SPECTROPHOTOMETRIC METHODS OF ANALYSIS

by

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To whom was looking forward to seeing this script, but, unfortunately, he shall be unable to see it anymore. To my Late Father.

A B S T R A C T

The direct spectrophotometric determination of trace amounts of three noble metals, silver (I), palladium (II) and gold (III) has been investigated. The indirect spectrophotometric determination, visual and photometric titration of cyanide has been also studied.

Two selective and rapid spectrophotometric methods for the determination of silver in aqueous solution and in organic media are described. The determination is based on the formation of ternary complexes between silver, 1,10-phenanthroline and the anionic reagent. Two reagents were employed, Bromophenol Blue, and Rose Bengal Extra. The two methods are sensitive especially after solvent extraction. Selectivity is achieved by masking agents.

A simple, sensitive and selective method for the indirect spectrophotometric determination of cyanide down to 0.0052 ppm in aqueous solution, based on the above ternary complexes involving silver, is described. By solvent-extraction, two reagents have been used for determining cyanide down to 0.131 ppm. Selectivity is achieved by masking-agents.

The use of 1,10-phenanthroline/dyestuff indicator

systems are proposed for the visual and photometric titration of cyanide with silver nitrate in the range 10^{-1}-10^{-4}M and 10^{-4}-10^{-5}M. Three dyestuffs have been proposed as indicators. Sharp, well-defined end-points are observed. Selectivity was obtained by masking-agents.

Rose Bengal Extra forms a mauve-coloured complex with the palladium bis-phenanthrolonium cation in aqueous media. This reaction is one of the most sensitive reactions for palladium (ϵ = 50,000). The method rendered selective using masking agents.

Another extremely sensitive and, selective reaction is proposed for determining palladium (II) spectrophotometrically in organic media, which is based on the extraction of the ternary complex formed between palladium (II), pyridine and Rose Bengal Extra into chloroform, with molar absorptivity of 125,000. Seven anions and 22 cations do not interfere using masking agents.

A simple and rapid method is proposed for the spectrophotometric determination of gold (III) in aqueous solution. This method is based on the formation of a ternary complex between gold (III), 1,10-phenanthroline and Rose Bengal Extra. This method is one of the most sensitive methods for the direct determination of gold (III) in aqueous solution (ϵ = 31,000).

A C K N O W L E D G E M E N T S

The work recorded in this thesis was carried out in the Chemistry Department of Imperial College of Science and Technology between 1965 and 1967. It is entirely original except where due reference is made and no part has been previously submitted for any other degree.

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F O R E W O R D

During recent years there has been a steadily growing interest in the constituents of certain materials present only in trace amounts. Such an interest is shown in the rapidly expanding area of metallurgy where there has been considerable research into the significance of trace elements.

Absorption spectrophotometry is undoubtedly one of the most serviceable and versatile techniques of trace metal analysis and it was decided at the outset of this programme to concentrate exclusively on this technique.

A survey of the literature revealed that there was a particular need for new methods of analysis for the noble metals and cyanide, especially, in aqueous solutions. For example, up to 1961, there was no direct spectrophotometric method for the determination of trace amounts of gold based on the formation of a soluble aqueous gold complex, except the bromoaurate method which is not sensitive. Also, the analysis of trace amounts of cyanide using

the widely recommended method of Aldridge, is becoming difficult owing to the carcinogenic properties of the reagent benzidine and its now prohibited manufacture.

Consequently, the need for more sensitive and selective spectrophotometric methods for the determination of the noble metals and cyanide is undoubtedly rather important.

C O N T E N T S

Page

INTRODUCTION

The term "trace" was first used to define or designate a minute quantity of a substance known to be present in a sample but which could not be determined quantitatively. This was because the amount was below that readily determinable with the existing titrimetric or gravimetric methods. To-day, trace analysis is no longer a very specialised activity applied almost exclusively in the study of particular chemical problems, but represents an important part of the daily routine work of many analytical laboratories. The term "trace" has come to represent amounts which constitute less than 0.01% of the matrix.

