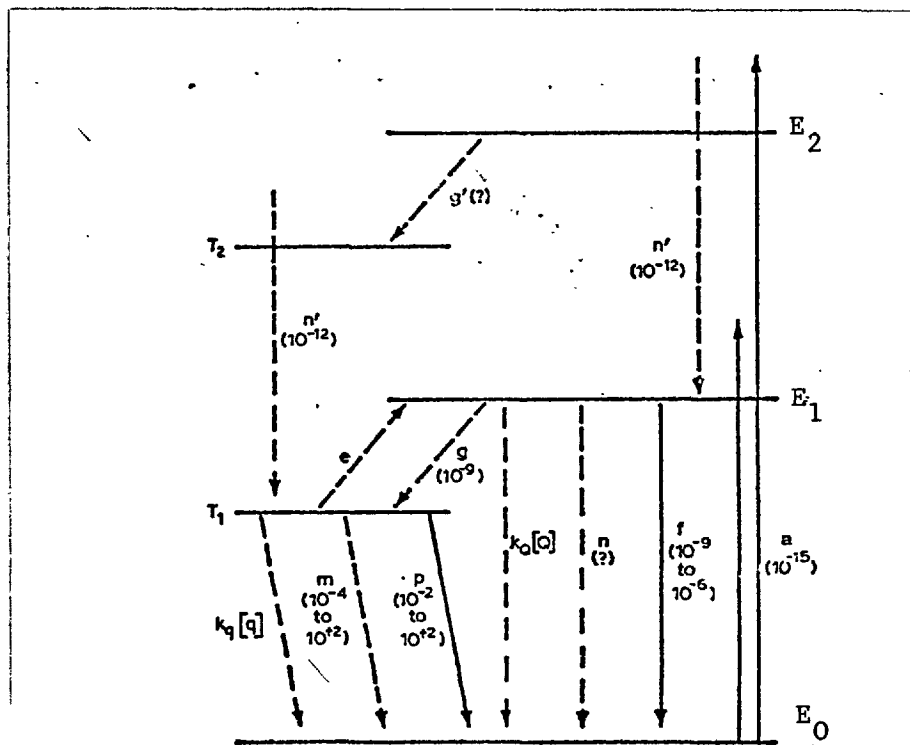
determination is only slightly slower than a conventional spectrophotometric determination. Some additional care must be taken in spectrophosphorimetry compared to spectrophotometry, however, to observe cleanliness when filling and cooling the sample tubes.

CHAPTER VI.

INTRODUCTION II.

Consideration of the mechanisms of formation of both excited singlet and triplet states and the subsequent emission of radiation as fluorescence or phosphorescence together with the time required for each of these processes is necessary if results obtained from the measurement of the lifetimes of luminescent species is to be correctly interpreted. Figure 6.1 illustrates the processes occurring together with their associated times.

FIGURE 6.1.



The radiative processes are shown as solid lines and the non-radiative processes as broken lines. The absorption of light (a) occurs within a period of 10^{-15} seconds. Normal fluorescence from E_1 to E_0 occurs between 10^{-9} seconds for allowed $\pi^*-\pi$ transitions, and 10^{-6} seconds for less probable $\pi^*-\pi$ transitions. The radiative lifetime (p) of the triplet state is in the region of 10^{-4} to 10^{+2} seconds. Internal conversion (n') from upper excited singlet and triplet levels occurs rapidly in approximately 10^{-12} seconds. This is the same length of time as that required for the loss of vibrational energy. Internal conversion to the ground state is represented by (n); little, however, is known about this process. The intersystem crossing (g) from the lowest excited singlet state takes time of the same order of magnitude as the radiative fluorescence, i.e. 10^{-9} seconds, and competes with the latter process. Internal conversion from higher states (g') has not been well examined but it must occur within a time of 10^{-12} seconds in order to compete with the normal radiationless transitions of the intersystem crossing processes. The transition (m) from the lowest excited triplet back to the ground state is slow and requires in the region of 10^{-4} to 10^{+2} seconds.

The symbol (e) refers to the rate of the overall process of thermal excitation followed by intersystem crossing for the excitation from T_1 to E_1 . It is this phenomena which is

responsible for E-type delayed fluorescence. However this occurs only when the separation between the two states is small enough to permit appreciable thermal excitation of the triplet molecule to a level equal to that of the lowest excited singlet level.

The mechanisms considered in Figure 6.1 are all first order with the exception of the absorption process, and therefore have reaction rate constants equal to the reciprocal of the lifetime of the initial state. Both the lowest excited singlet and triplet states have a sufficiently long lifetime for chemical reaction or luminescence quenching by collision with solute molecules to occur. Though this would obviously be a second order mechanism, the concentration of the quenching solute molecules is very much greater than that of the excited species. Their concentration is therefore effectively unchanged and the mechanism can be treated as a first order process with a rate constant of $K_Q[Q]$.

If a number of molecules n_0 are excited to a higher electronic state, and their return to the ground state is possible only by the emission of light, then the probability that one of these molecules will emit light and return to the ground state is independent of the presence of other excited molecules, and thus at any time t , the number of molecules emitting per second is proportional to the number, n , present at that time.

$$\frac{dn}{dt} = -k_f n \quad (1)$$

Where k_f is the first order rate constant for fluorescence emission.

Integration of equation (1) gives:

$$n = n_o e^{-k_f t} \quad (2)$$

The rate of emission of light Q is given by:

$$\begin{aligned} Q &= -\frac{dn}{dt} = k_f n_o e^{-k_f t} \\ &= Q_o e^{-k_f t} \end{aligned} \quad (3)$$

Therefore the fluorescence intensity decays exponentially.

The mean radiative lifetime of the fluorescence τ_R is defined as

$$\tau_R = \frac{1}{k_f} \quad (4)$$

and it is therefore the time required for the intensity to fall to $\frac{1}{e}$ of its initial value.

The value of e is 2.718, hence $\frac{1}{e} = 0.3678$; consequently the mean lifetime is the time required for the emitted radiation to fall to 36.78% of its original intensity.

The value of the radiative lifetime is related to the actual lifetime, τ , in the following manner:

$$\frac{1}{\tau} = k_f + k_n + k_g + k_Q [Q] \quad (5)$$

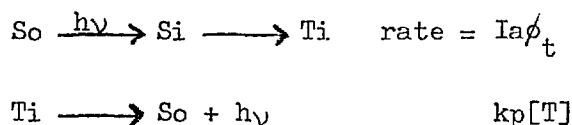
where k_f , k_n and k_g are the first order rate constants for the processes indicated in Figure 6.1. This equation applies for dilute solutions only where no quenching molecule has been added. Measurement of the fluorescence efficiency, ϕ_f , [37] [95-99] then provides sufficient data to calculate the radiative lifetime τ_R and k_f as:

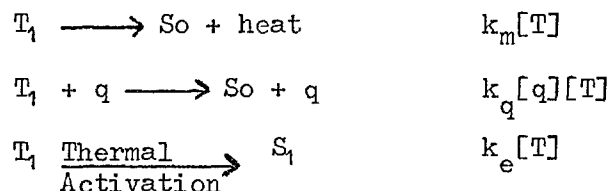
$$\phi_f = \frac{k_f}{k_f + k_n + k_g + k_Q[Q]} = k_f \tau = \frac{\tau}{\tau_R} \quad (6)$$

Therefore by measuring the value τ and ϕ_f using the spectrofluorimeter values of τ_R can be obtained. It should be pointed out that τ_R is the radiative lifetime, i.e. the lifetime which would be observed in the absence of all other processes by which the molecule will return to the ground state. The observed lifetime, τ , is nearly always less than the calculated value because of competing radiationless mechanisms.

