AN INVESTIGATION OF SOME REACTIONS APPLICABLE TO INORGANIC SPECTROFLUORIMETRIC ANALYSIS

by

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ABSTRACT

Several reactions involving purely inorganic species have been investigated in connection with their applicability to inorganic spectrofluorimetric analysis. The violet fluorescence of lead in hydrochloric acid-potassium chloride medium has been employed for the determination of 10-60 μg of lead. The sensitivity of the procedure compares favourably with those of spectrophotometric methods. Interference from some ions is eliminated by the use of masking agents.

The fluorescence characteristics of some inorganic complexes in hydrochloric and hydrobromic acids at liquid nitrogen temperature (-196°C) have been investigated. Several of these complexes which are not fluorescent at room temperature exhibit intense fluorescence emission at low temperature, while those which fluoresce at room temperature show much increased intensity of fluorescence at -196°C. Because of the small sample volume (0.5 ml) required for quantitative measurements in the spectrofluorimeter, very sensitive absolute detection limits have been obtained for many elements in both acid media.

The determination of tellurium by utilisation of the red fluorescence of the tellurium (IV) chloro-complex in hydrochloric acid at -196°C is described. The method is simple, sensitive and highly selective and illustrates the analytical application of inorganic spectrofluorimetry at low temperature. The

procedure has also been applied to the determination of traces of tellurium in lead samples.

The low temperature fluorescence of inorganic complexes in sulphuric, phosphoric and perchloric acid glasses have also been studied. Except for cerium (III) and uranium (VI), no fluorescence emission has been observed from other elements selected for the investigation in any of these three acids.

In the final chapter, the results of experiments conducted to compare intensities of several spectral sources are discussed, and some initial results for the determination of traces of other cations by low temperature spectrofluorimetry are described.

ACKNOWLEDGEMENTS

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CONTENTS

INTRODUCTION

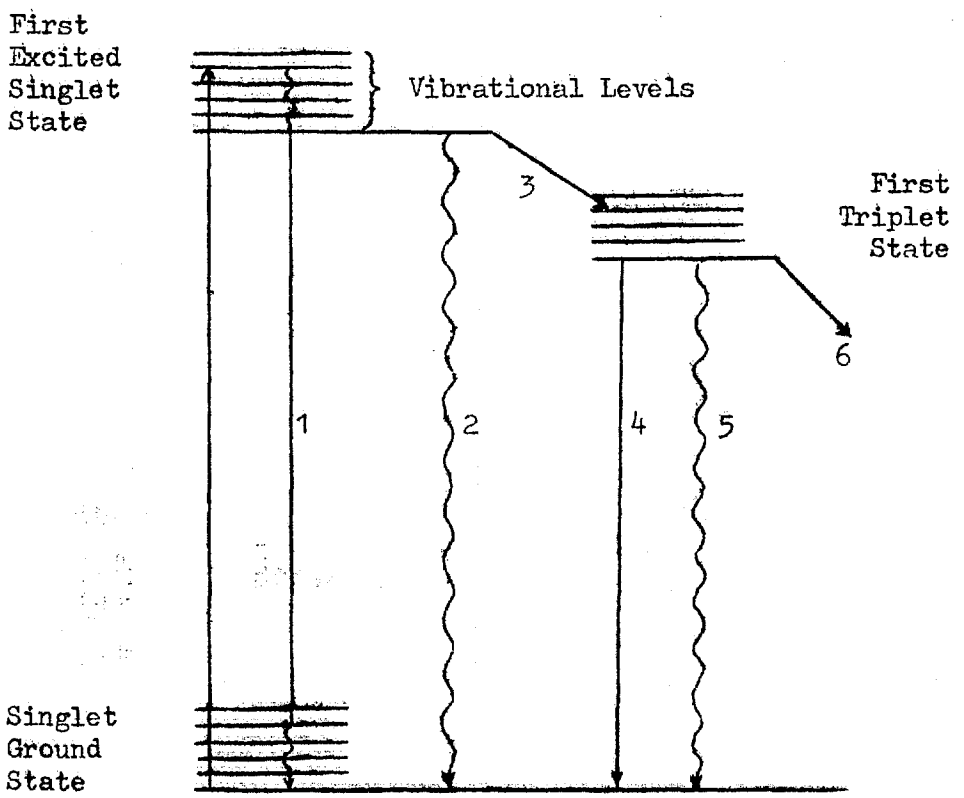
When a beam of light passes through a material, part of the light will be absorbed, part will be reflected, part will be transmitted and a part will be scattered in various ways. Absorption takes place in discrete units or quanta, the energies of which are equal to the product hv, where v is the frequency of the light and h is Planck's constant. The subsequent re-emission of the absorbed light, usually as quanta of lower energy, constitutes the phenomenon of luminescence. Luminescence which may be in the ultra-violet or visible region of the electromagnetic spectrum is shown by solids, liquids or gases and may be classified as fluorescence or phosphorescence. The essential difference between these two forms of luminescence is in the duration of the emission after the source of excitation is removed. Fluorescence decays almost instantaneously, i.e. usually within about 10^{-8} second, whereas phosphorescence may have a lifetime from 10^{-4} second up to tens of seconds.

Solution spectrofluorimetry is gradually becoming recognised as a useful technique of analysis in view of the remarkable analytical sensitivity and versatility which it can offer. Instrumental developments in the measurement of fluorescence since 1935 have extended the application of this technique to trace analysis. Its role in inorganic analysis has been greatly enhanced by the use of reactions yielding fluorescent products.

The theoretical and instrumental aspects of the technique of

spectrofluorimetric analysis have been well described by Bowen[1], Pringsheim[2], Bartholomew[3], Parker and Rees[4], West[5], Hercules[6] and Guilbault[7]. The application of the technique to the determination of trace metals has been reviewed in books by Radley and Grant[8], Schlezinger-Konstantinova[9], Bozhevol'nov[10] and White[11] in addition to the comprehensive surveys of White[12] in the Analytical Chemistry biennial reviews.

Figure 1



THEORY

The process of absorption and subsequent re-emission of radiant

energy is best described by reference to Figure 1 which shows an energy level diagram representing the electronic states of a light absorbing polyatomic molecule. Each of the electronic states has a number of vibrational sub-levels associated with it, and because of this, the energy of excitation does not correspond to a discrete wavelength, but to a range of wavelengths. Hence the absorption (and fluorescence) spectrum occurs as a band and not a sharp line.

When a molecule absorbs light it undergoes a transition from a vibrational level of the ground electronic state to some vibrational level of one of the upper electronically excited states. These energy states are designated singlet or triplet depending on whether the electron pairs have anti-parallel or parallel spins respectively. Within 10^{-12} sec, the excited molecule returns to the lowest vibrational level of the first excited singlet state by non-radiative transfer of the excess energy. This may be accomplished by collisional transfer to other molecules or by transfer to other vibrational and rotational modes of the molecule. The lifetime of this state is 10^{-9} to 10^{-7} sec, and the return of the molecule to the ground state with accompanying dissipation of energy can be achieved in several ways:-

1) Fluorescence - The molecule emits a photon corresponding to the energy difference between the lowest vibrational level of the first excited singlet state and any vibrational level of the

electronic ground state. The fluorescence decay time is effectively equal to the lifetime of the first excited singlet state.

2) Internal Conversion - With many molecules which do not possess rigid structures, the excess energy is largely spent by transfer into increased vibrational energy and thermal activity of the molecules which result in non-radiative intermolecular collisions.

3) Intersystem Crossing - Although population of triplet states by direct absorption from the ground state is insignificant, a very efficient process exists for the "forbidden" transition of the molecule from the first excited singlet state to a triplet state. A singlet-triplet transition is approximately 10^5 times less probable than a singlet-singlet transition. As radiationless vibrational processes (such as internal conversion) can occur in approximately 10^{-13} sec, the time required for a vibrational coupling of the excited singlet and triplet states would be approximately $10^{-13} \times 10^5$ i.e. 10^{-8} sec, which is the same order of magnitude as the lifetime of an excited singlet state. Hence, intersystem crossing can compete with fluorescence emission from the lowest vibrational level of the first excited singlet state.

4) Phosphorescence - If intersystem crossing occurs, then a radiative transition between the lowest triplet state (whose lifetime is ca. 10^{-4} to 10s) and the ground state may be observed, and this emission is called phosphorescence.

If all of the molecules excited by absorption of light return to the ground state with the emission of fluorescence, then the quantum efficiency of fluorescence, which is defined as the fraction of excited molecules that will fluoresce, is one. Because of factors discussed above, this does not happen in normal practice and for practically all molecules the quantum efficiency is less than one. By definition, the intensity of fluorescence equals the intensity of light absorbed (in quanta per unit time) multiplied by the quantum efficiency of the system, i.e.:-

$$F = I_o(1-10^{-\epsilon cl}) \cdot \phi$$

where F = total fluorescence intensity (in quanta per unit time)

I_o = intensity of exciting light (in quanta per unit time)

ϵ = molar absorptivity of the fluorescing solute

c = molar concentration of the solute

l = path-length of solution (in cm)

and ϕ = quantum efficiency of fluorescence

For a very dilute solution in which only a small fraction of the incident light is absorbed, the fluorescence equation simplifies to:-

$$F = I_o(2.3\epsilon cl)\,\phi$$

Thus it is seen that the fluorescence intensity is directly proportional to the intensity of the exciting light and the concentration of the solute. The linear equation serves to illustrate the basic difference between absorption spectrophotometry and

spectrofluorimetry. In the former, the basic equation is

$$A(\text{absorbance}) = \text{Log } \frac{I_o}{I_t}$$

where I_t = intensity of transmitted light

Any increase in I_o will produce a corresponding increase in I_t with no net gain in the analytical signal A. With fluorescence, however, any increase in I_o will produce a corresponding increase in the fluorescence signal F. Hence, the analytical sensitivity of spectrofluorimetry is inherently greater than that of absorption spectrophotometry.

As an analytical tool solution spectrofluorimetry is governed by two factors which limit the sensitivity of any fluorimetric method:

(a) With instruments which are not fitted with a blank "backing-off" device, the limit of determination is set by the value of the blank fluorescence. This may be due to the fluorescence of the reagent or impurities in the reagent used under the conditions of the determination, or it may arise from first and second order scattering of the exciting light and Raman scattering by the solvent[13]. The blank fluorescence due to impurities in the reagent may often be reduced or eliminated by purification but that due to Raman scattering by the solvent cannot be overcome in this way.

(b) With instruments which are fitted with a blank "backing-off" device the limit is set by the thermal noise of the photomultiplier

and circuit.

Apart from these two factors, other phenomena exist which have a deleterious effect on the efficiency of fluorescence of molecular species. Such phenomena which reduce the fluorescence may be classified as quenching effects i.e. those which reduce the quantum efficiency itself, or as inner-filter effects, i.e. those in which interference results mechanically from absorption of the incident or emitted radiation by a foreign species without having any effect on the value of ϕ, the quantum efficiency. Quenching processes may be due to several causes:-

(a) Intermolecular Collision and Temperature Effect

Collisional deactivation of excited state molecules with others, particularly the solvent molecules, results in a decrease or elimination of fluorescence. An increase in temperature produces an increase in collisional frequency which causes a marked decrease in the fluorescence. Generally, negative temperature coefficients of 1-2 percent per degree centigrade at room temperatures are very common. The use of low temperature will decrease inter-molecular collisions and result in increased sensitivities in fluorimetric measurements. Ohnesorge and Rodgers[14] have shown that several oxinate complexes are more intensely fluorescent at low temperature than at room temperature. Up to recent times, low temperature fluorimetry has found very few inorganic, analytical applications although the technique of phosphorimetry has been extensively employed in

analysis of organic compounds in various media. Probably the main reason may be attributed to the difficulty of finding suitable inorganic solvents that will form rigid, clear glasses at low temperature. Much of the author's work has been devoted to the study of some inorganic solvents suitable for use at liquid nitrogen temperature.

(b) Viscosity of medium

Quenching efficiency is decreased by an increase of the viscosity of the medium since the frequency of inter-molecular collisions is decreased.

(c) Effect of metal ions and ionic strength

Dissolved cations affect the fluorescence emission particularly when they complex the ground state of the organic solute. Frequently, heavy metal ions will quench fluorescence of organic molecules. The largest effects are often noted for paramagnetic transition-metal ions, suggesting that the paramagnetic species increases the rate constants for intersystem crossing in the organic molecule.

Fluorescence may also be influenced by variations of the ionic strength of the medium when the fluorescent species or the quenching agent or both exist as charged species. The ionic strength affects the activity of the ions whilst it may not affect their analytical concentration.

(d) Effect of dissolved oxygen

One problem of fluorimetry is the ability of molecular oxygen

to quench excited singlet states of many molecules, especially aromatic hydrocarbons, in solution. In some cases, oxygen "quenching" results from oxidation of the solute. Whereas oxygen quenching is pronounced in many organic systems, it does not appear to have effect on many inorganic-organic chelate systems. Although many mechanisms have been proposed to account for the efficiency of oxygen as a quencher of fluorescence, the one which is frequently invoked is concerned with the fact that the ground-state oxygen molecule is a triplet and therefore paramagnetic[15]. The formation of its singlet excited level requires relatively low energy. Quenching may, therefore, occur by long range dipole-dipole transfer of a singlet excited molecule with the triplet ground state oxygen molecule producing a singlet excited oxygen molecule and a triplet state form of the other.

(e) Excimer Formation

As the concentration of a fluorescent solute is increased, a decrease in fluorescence yield is frequently observed and this phenomenon is termed self-quenching. In many cases, this results from the formation of "excimers". An "excimer" is a dimer formed by reaction of a ground-state solute molecule with another in its lowest excited singlet state. Excimer formation may be minimised by increasing the viscosity of the medium.

Non-quenching processes also exist which may reduce fluorescence

without acting upon the quantum efficiency, ϕ, in any way. The most common of these processes is the inner-filter effect. This arises when a substance in the solution absorbs light at the wavelength of excitation or emission of the fluorescent solute when a reduction in the intensity of fluorescence will result. A "saturation inner-filter effect" may occur when there is a high concentration of fluorescent solute in solution. In such systems, the fluorescence signal varies with distance from the front face of the cuvette.

Progress in the application of the technique of solution spectrofluorimetry to inorganic analysis at the trace level has been reviewed periodically by White and Weissler[12]. Very few applications involve purely inorganic fluorescent systems. Of these may be mentioned the Ce/As redox system[16,17] where measurement of the fluorescence of Ce(III) formed on reduction of Ce(IV), has been shown to provide a method for the determination of arsenic. The fluorescence of thallium(I)[18] and lead[19] in the presence of chloride ions have also found analytical applications. Most fluorescence reactions, however, involve the formation of a metal chelate compound. Just as in absorption spectrophotometry where there are two possible routes (1) the production of colour, or (2) the diminution of pre-existing colour, so two analogous routes are open in spectrofluorimetry. A great many fluorescent reagents may have their fluorescence "quenched" by reacting them

with metal ions, e.g. Calcein[20] or Calcein Blue[21] by ions such as copper (II). A number of procedures are available where reaction of a metal ion with a non-fluorescent organic reagent produces a positive fluorescence e.g. gallium with Rhodamine B[22]. Lastly, a metal ion may react with a fluorescent reagent to produce a complex which fluoresces at a different wavelength e.g. aluminium or beryllium with 2-hydroxy-3-naphthoic acid[23].

A brief mention should be made of intramolecular energy systems which have been employed, particularly in the analysis of the rare earth elements. In these systems, the chelate absorbs energy characteristic of the ligand species, but re-emits energy which is characteristic of the metal. The chelates of many of the rare earths e.g. europium with benzoylacetone[24] are examples of such systems.

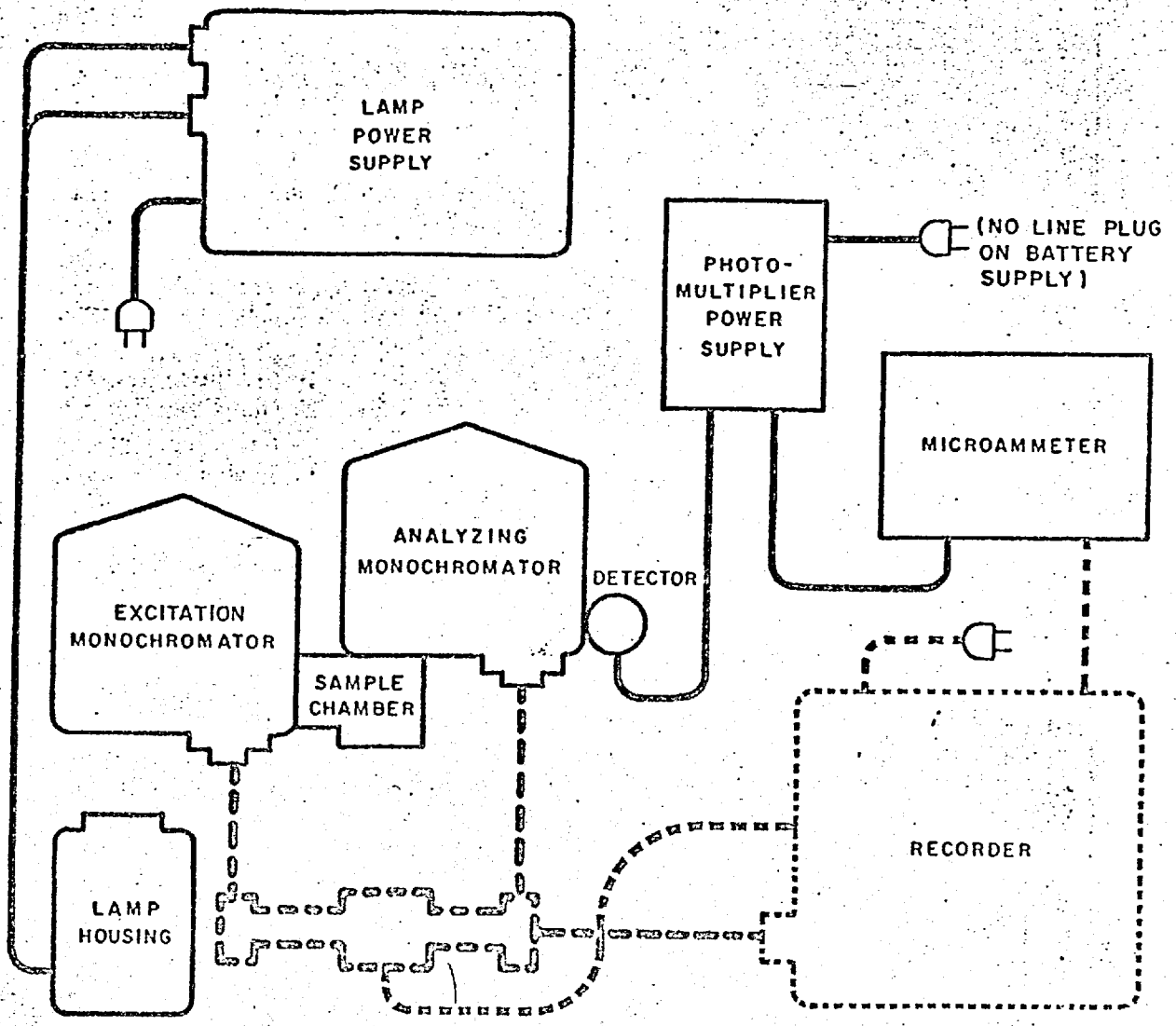
Instrumentation

Several instruments are now commercially available for the analytical application of fluorescence phenomenon. The author's work involved the use of two instruments, the Farrand spectrofluorimeter and the Aminco-Bowman spectrophotofluorometer.

Figure 2 shows the basic lay-out of the Farrand spectrofluorimeter. The optical system and the actual instrument are shown in Figs. 3 and 4.