The methods used for the determination of trace amounts of material are:

1. Colorimetry, spectrophotometry, and related methods (turbidimetry, nephlometry and fluorimetry)
2. Emission spectrography (arc, spark and flame)
3. X-ray absorption and emission
4. Radioactivation (neutron activation and isotope dilution).
5. Polarography (and other electrochemical methods).
6. Mass spectroscopy.

The bulk of present day trace analyses are made by omission spectrography and colorimetry (the term colorimetry is used here in its broadest sense and includes all methods based on absorption of light i.e. spectrophotometry, etc.)[1]

Colorimetry is the most common method used for the determination of trace amounts of material, because of its modest operative requirements with respect to apparatus and unskilled workers, it gives a sensitivity adequate for many present day purposes and an accuracy often as good as, if not better than, that of most other methods.[2] Cook et al.[3] reported that the precision of absorption spectrophotometric technique was greater than those others listed below which have been used for the determination of nuclear materials. The average standard deviation (S) obtained was:

Technique	S
Absorption Spectrophotometry	0.8
Neutron Activation	1.8
Polarography	2.1
Emission Spectrography	3.3

The main aspects of absorption spectrophotometry are briefly discussed in the following pages:

(a) RELATIONSHIP BETWEEN COLOUR AND CHEMICAL CONSTITUENTS.

The absorption of radiant energy in the visible region results in the displacement of electrons in the outer energy levels of the atoms constituting the ion or molecule. Thus when approximately 145,000 to 300,000 joules of energy are absorbed per mole, a characteristic spectral distribution is obtained in the visible region. If a larger amount of energy, possibly as large as 625,000 joules per mole, is absorbed, the characteristic spectral distribution will be found in the shorter wavelengths (ultraviolet) region of the electromagnetic spectrum.

The absorption of light is attributed to:

(i) the transition of non-bonding electrons of the cation or the anion.

(ii) the transition of nonbonding electrons of the reagent.

(iii) the transition of bonding electrons of non-ionic complexes.

It is also possible that an electron upon excitation to a higher quantum level can become coupled with the empty levels of the ligand, resulting in a partial transfer and causing a shift to the absorption of radiant energy of a longer wavelength.

Elements whose atoms have unpaired electrons in inner energy levels usually exhibit absorptivity in the visible or ultraviolet region. Thus, the solutions of many transition elements are coloured. Resonance occurs when two or more electronic structures of a most equal energy content are possible. Resonance involves a shift in the distribution of electrons within the molecule, the molecule structure remaining unchanged. Resonance may cause longer wavelengths of radiant energy to be absorbed. Because in the case of certain structures, one finds electron deficiency associated with unsaturation. However in order to obtain absorption in the ultraviolet or visible region, it is necessary that conjugation occurs. Because unsaturated structures permit resonance, they are often designated as resonators or oscillators and, if they are specifically responsible for colour, they are called "chromophores".[4]

Graebe and Libermann (1868) observed that all organic compounds became colorless on reduction and that therefore unsaturation was a characteristic of the absorption phemomenon. The first theory regarding the relation between constitution and colour was set forth in 1876 by Witt. According to Witt, every dyestuff

contains at least one group belonging to the class of unsaturated radicals which we called chromophores. The most important chromophores are: methine, carbonyl, azomethine, nitroso, nitro, azo, and azoxy. The molecule containing chromophores is called "chromogene". A chromogene may be coloured but does not yet represent a dye. To achieve this the further introduction of a salt-forming group called an "auxochrome", into the molecule is required. Hydroxy and amino, sulfonic and carboxylic acid radicals are examples of auxochromes.[5]

There have been many efforts to enlarge upon Witt's ideas and to formulate new approaches. In 1888 Nietzki added the quinonoid group to the list of chromophores and Armstrong developed a quinonoid theory of colour (1888) which was supported in 1900 by Fischer. Kauffmann in 1906 rejected a sharp dividing line between auxochromes or chromophores and his ideas were strengthened by the work of Willstater and Piccard which brought forth the theory of meriquinoid-haloquinoid isomerism with isorropesis (returning creation and breakage of linkages). Tautomerism and isomerism in the creation of coloured compounds were stressed by Baly (1904) and Hantzch

(1906), respectively.[5]