Several other methods not involving the use of a spectrofluorimeter exist for calculating values of the radiative lifetime have been proposed by Bowen [2], Förster [100] and Birks [101]. These methods all rely on formulae derived to relate the radiative lifetime and the extinction coefficient.

The rate at which the triplet is produced and consumed for low light intensities can be shown by the following equations:





where q represents the concentration of all quenching species present, $k_q[q]$ a pseudo first order rate constant for all quenching processes, and $k_e[T]$ the rate of thermal activation from the triplet back to the excited singlet level.

For steady state conditions

$$I_a \phi_t = (k_p + k_m + k_q[q] + k_e)[T]$$

As the rate of phosphorescence emission is $k_p[T]$, the phosphorescence efficiency ϕ_p is:

$$\phi_p = \frac{k_p[T]}{I_a} = \frac{k_p \phi_t}{k_p + k_m + k_q[q] + k_e}$$

The radiative lifetime of the triplet τ_R can be related to k_p by the equation:

$$k_p = \frac{1}{\tau_R}$$

The actual lifetime of the triplet, τ , is given:

$$\frac{1}{\tau} = k_p + k_m + k_q[q] + k_e$$

and therefore

$$\frac{\phi_p}{\phi_t} = \frac{\tau}{\tau_R}$$

At low temperatures k_e is small, and diffusion is also minimised so that $k_q[q]$ will be negligible. Therefore in rigid 'glass' media at liquid nitrogen temperature:

$$\frac{\phi_p}{\phi_t} = \frac{k_p}{k_p + k_m}$$

τ_R or k_p are characteristic of the substance and as such are temperature independent. Determination of these values involves the measurement of ϕ_p , τ and ϕ_t the triplet formation efficiency, and it is the measurement of ϕ_t which is particularly difficult. The value of ϕ_t is directly dependant on the processes which the singlet state undergoes, and in the absence of singlet quenchers is given by:

$$\phi_t = \frac{k_g}{k_f + k_n + k_g}$$

To avoid the difficult determination of ϕ_t , it was assumed that because the first excited state possessed such a short lifetime internal conversion was negligible, i.e.

$$k_n = 0$$

$$\therefore \phi_t \sim \frac{k_g}{k_f k_g}$$

$$\phi_f \sim \frac{k_f}{k_f k_g}$$

$$\therefore \phi_t \sim (1 - \phi_f)$$

This equation may be more closely obeyed at low temperature where the rate of internal conversion of the singlet is expected to decrease.

Several workers have indicated that this assumption is correct [102] [103] and this has been further supported by work carried out by Parker and Hatchard with ethanolic solutions of eosin [10] over the temperature range of $+ 70^{\circ}$ to $- 196^{\circ}\text{C}$

INSTRUMENTATION

Three different pieces of apparatus were employed by the author for measuring the lifetimes of the systems studied. The order of magnitude of the lifetime governing the choice of experimental arrangement employed. For lifetimes in the region of 10^{-4} seconds to 10 seconds either an Aminco Bowman Spectrophotofluorometer with phosphoroscope attachment or a Garton Discharge Tube apparatus was used, and for lifetimes of 10^{-8} to 10^{-4} seconds duration the T.R.W. instrumental assembly was employed.

(a) The Aminco-Bowman Spectrophotofluorometer

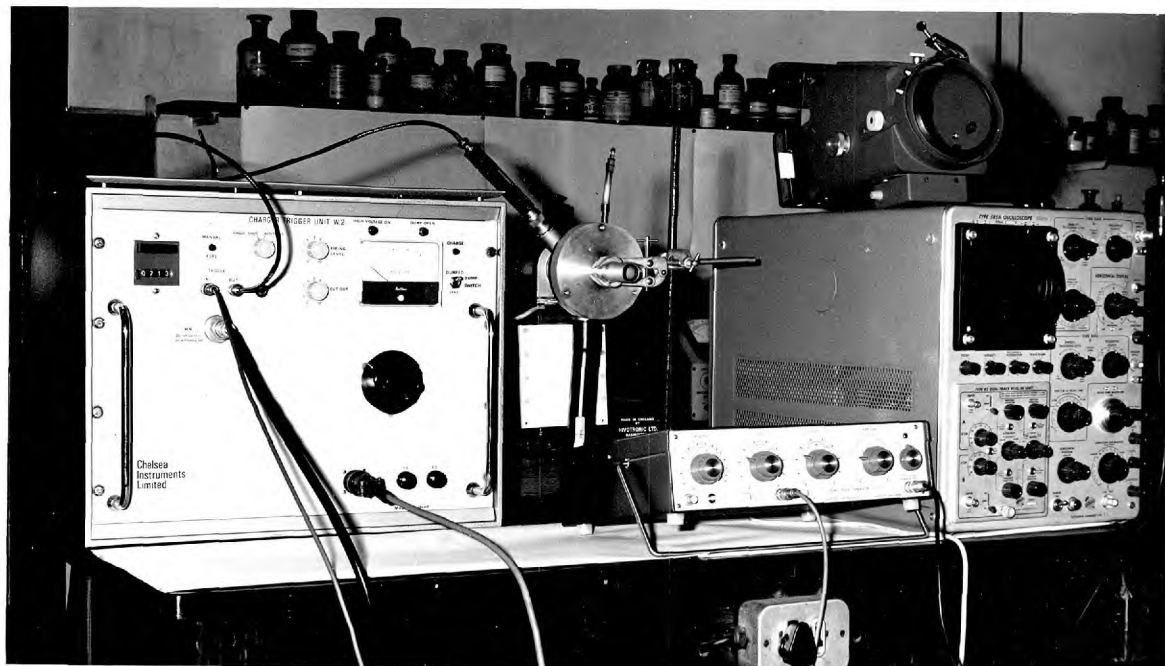
This was used in exactly the same manner as described previously for the determination of the lifetime of niobium oxinate. However, if the solution in question fluoresces only weakly then the voltage supply to the photomultiplier must be increased from 700 volts to 1000 volts D.C. This was achieved by using either a stabilised A.E.I. photomultiplier unit or eighteen B1702 Ever-Ready 60 volt batteries. The latter method

was the most successful as nearly all the background noise was effectively eliminated.

(b) Garton Discharge Tube

The flash tube was a development first described by Garton and co-workers in 1959 [104] [105], and though the instrument has been widely used for other pulse techniques [106] [107] it has not previously been applied to the field of molecular fluorimetry, and therefore a brief resumé of the problems incurred are thought to be of some value in this context.

A full illustration of the apparatus is shown in Figure 6.2. The tube was placed in the position that the Xenon arc normally occupies adjacent to the incident monochromator of the Aminco-Bowman optical unit. A standard IP21 or IP28 photomultiplier was employed to detect the signal. When the incident signal was monitored by placing both monochromators at exactly the same wavelength a distortion of the signal peak was observed. This was attributed to the high resistance of the dynode chain causing the interstage voltage to drop with a corresponding decrease in the photomultiplier tube gain when a high current signal flows. To overcome this undesirable effect the last three stages of the dynode were decoupled by adding 0.1 μF capacitors in parallel with the dynode chain



resistors, thereby maintaining the interstage voltage at a more reproducible value than before.