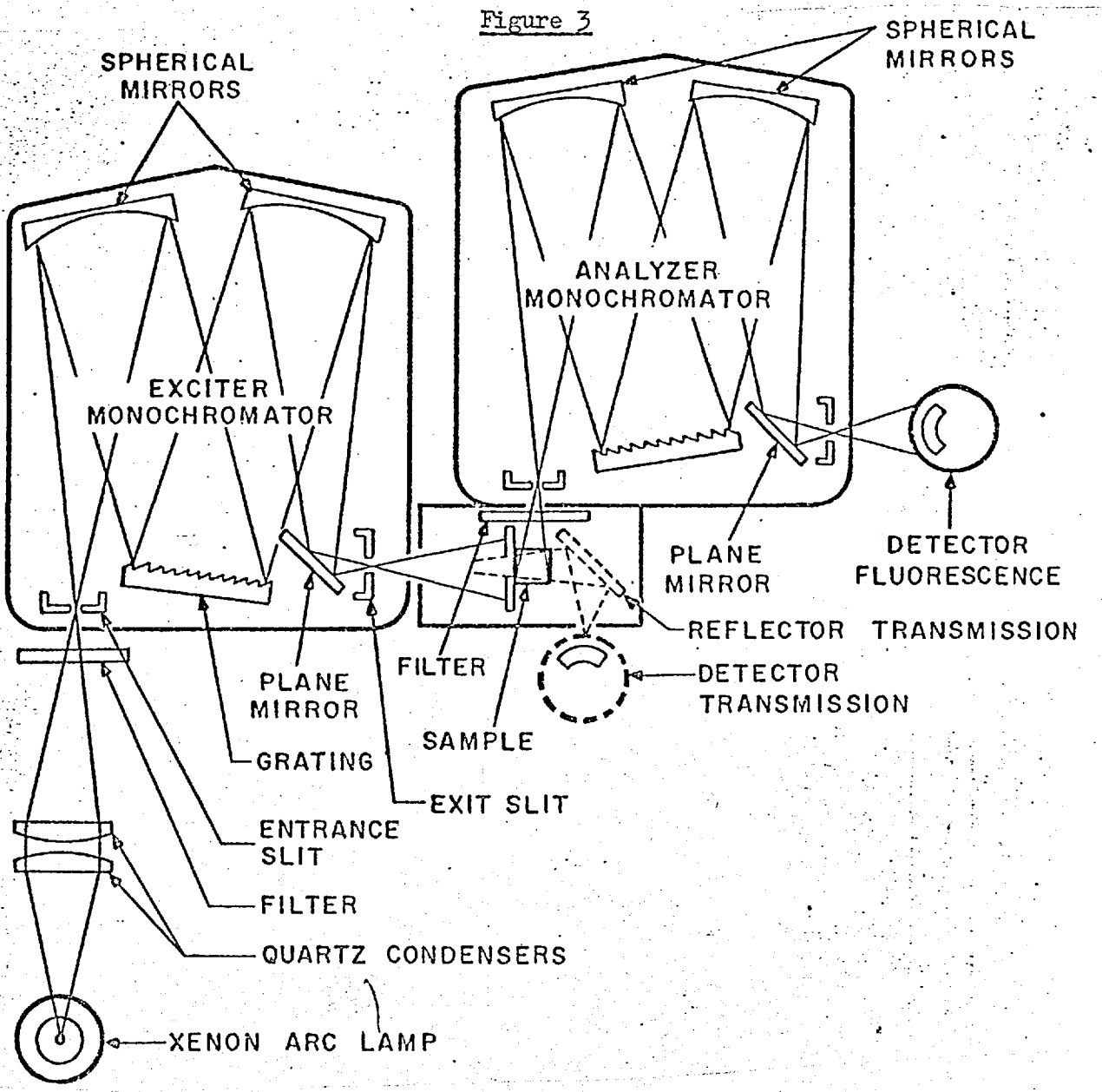
Radiation from a xenon arc lamp is focussed by an off-axis ellipsoidal reflector on the entrance slit of the excitation monochromator. Light of the selected wavelength is directed

Figure 2



from this monochromator into the sample chamber, and the resultant fluorescence, at right angles to the incident radiation, passes through a slit into the analysing monochromator. The signal from the photomultiplier is amplified and read on a microammeter or transferred to a chart recorder.

Figure 3



The light source is a high-pressure 150 watt D.C. xenon arc lamp which gives a continuous spectrum from 230 mμ to beyond 600 mμ. The lamp power supply uses A.C. mains input and rectifies this to D.C. During operation the lamp is cooled by a fan situated at the top of the lamp housing.

FIGURE 4

The monochromators each have a wavelength range of 220-650 mμ and use replica diffraction gratings with 14,400 lines per inch. Interchangeable metal slits with spectral halfbandwidths of 1,5,10 and 20 mμ are provided for the entrance and exit positions of each monochromator.

The sample compartment, situated between the two monochromators, is suitable for the use of 10 x 20 x 50 mm quartz cells (used in author's work) although it is also possible to use 10 x 10 x 50 mm and 3 x 3 x 40 mm cells. The cell compartment may be adapted to take a solid sample.

The analysing monochromator is identical to the excitation monochromator and is used in conjunction with an R.C.A. IP 21 or IP 28 photomultiplier tube. These tubes vary only slightly in their spectral response, and were operated from a mains input/900 volts D.C. output stabilised power supply.

The R.C.A. micro-ammeter has six decade sensitivity ranges which permit measurements of current from 0.0002 to 1,000 μ amps. This is used in conjunction with a Honeywell chart recorder, the motor of which is geared to drive either of the monochromators. The chart width is 10 inches and a complete spectrum scan (220-650 mμ) occupies 10 inches. A range of chart speeds, from $1\frac{2}{3}$ to 40 inches per minute, is available, but it is normally preferable to use the slowest possible speed to obtain optimum resolution of spectra.

It is also possible to use filters in this spectrofluorimeter. Filters are used to eliminate unwanted radiation within the monochromators which may result from internal scattering or second order diffraction. The filters supplied with the instrument were: A Corning 7-54 (>75% transmittance between 275 and 375 mμ) which can be used in connection with the excitation monochromator and Corning 3-72 and 3-73 (transmittance >75% above 490 mμ and above 455 mμ respectively) which can be used with the analysing monochromator.

The other instrument used in the author's work is the Aminco-Bowman spectrophotofluorometer (SPF). Figs. 5 and 6 show the SPF and its optical diagram, respectively. Essentially, the instrument is a three-component unit that includes (1) an optical unit, (2) a power supply for the xenon lamp, and (3) a photomultiplier microphotometer.

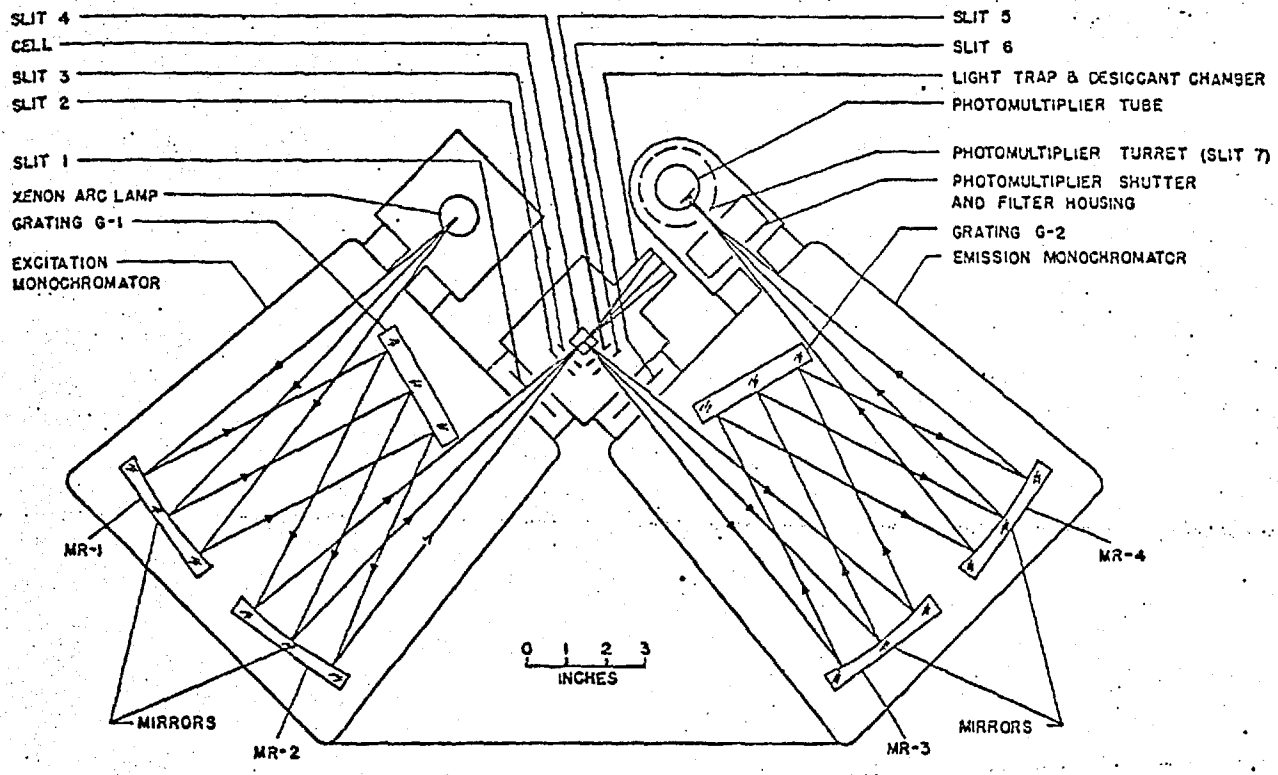
The light source is a high-intensity xenon arc lamp which produces a continuum peaking at 400 mμ and again at 900 mμ (beyond the range of the instrument) and which is located at the focus of the spherical mirror, MR4 (Fig. 6). The lamp power is supplied from a d.c. power supply which provides an output voltage of 20 volts to the lamp. Air from a blower cools the lamp during operation.

The monochromators are plane gratings, each having 600 grooves/mm and 52 x 52 mm ruled area. Both monochromators are optically identical

FIGURE 5


PHOTOMULTIPLIER MICROPHOTOMETER
AMERICAN INSTRUMENT COMPANY, INC.
SILVER SPRING, MARYLAND, U.S.A.
DARK CURRENT
METER MULTIPLIER
SENSITIVITY
ZERO ADJUST
OFF
ON
AMINCO-BOWMAN
SPECTROPHOTOFLUOROMETER
CYLINDER
MONOCHROMATORS
AMERICAN INSTRUMENT COMPANY, INC.
Bryans
Auto Plotter 2000 Series

FIGURE 6


SLIT 4
CELL
SLIT 3
SLIT 2
SLIT 1
XENON ARC LAMP
GRATING G-1
EXCITATION MONOCHROMATOR
SLIT 5
SLIT 6
LIGHT TRAP & DESICCANT CHAMBER
PHOTOMULTIPLIER TUBE
PHOTOMULTIPLIER TURRET (SLIT 7)
PHOTOMULTIPLIER SHUTTER AND FILTER HOUSING
GRATING G-2
EMISSION MONOCHROMATOR
MR-1
MR-2
MR-3
MR-4
MIRRORS
MIRRORS
0 1 2 3
INCHES

24

except for a difference in "blaze" wavelength between the two gratings. The excitation grating is blazed to produce maximum intensity at 300 mμ, thus reinforcing the output of the xenon lamp which falls off below 400 mμ. The emission grating is blazed at 500 mμ (1st order) to improve the response to fluorescence at wavelengths from 400-600 mμ. Each monochromator has a wavelength range of 200 to 800 mμ and the time required for a complete scan varies from 90 to 270 seconds. The monochromator gratings are oscillated by motor-driven cams to which are coupled graduated discs for visual observation and manual adjustment of wavelength. Potentiometers, coupled to the gratings, supply wavelength information in the form of a d.c. signal to the horizontal (X) axis of the oscillograph or the X-Y recorder.

Seven slits are used to define the light in the vicinity of the sample cell and photomultiplier tube, and five slit arrangements are possible. Slits 1 through 6 are 4.8 mm high and the photomultiplier slit 7 is 16 mm high. Some of these slits serve as baffles to reduce instrumental scatter.

Fused quartz cells, 12.5 x 12.5 mm square outside, 10 x 10 mm square inside and 48 mm high are used for fluorimetric measurements at room temperature. The instrument may be modified for use in low-temperature fluorimetry by incorporating a different cell-holder, a Dewar holder assembly, a Dewar flask and a micro sample tube. It may also be adapted for phosphorescence analysis, with

or without polarization, by using an Aminco-Keirs phosphoroscope. The Dewar housing has an inlet provided to which gas or air may be connected to remove condensation on the unsilvered portions of the Dewar. In the author's work, modified quartz sample tubes from Jencons' have been used in place of the Aminco-Bowman micro sample tubes. The cell compartment can also accommodate filters and polarisers which are used for fluorescence polarization measurements.

The detector system employs RCA type IP 21 and IP 28 photomultiplier tubes. The photomultiplier housing includes a manually operated rotary slit-turret and filter holder with shutter control.

The photomultiplier microphotometer amplifies the weak signal from the detector and the photometer output is indicated on the self-contained meter. This output signal may also be connected to the vertical (Y) axis of either an oscillograph or an X-Y recorder. Sensitivity is controlled by a meter-multiplier switch and sensitivity potentiometer. Gross sensitivity adjustments are made with a meter-multiplier switch which reduces oscillograph and recorder output signals, together with meter readings, in fixed steps of 1/3, 1/10, 1/30, 1/100, 1/300, 1/1000. The meter-multiplier (MM) positions are numbered 1, 0.3, 0.1, 0.03, 0.01, 0.003, and 0.001 in order of increasing sensitivity. Fine sensitivity adjustments are made with a sensitivity potentiometer which continuously adjusts recorder output signal and meter readings

over a range of 3.5 to 1. The angular position of the sensitivity potentiometer wiper is indicated by a graduated scale numbered from 0 to 50 in order of increasing sensitivity. A dark-current control cancels photomultiplier-tube dark current by application of an equal current of opposite polarity to the anode current.

A Bryans X-Y recorder (Model 21001) was used in conjunction with the spectrophotofluorometer. Excitation and emission spectra can be suitably plotted on graph paper which are held down by magnetic strips placed on the plotting surface. The pen is of ball point pattern, with readily interchangeable refills of various colours.

Most commercial spectrofluorimeters, including the Farrand and the SPF, are single beam devices which record "apparent fluorescence emission spectra" and "apparent fluorescence excitation spectra". These spectra are uncorrected for the emission characteristics of the source, transmission characteristics of the monochromators, and the spectral response of the photomultiplier. Methods of determining true spectra have been described in detail by Parker and Rees[25]. More recently, corrections of instrumental characteristics for the Farrand[26] and the SPF[27] have been described. Self-correcting instruments which permit the recording of energy corrected spectra have also been devised[28,29]. Although true spectra are necessary for comparison of results obtained with other instruments, the "apparent" spectra, i.e. those recorded by the

instrument under a given set of experimental conditions, are more useful for practical, analytical purposes since the spectra obtained on one particular instrument will be reproducible. However, because the sensitivities of the instrumental components may vary from day to day, the fluorescence signals obtained from a given solution consequently vary. For example, the xenon arc lamp may strike different arcs from time to time, and thus produce different intensities of light for excitation of fluorescence. Thus, a fluorescence standard is necessary for checking the sensitivity of the instrument. Further, the use of a standard substance of known quantum efficiency is imperative if a comparison of fluorescence intensities between laboratories is to be made. Several substances have been studied as possible standards for fluorimetric measurements[25]. A solution of quinine bisulphate in 0.1M sulphuric acid has been shown to be the most suitable for the purpose[25], and has become widely used as a fluorescence standard.[30]

As stated earlier, few fluorescence reactions of purely inorganic species in solution are known. The objectives of the work presented in this thesis were to investigate the analytical potentiality of some simple inorganic systems for spectrofluorimetric applications. Such systems should have the advantage over the generally employed inorganic-organic chelate systems in having much lower "blank" readings since organic reagents are frequently contaminated by traces of organic impurity or photochemical decom-

position products.

The procedure for lead[19] exploits the violet fluorescence of the species $PbCl_4^{2-}$ under conditions similar to those used for the determination of thallium[18]. The sensitivity of the method compares favourably with those obtained by spectrophotometric methods. A few interferences were encountered but most of them can be eliminated by the use of suitable masking agents or solvent extraction technique.

The analytical potentiality of low-temperature fluorimetry has been investigated. The study of some inorganic acid solvents reveals that several of these form clear, rigid glasses at liquid nitrogen temperature. This permits the study of the fluorescence characteristics of inorganic complexes in these acids at low temperature using the conventional right-angle arrangement. Several halide complexes which are not fluorescent at room temperature, show characteristic fluorescence bands at liquid nitrogen temperature[31,32]. In those cases where the complexes are fluorescent at room temperature, several fold increase in sensitivity is obtained by the use of low temperature technique.

The method described for the determination of tellurium as the fluorescent chloro-complex at -196°C is simple, sensitive and highly selective, and may be applied to the determination of traces of tellurium in lead samples[33].

CHAPTER I

The Spectrofluorimetric Determination of Lead

Several colorimetric methods are available for the determination of small amounts of lead in aqueous solution; the best known methods are based on the use of the reagents dithizone[34], diethyldithiocarbamate[35], 4-(2-pyridyl)-resorcinol (PAR)[36] and 1,1'-dipyridyl[37]. Methods utilising the absorption of the anionic chloro-complex of lead in the ultra-violet at 271 mμ have also been reported.[38,39] While the spectrophotometric determination of lead with these reagents is frequently sensitive, the reaction between lead and the reagent in solution is usually unselective, and recourse is necessary to prior separation of the lead from other ions or to extensive use of masking agents.

Bozhevol'nov and Solov'ev[40] have proposed a fluorimetric procedure for lead which is based on recording the fluorescence observed from lead in hydrochloric acid at -70°C. No other spectrofluorimetric method for the determination of lead is available, although several spot tests have been reported for the detection of lead which exploit the formation of insoluble fluorescent complexes of lead with organic reagents. For example, when potassium iodide and pyridine are added to a solution containing lead, as little as 0.25 μg of lead suffices to give a precipitate of $Pb(C_5H_5N)_2I_2$ which shows a strong yellow-brown fluorescence under ultra-violet

light[41]. An equally sensitive test can be obtained for lead with morin; a yellow-green fluorescence is obtained[41].

This chapter describes the investigation of the fluorescence observed for lead in the presence of potassium chloride in concentrated hydrochloric acid and the development of a method for the determination of microgram amounts of lead using the violet fluorescence produced. The fluorescence of lead and thallium (I) in concentrated chloride media was first reported by Pringsheim and Vogels[42], and the spectrofluorimetric determination of thallium in this way has been reported[18]. Lead, copper (I), tin (II) and cerium (III) also show characteristic fluorescence emission under similar conditions[18], but only the lead emission is of sufficient intensity to be analytically useful. The violet fluorescence for lead has been attributed by Pringsheim and Vogels[42] to the complex anionic $PbCl_4^{2-}$ species. The work of Merritt, Hershenson and Rogers[38] suggests that the absorption spectrum observed for lead in concentrated chloride medium is characteristic of the species $PbCl_4^{2-}$, and this is most probably the species also responsible for the fluorescence emission. This fluorescence is only observed in the presence of very large amounts of alkali chloride and hydrochloric acid. Consequently, the standard optical methods (mole ratio, slope ratio and continuous variations procedures) for elucidation of the empirical formula of the fluorescent complex cannot be applied. In the method reported here the fluorescence

emission is measured at 480 mμ using an excitation wavelength of 270 mμ in a concentrated hydrochloric acid-potassium chloride medium. The optimum conditions for the determination of lead have been established, and the effect of numerous ions has been investigated. The interference from several ions may be eliminated by the addition of masking agents.

EXPERIMENTAL

Reagents

Standard Lead Solution

A 10^{-3}M lead solution was prepared by dissolving 0.3312 g of Analar lead nitrate in water and diluting to 1 litre, using water from an all-glass distillation apparatus. This stock solution was diluted to 10^{-4}M as required.

Hydrochloric acid

Analar grade was used.

Saturated Potassium Chloride Solution

This was prepared by dissolving ca. 150g of Analar grade potassium chloride in 500 ml. of boiling water, and allowing it to crystallise on cooling. The saturated solution was approximately 4.1 M in potassium chloride.

Stannous Chloride

A 10^{-2}M solution was prepared using general purpose reagent

grade salt.

Sodium Sulphite

Analar grade salt was used.

Foreign Ions

0.01M solutions of Analar grade salts were used.

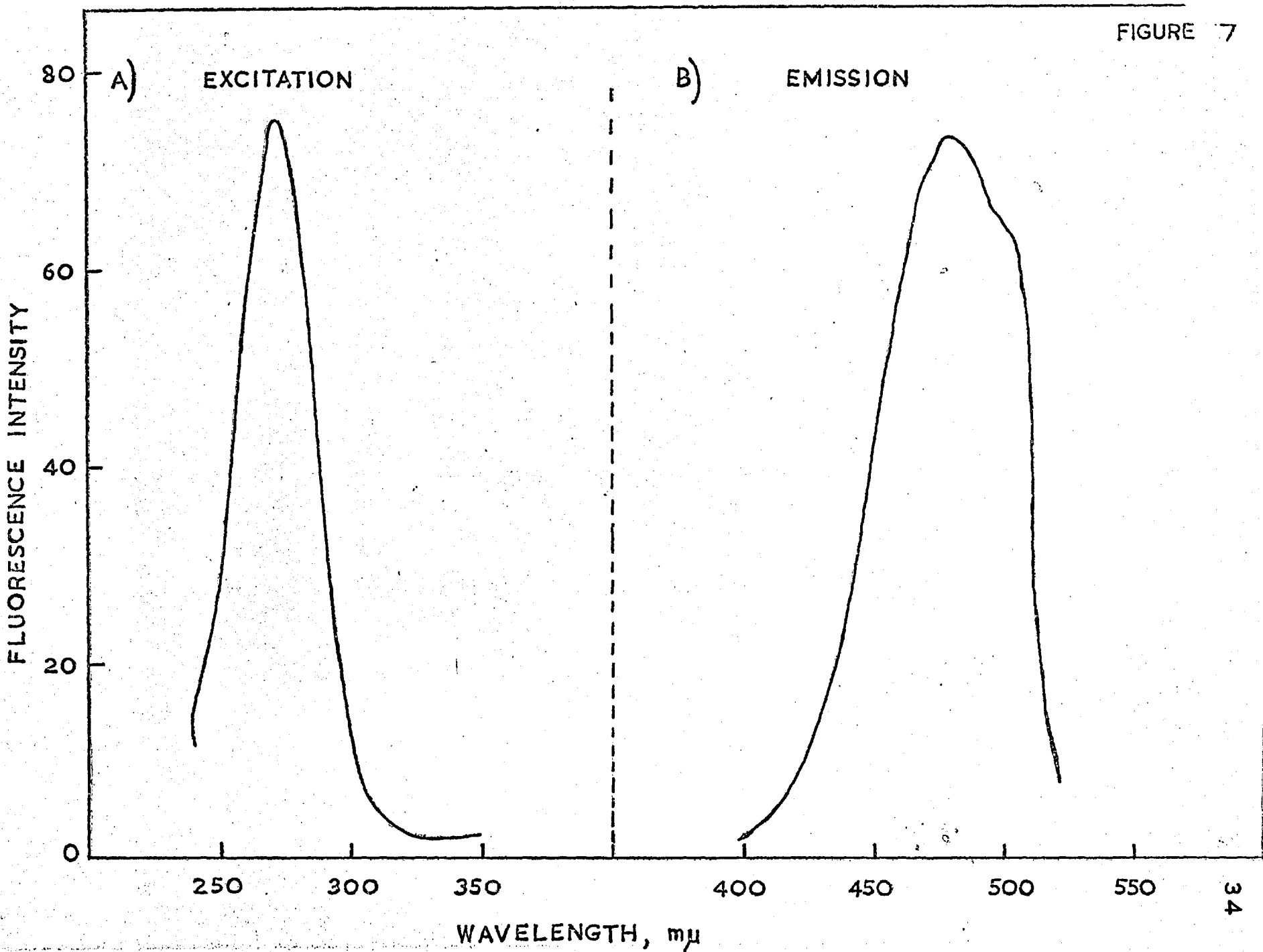
Apparatus

Fluorescence measurements were made with a Farrand spectrofluorimeter (Farrand Optical Co. Cat. No. 104244) described in 'Introduction". Fused quartz cells (10 x 20 x 50 mm) were used throughout the work. Fluorescence was measured at right angles to the incident light such that the mean solution path-length of the exciting radiation is 5 mm and that of the fluorescence emission is 10 mm. 20 mμ bandwidth slits were used in both the exciting and analysing monochromators, and no filters were used during these experiments.

Spectral Characteristics

Fig. 7 shows the excitation and emission spectra for the lead (II) ion in hydrochloric acid-potassium chloride solution. The lead concentration used was 3.5×10^{-4} M and the spectra were plotted on the XI sensitivity scale. Curve (A) was obtained by measuring the emission at 480 mμ while for curve (B) the excitation wavelength was set at 270 mμ. These spectra are uncorrected for

FIGURE 7


A) EXCITATION
B) EMISSION
80
60
40
20
0
FLUORESCENCE INTENSITY
250
300
350
400
450
500
550
WAVELENGTH, mμ

variations in the emission characteristics of the lamp, the transmission of the two monochromators and the response characteristics of the IP 28 photomultiplier. The relevant correction curves are shown in Fig. 8. Curve (B) is supplied by the manufacturers and relates the photomultiplier sensitivity with wavelength. Curve (A) shows the spectral characteristics of the lamp and the excitation monochromator after correction for the photomultiplier response[16].

The excitation maximum occurs at 270 mμ and the fluorescence emission maximum at 480 mμ. Fig. 9 shows the uncorrected emission spectra of more dilute solutions at much increased sensitivity with wide (20 mμ) slits and no protective filters. These spectra were plotted on the X0.1 sensitivity scale using an excitation wavelength of 270 mμ. Curve (A) was obtained with a lead concentration of 10^{-6}M and curve (B) with no lead present. The peak at approximately 550 mμ is attributed to second-order diffraction from the analysing monochromator grating. The peak at approximately 350 mμ may have been caused by fluorescent impurities in the solvents used, but Woodward has demonstrated for thallium (I) that the main cause is due to stray radiation within the monochromators[16]. The tails of the two peaks shown in Fig. 9 make up the blank fluorescence at 480 mμ. The signal at this wavelength is directly proportional to the lead concentration, but calibration curves plotted at this level of concentration pass above the origin for reasons mentioned above.

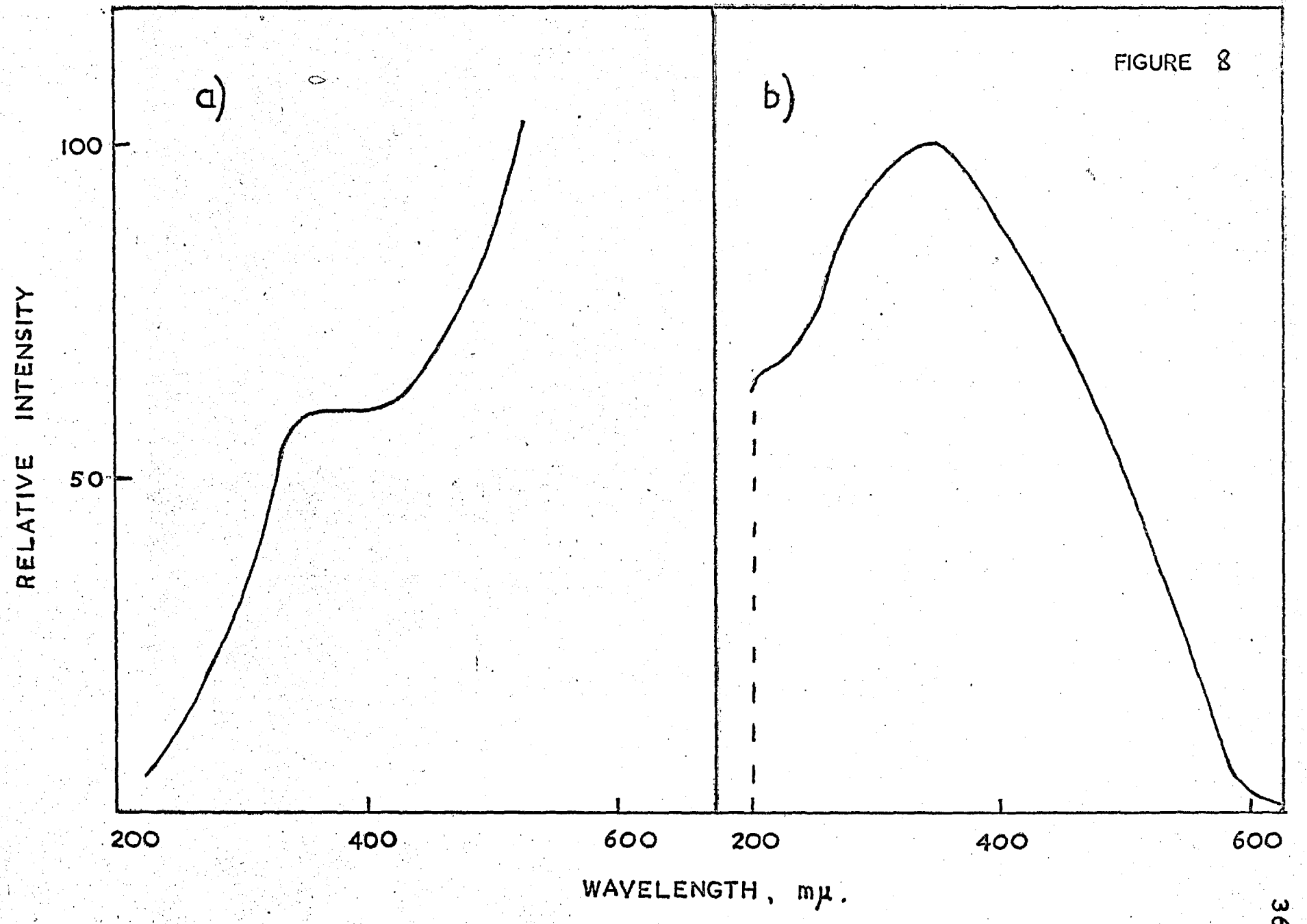


FIGURE 8
a)
b)
100
50
RELATIVE INTENSITY
200
400
600
200
400
600
WAVELENGTH, mμ.

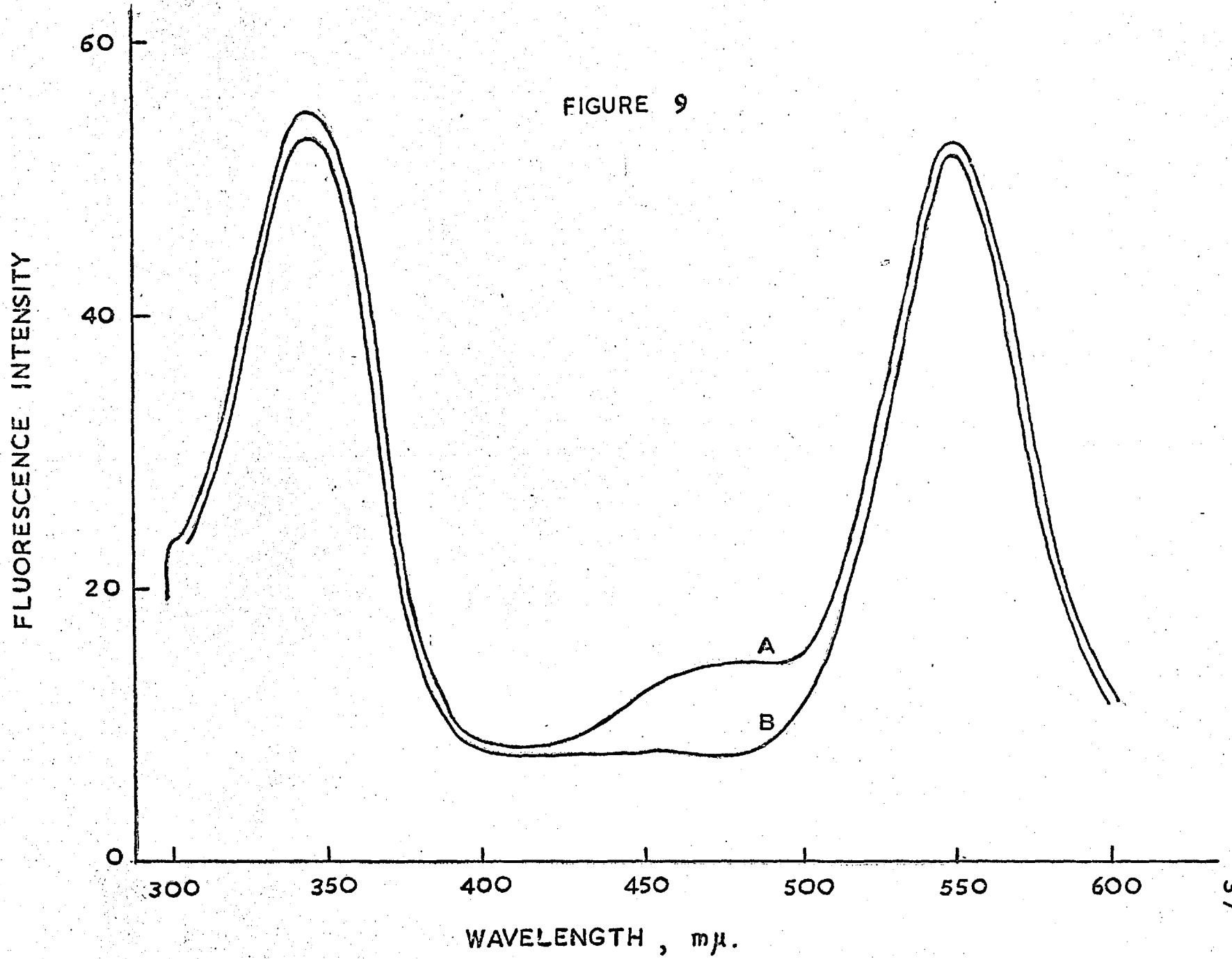


FIGURE 9
FLUORESCENCE INTENSITY
60
40
20
0
A
B
300
350
400
450
500
550
600
WAVELENGTH , mμ.

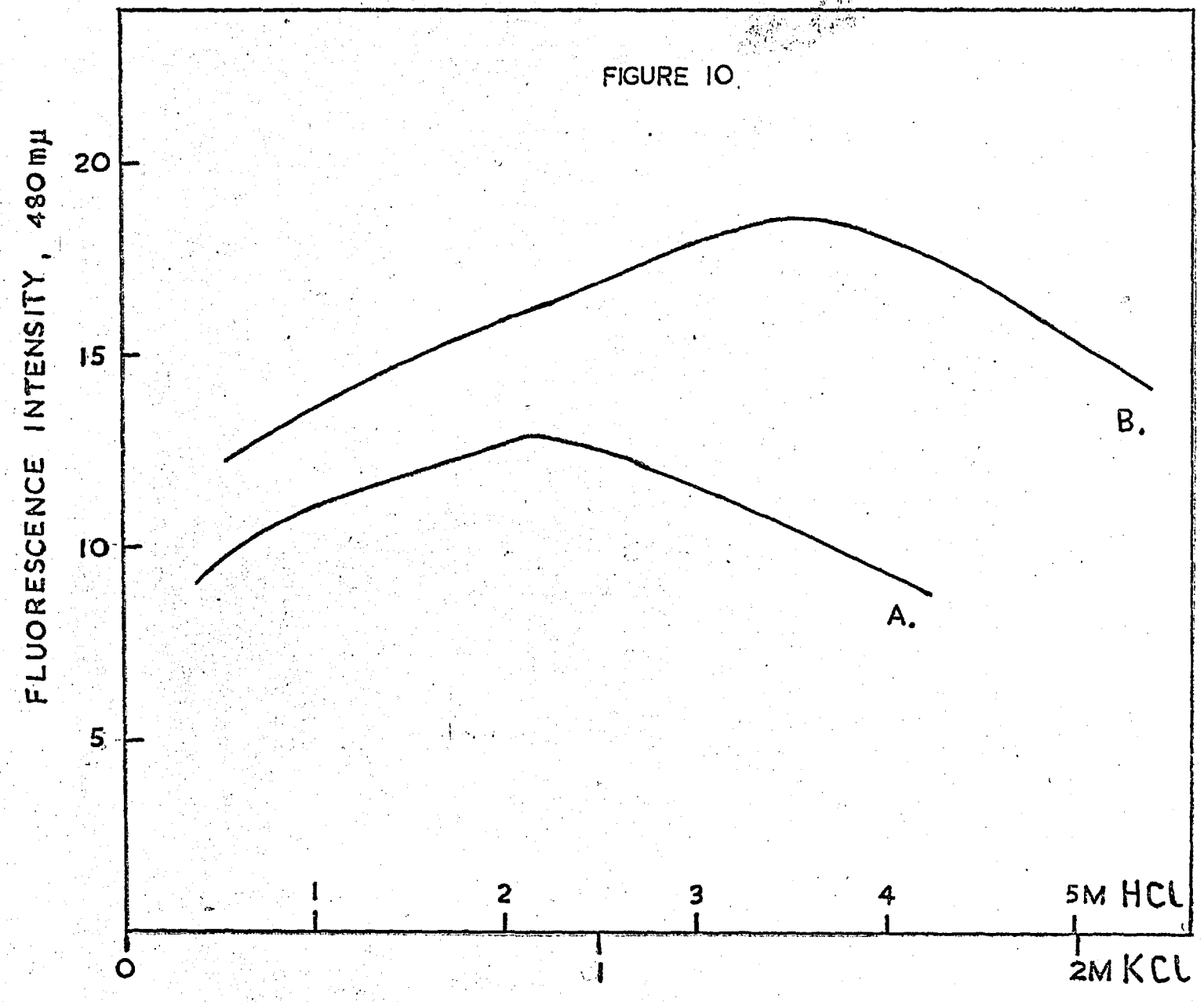
Effect of Hydrochloric Acid and Potassium Chloride Concentrations

Tests were carried out to establish the optimum amounts of hydrochloric acid and potassium chloride for the determination of lead by varying their concentrations dependently. In a solution 3.3M in hydrochloric acid, the fluorescence intensity increases with increase in potassium chloride concentration and attains a maximum when the solution is 0.8M in potassium chloride. The fluorescence intensity decreases slightly beyond this level and potassium chloride tends to precipitate by the common ion effect at higher concentrations of the salt (Curve A, Fig. 10). Similarly, by keeping the potassium chloride concentration constant at 0.8M, it was shown that a 3.3M hydrochloric acid concentration is necessary to produce maximum fluorescence (Curve B, Fig. 10). Thus, the best solution should be approximately 3.3M in hydrochloric acid and 0.8M in potassium chloride, i.e. 100 ml. of solution contains 30 ml. of concentrated hydrochloric acid and 20 ml. of saturated potassium chloride.

Effect of Time

The variation of fluorescence intensity of dilute lead solutions with time was studied. A 4×10^{-6} M lead solution prepared by the recommended procedure showed a gradual reduction in fluorescence over a period of two hours when stood in the dark, after which the fluorescence had fallen by 21% from the time of

FIGURE 10.


FLUORESCENCE INTENSITY, 480 mμ
20
15
10
5
0
B.
A.
1
2
3
4
5M HCl
1
2M KCl

measurement immediately after mixing. A similar reduction in fluorescence intensity was obtained after standing the solution for two hours in normal laboratory conditions i.e. under fluorescent tube lighting, and continuous irradiation of the solution at 270 mμ in the spectrofluorimeter for a similar period also caused a reduction in intensity of 20%. The fluorescence is therefore quite stable during the time required for its measurement even if standards are not prepared at the same time as sample solutions.

Effect of Temperature

Over the temperature range investigated, i.e. 10-40°C, a decrease of fluorescence intensity with increase in temperature of development was observed which corresponded to a temperature coefficient of approximately 1.2% per °c. All measurements of the lead fluorescence were made under normal laboratory conditions i.e. at 23 ± 3°, and the observed fluorescence intensities were compared with standards prepared simultaneously, so that the existence of the temperature coefficient did not invalidate the results obtained. However, in order to minimise the generation of heat of mixing between concentrated hydrochloric acid and water during the preparation of samples for fluorescence measurements, the acid should be added to as large a volume of water as possible and mixed thoroughly immediately.

Precision

The precision of the method at its maximum sensitivity is

compounded from a) the chemical precision, i.e. the reproducibility in fluorescence signals of a series of identical solutions and b) the instrumental precision, i.e. the reproducibility in scale reading using the instrument on its most sensitive scale.

a) was estimated by repetitive determination of a relatively high concentration of lead (6 ppm) to give readings on a less sensitive scale (XO.1) where instrumental noise is negligible (see Table 1). The instrumental precision b) was estimated using a single more dilute solution of lead (0.6 ppm) to give repetitive readings on the most sensitive scale (XO.01) where instrumental noise is appreciable (see Table 2). The results shown in Table 1 gave a lead response of 72.3 $\pm$ 0.9 units which indicated a chemical precision of $\pm$ 1.3%, whilst Table 2 gave a response of 57.1 $\pm$ 0.9 units, corresponding to an instrumental precision of $\pm$ 1.6%.

Accuracy

Chemical analyses for lead were carried out on unknown sample solutions by the recommended procedure in order to assess the accuracy of the method. Two standards were prepared and measured with each group of samples. The results of these analyses are shown in Table 3.