This procedure enable the source to be used satisfactorily, i.e. no distortion occurs when a large pulse is passed and a large amount of current is rapidly required. Attenuation of the light intensity was necessary only if a signal of > 0.4 volts was observed on the oscilloscope. In order to achieve this attenuation, either a weaker sample solution was used, or several pieces of frosted quartz were placed at the entrance slit of the incident monochromator of the Aminco optical unit.

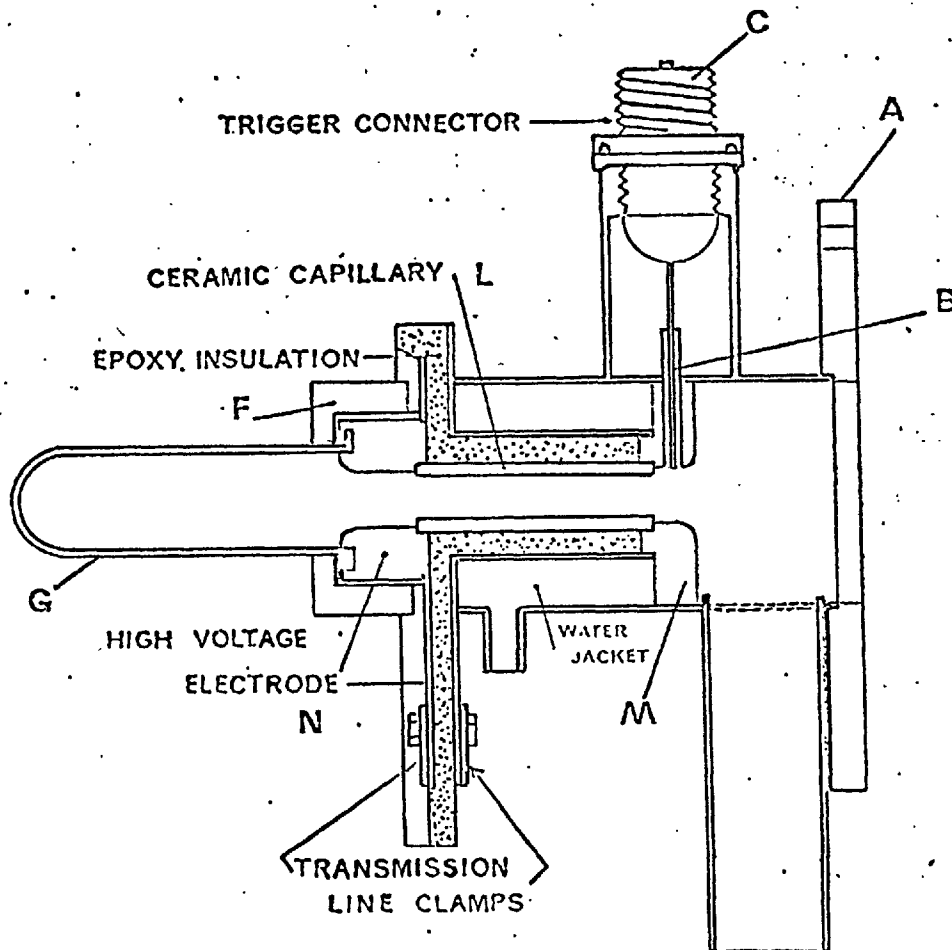
A terminal resistance of 1 megohm was incorporated in the oscilloscope and the capacitance of the cable from the photomultiplier anode was measured to be $0.0002 \mu\text{F}$. This gave a time constant of $2 \cdot 10^{-4}$ seconds. Time constant (seconds) = megohms x microfarads.

As the time constant of the measuring circuit is too large for measurement of lifetimes less than 10^{-3} seconds, and the fact that the cable capacitance could be only marginally decreased, the cable termination had to be decreased to 4.7 K ohms. This produced a circuit time constant of 10^{-6} seconds and though an overall decrease in sensitivity of 200 times was incurred, this was easily compensated for by the excess sensitivity available from the very high intensity of the source.

For measurement of long lifetimes extra capacitance was added in parallel with the input. This was necessary because of the discreet nature of the photomultiplier output. Care being taken at all times to ensure that the time constant was always less than one-tenth of the lifetime to be measured.

The Garton Discharge Tube, Figure 6.4, consists of two electrodes M and N connected via a strip transmission to the terminals of a 10 μ F, 10 K volt rapid discharge capacitor.

FIGURE 6.4.



During operation the tube was evacuated using a Genevac high vacuum rotary oil pump (Type NRD 1), together with a liquid nitrogen cold trap, to achieve a pressure of less than $2 \cdot 10^{-2}$ Torr. The tube was fired by applying a trigger pulse from a Marconi TF 2010 pulse generator, via a pulse transformer. A second output from the pulse generator simultaneously triggered the oscilloscope trace. This produces a local discharge at the ground electrode M that initiates a main discharge which occurs through the 1 cm. bore capillary L. This main discharge takes place between M and N and the wall material, which is used, is compressed by means of a magnetic pinch effect and thus raised to a high temperature radiating a strong and intense continuum.

The continuum extends throughout the visible and ultra violet region to less than $500\text{\AA}$, and the pulse itself has an approximate half width of 4μ sec. This enables determination of lifetimes longer than 40μ secs. The pulse intensity was found to be quite reproducible ($\pm 5\%$ at 7 kV).

Because of its very high intensity, the continuum nature of the spectra produced throughout the region of interest, and its rapid pulse, this instrument should prove a great asset to future workers studying molecular fluorimetry.

(c) T.R.W. Nanosecond Pulse Source

This instrument, Figure 6.3, has been the subject of previous work in the field of molecular fluorimetry [108] [109] [110] and the measurement of lifetimes in the region of 10^{-3} to 10^{-9} seconds. The author found several problems with the instrument, however;

1. The very low intensity of the available nitrogen and deuterium sources produced only small fluorescence signals which were difficult to monitor on the oscilloscope. This problem was aggravated when the time constant of the measuring circuit had to be reduced sufficiently to enable lifetimes in the region of 10^{-8} seconds to be measured.
2. The spectral distribution of the available lamp sources.
3. The electrical interference caused by the pulsed source seriously affected the performance of the photomultiplier tube, which had to be carefully screened.

The use of the source in connection with the Aminco-Bowman optical unit was not possible because the light losses incurred were too great to enable detection of a fluorescence signal. However a single monochromator on the emission side, together with an ordinary glass filter for the excitation side proved a limited success.

Several other methods for measuring fluorescence lifetimes have been employed. These involved the use of phase fluorimeters,

which incorporate a light beam modulated at high frequency to excite the fluorescence. The modulation is produced by application of the Kerr effect, or by use of an ultrasonic standing wave diffraction grating (formed in a liquid by means of a quartz crystal transducer) through which the steady beam of exciting light passes [111] [112] [113] [114]. A further method involving an air discharge tube driven by a high frequency oscillator has been described [115] and a hydrogen lamp fed from a suitably modulated current source has also been employed [116], [117]. Both these methods produce modulated light directly.