Influence of Foreign Ions

The effect of 32 foreign ions on the lead fluorescence

Table I

Sample Number	Scale reading(XO.1)	Net lead response	Deviation	Variance
1	80.2	73.2	+0.9	0.81
2	78.2	71.2	-1.1	1.21
3	79.7	72.7	+0.4	0.16
4	78.0	71.0	-1.3	1.69
5	79.9	72.9	+0.6	0.36
6	80.2	73.2	+0.9	0.81
7	79.0	72.0	-0.3	0.09
Blank	7.0	-		
		Mean = 72.3		

Standard deviation = $\sqrt{\frac{\Sigma \Delta^2}{n-1}} = \sqrt{\frac{5.13}{6}} = \sqrt{0.85} = 0.92$ units

Table 2

Sample Number	Scale reading(XO.01)	Net lead response	Deviation	Variance
1	73.5	57.0	-0.1	0.01
1	74.0	57.5	+0.4	0.16
1	73.0	56.5	-0.6	0.36
1	73.5	57.0	-0.1	0.01
1	73.0	56.5	-0.6	0.36
1	75.5	59.0	+1.9	3.61
1	73.0	56.5	-0.6	0.36
Blank	16.5	-		
		Mean = 57.1		

Standard deviation = $\sqrt{\frac{\Sigma \Delta^2}{n-1}} = \sqrt{\frac{4.87}{6}} = \sqrt{0.81} = 0.90$ units

Table 3

Analysis of Lead solutions treated as unknown samples

Sample	Lead, µg		Error		Foreign Ions present, µg.
	Present	Found	µg	%	
1	31.08	31.08	-	-	-
2	33.15	34.18	+1.03	+3.1	-
3	49.72	51.80	+2.08	+4.2	-
4	24.86	26.93	+2.07	+8.3	Ba(2060)
5	53.87	53.87	-	-	Mg(365)
6	45.58	44.55	-1.03	-2.3	Sr(1314)
7	37.29	37.29	-	-	Zn(981)
8	62.16	63.19	+1.03	+1.7	Ni(881)
9	20.72	20.72	-	-	Cd(1686)
10	49.73	49.31	-0.42	-0.8	Cr(VI)(780) Mn(II)(824)
11	41.44	43.50	+2.06	+4.9	Ni(881), Fe(III) (838)
12	45.58	49.72	+4.14	+9.1	Ni(881), Fe(III) (838)
13	62.16	62.16	-	-	Co(II)(884), Fe(III) (838)
14	29.01	31.07	+2.06	+7.1	Co(II)(884), Fe(III) (838)
15	53.87	49.73	-4.14	-7.7	Co(II)(884), V(V) (764)

in pure solution was investigated. The study was made by observing the effect of a fifty-fold molar excess of each ion on the determination of 60 µg of lead. The ions investigated were considered to interfere at this level when they caused a variation of fluorescence

intensity of greater than or equal to ±5%. The investigation revealed that the following ions do not interfere under the above conditions: barium, cadmium, calcium, chromium (III), cobalt (II), iron (II), magnesium, manganese (II), mercury (II), nickel, silver, strontium, tin (II), titanium (IV), zinc, citrate, fluoride, nitrate, oxalate, sulphate, sulphite and tartrate. The presence of a 50-fold excess of the following ions causes the error in the fluorescence intensity given in parentheses: bismuth(-8%), chromium (VI)(-33%), copper (II)(-11%), iron (III)(-44%), molybdenum (VI)(-26%), palladium (II)(-89%), thallium (I)(+100%), vanadium (V)(-15%), ascorbic acid (-29%), and metabisulphite (-34%).

Attempts were made to eliminate the interferences by the use of suitable masking agents. These experiments were conducted for the determination of 60 µg of lead (0.6 ppm) in the presence of a 50-fold molar excess of each interfering ion and the appropriate masking agent. The interference of chromium (VI) is eliminated by its reduction to chromium (III) by the addition of a 300-fold molar excess (over lead) of the sulphite ion. The interference from iron (III) and vanadium (V) are removed similarly by the addition of 100-fold and 150-fold molar excesses (over lead) respectively of tin (II) chloride to the sample and standard solutions. Under the conditions of the determination, hydroxylamine hydrochloride, tin (II) chloride and sodium sulphite fail to eliminate the interference caused by copper (II) or molybdenum

(VI). Investigation of the determination of 60 μg of lead in the presence of varying amounts of copper (II), molybdenum (VI) and bismuth reveal that less than 5% negative error in the fluorescence intensity due to lead is produced when a 10-fold molar excess of copper, 5-fold molar excess of molybdenum (VI) or 30-fold molar excess of bismuth is present. Of the ions studied, thallium (I) causes the most serious interference in the procedure. This interference is not readily overcome by oxidation of the thallium (I) to thallium (III) with hydrogen peroxide or potassium bromate, and it is necessary to resort to separation of the thallium from lead by the ether extraction of thallium chloride from hydrochloric acid medium as described previously[18]. Large amounts of copper may be separated from small amounts of lead by extraction of copper diethylammonium diethyldithiocarbamate away from lead into chloroform from 2N hydrochloric acid solution[43]. The presence of large amounts of nitrate ion (ca. 1000-fold excess over lead), which would frequently be present after dissolution or destruction of biological materials to be analysed for lead by wet digestion with nitric acid, has been shown not to affect the fluorescence produced at the lead concentrations encountered in the recommended procedure.

Calibration Curve

To 20 ml. of saturated potassium chloride solution, 30 ml. of water and 30 ml. of concentrated hydrochloric acid in a 100 ml.

volumetric flask, pipette accurately between 0.5 and 3.0 ml. of standard lead (II) solution (10^{-4}M ≡ 20.72 µg/ml) and dilute to volume with water. Allow the solutions to stand for 15 minutes, then measure the intensity of the fluorescence at 480 mµ at an excitation wavelength of 270 mµ. The plot of fluorescence intensity against lead concentration (0.1-0.6 ppm) is a straight line and passes above the origin (Fig. 11).

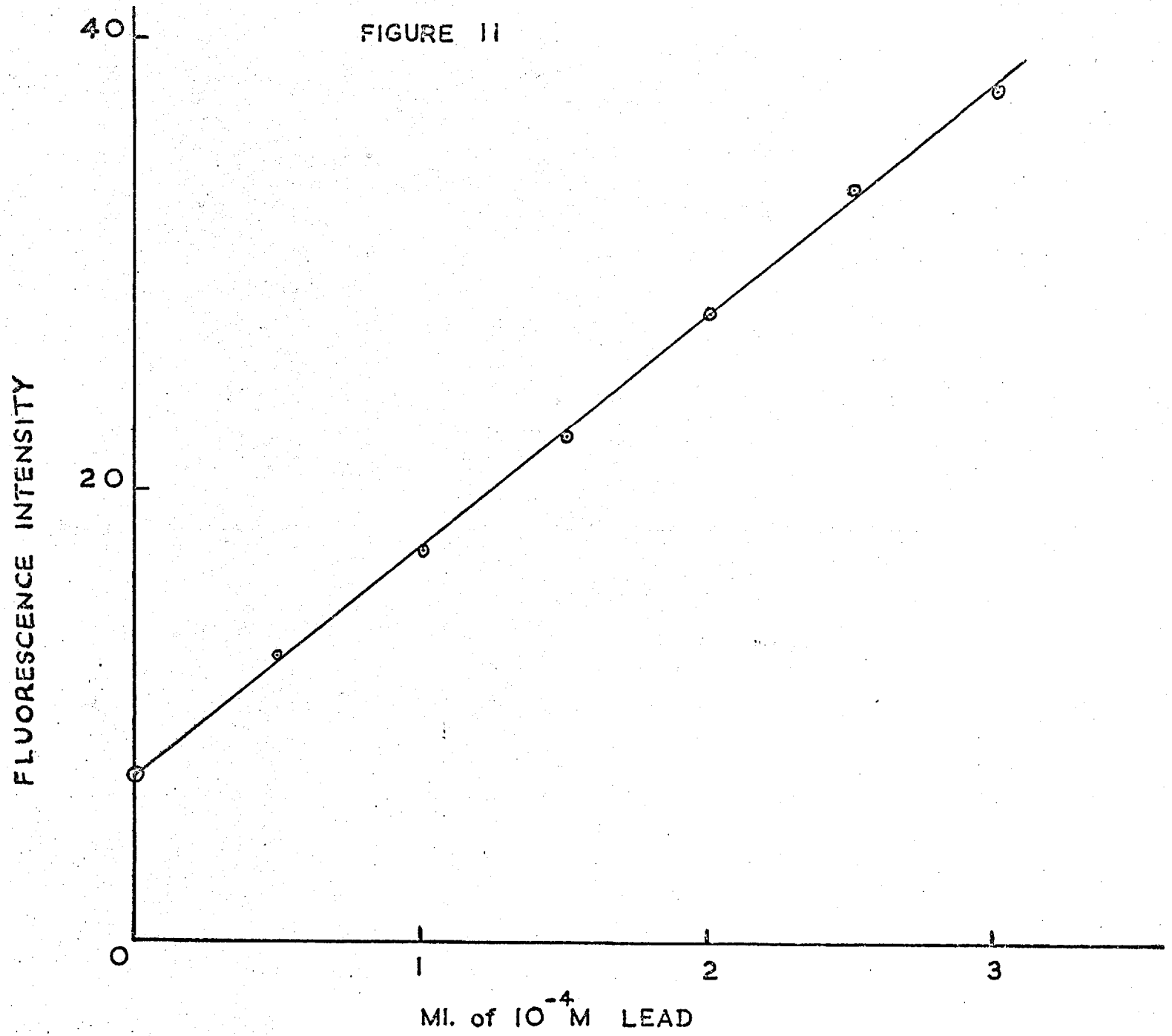
Prepare and measure two standards with each group of samples, using 0 and 3 ml. of the lead (II) solution (20.72 µg/ml.), respectively.

Discussion

A simple and rapid method has been developed for the spectrofluorimetric determination of 10-60 µg of lead. The sensitivity of the procedure, although not as great as that reported for thallium, compares favourably with that of spectrophotometric methods. The method is susceptible to some interferences but the elimination of the more important interferences is easily achieved by the use of masking agents.

The linear dependence of intensity of fluorescence on the intensity of the exciting source suggests that the sensitivity of the method may be increased by using a more intense source than the xenon arc lamp used for excitation of the lead fluorescence. Consequently, experiments were conducted using a mercury vapour discharge lamp and a microwave-excited mercury electrodeless

FIGURE 11



discharge tube as spectral sources, but these have been shown to be inferior to the xenon arc lamp as excitation source for molecular fluorescence analysis[44].

CHAPTER II

Low-Temperature Fluorimetry

Many inorganic solids which are not fluorescent at room temperature have been shown to produce fluorescence emission at low temperature[45]. In several instances, the fluorescence is a feature of the pure substance but in others, it is due to the presence of impurities in the solid and thus an examination at low temperature will provide a more sensitive test of purity than the normal procedure. Most low temperature luminescence measurements have been utilised for the quantitative determination of organic compounds. McGlynn et al[46] have demonstrated the usefulness of measuring low-temperature luminescence for determination of several hydrocarbons of petrochemical interest. Hood and Winefordner have applied similar techniques to determine a mixture of carcinogens.[47] Relatively few inorganic applications of low temperature fluorimetry are known,[14,48] and much work remains to be done in this field of research.

Fluorescence spectra can be obtained either in liquid solutions or, when the solution is frozen, in a glassy or (less favourable) crystalline environment. A number of important changes in fluorescence spectra occur when a liquid solution is frozen to yield a glass. Vibrational structure of fluorescence spectra is invariably much more fully resolved in frozen glasses, compared with the diffuse spectra commonly obtained in liquid

solution and this is often seen in the fluorescence spectra of aromatic hydrocarbons at low temperature.

It is commonly observed that both intensities and energies of fluorescence are greater in low-temperature glasses than in liquid solution. The larger quantum yield in glasses can arise from several factors. One important reason is that loss of excitation energy by collisions of excited solute with solvent molecules will clearly be less extensive if the medium is rigid. Also, the radiationless processes which compete with fluorescence often appear temperature-dependent, increasing in efficiency with increasing temperature[49]. The variation of fluorescence yield with temperature can frequently be represented by an equation of the form[50],

$$\frac{1}{\phi_F} - 1 = A \exp.\left(-\frac{E}{RT}\right)$$

which resembles the common Arrhenius rate equation. The rate constant which varies with temperature is not that for radiative decay of the excited singlet, but instead represents one or more temperature-dependent radiationless processes[51]. The increase in energy of fluorescence brought about by freezing a liquid solution results from the fact that solvent reorientation following excitation is considerably less facile in a rigid medium than in solution. Hence, the Franck-Condon excited state is effectively "frozen in" at low temperature[52] and produces the "low temperature blue shift"

Since the advent of low temperature emission and absorption spectroscopy, extensive study has been made of the suitability of a large number of solvents for use in these techniques. The main requirement of solvents is that they must form clear, uncracked glasses when cooled. Further, these solvents must have good solubility characteristics for the compounds to be studied, must be readily available and inexpensive and must neither absorb strongly nor luminesce greatly in the spectral regions of interest. Results have shown that relatively few pure solvents form clear rigid glasses the majority of the time but a number of solvent mixtures form good media for low temperature fluorimetric analysis.[53,54,55]

Even if suitable solvents are available, the ultimate success of an analysis depends on the careful handling of the sample tube. If the sample tube is dirty or contains scratches, the solvent will generally crack on cooling and spurious signals will be obtained. Again if the sample tube is struck against the side of the Dewar flask during cooling, the vibration may result in cracking. Just as in the process of precipitation where the availability of nucleation sites results in growth of the crystals, the availability of small dust particles or scatches apparently results in sites for cracking. One must therefore exercise reasonable care to obtain good, reproducible glasses. The amount of sample needed for analysis is often extremely small because of the small sample volume needed for measurement and the good sensitivity of analysis.

Fluorescence Characteristics of Inorganic Complexes in Hydrochloric Acid Medium at Liquid Nitrogen Temperature

Several workers have demonstrated that certain metal chelate complexes may show increase in their fluorescence intensity at low temperatures compared to that obtained at room temperature.[14,48] Bozhevol'nov and Solov'ev[56] have studied organic chelate complexes of elements such as magnesium, niobium and gallium and shown, for example, that a 100-fold increase in the intensity of the fluorescence of the niobium complex of 2,2',4'-trihydroxy-5-chloro-(1-azo-1')-benzene-3-sulphonic acid is obtained at -196°C compared to the intensity at room temperature. These workers have also described the increase in fluorescence intensity which is obtained for lead and thallium in hydrochloric acid medium at -70°C and -196°C respectively compared to the intensity at room temperature[57,58], and also report that the fluorescence of tin in concentrated sulphuric acid at -70°C may be used for its determination.[40] The available optical geometries for fluorimetric analysis have been reviewed by Parker and Rees[4]. Much previous work[40] in low temperature fluorimetry of inorganic materials has employed the technique of "frontal illumination", in which the fluorescence radiation from the surface of the sample is viewed along an axis which makes an acute angle to the optical axis of the incident radiation used for excitation of the fluorescence. This technique is adopted because clear, rigid glasses suitable for use with the conventional fluorimetric "right angle" optical geometry are difficult to produce in conventional sample cells for aqueous samples. Although many solvents which form suitable

glasses at low temperatures have been described[53,54,55], these are almost all organic liquids at room temperature.

The present chapter describes some inorganic acid solvents which form clear glasses at liquid nitrogen temperature, and their use in a simple sample cell which may be used with the conventional fluorimetric "right angle" geometry with the low temperature attachment of a commercial spectrofluorimeter. An investigation of the fluorescence emission characteristics of the ions of 55 elements in hydrochloric acid medium at - 196°C was undertaken. Antimony (III), antimony (V), bismuth, cerium (III), copper (I), lead, tellurium (IV), thallium (I), tin (IV) and uranium (VI) exhibit characteristic fluorescence under these conditions. The spectral characteristics, effect of hydrochloric acid concentration, stability of fluorescence emission and limits of detection for seven of these elements have been studied.

EXPERIMENTAL

Apparatus

Fluorescence measurements were made with an Aminco-Bowman spectrofluorimeter (American Instrument Co.) fitted with a 150 watt xenon arc lamp and RCA IP 28 photomultiplier tube, and equipped with a Bryans X-Y recorder. The Aminco low temperature housing and Dewar flask with fused silica base supplied for spectrophosphorimetry was employed to hold the sample tubes. Precision

bore transparent silica sample tubes (Jencons Ltd., Hemel Hempstead, England) of length 20 cm., internal diameter 3 mm. and 1 mm. wall thickness were employed. A sample volume of 0.5 ml. is enough to fill these tubes sufficiently for work in the Aminco spectrofluorimeter. Sample solutions in hydrochloric acid in these thick-walled tubes may be placed directly into liquid nitrogen in the Dewar flask, and may subsequently be brought back to room temperature after measurement, without fracture of the tubes.

In order to obtain maximum sensitivity compatible with good definition of maxima, 3 mm. slits corresponding to ca. 30 mμ band-pass (Aminco-Bowman slit arrangement no. 3) were used in the excitation and analysing monochromators.

Reagents

The semi-quantitative survey of the low-temperature characteristics of the 55 elements examined was conducted using analytical-reagent grade salts and hydrochloric acid ("Analar", Hopkin and Williams Ltd.).

Quantitative measurements of the fluorescence emission characteristics of the ten elements which show intense emission were conducted using analytical-reagent grade salts (antimony potassium tartrate, bismuth nitrate, cerium (III) nitrate, lead nitrate, thallium (I) sulphate, uranyl nitrate) to prepare stock 10^{-2}M solutions. Tellurium powder (Johnson and Matthey, Specpure),

stannic chloride (general purpose reagent grade, Hopkin and Williams Ltd.), antimony pentachloride (technical grade, British Drug Houses) and copper sulphate (Analar, Hopkin and Williams) were used as starting materials for the preparation of stock 10^{-2}M solutions containing the ions Te (IV), Sn(IV), Sb(V) and Cu(I). For these quantitative studies extra pure analytical-reagent grade hydrochloric acid ("Aristar" grade, British Drug Houses Ltd.) was employed.

RESULTS AND DISCUSSION

Low Temperature Glass Formation

The application of spectrofluorimetric analysis at low temperatures to inorganic trace analysis has been restricted by the lack of solvents which form rigid, clear glasses rather than 'snows' or extensively cracked glasses under these conditions. Thus while some complexes which may be extracted into organic solvents from aqueous medium may be examined in one of the wide-range of organic solvent mixtures available, there is a need for aqueous solvents in which other inorganic complexes may be examined at low temperature. The author has examined the properties of a range of acids for this purpose. Concentrated hydrochloric, hydrobromic, sulphuric, nitric, phosphoric and perchloric acids were found to produce good clear glasses reproducibly at -196°C in the thick-walled sample tubes used in

this study. Concentrated acetic, formic, boric and oxalic acid solution invariably formed opaque "snows" on rapid cooling in liquid nitrogen. Hydriodic acid, which always contains traces of free iodine, usually produced a yellow, extensively cracked glass. With the concentrated mineral acids which form good, clear glasses it is also possible to obtain transparent glasses with less concentrated solutions. Thus on rapid cooling of the thick-walled sample tubes containing aqueous hydrochloric acid solutions, transparent glasses are formed reproducibly at all concentrations higher than 6M, whereas below 5M a snow is invariably formed.

General study of elements in hydrochloric acid

The general preliminary study was conducted using a 2×10^{-3}M solution of the purest available salt of each element in a 6M hydrochloric acid solution. An aliquot of each solution (0.5 ml.) was transferred to a silica sample tube and placed in the spectrofluorimeter Dewar flask containing liquid nitrogen. The glass produced was examined visually through the silica walls of the low temperature Dewar flask under a mercury vapour discharge lamp. The quality of the glass and any fluorescence emission was noted. The Dewar was then transferred to the spectrofluorimeter and the fluorescence was then specifically sought instrumentally. No fluorescence emission was observed under these conditions for the following 45 ions: aluminium, arsenic (III), arsenic (V), beryllium, cadmium, cerium (IV), chromium (III),

cobalt, copper (II), dysprosium, erbium, europium, gadolinium, gallium, holmium, indium, lanthanum, magnesium, manganese (II), mercury (II), molybdenum (VI), neodymium, nickel, niobium (V), palladium, platinum (II), platinum (IV), praseodymium, ruthenium, samarium, scandium, selenium (IV), silver, strontium, tantalum, terbium, thorium, thulium, tin (II), titanium (IV), vanadium (V), ytterbium, yttrium, zinc and zirconium. Under the same conditions the following 10 ions were found to exhibit fluorescence emission: antimony (III), antimony (V), bismuth (III), cerium (III), copper (I), lead, tellurium (IV), thallium (I), tin (IV) and uranium (VI). Table 4 shows the colour of the fluorescence observed visually for these ions and the wavelengths of maximum excitation and emission.

The fluorescence emission of uranium (VI) in solution and boric acid glasses at room temperature is well-characterised in the literature and thus no examination was made of the emission which was observed in concentrated hydrochloric acid at -196°C. The emission observed from antimony (V) and copper (I) (in the presence of ascorbic acid reductant) was not very intense. The investigation of the analytical utility of low temperature spectrofluorimetric measurements at -196°C in hydrochloric acid was therefore restricted to the seven ions Sb(III), Bi(III), Ce(III), Pb, Te(IV), Tl(I) and Sn(IV).

TABLE 4

Ions found to fluoresce in 6M hydrochloric acid at -196°C

Ion	Colour of Fluorescence	Excitation Maximum, mμ.	Emission Maximum, mμ
Sb(III)	red	306	582
Sb(V)	faint red	390	580
Bi(III)	blue	330	410
Ce(III)	-	252	348
Cu(I)	green-blue	284	440
Pb	-	276	390
*Te(IV)	red	326	550
	red	380	586
Tl(I)	-	256	380
Sn(IV)	-	272	390
U(VI)	green	302	494 strong 514 strong 540 weak 565 weak

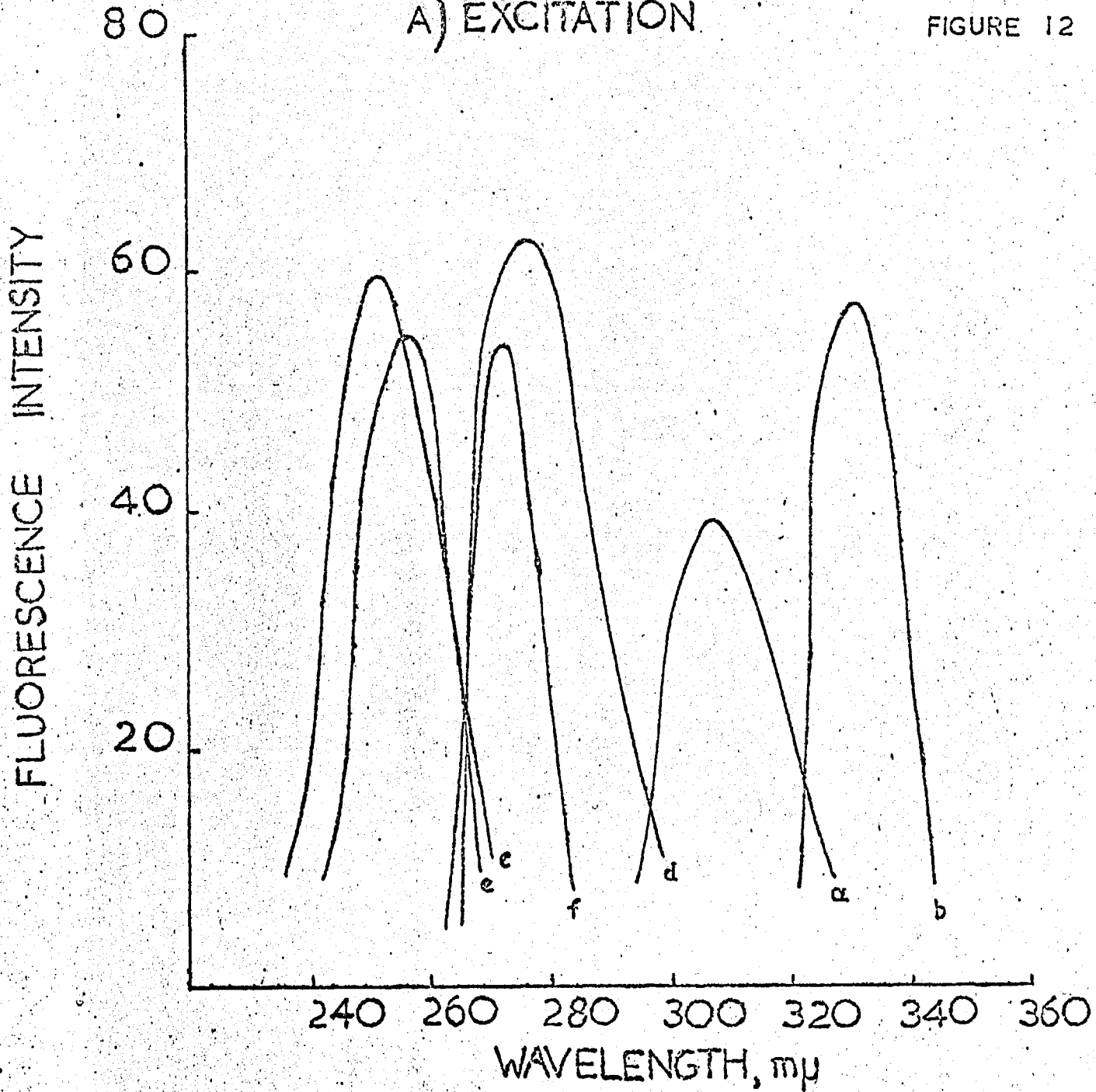
* Tellurium (IV) shows two different characteristic excitation and emission spectra depending on the concentration of hydrochloric acid employed. In 6M HCl excitation 326 mμ/emission 550 mμ, and above 8M excitation 380 mμ/emission 586 mμ.

Spectral Characteristics

Figure 12 shows the excitation and emission spectra for six of the seven most intensely fluorescent ions in 6M hydrochloric acid at -196°C. These spectra are uncorrected for variation in emission characteristics of the xenon arc lamp and response characteristics of the monochromators and the photomultiplier. Corrections of these spectra have been described by Chen[27]. Variation of the hydrochloric acid concentration between 6 and 10M produces no change in the wavelengths of maximum excitation and emission for the ions studied, with the exception of tellurium (IV).

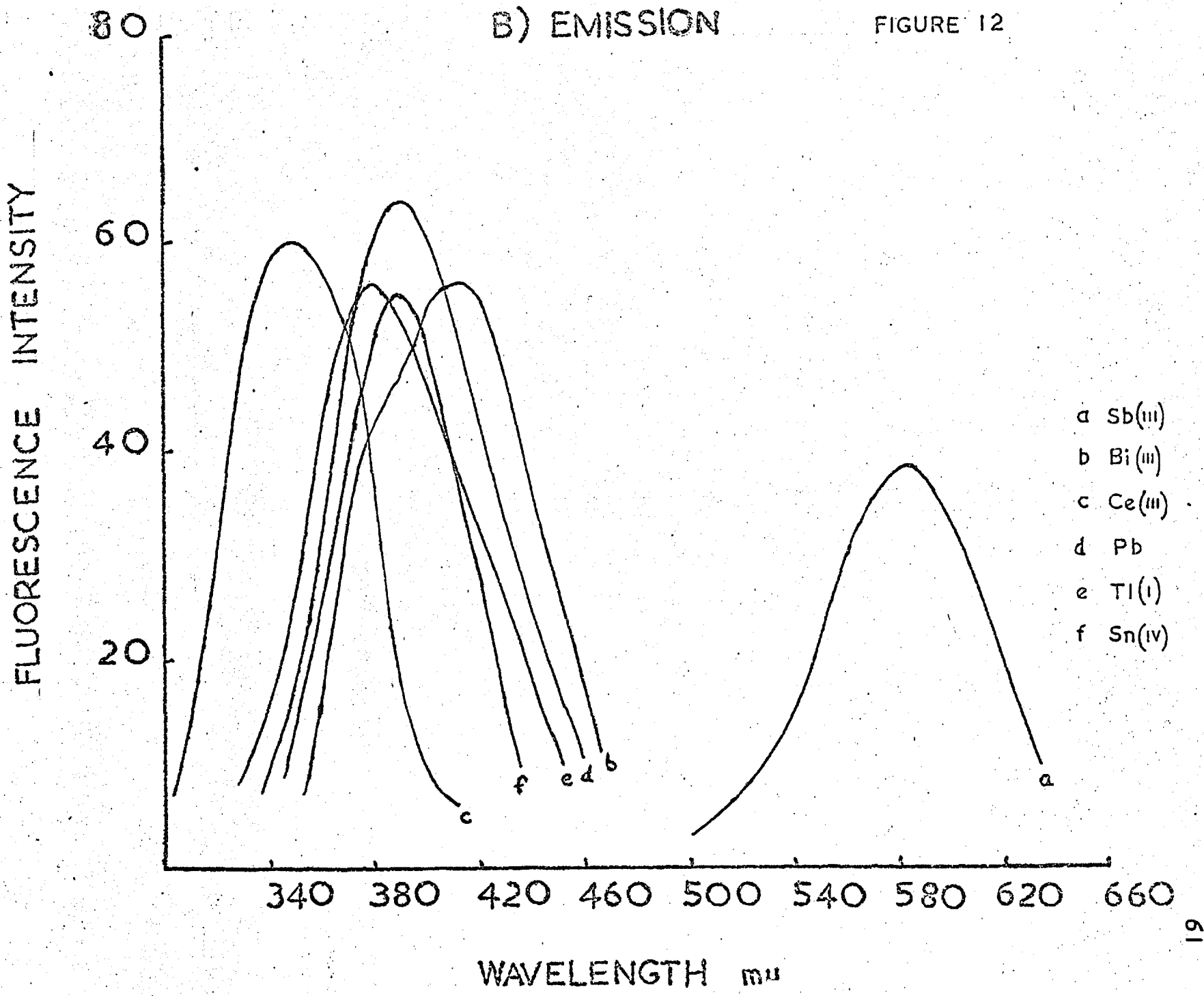
Effect of hydrochloric acid concentration

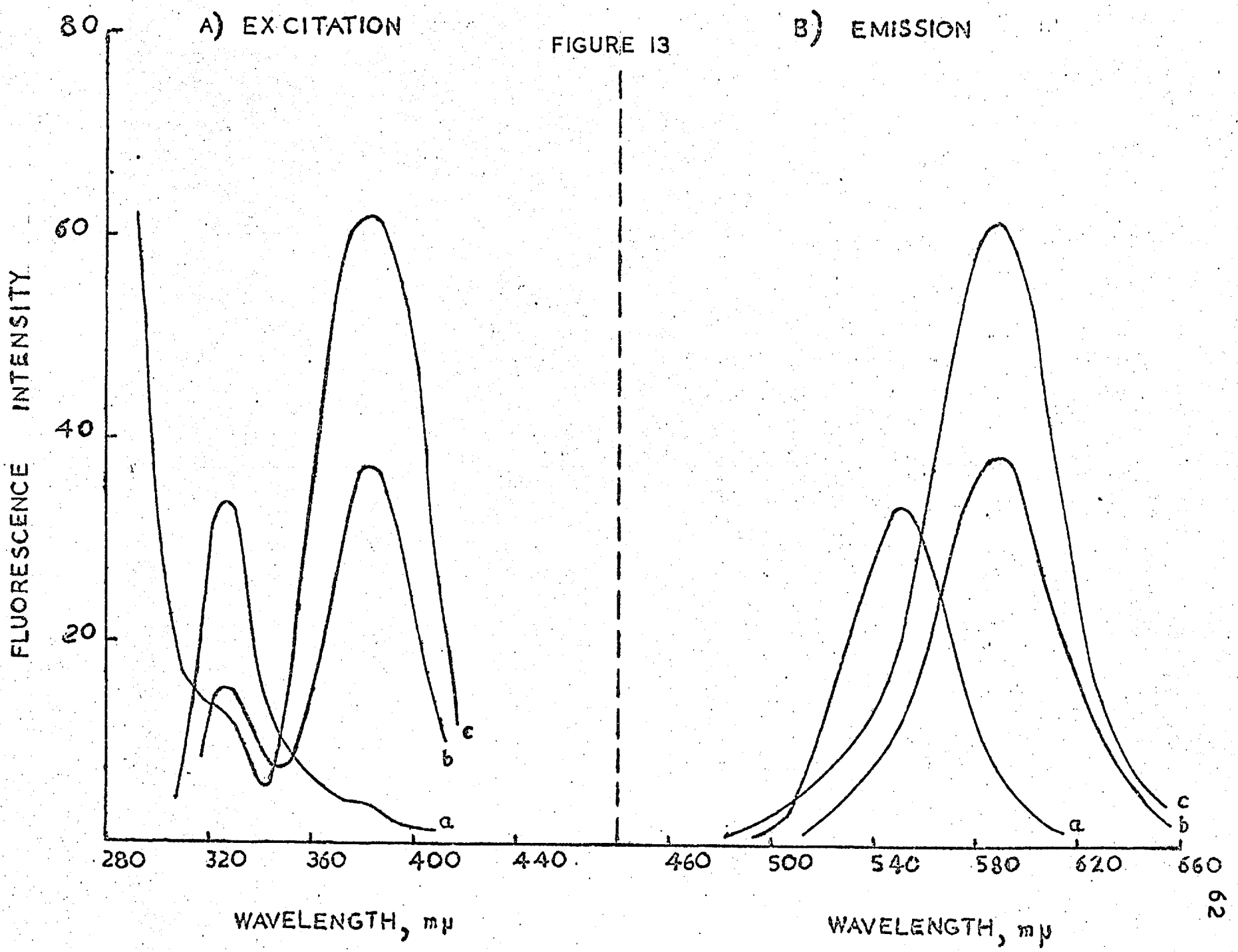
The wavelengths of excitation and emission for the fluorescence observed from tellurium (IV) are affected by the hydrochloric acid concentration. Figure 13 shows the excitation and emission spectra obtained at hydrochloric acid concentrations between 6 and 10M (a = 6M HCl, b = 8M HCl, c = 10M HCl). In 6M HCl the excitation spectrum shows a maximum at 326 mμ and a less intense peak at 380 mμ. Under these conditions the wavelength of maximum emission occurs at 550 mμ. When more concentrated hydrochloric acid solutions are used, the excitation maximum at 326 decreases, while that at 380 mμ increases. The wavelength of maximum emission moves to longer wavelength with increase in acid concentration, and in 10M hydrochloric acid occurs at 586 mμ.


A) EXCITATION
FIGURE 12
80
60
40
20
FLUORESCENCE INTENSITY
240
260
280
300
320
340
360
WAVELENGTH, mμ
a
b
c
d
e
f
a Sb(III)
b Bi(III)
c Ce(III)
d Pb
e Tl(I)
f Sn(IV)

B) EMISSION

FIGURE 12

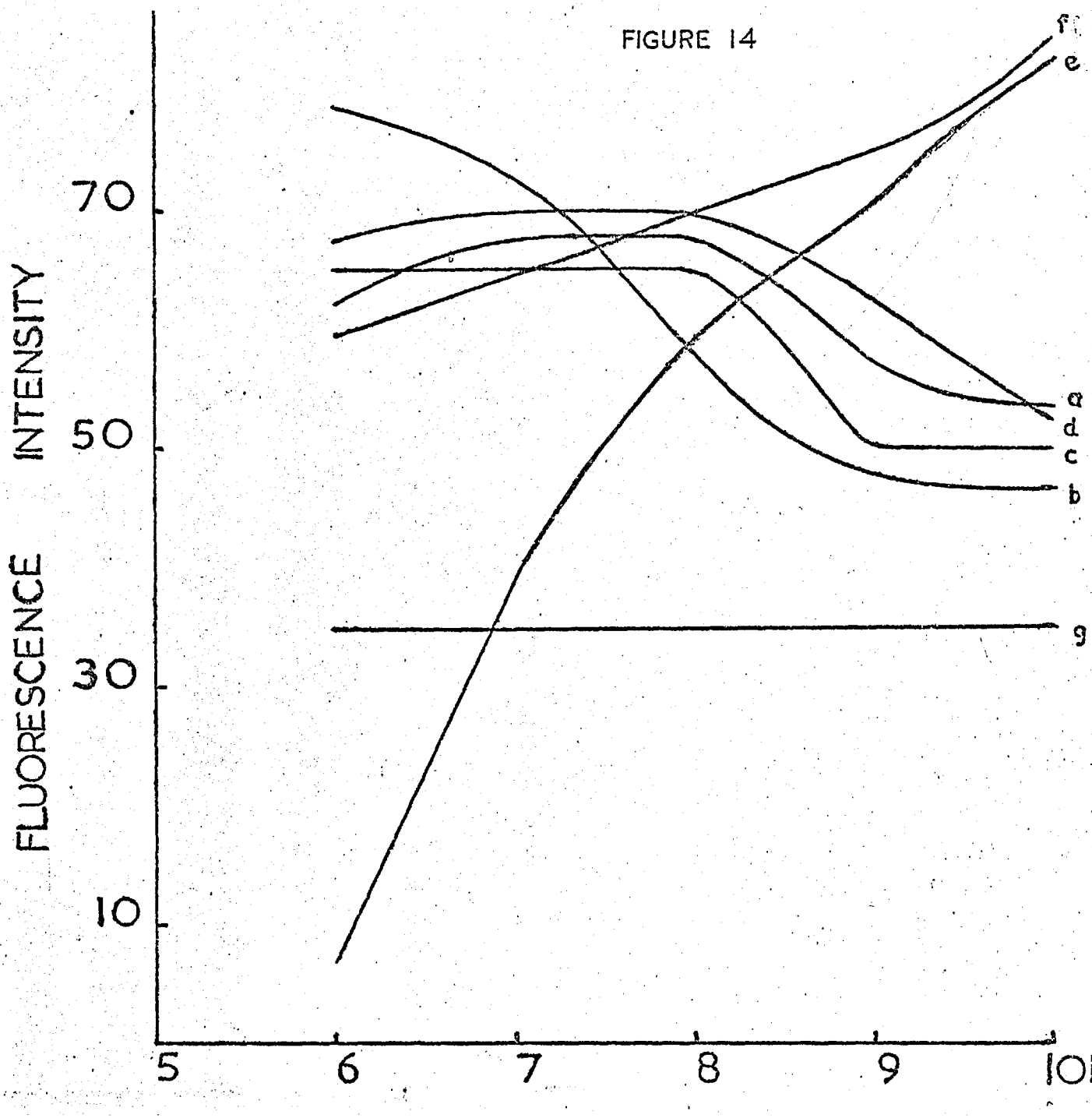



A) EXCITATION
B) EMISSION
FIGURE 13
FLUORESCENCE INTENSITY
80
60
40
20
280
320
360
400
440
460
500
540
580
620
660
WAVELENGTH, mμ
WAVELENGTH, mμ
a
b
c
a
b
c

These results suggest that the intense red fluorescence observed for tellurium (IV) is shown by two different tellurium complexes, and that the relative concentrations of these depend on the hydrochloric acid concentration. When the effect of additional chloride and hydronium ion on a 6M HCl solution of tellurium (IV) was investigated, it was found that by increasing the acidity (by addition of concentrated sulphuric acid) the *same* change in the absorption and emission spectra was produced. The addition of chloride to a 6M HCl solution of tellurium (IV), on the other hand, has no effect on the wavelengths of excitation and emission. These observations suggest that the two species present might be $TeCl_6^{2-}$ and $HTeCl_6^-$ or H_2TeCl_6.

As mentioned above, no change in the wavelengths of maximum excitation and emission occurs over the range 6-10M hydrochloric acid for Sb(III), Bi(III), Ce(III), Pb, Tl(I) and Sn(IV). The emission intensity, however, is somewhat affected, and Figure 14 shows the effect of HCl concentration on the fluorescence emission intensity at the optimum wavelengths of excitation and emission. The curve for tellurium reflects the increase in intensity at 380 mμ/586 mμ and decrease at 326 mμ/550 mμ corresponding to the change in relative proportions of the two chlorocomplexes present. The tellurium complex formed at high HCl concentrations is also much more intensely fluorescent than that present at lower acidity, and consequently measurement of the

FIGURE 14



a Sb(III)
b Bi(III)
c Ce(III)
d Pb
e Te(IV)
f Tl(I)
g Sn(IV)

fluorescence of this species gives higher sensitivity in analytical work.

Effect of time on fluorescence emission

The effect of time on the intensity of the fluorescence of the seven ions studied was investigated at their optimal hydrochloric acid concentrations:

(a) when the solution was stored in darkness for 2 hours,

(b) when the solution was allowed to stand under normal laboratory conditions (fluorescent strip lighting) for 2 hours,

(c) on continuous irradiation of the solution in the spectrofluorimeter for 1 hour.

The results are shown in Table 5. The fluorescence of the chloro-complexes is quite stable, certainly over the time (1-2 minutes) required for measurement of the fluorescence emission intensity of sample solutions. Continuous irradiation of the thallium (I) solution for one hour causes a reduction in fluorescence intensity of 60%, probably due to oxidation of thallium (I) to thallium (III)[18].

Calibration curves and sensitivity

Under optimum conditions the graph of fluorescence intensity *vs.* concentration is linear for each ion studied. Table 6 shows the concentration range for each ion over which this linearity

TABLE 5

Effect of Time on Fluorescence Emission Intensities

Solution	Reduction in Fluorescence Intensity, %		
	Standing in Darkness (2 hr)	Under Laboratory Lighting (2 hr)	Continuous Irradiation (1 hr)
10^{-5}M Sb(III) in 7M HCl	not detectable	not detectable	5
10^{-7}M Bi(III) in 6M HCl	7.5	14	10
10^{-5}M Ce(III) in 7M HCl	not detectable	not detectable	13
10^{-6}M Pb in 7M HCl	not detectable	6	4
10^{-6}M Te(IV) in 10M HCl	3	6	5
10^{-5}M Tl(I) in 10M HCl	4	7	60
10^{-3}M Sn(IV) in 7M HCl	8	8	3

TABLE 6

Element	Concentration range of calibration curve
Sb(III) in 7M HCl	10^{-6}M - 10^{-5}M
Bi(III) in 6M HCl	10^{-8}M - 5×10^{-8}M
Ce(III) in 7M HCl	10^{-7}M - 10^{-6}M
Pb in 7M *HCl	10^{-8}M - 10^{-7}M
Te(IV) in 10M *HCl	10^{-7}M - 10^{-6}M
Tl(I) in 10M HCl	10^{-6}M - 8×10^{-6}M
Sn(IV) in 7M HCl	10^{-4}M - 10^{-3}M

* B.D.H. Aristar HCl

was confirmed. No attempt was made to establish the upper range of linearity by working at a lower gain setting. The lower concentration limits of these calibration graphs represent a realistic detection limit (signal: noise = 1) for the fluorescence of the element above the background blank for the hydrochloric acid employed. Thus even the trace impurities in the best available hydrochloric acid affect the available sensitivity. The thick-walled silica tubing also exhibits a slight "blank" fluorescence. The characteristics of this emission are similar to those of the lead, thallium and tin fluorescence, and consequently this blank limits the sensitivity for these elements. As only 0.5 ml. of

sample solution is required, the absolute detection limits are Sb(III), 0.06 μg; Bi(III), 0.001 μg; Ce(III), 0.007 μg; Pb, 0.001 μg; Te(IV), 0.006 μg; Tl(I), 0.1 μg; Sn(IV), 6 μg.

Conclusion.