Pulse source equipment has also been fully described by several workers [118- 122] and this appears to provide the most satisfactory method for fluorescence lifetime measurement.

CHAPTER VII

Lifetime measurements of inorganic species in Hydrochloric acid media at Low temperature.

Evaluation of both the Garton Flash Tube and the T.R.W. instrument disclosed that the half width of the emission from the Garton Tube was 6μ seconds, and the pulses emitted by the T.R.W. equipment 15 nanoseconds half width if run at 2 KHz. (The pulse width varied slightly with the repetition rate, the slower the repetition rate the smaller the half width). The value of 15 nanoseconds is for the more commonly used nitrogen lamp, the deuterium lamp which was also available gave a 12 nanosecond pulse half width. All readings were made directly from the screen of a type 585A Tektronix oscilloscope which incorporated a type 82 dual trace plug in.

Determination of the lifetime of niobium oxinate in E.P.A. solvent at liquid nitrogen temperature using the Garton Tube was carried out in order to determine any malfunction of the instrument and its associated circuitry. A 0.1 ml. aliquot of $2 \cdot 10^{-4}$ M niobium solution was added to 6 ml. of pH 9.4 buffer solution (3 ml. of 4% citric acid solution and 3 ml. of M ammonia solution), in a 10 ml. volumetric flask. 2 ml. of a 1% 8-hydroxyquinoline solution in chloroform was added, and the whole made up to the mark with distilled water.

After thorough shaking for 2 minutes, 1 ml. of the chloroform phase was removed by means of a syringe, and diluted to 10 ml. using E.P.A. solvent. A small aliquot of this sample solution was cooled to -196°C and the quartz sample dewar then placed in the sample compartment of the Aminco optical unit in the normal fashion. The excitation monochromator was set at 398 nm and the emission monochromator at 580 nm. The Garton Tube was triggered at 7 kV. The IP21 photomultiplier was run at 800 V D.C. using the A.E.I. power pack.

The resulting trace was photographed using a Hewlett Packard (Model 196B) oscilloscope camera, and measurement from the photograph gave a lifetime of 6.4 m seconds. The lifetime obtained earlier using the Aminco instrument was 7.5 m seconds and though the two results do not exactly agree they are within the range of experimental error of $\pm 10\%$.

Determination of the lifetimes of quinine bisulphate in 0.1 N sulphuric acid and 9.10 diphenyl-anthracene in benzene gave values of 20.6 nanoseconds and 10 nanoseconds respectively. These values agree closely with previous investigations [56] [123]. Both results were obtained using the T.R.W. instrument. The traces in Figure 7.1 and Figure 7.2 show the rapid light pulse decay curves and the longer fluorescence decay curves for the quinine bisulphate and 9.10 diphenyl-anthracene sample solutions. Both signal leads to the Tektronix 585A oscilloscope were terminated in 50 ohms.

FIGURE 7.1 Quinine Bisulphate Decay Curve (Oscilloscope
time base 50 nanoseconds/cm.).

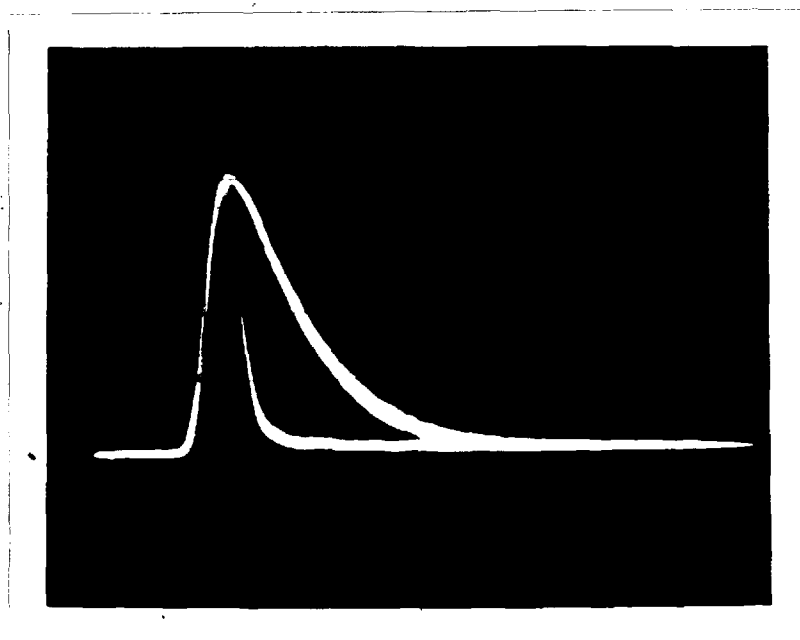
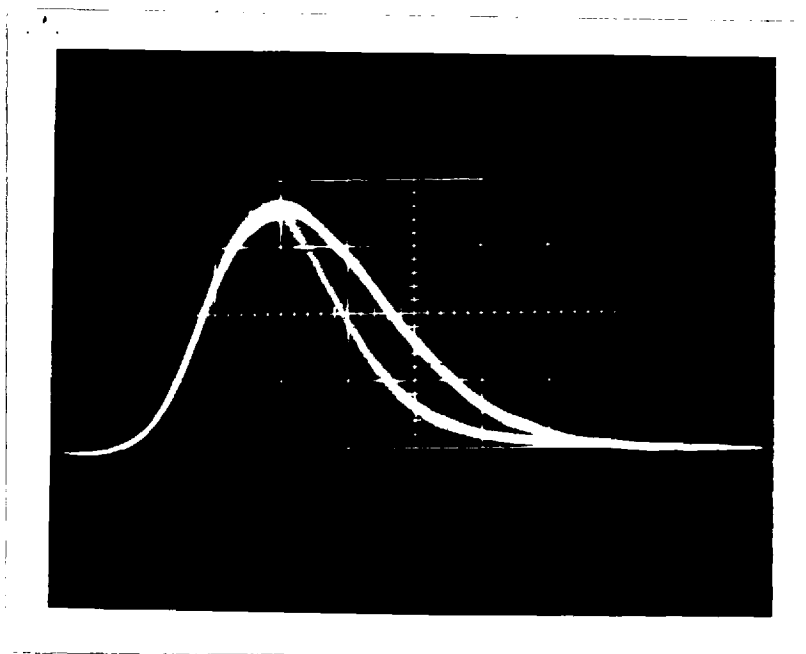


FIGURE 7.2 9.10 Diphenyl-anthracence Decay Curve (Oscilloscope
time base 10 nanoseconds/cm.).



From these results it was seen that all the equipment was functioning correctly and that the time constant of the two measuring circuits was sufficiently low.

In order that the time constant of the measuring circuit could be altered to suit any measurement a circuit was constructed containing resistors from 50 ohms to 470 K ohms, and capacitors from 100 pF to 1880 pF. Table 7.1 shows the time constant in m seconds of the measuring circuit incorporating these values.