Bismuth (III), tellurium (IV) and antimony(III) do not show fluorescence in HCl at room temperature. Although fluorescence has been observed from tin (II) in hydrochloric acid at room temperature[18], tin (IV) does not appear to fluoresce under these conditions. At -196°C, however, tin (IV) shows fluorescence emission (although not strikingly intense), whereas no fluorescence emission has been detected from tin (II). With the experimental arrangement used by the author, thallium (I), cerium and lead show much increased fluorescence intensity (5, 50 and 1000-fold respectively) at -196°C compared to that obtainable under otherwise similar conditions at room temperature.

Although the chloro-complexes of the ions examined exhibit relatively broad fluorescence emission spectra at -196°C, the half-intensity widths of the corresponding excitation spectra are relatively narrow. The intense fluorescence emission of the seven elements examined in detail provides very sensitive methods for their determination. Owing to the separation of the excitation and emission maxima, it is possible to determine several of these elements simultaneously by selection of suitable excitation and emission wavelengths.

Chapter IV

Low Temperature Fluorescence of Some Bromide Ion-Association Complexes in Hydrobromic Acid Glasses at -196°C

The utilisation of increased intensity of fluorescence at low temperatures for the determination of lead[57] and thallium[58] by a frontal illumination technique has been mentioned in the previous chapter. Several inorganic acids which form clear glasses at the temperature at which liquid nitrogen boils under atmospheric pressure (-196°C) have been examined to assess their suitability as media for low temperature fluorescence employing the conventional right-angle excitation-fluorescence system. Both hydrochloric and hydrobromic acids form suitable glasses and give ion-association complexes with several metals which fluoresce strongly at this temperature. The behaviour of the hydrochloric acid system has been discussed previously.

This chapter presents the results of a continuation of the author's investigations and a study of the fluorescence emission characteristics of ions of 58 elements in hydrobromic acid at -196°C. Strong fluorescence signals were obtained for antimony (III) and (V), arsenic (III) and (V), bismuth, cerium (III), copper (I), lead, tellurium (IV), thallium (I), tin (II) and uranium (VI).

Apparatus

Aminco-Bowman Spectrofluorimeter (American Instrument Co.) and low temperature attachment as described in "Introduction". Sample tubes were made from precision bore transparent silica tubing (Jencons Ltd., Hemel Hempstead, England) of length 20 cm, internal diameter 3mm, and wall thickness 1mm. A sample volume of 0.5 ml. is enough to fill these tubes to a sufficient depth for use in the instrument. Excitation and emission spectra were recorded on an XY recorder (Bryans Ltd., Mitcham, England). 3 mm slits corresponding to ca. 30 mμ band pass were used in both monochromators.

The absorption spectra of As(III) and As(V) in hydrobromic acid were recorded using a Unicam SP.800A Ultraviolet Spectrophotometer (Unicam Instruments Ltd., Cambridge, England), and 1 cm quartz cells.

Reagents

Hydrobromic Acid: redistilled 48% general-purpose HBr (Hopkin and Williams Ltd., Chadwell Heath, Essex, U.K.). The hydrobromic acid, when not redistilled, exhibited a faint blue fluorescence at -196°C whereas the distilled acid showed virtually none.

Metal Salts: 10^{-2}M aqueous stock solutions of analytical reagent grade antimony potassium tartrate, arsenious oxide, bismuth nitrate, copper sulphate, lead nitrate, sodium arsenate, stannous chloride,

thallous sulphate and uranyl nitrate. Tellurium metal (Johnson and Matthey, Specpure), cerous nitrate (BDH, Laboratory reagent grade) and antimony pentoxide (Hopkin and Williams) were used as starting materials for the remaining ions which showed strong fluorescence.

The other ions which exhibited no fluorescence were prepared from the purest materials available.

Results and Discussion

A general survey of 58 elements was made by preparing a 10^{-3}M solution of the element in 6M hydrobromic acid solution. A 0.5 ml. aliquot of each was placed in a silica tube and the latter was cooled by immersing it in liquid nitrogen in the micro Dewar flask of the spectrofluorimeter. The glass thus produced was examined visually in the screening tests by placing it under a mercury vapour discharge lamp and observing any fluorescence. The Dewar flask was then transferred to the spectrofluorimeter and the fluorescence signal was examined instrumentally by scanning each monochromator in turn whilst maintaining the other fixed at a suitable position on the wavelength scale.

Under these conditions no fluorescence signal was observed for 46 of the elements examined viz. aluminium, barium, beryllium, cadmium, calcium, cerium (IV), chromium (III), cobalt, copper (II), dysprosium, erbium, europium, gadolinium, gallium, gold, holmium,

indium, lanthanum, lutetium, magnesium, manganese (II), mercury (II), molybdenum (VI), neodymium, nickel, niobium, palladium (II), praseodymium, ruthenium, samarium, scandium, selenium (IV), silver, strontium, tantalum, terbium, thorium, thulium, tin (IV), titanium (III), titanium (IV), vanadium (V), ytterbium, yttrium, zinc and zirconium.

Fluorescence emissions were observed for 12 ions viz. antimony (III), antimony (V), arsenic (III), arsenic (V), bismuth, cerium (III), copper (I), lead, tellurium (IV), thallium (I), tin (II) and uranium (VI). Table 7 shows the visually observed fluorescence colours for these ions and the instrumentally recorded maxima for excitation and fluorescence. These maxima are uncorrected for instrumental parameters such as diffraction grating efficiency at varying wavelengths, detector response and source emission intensity.

The wavelengths of maximal excitation and emission for Te(IV) in hydrobromic acid are independent of the concentration of the latter. This is in marked contrast to the behaviour in hydrochloric acid where the dependence is quite pronounced (see Chapter III). The intensity of Te(IV) fluorescence is much weaker in HBr than in HCl. The fluorescence of copper (I) in hydrobromic acid is also very weak. For this reason the study of the analytical utility of low temperature fluorescence of bromo ion-association complexes in hydrobromic acid was confined to the remaining ten ions.

TABLE 7

Ions found to fluoresce in 6M hydrobromic acid at -196°C

Ion	Colour of Fluorescence	Excitation Maximum, mμ	Emission Maximum, mμ
Sb(III)	red	360	586
Sb(V)	red	360	586
As(III)	faint red	356	584
As(V)	faint red	356	566
Bi(III)	blue	378	450
Ce(III)	-	250	350
Cu(I)	faint blue	286	434
Pb	blue	304	414
Te(IV)	faint red	352	560
Tl(I)	-	270	410
Sn(II)	orange	314	550
U(VI)	green	327	494 strong
			516 strong
			540 weak
			565 weak

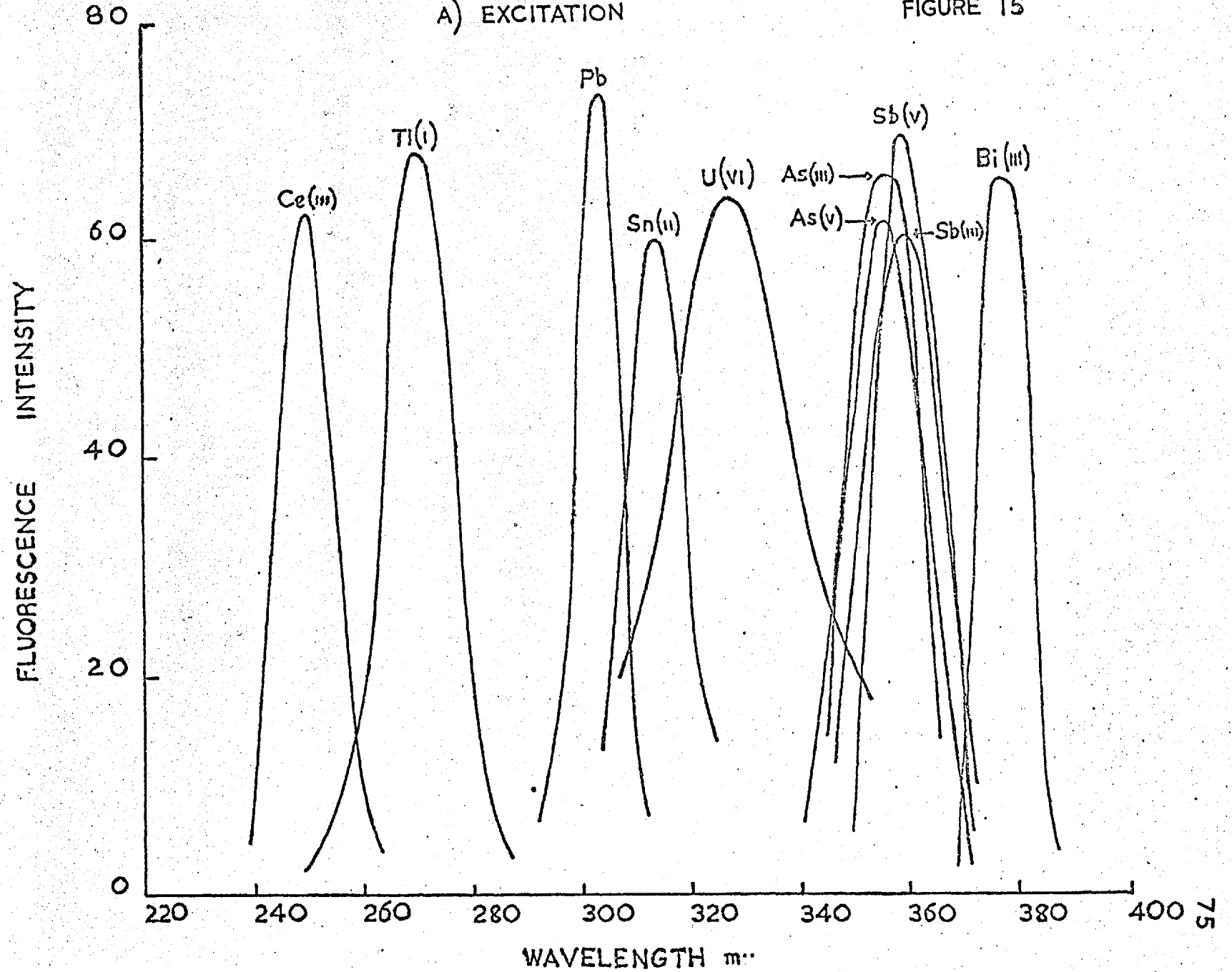
Spectral Characteristics

Figure 15 shows the excitation and emission spectra of the ten ions in 6M HBr at -196°C. These spectra are uncorrected for variations in detector sensitivity, lamp emission or grating transmission against wavelength. The relevant correction methods appear elsewhere.[27]

Hydrobromic Acid Concentration

Variation of the hydrobromic acid concentration between 6 and 9M did not affect the wavelengths of maximal excitation or fluorescence in any way for antimony (III) or (V), arsenic (III) or (V), bismuth (III), cerium (III), lead, thallium (I) and tin (II). With uranium (VI) the maximal wavelength of excitation increases steadily from 327 mμ in 6M HBr to 345 mμ in 9M HBr. The wavelength of maximal-fluorescence does not alter with acidity in this region. However, whilst the wavelengths of maximal fluorescence do not change with acidity, the intensities of fluorescence are affected. Figure 16 shows the effect of hydrobromic acid concentration on the intensity of fluorescence of the various ions under optimised conditions.

It was further observed that variation of hydrobromic acid concentration affects the colour of the solutions of certain ions e.g. arsenic (V). A solution of arsenic (V) in 6M HBr is light yellow


A) EXCITATION
FIGURE 15
80
60
40
20
0
FLUORESCENCE INTENSITY
Ce(III)
Tl(I)
Pb
Sn(II)
U(VI)
As(III)
As(V)
Sb(V)
Sb(III)
Bi(III)
220
240
260
280
300
320
340
360
380
400
WAVELENGTH m··
75

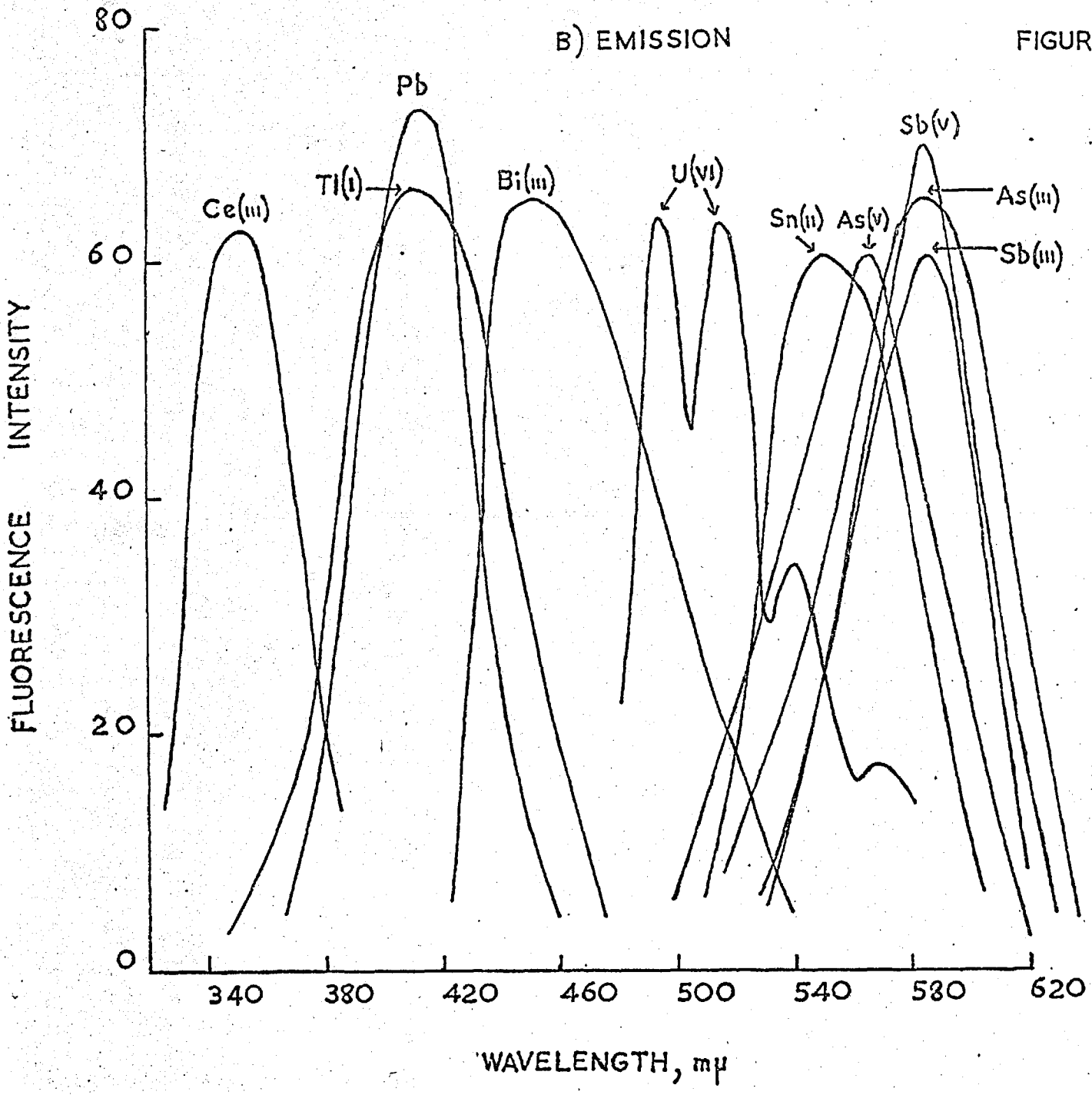
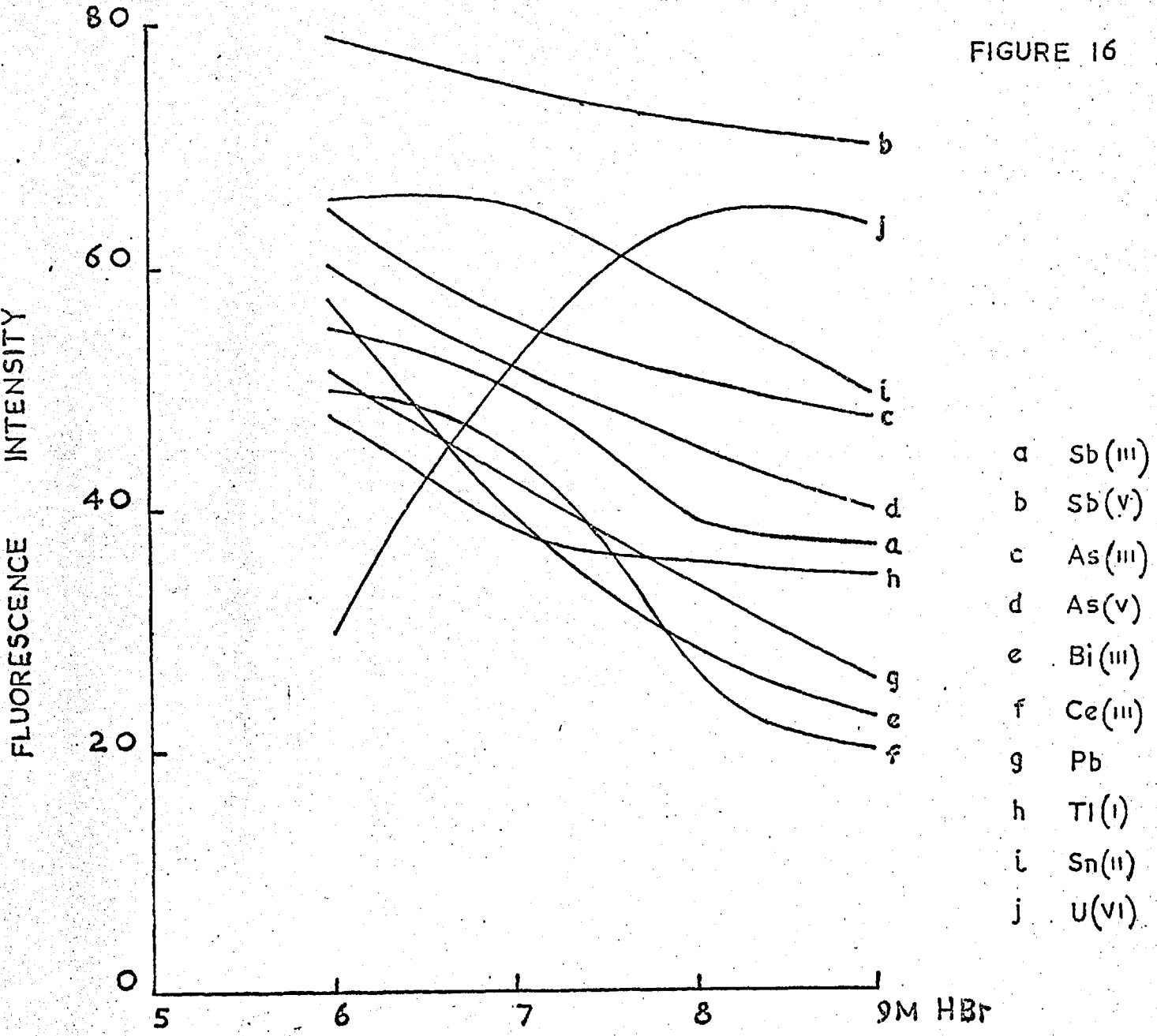

B) EMISSION
FIGURE 15
80
60
40
20
0
FLUORESCENCE INTENSITY
Ce(III)
Tl(I)
Pb
Bi(III)
U(VI)
Sn(II)
As(V)
Sb(V)
As(III)
Sb(III)
340
380
420
460
500
540
580
620
WAVELENGTH, mμ