TABLE 7.1

Resistance	Added Capacitance pF					Region of Measurement
ohms	0	100	470	880	1880	10xR.C. value
50	<u>0.002</u>	0.007	0.025	0.05	0.1	20-1000 n sec.
200	0.02	0.04	0.12	0.2	0.4	200-4000 n sec.
1 K	0.12	0.22	0.59	1.0	2.0	1 - 20 μ sec.
4.7 K	0.56	1.0	2.7	4.7	9.4	5 - 100 μ sec.
10 K	1.2	2.2	5.9	10	20	12 - 200 μ sec.
15 K	1.8	3.3	8.8	15	30	18 - 300 μ sec.
27 K	3.2	5.9	15	27	54	32 - 540 μ sec.
47 K	5.6	10	27	47	94	56 - 940 μ sec.
100 K	12	22	59	100	200	120-2000 μ sec.
270 K	32	59	150	270	540	.32 - 5.4 m sec.
470 K	56	100	270	470	940	.56 - 9.4 m sec.
1 Meg	120	220	590	1000	2000	1.20 - 20 m sec.

The capacitance of the cable from the photomultiplier, through the aluminium resistance and capacitance box to the oscilloscope was measured as 120 pf using a Marconi 0.1% Universal Bridge, Type TP 1313A. In order to decrease the line constant by a further factor so that lifetimes in the region of 20 n secs. could be measured the resistor box was replaced by a 50 ohm resistor soldered directly into the oscilloscope input; this reduced the value from 120 pf to 40 pf. (At a later stage 50 ohm Tektronix cable terminators were available and these were substituted for the soldered resistor). In all measurements made using either the Garton or T.R.W. apparatus, 50 ohm co-axial cable, terminated in 50 ohm B.N.C. connectors, was used.

In order to ascertain the mechanism of luminescence associated with the hydrobromic and hydrochloric acid matrices the lifetimes of several of the ions causing luminescence were measured in the following manner:

1. Antimony(III) in hydrobromic and hydrochloric acids
using the T.R.W. instrument.

	Hydrobromic Acid	Hydrochloric Acid
Lamp	N ₂	N ₂
Lamp Power	80%	80%
Repetition Rate	5 KHz	5 KHz

	Hydrobromic Acid	Hydrochloric Acid
Excitation Wavelength	360	306
Emission Wavelength	586	582
Monochromator Setting	0°	0°
Termination Resistor	1000 ohms	1000 ohms
External Photomultiplier Gain	< 3	< 2
Measured Lifetime	$3.1 \pm 0.3 \mu$ seconds	$2.0 \pm 0.2 \mu$ seconds

In both the above mentioned cases normal 2 inch x 2 inch glass filters were used to select the excitation and emission wavelengths. Spectral overlap of these two filters could not be tolerated as detection of scattered light directly from the source produced very distorted decay curves.

2. Arsenic(III) in hydrobromic acid using the T.R.W. instrument

	Hydrobromic Acid
Lamp	N ₂
Lamp Power	85%
Repetition Rate	5 KHz
Excitation Wavelength	356
Emission Wavelength	580

Hydrobromic Acid

Monochromator Setting	0°
Termination Resistor	1000 ohms
External Photomultiplier Gain	< 2
Measured Lifetime	$1.3 \pm 0.2 \mu \text{ secs.}$

Normal glass filters were again used to select the optimum wavelengths.

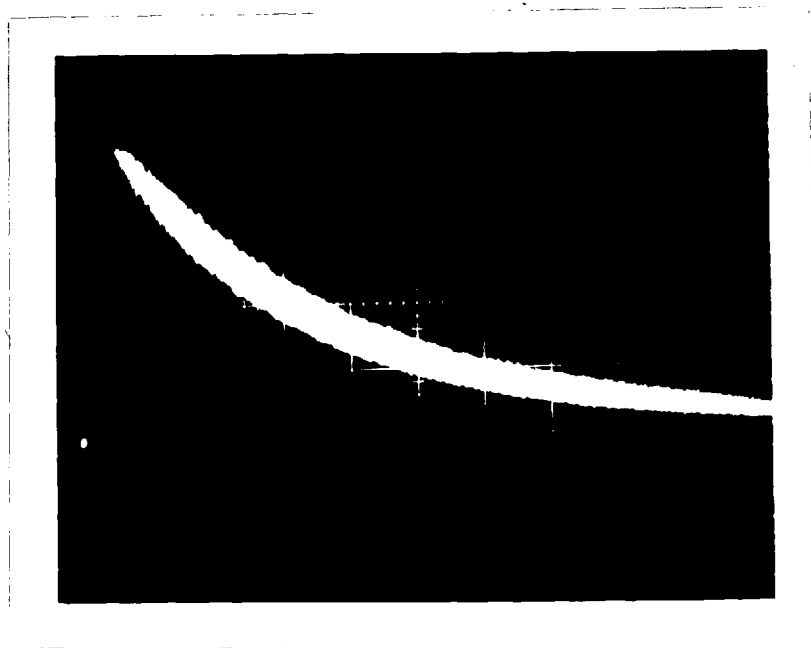
3. Bismuth(III) in hydrobromic and hydrochloric acids using the Garton Discharge Tube in conjunction with the T.R.W. optical unit.

Measurement using the T.R.W. instrument was prevented due to the long lifetime of bismuth in both matrices, and the Garton Tube was therefore used as the source, in conjunction with monochromators, sample compartment and photomultiplier tube and housing of the T.R.W. apparatus.

A normal glass filter was used as the excitation monochromator and an interference filter (450-470 nm) as the emission monochromator. A neutral density filter was placed between the excitation monochromator and Garton Tube to attenuate the incident light, and the lead connecting the photomultiplier and the oscilloscope was terminated with a 4.7 K ohm resistor.

Lifetimes of 0.85 ± 0.1 m seconds for bismuth in hydrobromic acid and 2.45 ± 0.3 m seconds for bismuth in hydrochloric acid were measured.

FIGURE 7.3 Bismuth in 6M Hydrochloric Acid Decay Curve
(Oscilloscope time base 1.0 m. seconds/Cm.).



The above results are quoted as an average of at least three measurements made using the geometrical centre of the decay curve. This method was used in all other cases where the decay curve had such a diffuse appearance as above.

4. Tellurium in hydrochloric acid using the T.R.W. instrument.

	Hydrochloric Acid
Lamp	N ₂
Lamp Power	65%
Repetition Rate	5 KHz
Excitation Wavelength	326
Emission Wavelength	550
Monochromator Setting	0°
Termination Resistor	4,700 ohms
External Photomultiplier Gain	< 2
Measured Lifetime	3.5 $\pm$ 0.4 μ seconds

Normal glass filters were again used in both monochromators

5. Tin(II) in hydrobromic acid using the T.R.W. instrument.

	Hydrobromic Acid
Lamp	N ₂
Lamp Power	70%
Repetition Rate	5 KHz
Excitation Wavelength	318
Emission Wavelength	550

	Hydrobromic Acid
Monochromator Setting	0°
Termination Resistor	2,700 ohms
External Photomultiplier Gain	< 2
Measured Lifetime	$2.1 \pm 0.2 \mu \text{ secs.}$

The same two glass filters as before were used in both the monochromators.

6. Uranium(VI) in hydrobromic and hydrochloric acids using the T.R.W. apparatus.

	Hydrobromic Acid	Hydrochloric Acid
Lamp	N ₂	N ₂
Lamp Power	70%	75%
Repetition Rate	.3 KHz	.3 KHz
Excitation Wavelength	325	302
Emission Wavelength	494	494
Monochromator Setting	10°	10°
Termination Resistor	.1 megohm	.1 megohm
External Photomultiplier Gain	< 2	< 2
Measured Lifetime	$0.28 \pm 0.03 \mu \text{ seconds}$	$0.48 \pm 0.05 \mu \text{ seconds}$

A glass filter was placed in the excitation monochromator and an interference filter (470-490 nm) inclined at 10° acted as the emission monochromator.