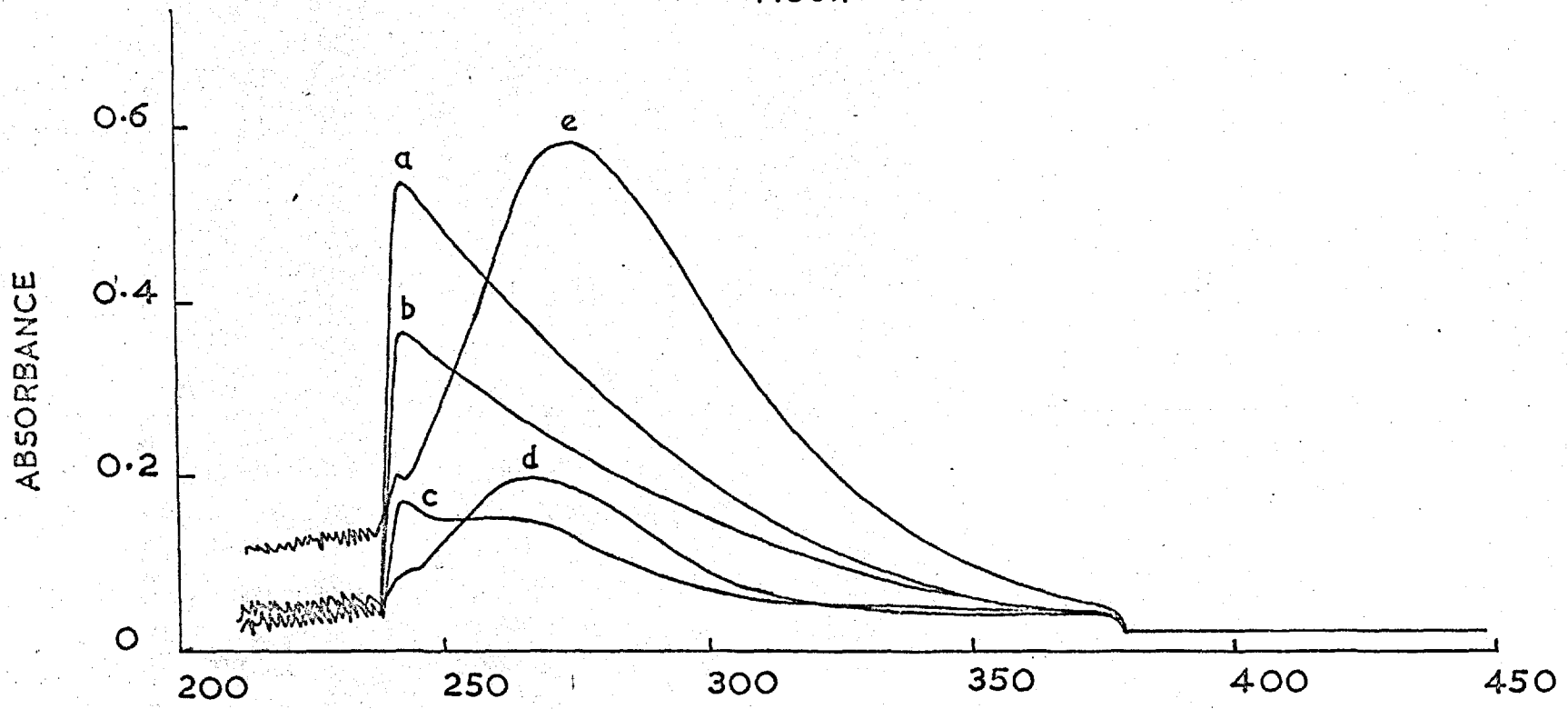
FIGURE 16


80
60
40
20
0
FLUORESCENCE INTENSITY
5
6
7
8
9M HBr
b
j
i
c
d
a
h
g
e
f
a Sb(III)
b Sb(V)
c As(III)
d As(V)
e Bi(III)
f Ce(III)
g Pb
h Tl(I)
i Sn(II)
j U(VI)

while
a similar solution in 9M HBr is deep yellow. On the other hand, solutions of arsenic (III) in 6-9M HBr are not coloured. Arsenic (V) bromo-complex may be yellow in colour, but these visual observations also may suggest the possibility of reduction of arsenic (V) to arsenic (III) in hydrobromic acid solution with corresponding release of bromine and a fluorescence from arsenic (III) bromo-complex. The spectral characteristics of the fluorescence emission observed from arsenic (III) and arsenic (V) samples in hydrobromic acid glass are very similar. Consequently, to confirm the valency state of arsenic which is responsible for the fluorescence from solutions containing arsenic (V) in hydrobromic acid, the absorption characteristics of arsenic (III) and (V) in hydrobromic acid were examined over the range 200-450 mμ. Figure 17 shows the absorption spectra for these ions and bromine in 6M HBr recorded against 6M HBr as blank. Although the absorption spectra for arsenic (V) and bromine in HBr are very similar, the wavelengths of maximum absorption being 268 mμ and 272 mμ, respectively, both spectra differ completely from the spectrum of the arsenic (III) ion which suggests that the arsenic (V) ion exists in 6M HBr.

The absorption maximum for the arsenic (III) bromo-complex in HBr occurs below 245 mμ but is not shown in the figure since the spectrophotometer used for recording these spectra is insensitive below this region. The arsenic (III) spectra clearly show, however, that the arsenic (III) peak decreases with gradual addition of

FIGURE 17



a 10^{-4} M As(III) in 6M HBr
b (a) + 1 drop bromine water
c (a) + 2 drops bromine water
d 10^{-4} M As(V) in 6M HBr
e Bromine in 6M HBr

bromine to identical solutions of arsenic (III) in 6M HBr. At the same time a shoulder at approximately 268 mμ (the absorption peak for arsenic (V)) starts to build up. This experimental evidence appears to indicate that in hydrobromic acid solution arsenic (III) is oxidised to arsenic (V) on addition of bromine, and that arsenic (V) is stable under these conditions. The fluorescence emission observed from arsenic (V) in hydrobromic acid glass may, therefore, be attributed to the arsenic (V) bromo-complex.

Effect of time on fluorescence emission

The effect of time on fluorescence intensity was studied under optimised conditions of excitation, acidity etc., for the various ions by:-

(a) Allowing the solution to stand in darkness for 2 hours.

(b) Allowing the solution to stand under normal laboratory conditions (fluorescent strip-lighting) for 2 hours.

(c) Allowing the solution to be irradiated continuously in the spectrofluorimeter cell for 1 hour.

These experiments, cf. Table 8 revealed that the only detectable difference occurred with thallium (I) standing under normal laboratory fluorescent lighting for 2 hours. In this instance the fluorescence was almost completely destroyed probably due to oxidation of Tl(I) to Tl(III).[18]

TABLE 8

Effect of Time on Fluorescence Emission Intensities

Solution (in 6MHBr)	Reduction in fluorescence intensity %		
	Standing in darkness (2 hrs.)	Under laboratory lighting (2 hrs.)	Continuous irradiation (1 hr.)
10^{-6}M Sb(III)	not detectable	not detectable	4
10^{-6}M Sb(V)	4	5	not detectable
10^{-4}M As(III)	not detectable	not detectable	not detectable
10^{-4}M As(V)	3	4	not detectable
10^{-6}M Bi(III)	4	12	4
3×10^{-6}M Ce(III)	2	10	7
10^{-6}M Pb	not detectable	not detectable	2
10^{-5}M Tl(I)	33	90	25
10^{-5}M Sn(II)	not detectable	not detectable	not detectable
3×10^{-6}M U(VI) (in 8M HBr)	not detectable	not detectable	2

Analytical Calibration Curves

Table 9 shows the range of linearity of analytical curves for each of the ten elements under the appropriately optimised conditions. No attempt was made to establish the upper limit of linearity. The limit of detection, defined as the concentration in μg/ml, required to produce a signal:noise ratio of unity is given in column 3. Because only 0.5 ml. samples were used to produce the frozen glass, the absolute detection limits are as follows:-

Sb(III), 6×10^{-4} μg; Sb(V), 6×10^{-3} μg; As(III), 3.7×10^{-1} μg; As(V), 7.5×10^{-1} μg; Bi, 6×10^{-3} μg; Ce(III), 5.6×10^{-2} μg; Pb, 2×10^{-3} μg; Tl(I), 2×10^{-1} μg; Sn(II), 1.2×10^{-1} μg; U(VI), 7×10^{-2} μg.

Even with redistilled hydrobromic acid, a slight background fluorescence is obtained at the highest instrumental sensitivities. The thick-walled silica tubing itself exhibits a slight blank fluorescence at these settings.

Conclusion

With the exception of tin (IV), all the elements which exhibit fluorescence as chloro-complexes in hydrochloric acid glasses at -196°C also exhibit fluorescence in hydrobromic acid glasses. Tin (II), which exhibits no fluorescence in HCl glass, exhibits strong fluorescence in hydrobromic acid. This permits tin to be determined in HBr down to 0.12 μg as Sn(II), whereas in HCl the limit

TABLE 9

Ion (in 6M HBr)	Concentration range of calibration curve	Limit of detection(μg/ml.)
Sb(III)	10^{-8}M → 10^{-7}M	0.0012
*Sb(V)	10^{-7}M → 10^{-6}M	0.012
As(III)	10^{-5}M → 10^{-4}M	0.75
As(V)	2×10^{-5}M → 10^{-4}M	1.50
Bi(III)	6×10^{-8}M → 3×10^{-7}M	0.012
Ce(III)	8×10^{-7}M → 10^{-5}M	0.112
Pb	2×10^{-8}M → 4×10^{-7}M	0.004
Tl(I)	2×10^{-6}M → 10^{-5}M	0.40
Sn(II)	2×10^{-6}M → 10^{-5}M	0.24
U(VI)in 8M HBr	6×10^{-7}M → 4×10^{-6}M	0.14

* This detection limit is only approximate as the salt used in the investigation is of approximate composition.

is 6 μg as Sn(IV). The detection limits obtained for antimony both as antimony (V) and antimony (III) are 10 and 100 times lower respectively in HBr than in HCl, where only antimony (III) fluoresces appreciably (detection limit 6 x 10^{-2} μg). As(III) and (V), which exhibit no fluorescence in HCl glass, fluoresce strongly in HBr at -196°C.

A comparison of the detection limits in HCl (see Chapter III) and HBr glasses shows that the former medium is more sensitive for Bi, Ce(III), Pb, Tl(I) and Te(IV). Lastly, it may be mentioned that because of the good separation between excitation and emission maxima it is possible to determine several of these elements simultaneously by suitable choice of excitation and emission wavelengths.

CHAPTER V

The Determination of Trace Amounts of Tellurium by Inorganic Spectrofluorimetry at Liquid Nitrogen Temperature

The increase in the industrial usage of tellurium, especially in semiconductor technology, creates new problems in the development of rapid and accurate methods for the determination of traces of the element in various materials e.g. semiconductors, steels, alloys, etc. The determination of traces of tellurium by absorption spectrophotometry of elementary tellurium as a hydrosol is complicated by the dependence of the spectral characteristics and sensitivity upon size and geometric characteristics of sol particles.[59] Spectrophotometric methods employing the reagents thiourea,[60] diethyldithiocarbamate,[61] bismuthiol II[62,63] and thioglycollic acid[64] have been proposed as well as others based on the absorption of light by the coloured halogeno-complexes of tellurium.[65,66,67] These methods are often unselective. The determination of tellurium in arsenic by solution spectrofluorimetry of the ion-association complex between butylrhodamine and the anionic tellurium bromide complex after preliminary extraction of tellurium with sodium diethyldithiocarbamate has been reported.[68] Bismuth, indium and thallium interfere.

In earlier chapters the author has reported that tellurium (IV) in strong hydrochloric acid medium at -196°C exhibits intense

fluorescence emission while the fluorescence emission in hydrobromic acid glass is comparatively weak. The present chapter describes a simple, selective method for the determination of tellurium in the range 0.02-0.64 ppm. utilising the red fluorescence of the chloro-complex of tellurium (IV) in hydrochloric acid at liquid nitrogen temperature (-196°C). The fluorescence emission is measured at 586 mμ with an excitation wavelength of 380 mμ. Optimum conditions have been established for the determination and the potential interference of 50 ions has been investigated. Because large amounts of lead do not interfere, the present method may be applied to the determination of traces of tellurium in lead.

EXPERIMENTAL

Apparatus

Fluorescence measurements were made with an Aminco-Bowman spectrofluorimeter using slits giving ca. 30 mμ bandwidth in both monochromators. The usual precision bore transparent silica sample tubes (Jencons Ltd., Hemel Hempstead, England) were employed. A sample volume of 0.5 ml. is sufficient to fill these tubes for quantitative measurements in the spectrofluorimeter.

Reagents

Tellurium (IV) solution (10^{-2}M). Dissolve 1.276 g of chemically refined tellurium powder (Johnson, Matthey and Co., Ltd.) in

10 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid. Warm gently to aid dissolution and heat to expel brown fumes. Cool the solution, transfer to a 1-litre volumetric flask and add sufficient concentrated hydrochloric acid to make the final acidity approximately 1M with respect to acid. Dilute to volume with distilled water. This stock solution was diluted to 10^{-4}M with 1M hydrochloric acid as required.

Lead (II) solution. A 10^{-1}M lead stock solution was prepared from lead nitrate (Analar).

Hydrochloric acid. "Aristar" grade, British Drug Houses.

Diverse ions. 0.1M or 0.01M solutions of analytical-reagent grade salts were used. All other reagents were analytical reagent grade.

Construction of Calibration Curve

Transfer accurately between 0.05 and 1.25 ml. of 10^{-4}M tellurium (IV) solution (10^{-4}M ≡ 12.76 µg/ml) to 25 ml. volumetric flasks. Add 20 ml. of concentrated hydrochloric acid and dilute to volume with water from an all-glass distillation apparatus. After 10 minutes measure the intensity of the fluorescence of the solution at -196°C at 586 mµ, using an excitation wavelength of 380 mµ. The plot of fluorescence intensity against tellurium concentration (0.02-0.64 ppm) is a straight line and passes above the

origin due to the fluorescence of the hydrochloric acid reagent blank. The linearity of the calibration curve beyond 16 µg of tellurium was not examined.

Prepare and measure a blank and a 0.64 ppm standard with each group of samples.

Results

Spectral Characteristics

The wavelengths of maximal excitation and emission for tellurium (IV) in hydrochloric acid are dependent on the concentration of the latter.[31] Figure 13 shows the excitation and emission spectra obtained at hydrochloric acid concentrations between 6 and 10M (a = 6M HCl, b = 8M HCl, c = 10M HCl). These spectra are uncorrected for variations in the emission characteristics of the lamp, monochromator response and detector sensitivity. The relevant correction curves appear elsewhere.[27]

Effect of hydrochloric acid concentration and time on fluorescence intensity

In 6M HCl, the excitation spectrum for the tellurium (IV) chloro-complex shows a maximum at 326 mµ and a small peak at 380 mµ. At this acidity, the fluorescence emission maximum occurs at 550 mµ. With increase in hydrochloric acid concentration, the excitation maximum at 326 mµ decreases with accompanying increase in the maximum at 380 mµ. The emission maximum is moved to longer

wavelength with increasing acid concentration and in 9M HCl occurs at 586 mμ. It seems probable that two different tellurium chloro-complexes, whose relative concentrations depend on the hydrochloric acid concentration, are responsible for the fluorescence emission.[31] The tellurium complex formed at high hydrochloric acid concentration is much more intensely fluorescent than that found at lower acidity. Consequently, all quantitative determinations of tellurium were made in 9M hydrochloric acid solution utilising an excitation wavelength of 380 mμ and an emission wavelength of 586 mμ.

A 10^{-6}M solution of tellurium (IV) prepared by the recommended procedure showed an average reduction in fluorescence intensity of 3% and 6% after standing for 2 hours in darkness and under normal laboratory fluorescent lighting, respectively. The fluorescence is thus stable over the period normally required for its measurement.

Precision

The combined chemical and instrumental precision was determined by multiple measurements of the fluorescence of dilute tellurium solutions (0.13 ppm). The standard deviation indicated an overall precision of 2.2% for low concentrations.

Effect of Foreign Ions

The effects of a 50-fold weight excess of 50 foreign ions

on the determination of 16 μg of tellurium were investigated. An acceptable variation of fluorescence intensity from that of standard solutions was taken as $\leq 5\%$. Under these conditions, aluminium, antimony (III), arsenic (III), arsenic (V), barium, beryllium, bismuth, cadmium, calcium, cerium (III), cerium (IV), chromium (III), cobalt (II), copper (I), copper (II), gallium, germanium, gold, lanthanum, lead, magnesium, manganese (II), mercury (II), molybdenum (VI), nickel, niobium, palladium (II), platinum (IV), potassium, selenium (IV), silver, sodium, strontium, tantalum, thallium (I), thorium, tin (IV), titanium (IV), tungsten (VI), vanadium (V), zinc, zirconium, bromide, nitrate, phosphate, sulphate and sulphite do not interfere. Iron (III) and iodide which form very strong, yellow-coloured solutions, cause serious errors by absorption of the incident radiation. Tin (II) interferes by reducing tellurium (IV) to elemental tellurium. The interference of tin (II) may be eliminated by preliminary oxidation. The interference from iron (III) cannot be removed by reduction to iron (II) but a negative error of less than 5% was obtained when a 5-fold weight excess of iron (III) is present. However, tellurium may be separated from larger amounts of iron before application of the procedure either by extraction of tellurium thioglycollate into ethyl acetate[64] or by extraction of tellurium diethyldithiocarbamate in the presence of masking agents into carbon tetrachloride.[69]

Accuracy

The results of analyses of solutions for tellurium by the recommended procedure (see Experimental) are shown in Table 10. For the analysis of tellurium in lead samples, synthetic solutions of lead to which traces of tellurium had been added were employed. The results of three analyses are shown in the same table, and indicate the feasibility of application of the method to the determination of small amounts (down to ca. 0.03%) of tellurium in lead.

Conclusion

The method described for the determination of tellurium is rapid and sensitive and demonstrates the analytical application of inorganic spectrofluorimetry at low temperatures. The small sample volume required gives rise to a very high absolute sensitivity. Thus the absolute lower limit of determination of tellurium in the recommended procedure is 10^{-2} µg. The detection limit for tellurium, however, based on a fluorescence signal to noise and detector noise ratio of unity, is somewhat lower (ca. 6×10^{-3} µg Te).[31] The sensitivity of detection of the red fluorescence of the tellurium (IV) complex may be increased further by special selection of a photomultiplier tube for the spectrofluorimeter whose spectral sensitivity in the red region at 586 mµ is greater than that of the RCA IP 28 tube fitted in the instrument employed in this

Table 10

Analysis of Tellurium (IV) solutions treated as unknown samples

Sample	Tellurium		Error		Foreign ions
	Present, μg	Found, μg	μg	%	μg
1	12.76	12.38	-0.38	-2.9	V(V)(800)
2	15.31	14.04	-1.27	-8.3	As(III)(800)
3	2.55	2.68	+0.13	+5.0	Sb(III)(600)
4	3.19	3.44	+0.25	+7.9	Bi(III)(800)
5	1.53	1.40	-0.13	-8.4	Cu(II)(160)
6	1.91	1.90	-0.01	-0.6	Pb(828)
7	2.81	2.68	-0.13	-4.6	Cu(II)(160) Pb(828)
8	3.19	3.32	+0.13	+4.1	Ce(III)(1400) Be(900)
9	0.64	0.60	-0.04	-6.2	Mg(486) Ba(410)
10	6.38	6.76	+0.38	+5.9	Sn(IV)(950) Sb(III)(852)
11	1.53	1.40	-0.13	-8.5	Se(IV)(150) Cu(II)(160)
12	0.89	0.83	-0.06	-6.7	Co(II)(100) Ni(117)
13	1.21	1.15	-0.06	-5.2	Mn(II)(200) Bi(III)(209)
14	4.47	4.59	+0.12	+2.7	Cr(III)(806) Tl(I)(1020)
15	1.15	1.21	+0.06	+5.2	Ag(540) Se(IV)(150)
16	2.30	2.42	+0.12	+5.2	Cu(II) (310) Hg(II)(1003)
17	3.19	3.51	+0.32	+10.0	Pb(6380)
18	7.02	7.66	+0.64	+9.1	Pb(17,500)
19	1.78	1.92	+0.14	+7.9	Pb(2625)

study. The determination of tellurium by the procedure recommended here is highly selective. The high selectivity results largely from the spectral characteristics of the tellurium (IV) chloro-complex. Thus the wavelengths of maximum excitation (380 mμ) and emission (586 mμ) are well resolved from and much higher than those of the other cations which produce fluorescent complexes in concentrated hydrochloric acid medium (e.g. Pb, Bi, Tl(I), Ce(III), Sb(III), and Sn(IV)). No fluorescence is, therefore, stimulated from these cations under the recommended conditions, and they, therefore, do not interfere. In a similar fashion the wavelength of maximum excitation at 380 mμ is long enough to ensure that many yellow coloured ions do not interfere seriously by attenuating the incident radiation intensity at 380 mμ, while the emission maximum at 586 mμ is long enough to ensure that few species can interfere by absorption of the emitted radiation. Additionally, as the tellurites of most of the heavy metals are insoluble in water but soluble in hydrochloric acid, no interference due to formation and precipitation of these species is encountered.

CHAPTER VI

A Study of the Fluorescence Characteristics of Inorganic Complexes in other Inorganic Acids at -196°C

In addition to hydrochloric and hydrobromic acids, it was mentioned in Chapter III that other inorganic, acid solvents also form good, reproducible glasses at liquid nitrogen temperature. The intense fluorescence emission exhibited by several complexes in hydrochloric acid and hydrobromic acid media at -196°C suggests that the investigation of the scope of the technique be extended to the study of inorganic complexes in other glass-forming solvents. Numerous inorganic complexes in sulphuric, phosphoric and perchloric acids are known but only the cerium (III)[17] and tin[40] complexes in sulphuric acid have been utilised in fluorescence analysis.

The results of the investigation of the fluorescence characteristics of the ions of several elements in sulphuric, phosphoric and perchloric acids at -196°C are presented in this chapter. Of the ions selected for the investigation, uranium (VI) exhibits a green fluorescence emission in all three acid solvents under the respective experimental conditions. Fluorescence emission has also been detected from cerium (III) in sulphuric acid medium.

EXPERIMENTAL

Apparatus:

The instrumentation used for fluorescence measurements is similar to that described in earlier chapters.

Reagents

The study of the fluorescence characteristics at -196°C of several elements in sulphuric, phosphoric and perchloric acids, was conducted using the purest available salt of each element. "Analar" grade (Hopkin and Williams Ltd.) sulphuric and perchloric acids and orthophosphoric acid (General Purpose Reagent, Hopkin and Williams Ltd.) were employed in the investigation.