FIGURE 7.4 Uranium(VI) in 6M Hydrochloric Acid - Decay
Curve (Oscilloscope time base 0.2 m.sec./cm.).



For the above results 6 M acid solutions containing 10^{-2} M concentrations of the ions under consideration were used. Variation of both acid strength and element concentration appeared to make no measurable difference to the lifetime values. Each result quoted is the arithmetic mean of at least 3 measurements, and the value quoted is that calculated directly from the polaroid photograph. Measurement using the T.R.W. calculator was also made, but because the decay curve had first to be traced on the oscilloscope screen and then the standard wave superimposed on the trace before calculation could be carried out, the process appeared to be less accurate.

The lifetimes of the remaining elements which cause luminescence in the acid matrices could not be measured because no suitable glass and interference filters were available

Stoke's shift values obtained for those elements whose lifetime has been calculated are given in Table 7.1.

TABLE 7.1

	Hydrobromic Acid		Hydrochloric Acid	
	Lifetime	Stokes Shift (eV)	Lifetime	Stokes Shift (eV)
Sb(III)	3.1 μ sec.	1.33	2.0 μ sec.	1.92
As(III)	1.3 μ sec.	1.36	-	-
Bi(III)	0.85 m sec.	0.53	2.45 m sec.	0.74
Te(IV)	-	-	3.5 μ sec.	1.55
Sn(II)	2.1 μ sec.	1.70	-	-
U(VI)	0.28 m sec.	1.28	0.48 m sec.	1.4

No clear pattern may be observed from these results but two factors should be illustrated. Firstly that the luminescence of uranium, attributed to the uranyl ion [3] [125] [126] [127], cannot be compared with the measurements obtained for the other elements, and secondly the very long lifetime for bismuth in comparison with the remainder of the results.

A phosphorescence mechanism may be expected from those elements exhibiting long lifetimes and large Stoke's shifts values. However a solution of antimony(III) in hydrochloric acid which has a Stoke's shift of 1.92 eV still shows a relatively short lifetime of 2.0 μ seconds. The involvement of a normal phosphorescence mechanism does not therefore seem possible. It seems improbable that the bismuth solutions

which show the smallest Stoke's shift and longest lifetimes exhibit normal phosphorescence, though a delayed fluorescence mechanism appears possible if only these two factors are considered. The probability of E-type delayed fluorescence seems small because at the temperature of liquid nitrogen the energy available would be insufficient to promote the required transition from the triplet to the first excited singlet state. P-type delayed fluorescence though it has been reported several times at liquid nitrogen temperatures [128-131] is unlikely because of the very low mobility of the molecule at these low temperatures.

Proof of the presence of triplet state molecules were sought by placing very strong sample solutions, at liquid nitrogen vapour of -185°C , in the cavity of a Varian V 4500-15 At-X Band E.S.R. instrument while simultaneously focussing light from a mercury vapour discharge lamp onto the sample tube. Molar solutions of antimony(III), bismuth(III) and tellurium(IV) in hydrochloric acid, and cerium(III) in hydrobromic acid were investigated and though no triplet peak was obtained, the triplet concentration would have been extremely low and the absence of a peak would not necessarily prove the absence of the triplet state. To attempt any definite conclusions from this experiment therefore would be incorrect.

Interpretation of the results obtained to date appears somewhat complex as several conflicting pieces of evidence have been obtained concerning the luminescence mechanisms involved within the hydrobromic and hydrochloric acid media.

With several lifetime measurements within the region of 10^{-6} seconds which is midway between the those expected values for the two defined processes of fluorescence and phosphorescence no definite decision can be made on this basis alone. The fact that several ions do give rise to luminescence at room temperature under very similar conditions of ionic strength, e.g. cerium(III) in chloride, copper(I) in chloride, lead in chloride [75], thallium in bromide and chloride [77] [132], and tin in chloride [133], is a strong indication that a fluorescence mechanism predominates for these elements at this temperature (phosphorescence at room temperature is seldom observed [9]). As the spectral characteristics at low temperature are very similar, it seems probable that fluorescence is again the mechanism involved, though phosphorescence does appear possible for bismuth(III) which has a long lifetime. It is difficult to explain the relatively large values for the Stoke's shift, however, for the majority of the systems possessing short lifetimes.

A preliminary conclusion that a charge transfer mechanism is responsible for the fluorescence mechanism is suggested for the following reasons:

1. The shape of the emission spectra is of a characteristic width attributable to a charge transfer process [134], and no fine structure can be determined even at low temperatures.
2. All the elements giving rise to fluorescence possess readily attainable higher oxidation states, and the complexing atom involved is highly electronegative in character [134] [135].
3. The lifetime measurements are in the region expected for this type of mechanism.

In order to fully clarify the situation results for lifetimes of all the species in both bromide and chloride media at temperatures including and between those of liquid nitrogen and +25^o C are required. This was not possible, however, at the present time because of the shortage of suitable interference filters, and it is hoped that as soon as this apparatus is available clarification of the situation will be possible.

CHAPTER VIII

Suggestions for Future Work

All the work described in this thesis, with the exception of the niobium determination, deals with the luminescence characteristics of several inorganic species when present in strong acid solutions. This work plays only a small part in deciding on the mechanisms and reasons why the phenomena which have been observed actually take place, and much remains to be done before a satisfactory answer to these questions can be derived.

It is hoped that the lifetimes of those systems that were not measured can be readily obtained as soon as the appropriate apparatus is available.

Several ions have also been found to give rise to luminescence when added to strong solutions of fluoride, chloride, bromide and iodide salts which are then cooled to liquid nitrogen temperature in the normal fashion. The use of the salts of these acids means that the strong acid conditions previously required can now be dispensed with, and also fluoride and iodide systems, that were previously impracticable, can be readily studied. Measurement of luminescence lifetimes under these conditions can provide a useful indication as to the mechanisms involved.

The problem of the exact mechanisms involved therefore appears to be the biggest barrier at the present time, and once this has been solved it may be possible to predict future useful analytical methods using this information as a pointer.

Within the field of fluorimetry generally many areas remain relatively undeveloped. The requirements for many more reagents if the technique is to achieve wider applications is important, while an improvement of the commercial instrumentation is also needed; With the development of a good double beam instrument being the most important. A second important improvement that is also required in this field is an alteration of the sample system for low temperature measurements.

At the present time the narrow bore quartz tubes that are available with the Aminco Bowman instrument must be firmly fixed in order to overcome positional errors during measurement. This is not easily achieved with the liquid nitrogen bubbling around the base of the tube. The use of wider bore tubing, however, partially overcomes this effect but it is by no means a total answer to the problem.

The use of a narrow bore sample tube also means that it must be very carefully washed out between samples. Insufficient cleaning has been found on many occasions to be the cause of spurious results, on the other hand to avoid this error is a very time consuming occupation. If therefore a more practical

shaped sample container could be devised a great saving in time and an improvement in accuracy would definitely result.

REFERENCES

1. Bowen, E.J., Quarterly Reviews, 1947, 1, 1.
2. Bowen, E.J. and Wokes, F., Fluorescence of Solutions, Longmans, Green and Co. London, 1953.
3. Pringsheim, P., Fluorescence and Phosphorescence, Interscience, New York, 1949.
4. Bartholomew, R.J., Reviews of Pure and Applied Chemistry, 1958, 8, 265.
5. White, C.E. and Weisser, A., W. Maates, L. (ed), Handbook of Analytical Chemistry, McGraw Hill, 1964.
6. West, T.S., Laboratory Practice, 1965, 14, 922; 14, 1030.
7. Hercules, D.M. (ed), Fluorescence and Phosphorescence Analysis, Interscience Publishers Inc., New York, 1966, 41.
8. Parker, C.A., Photoluminescence of Solutions, Elsevier Publishing Company, London, 1968.
9. Parker, C.A., Hatchard, C.G., J. Phys. Chem., 1962, 66, 2506.
10. Parker, C.A., Hatchard, C.G., Trans. Faraday Soc., 1961, 57, 1894.
11. Parker, C.A., Hatchard, C.G., Trans. Faraday Soc., 1963, 59, 284.
12. Stevens, B., Walker, M.S., and Hutton, E., Proc. Chem. Soc., 1963, 62.
13. Parker, C.A., Hatchard, C.G., Trans. Faraday Soc., 1963, 284.

14. Parker, C.A., *Analyst*, 1969, 84, 446.
15. Weber, G., Teale, F.W.J., *Trans. Faraday Soc.*, 1957, 53, 646.
16. Bowen, E.J., West, K.J., *Chem. Soc.*, 1955, 4394.
17. Bowen, E.J., Sahu, J., *J. Phys. Chem.*, 1959, 63, 4.
18. McCarthy, W.J., Dunlap, K.L., *Talanta*, 1970, 17, 305.
19. Kasha, M., *J. Phys. Chem.*, 1952, 20, 71.
20. McGlynn, S.P., Reynolds, M.J., Daigre G.W., and Christodouleas, N.D., *J. Phys. Chem.*, 1962, 66, 2499.
21. Van Dauren, B.L., *Chem. Rev.*, 1963, 63, 325.
22. Bowen, E.J., Seaman, D., in Kallman, H. and Spruch, G.M., (eds.), *Luminescence of Organic and Inorganic Materials*, John Wiley and Sons, Inc., New York, 1962.
23. Spiro T.G., *Inorg. Chem.*, 1965, 4, 73.
24. Allison, J.B., Becker, R.S., *J. Chem. Phys.*, 1960, 32, 1410.
25. Leonhardt, H., Weller, A., *Z. Physik. Chem.*, 1961, 29, 277.
26. Perrin, J., in 2eme. Conseil de Chimie Solvay, Brussels, 1924, Gauthier-Villars, Paris, 1925.
27. Perrin, J. *Compt. Rend.*, 1927, 184, 1097.
28. Förster, Th., *Ann Physik*, Series 6, 1948, 2, 55.
29. Förster, Th., *Discussions Faraday Soc.*, 1959, 27, 7.
30. Terenin, A., Ermolaev, V., *Trans. Faraday Soc.*, 1956, 52, 1042.

31. Porter, G., Wilkinson, F., Proc. Roy. Soc. (London) A, 1961, 264, 1.
32. Sandros, K., Backstrom, H.L.J., Acta Chem. Scand., 1962, 16, 958.
33. Parker, C.A., Hatchard, C.G., Joyce, T.A., Nature, 1965, 205, 1282.
34. Parker, C.A., Hatchard, C.G., Proc. Roy. Soc. (London) A, 1962, 269, 574.
35. Parker, C.A., Hatchard, C.G., Proc. Chem. Soc., 1962, 147.
36. Parker, C.A., Rees, W.T., Analyst, 1962, 87, 83.
37. Parker, C.A., Rees, W.T., Analyst, 1960, 85, 587.
38. Chen, R.F., Analyst. Biochem., 1967, 20, 339.
39. White, C., Ho, M., Weimer, E., Anal. Chem., 1960, 32, 438.
40. Drushel, H., Sommers, A., Cox, R., Anal. Chem., 1964, 35, 2166.
41. Argauer, R., White, C., Anal. Chem., 1964, 35, 368.
42. Melhuish, W.H., J. Opt. Soc. Am., 1962, 52, 1256.
43. American Instrument Co., Inc., Aminco-Bowman Spectrophotofluorometer, Bulletin 1968, 2392-F, 14.
44. Melhuish, W.J., J. Phys. Chem., 1960, 64, 762.
45. Melhuish, W.J., J. Phys. Chem., 1961, 65, 229.
46. Lott, P.F., J. Chem. Education, 1964, 41, A327.
47. Cheng, K.L., in Trace Analysis: Physical Methods, Morrison G.H. (ed.), Interscience Publishers, New York, 1965, 161.

48. Slavin, W., Mooney, R.W., Palumbo, D.T., J. Opt. Soc. Am., 1961, 51, 93.
49. Turner, G.K., Science (No. 3641), 1964, 146, 183.
50. Kasha, M., in McElroy, W.D., Glass, B., (eds.), Light and Life, John Hopkins Press, 1961.
51. Sidman, J., Chem. Rev., 1958, 58, 689.
52. Collat, J.W., Rogers, L.B., Anal. Chem., 1956, 27, 961.
53. West, T.S., in Meinke, W.W., Scribner, B.F., Trace Characterisation, Chemical and Physical, Monograph 100, Nat. Bureau of Standards, Washington, 1968.
54. White, C.E., Anal. Chem., 1949, 21, 104; 1950, 22, 69; 1952, 24, 85; 1954, 26, 129; 1956, 28, 621; 1958, 30, 729; 1960, 32, 47R.
55. White, C.E., Weissler, A., Anal. Chem., 1962, 34, 81R; 1964, 36, 116R; 1966, 38, 155R; 1968, 40, 116R; 1970, 42, 57R.
56. Berlman, I.B., Handbook of Fluorescent Spectra of Aromatic Molecules, Academic Press, New York, 1965.
57. Passwater, R.A., Guide to the Fluorescence Literature, Plenum Press, New York, 1967.
58. Becker, R.S., Theory and Interpretation of Fluorescence and Phosphorescence, Wiley Interscience, New York, 1969.
59. Konstantinova-Schlezing, M.A., (ed.), Fluorimetric Analysis, Israel Program for Scientific Translation, Jerusalem, 1965 (From Russian).

60. Nielsch, W., Bolz, G., Z. Anal. Chem., 1954, 143(2), 81.
Anal. Abstr. 1955, 601.
61. Jean, M., Anal. Chim. Acta, 1952, 7, 462.
62. Kristaleva, L.B., Zavodsk Lab., 1969, 25, 1294, Anal.
Abstr., 1960, 3201.
63. Webster, S.H., Fairhall, L.T., J. Ind. Hygiene and
Toxicol., 1945, 27, 184.
64. MacNulty, B.J., Woolard, L.D., Anal. Chim. Acta, 1955,
13, 64.
65. Christopher, D.H., West, T.S., Talanta, 1966, 13, 507.
66. Nielsch, W., Bolz, G., Mikrochim. Acta, 1954, 313:
Anal. Abstr. 1954, 2389.
67. Cherkesov, A.I., Busev, A.I., Zh. Analit. Khim., 1957,
12, 268; Anal. Abstr., 1958, 457.
68. Blumental, H., Z. Anal. Chem., 1928, 74, 33.
69. Kirkbright, G.F., Saw, C.G., West, T.S., Talanta, 1969,
16, 65.
70. Kirkbright, G.F., Saw, C.G., West, T.S., Analyst, 1969,
94, 538.
71. Kirkbright, G.F. Saw, C.G., West, T.S., Analyst, 1969,
94, 457.
72. Marczenk, Z., Chem. Anal., Warsaw, 1963, 8(6), 849.
73. Kemula, W., Glodowski, S., Chem. Anal. Warsaw, 1963,
8(3), 369.