Results

(a) General study of elements in sulphuric acid

The survey was performed using a 10^{-3}M solution of the ion of the element in 9M sulphuric acid solution. In common with the preliminary survey in hydrochloric and hydrobromic acids, the study of the fluorescence emission in sulphuric acid glass at -196°C was made first, visually and then, instrumentally as described previously. Under the conditions of the investigation, no fluorescence emission was observed from the following 29 ions: aluminium, antimony (III), arsenic (III), arsenic (V), bismuth (III), cerium (IV), chromium (III), chromium (VI), cobalt, erbium, europium, gadolinium, gallium, lanthanum, lutetium, manganese (II),

mercury (II), nickel, samarium, scandium, terbium, thallium (I), thorium, tin (II), tin (IV), vanadium (V), ytterbium, yttrium and zirconium. Cerium (III) and uranium (VI), however, fluoresce under the same conditions. The excitation maximum for the cerium complex occurs at 270 mμ with a fluorescence emission maximum at 320 mμ. The uranium complex emits a bright green fluorescence with emission maxima at 490, 510, 534 and 560 mμ and an excitation maximum at 304 mμ.

(b) Investigation of inorganic complexes in phosphoric acid medium

The investigation of the low temperature fluorescence characteristics of 31 ions in phosphoric acid was made using a 10^{-3}M solution of each ion in 7M phosphoric acid solution, and in a manner similar to that adopted for previous acid media. Of the ions selected for the study, only uranium (VI) was found to fluoresce strongly. The fluorescence is visible as a green emission, and the excitation and emission maxima for the complex are 320 mμ and 490, 514, 530 and 565 mμ respectively. No fluorescence emission was detected for the following 30 ions: aluminium, antimony (III), arsenic (III), arsenic (V), beryllium, cerium (III), chromium (III), dysprosium, erbium, europium, gadolinium, holmium, lanthanum, lead, lutetium, manganese (II), neodymium, praseodymium, samarium, scandium, terbium, thallium (I), thorium, thulium, tin (II), tin (IV), vanadium (V), ytterbium, yttrium and zirconium.

(c) Investigation of inorganic complexes in perchloric acid glass

For this investigation, a 10^{-3}M solution of each ion in 7M perchloric acid was employed. The results revealed that among 11 ions used in the study, only uranium (VI) is fluorescent in perchloric acid medium at liquid nitrogen temperature. This fluorescence emission from the uranium complex is similar to that exhibited by uranium in other acid media at -196°C that have been employed by the author. The complex in perchloric acid glass is characterised by an excitation maximum at 320 mμ and emission maxima at 490, 510, 530 and 560 mμ. Under the same experimental conditions, the following 10 ions do not fluoresce: antimony (III), bismuth (III), cerium (III), lanthanum, manganese (II), mercury (II), molybdenum (VI), neodymium, thorium and zirconium.

CHAPTER VII

Conclusion

The application of the technique of solution spectrofluorimetry to inorganic trace analysis has been overshadowed, in recent years, by the growing popularity of atomic absorption spectrophotometric and atomic fluorescence spectroscopic methods of analysis. As an analytical technique, spectrofluorimetry is inherently more sensitive than several other instrumental methods e.g. solution spectrophotometry, but it suffers from the disadvantage that it is often susceptible to many interferences that arise from different causes e.g. quenching and inner-filter effects. In the face of great competition from other analytical methods, especially current atomic methods, future fluorimetric procedures for inorganic materials will have to produce very high sensitivities to compensate for the lack of selectivity if the technique is to retain its status. One possible approach to obtain greater sensitivity in fluorimetric determinations is to employ a very intense light source to excite the fluorescence emission since the intensity of fluorescence is directly dependent on the intensity of the exciting source. The light source in both spectrofluorimeters used in the author's work was a 150 watt xenon-arc lamp whose energy output, particularly in the ultra-violet, is of a low order of magnitude. It is, therefore, highly desirable to find

a more intense source to replace the xenon-arc lamp if improvements in sensitivities are to be expected. With this object in mind, the author conducted some experiments in which the intensities of emission from several sources of radiation were compared with that given by the xenon-arc lamp.

As spectral sources, electrodeless discharge tubes (E.D.T.'s) excited by microwaves are known to emit very sharp and intense lines, and have been used in the past chiefly for spectral elucidation studies.[70,71] Recently, however, they have been employed to replace hollow-cathode lamps as sources in the techniques of atomic absorption spectrophotometry (A.A.S.) and atomic fluorescence spectroscopy (A.F.S.) in which they have proved to be highly successful.[72] The distinct advantages of an E.D.T. over other sources used in atomic, analytical methods such as hollow-cathode and high intensity lamps are their high intensity, ease of preparation, low cost of production and long "shelf-life". The successful application of E.D.T.'s to A.A.S. and A.F.S. suggests their possible application also as spectral sources in molecular fluorescence analysis. The results of experiments performed to compare the intensities of several E.D.T.'s and a mercury vapour discharge lamp with the intensity emitted by the 150-W xenon-arc lamp fitted to the Farrand spectrofluorimeter are presented below. The E.D.T.'s employed in this study were prepared in the manner described by Dagnall, Thompson and West.[72]

For excitation of these tubes, a "Microtron 200" microwave generator (2450 Mc/sec) was used in conjunction with a resonant cavity (Electro-Medical Supplies Ltd., London W.1. Type 214L). Initiation of the discharge, which relies on the production of free electrons, was achieved with a simple Tesla coil vacuum tester.

The spectral characteristics of the sources and all measurements of intensities were recorded using the Farrand spectrofluorimeter by employing a dull surface aluminium mirror provided for direct measurement of transmission and placing the photomultiplier in the alternative position next to the cell compartment (see Fig. 3). To maintain similar experimental conditions, the study of each source selected for investigation was made by positioning the source in the position occupied by the xenon-arc lamp in the spectrofluorimeter. Figures 18 and 19 show the emission spectra of the seven sources viz, xenon-arc lamp, mercury vapour discharge lamp, mercury e.d.t., sulphur e.d.t., carbon monoxide e.d.t., argon e.d.t. and xenon e.d.t. The legends to the figures are as follows:

Figure 18

A Mercury vapour discharge lamp and mercury e.d.t. (sensitivity scale: x 100)

B Xenon-arc lamp (sensitivity scale: x 1000)

C Xenon e.d.t. (sensitivity scale: x 0.1)

FIGURE 18

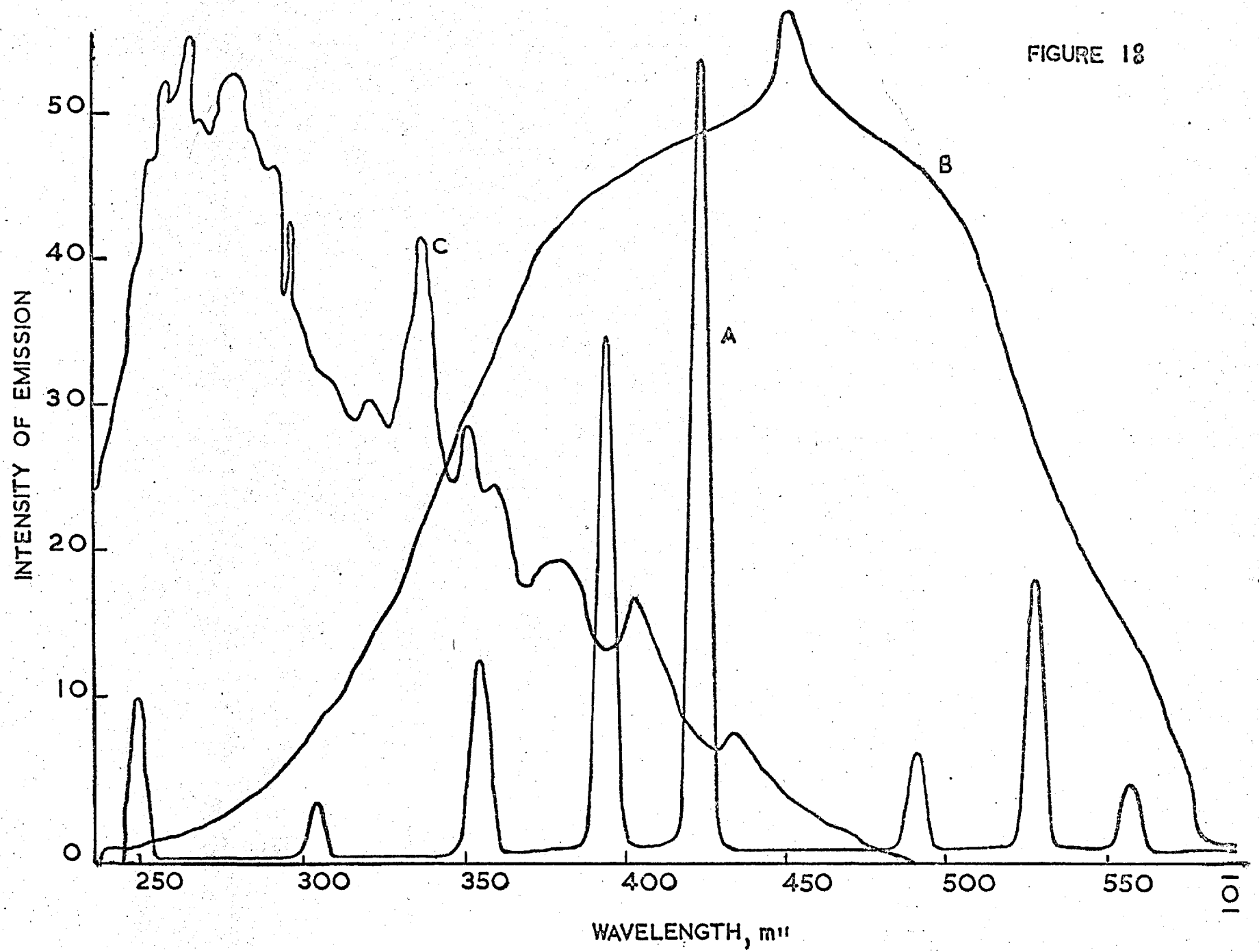

INTENSITY OF EMISSION
0
10
20
30
40
50
250
300
350
400
450
500
550
WAVELENGTH, mμ
A
B
C

FIGURE 19

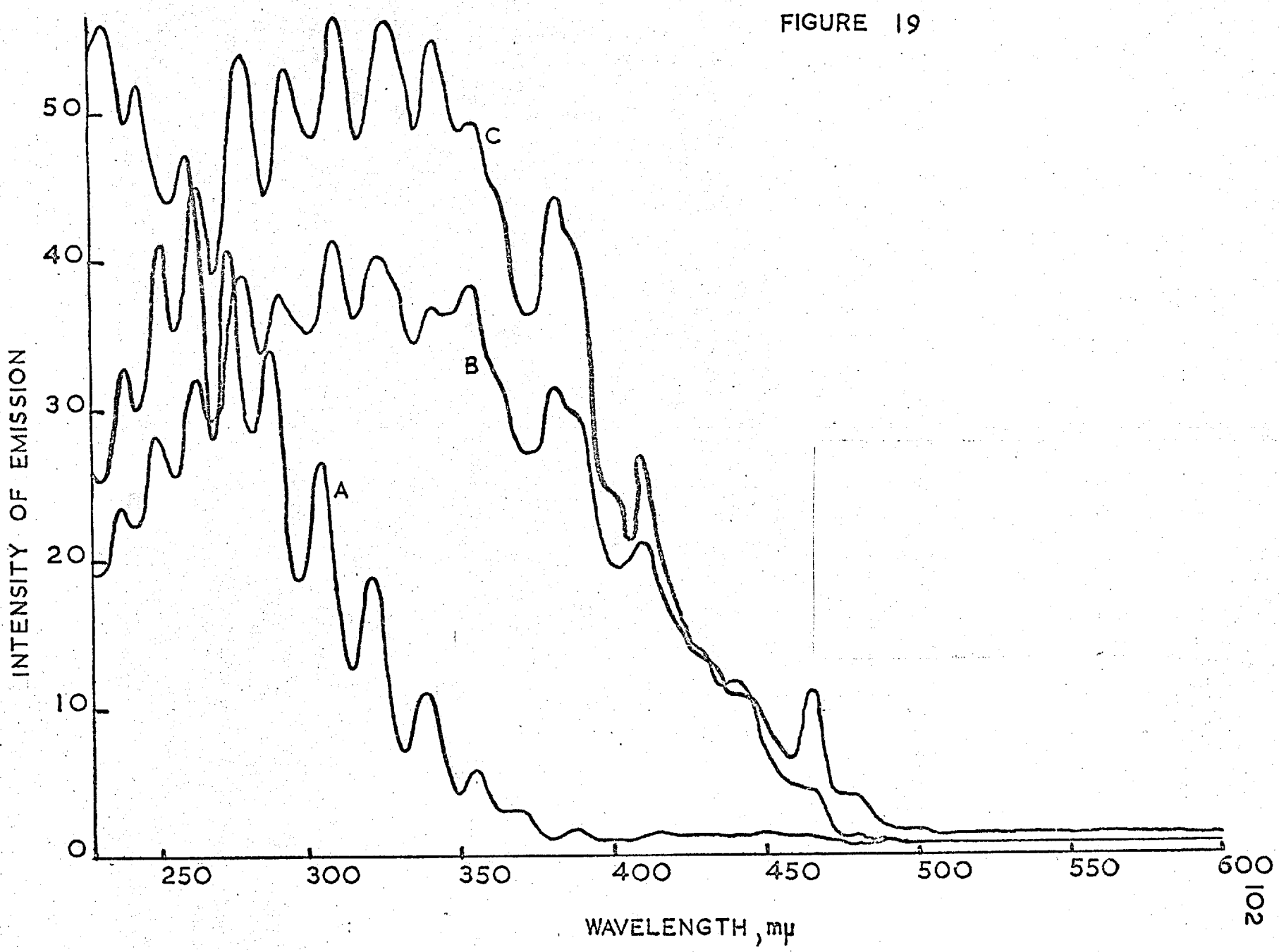

INTENSITY OF EMISSION
0
10
20
30
40
50
A
B
C
250
300
350
400
450
500
550
600
WAVELENGTH, mμ

Figure 19

A Sulphur e.d.t. (sensitivity scale: x 10)

B Argon e.d.t. (sensitivity scale: x 1)

C Carbon monoxide e.d.t. (sensitivity scale: x 1)

The sharp line-emission spectra for the mercury vapour discharge lamp and the mercury e.d.t. are similar, while the remaining five sources produce continua over the spectral range investigated. With the mercury e.d.t., no significant change in the intensities of emission was observed by placing the tube directly in front of the entrance port of the excitation monochromator which revealed that an efficient optical system exists in the instrument for direction of incident radiation.

The emission at 250 mμ was selected for the purpose of comparing the source intensities. The results (using 5 mμ bandwidth slits) show that the xenon-arc lamp is superior to the other sources, the order of intensity being: xenon-arc lamp $>$ mercury vapour discharge lamp $\approx$ mercury e.d.t. $>$ sulphur e.d.t. $>$ carbon monoxide e.d.t. $>$ argon e.d.t. $>$ xenon e.d.t. The same order of intensity was obtained from the fluorescence signals at 430 mμ of identical thallium (1) solutions in hydrochloric acid-potassium chloride medium which were excited at 250 mμ.[18] By using wider slits, 20 mμ band pass slits, the superiority of the xenon-arc lamp over a mercury e.d.t. is further enhanced. Thus it would appear that,

while e.d.t.'s emit sharp and intense lines which are much desired in A.A.S. and A.F.S. procedures, they are not likely to find application in solution spectrofluorimetry as sources of excitation. Here, the excitation spectrum of the fluorescent complex generally appears as a broad band so that the energy of excitation may be represented by the integrated area of the curve over the absorption profile. A continuous source such as the xenon-arc lamp is likely to satisfy this energy requirement far better than a line source since its total energy output over a relatively broad absorption profile is higher than that of the latter considered over an identical absorption range. Justification of this fact is seen in the increased intensity at 250 mμ of the xenon-arc lamp over the mercury e.d.t. obtained by changing the bandwidth in the experiments from 5 to 20 mμ, and from the stronger fluorescence signals given by the thallium (I) complex when using the xenon-arc lamp as exciting source.

An alternative way to achieve better sensitivity in spectrofluorimetric methods is to perform measurements at low temperature where, as discussed in Chapter II, processes having an adverse effect on the quantum efficiency of fluorescence are much reduced. The work of Ohnesorge and Rogers[14] on the low temperature fluorescence of oxinate complexes of metals of Group IIIA indicates the possibility of obtaining lower limits of determination of metal ions via the formation of fluorescent chelate complexes with organic

reagents by extracting these complexes into suitable solvents or mixtures of solvents which form clear glasses at -196°C. The work described in previous chapters of this thesis illustrates how the technique of solution spectrofluorimetry may be successfully applied at low temperatures to extend the range of elements that may be determined by fluorescence reactions. A very sensitive and selective method has been described for tellurium.

Mention has already been made that the fluorescence emission from antimony (III) in hydrobromic acid glass is 100 times more intense than in hydrochloric acid glass, and that a very sensitive detection limit (10^{-8}M) for antimony in the former medium at liquid nitrogen temperature has been obtained. Consequently, a method is being currently developed for the determination of antimony which is based on measurement of the red fluorescence of the antimony (III) bromo-complex in hydrobromic acid at -196°C. The optimum conditions employed in this determination have been established in an earlier study (see Chapter IV). A preliminary investigation of the potential interference of a 50-fold molar excess of numerous foreign ions on the determination of 2×10^{-6}M antimony (6 μg in 25ml.) reveals that the following ions caused a variation of fluorescence intensity of $\leqslant \pm 5\%$ of the fluorescence intensity value obtained in the absence of foreign ions: aluminium, arsenic (III), barium, beryllium, bismuth, cadmium calcium, cerium (III), chromium (III), cobalt, copper (II), gallium, germanium, indium, iron (III),

lanthanum, lead, magnesium, manganese (II), mercury (II), nickel, potassium, scandium, selenium (IV), silver, sodium, strontium, tellurium (IV), thallium (I), tin (II), tin (IV), titanium (IV), vanadium (V), zinc, zirconium, acetate, chloride, citrate, fluoride, nitrate, oxalate, perchlorate, phosphate, sulphate, tartrate and thiocyanate.

In common with the method reported for tellurium,[33] the determination of antimony in the manner described above is marked by the high selectivity of the procedure. As with tellurium this selectivity for antimony is mainly due to the spectral characteristics of the antimony (III) bromo-complex which are well separated from those of several other cations which exhibit fluorescence emission in hydrobromic acid glass. The absence of interference from many strongly coloured ions in the methods for tellurium and antimony may be explained again by reference to the spectral characteristics of the respective complexes, but in these instances the explanation is facilitated further by a very significant change which occurs when these coloured solutions are cooled to liquid nitrogen temperature. Several strongly coloured solutions in hydrochloric and hydrobromic acids when frozen at -196°C were observed to show either a considerable dilution of colour or a change to a different and weak colour. Thus the strong yellow colour of iron (III) in hydrochloric acid is reduced to pale yellow at -196°C while the orange colour of the same ion in hydrobromic

acid changes to pale pink at low temperature. These observations probably account for the non-interference of iron (III) in the determination of antimony, and for the tolerance limit of a 5-fold weight excess of iron (III) in the determination of tellurium. Likewise, the yellow colour characteristic of the ions Cu(II), V(V), Au, Pt(IV), etc. in hydrochloric acid and the purple colour of the Cu(II) ion in hydrobromic acid do not interfere in these determinations. One important consequence of the effect of lowering of temperature on the colour of bright solutions may be mentioned here. Several methods that have been proposed for trace metals and which depend on the absorption of light in the ultraviolet by their halogeno-complexes are subject to interference from many foreign ions which form coloured halogeno-complexes and thus reduce the intensity of the incident radiation. However, if spectrophotometric measurements are made at low temperature, these interferences may be considerably minimised or even eliminated. The importance of low temperature absorption spectroscopy has been recognised for years, but relatively little work has been reported in the field because of the experimental difficulties which exist. Recently, several workers[53,73] have attempted to remove some of these experimental problems by designing low temperature absorption cells for various spectrophotometers.

The author's investigation of low temperature fluorescence reactions in inorganic acid media has produced some encouraging

results. Nevertheless the technique is still in an early stage of development and undoubtedly a number of practical problems will have to be solved before it can acquire wide acceptance and application. The problem of cracking of the silica sample tubes used in these studies may be improved by employing thicker-walled tubes to contain the sample solution. When a crack in the glassy medium occurs, the internal pressures set up frequently cause rupture of the sample tube. Hence the greater "strength" of thick-walled tubes should allow them to resist the strains more effectively. The need for careful positioning of the sample tube for reproducibility of results presents another difficulty encountered in the technique. Quite recently, Hollifield and Winefordner[74] have described a rotating sample cell for use in phosphorimetry by means of which they have obtained improvements in the precision of measurements. Spectrofluorimetry at low temperature would thus appear to be a technique of trace analysis which may yield valuable results in the years to come.

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