74. Bozhevolnov, E.A., Solovev, E.A., *Zh. Analit. Khim.*, 1965, 20, (12), 369.
75. Kirkbright, G.F., Saw, C.G., West, T.S., *Talanta*, 1968, 15, 570.
76. Bozhevolnov, E.A., Solovev, E.A., *Zavodsk. Lab.* 1964, 30 (4) 412.
77. Kirkbright, G.F., West, T.S., Woodward, C., *Talanta*, 1965, 12, 517.
78. Lewis, G.N., Lipkin, D., *J. Am. Chem. Soc.*, 1942, 64, 2801.
79. McClain, W.M., Albrecht, A.C., *J. Chem. Phys.*, 1965, 43, 645.
80. Lim, E.C., Lazzara, C.P., Yang, M.Y., Swenson, G.W., *J. Chem. Phys.*, 1965, 43, 970.
81. Brocklehurst, B., Gibbons, W.A., Lang, F.T., Porter, G., Savadatti, M.I., *Trans. Faraday Soc.*, 1966, 62, 1793.
82. Price, G.R., *Anal. Chem.*, 1953, 25, 322.
83. Wright, J.R., *Analyst* 1966, 91, 87.
84. Ramakrishna, T.V., Rahim, S.A., West, T.S., *Talanta*, 1969, 16, 847.
85. Belcher, R., Ramakrishna, T.V., West, T.S., *Talanta*, 1965, 12, 681.
86. Williams, A.I. *Analyst*, 1967, 92, 43.
87. Wood, E.F., Jones, J.T., *Analyst*, 1968, 93, 131.
88. Pakalns, P., Wanfy, A.B., *Anal. Chim. Acta*, 1968, 41, 139.

89. Pakalns, P., Anal. Chim. Acta, 1968, 41, 283.
90. Belcher, R. , Ramakrishna, T.V., West, T.S., Talanta, 1962, 9, 943; 1963, 10, 1013.
91. Elinson, S.V., Pobedina, L.I., Rezova, A.T., Zh.Analit. Khim., 1965, 20, 676.
92. Klimov, V.V., Didkovskaya, O.S., Tr, Vses. Nauchn. Issled. Inst. Khim. Reaktivov, (1963), 25, 195.
93. Kassner, J.L., Garcia-Porrata, A., Grove, E.L., Anal. Chem. 1955, 27, 492.
94. Motojima, K., Hashitani, H., Anal. Chem., 1961, 33, 48.
95. Bowen, E.J., Sawtell, J.W., Trans. Faraday Soc., 1937, 33, 1425.
96. Forster, L.S., Livingston, R., J. Chem. Phys., 1952, 20, 1315.
97. Gilmore, E.H., Gibson, G.E., McClure, D.S., J. Chem. Phys., 1952, 20, 829.
98. Weber, G., Teale, F.W.J., Trans. Faraday Soc. 1951, 53, 646.
99. Parker, C.A., Hatchard, Analyst, 1962, 87, 664.
100. Forster, Th., Fluoreszenz Organischer Verbindungen, Vandenhoecik and Rupprecht, Gottingen, 1951.
101. Birks, J.B., Dyson, D.J., Proc. Roy. Soc. (London) A, 1963, 275, 135.
102. Medinger, T., Wilkinson, F. Trans. Farady Soc. 1965, 61, 520.

103. Parker, C.A., Joyce, T.A., Trans Faraday Soc., 1966, 62, 2785.
104. Garton, W.R.S., J. Sci. Instrum., 1959, 36, 11.
105. Garton, W.R.S., Celnick, I.W., Hessberg, H. Weaton, J.E.G., Upsala 1959, Published 1960 North Holland, 518.
106. Parkinson, w.h., Reeves, E.M. Proc. Phys. Soc.,A 1961, 262, 409.
107. Wheaton, J.E.G., Applied Optics, 1964, 3, 11, 1297.
108. Pollack, S.A., Applied Optics, 1966, 5, 11, 1749.
109. Chen, R.F., Vurek, S., Alexander, P.L., Science, 1967.
110. Meserve, E.T., TR.W. Application Note 6, 1968.
111. Bailey, E., Rollefson, G., J. Chem. Phys., 1953, 21, 1315.
112. Venetta, B.D., Rev. Sci. Instr., 1959, 30, 450.
113. Scharmann, A., Z. Naturforsch, 1956, 11A, 398.
114. Schmillen, A., Z. Physik, 1953, 135, 294.
115. Birks, J.B., Little, W.A., Proc. Phys. Soc. (London)A, 1953, 66, 921.
116. Birks, J.B., Dyson, D.J., J. Sci. Instr., 1961, 38, 282.
117. Malmberg, J.H., Rev. Sci. Instr., 1957, 28, 1027.
118. Brody, S.S., Rev. Sci. Instr., 1957, 28, 1020.
119. Birks, J.B., King, T.A., Munro, I.M., Proc. Phys. Soc. (London), 1962, 80, 355.
120. Hendee, C.F., Brown, W.B., Philips Tech. Rev., 1957, 19, 50.
121. Bennett, R.G., Rev. Sci. Instr., 1960, 31, 1275.

- 122. Mataga, N., Tomura, M., Nishimura, H., Mol. Phys. 1965, 9, 367.
- 123. Ware, W., Baldwin, B., J. Chem. Phys., 1964, 40, 1703.
- 124. Muel, B., Compt. Rend., 1962, 255, 3149.
- 125. Pant, D.D., Pant, C., J. Ind. Chem. Soc., 1966, 6, 1409.
- 126. Gobrecht, H., Hahn, D., Gretzinger, B., Z. Phys. 1954, 139, 309.
- 127. Nichols, E.L., Howes, H.L., Fluorescence of the Uranyl Salts, Carnegie Institute, Washington, 1919, 298.
- 128. Dupuy, F., Thesis, University of Bordeaux, 1964.
- 129. Azumi, T., McGlynn, S.P., J. Chem. Phys., 1963, 39, 3533.
- 130. Smith, F.J., McGlynn, S.P., J. Chem. Phys., 1965, 42, 4308.
- 131. Parker, C.A., Trans Faraday Soc., 1964, 60, 1998.
- 132. Curtice, R.E., Scott, A.B., Inorganic Chemistry, 1964, 3, 10, 1383.
- 133. Woodward, C., Ph.D. Thesis, Imperial College, University of London, 1966.
- 134. Paris, J.P., Brandt, W.W., J. Am. Chem. Soc., 1959, 81 5001.
- 135. Paris, J.P., Ph.D. Thesis, University of Purdue, 1960.
- 136. Gentry, C.H.R., Sherrington L.G., Analyst, 1950, 75, 71.
- 137. McKaveney, D., Ph.d. Thesis, University of Pittsburg, 1957,