Partly on the basis of work done by Pfeffier in 1910-1916, Dilthey published in 1924 his conception of a new theory concerning chromophores which was augmented by Wizinger's ideas on new auxochromes. Whereas, according to the then existing theories, chromophores were represented by a plurality of doubly bonded unsaturated groups, the theories of Dilthey and Wizinger postulates the existence of coordinatively unsaturated single atoms, there being no colour without the presence of such a chromophore. For the production of deep and intensive colour, however, the chromophore must be charged positively or negatively, or expressed differently. The transformation of a co-ordinated unsaturated atom (the chromophore) into the ionic state results in a great intensification in the light absorption. This electrical charge is introduced by the auxochrome, of which Wizinger distinguishes three kinds[5]

(i) Positive Auxochromes

These are radical such as methoxy, hydroxy, amino, dimethylamino, and anilino which favour the electropositive ions having a co-ordinatively unsaturated central atom. Their effect is bathochromic.

(ii) Negative Auxochromes or Antiauxochromes

Examples of such groups are nitroso, nitro, carbonyl, cyano, sulphonyl and azo. These radicals favour the electronegative state and intensify the colour of negative ions containing a co-ordinatively unsaturated central atom. Their effect is likewise bathochromic.

(iii) Amphoteric Auxochromes

Such auxochromes are, for example, aryl and vinyl radicals, which favour ionisation toward either the positive or negative ions having a co-ordinatively unsaturated atom.

The theories discussed so far are based mainly on the structural characteristics associated with colour. As a bridge to the modern concepts of resonance as related to colour, Sieglitz's views may be cited. Stieglitz maintains the colour is produced by oscillation of electrons involved in an intramolecular oxidation-reduction process. A dyestuff contains both oxidizing and reducing groups (chromophores and auxochromes) and a conjugated system connecting both serves as a means of communication.

The modern interpretation of the auxochromes and chromophores is based largely on the work of Bury (1935). Lewis (1940), Schwarzenbach (1939) Pauling (1939), Ingold (1929), and Adams and Rothstein (1914), Beyer (1917), has suggested that the colour of the triphenylmethane dyes was due to the oscillation of an atom in the molecule[5]

(b) ABSORBTION INTENSITY AND TRANSITION PROBABILITY.

Absorption intensity is expressed in terms of absorption or extinction coefficients, defined on the basis of the Beer - Bouger - Lambert[1] Law[6,7] which states that the fraction of incident light (Io) absorbed is proportional to the number of molecules in the light path i.e. to the concentration (c) and path length (b). If (Io) and (I) represent the intensities of incident and transmitted light, the fraction absorbed is approximately (Io) - I) / Io, or more precisely,

$$\int_{I=I}^{I=I_o} dI/I = 2.3 \log_{10} (Io/I)$$

since the effective incident intensity is undergoing continuous change on passage through a finite length of absorbing layer. Thus:

$$\text{Log}_{10} (Io/I) = A = \epsilon lc$$

$$\therefore \quad \epsilon = A/lc$$

where

A = absorbance or optical density

c = concentration of coloured species (mole / 1.)

l = light path length (cm)

and ϵ = molar absorptivity.

Molar absorptivity may be expressed with regard to one gram atom of the element determined per litre of solution instead of to one mole of the coloured species. In the first case the molar absorptivity, may be termed the "ionic molar absorptivity".[8]

The analytical application of this law depends on measurements of optical density at either constant path length with varying concentration or at constant concentration with varying path length; thus, calibration graphs, which will be linear if the Lambert-Beer law is obeyed, can be plotted relating optical density to either of these variables.

Deviations from the law, real or apparent, occur in practice because of the displacement of equilibria involving absorbing materials, interaction between molecules, stray radiation at high optical densities, fluorescence of solutions, or because the radiant energy is not monochromatic; The greater the range of wavelengths, the greater the apparent departure from the law.[6]

When solutions do not obey, or appear not to obey, the Lambert-Beer's law, alternative methods of calculation can be employed; for a single solute, a working graph relating (A) to (c) under specified conditions of wavelength, cell length, type of filter, type of instrument, solvent and concentration range limits can be constructed by the use of solutions of known strength, and the graph may then be used for the analysis of sample solutions.

Holzapfel[9] proposed another method if Beer's law is invalid for a photometric method, the means of absorptivities, $(\bar{\epsilon}c), \bar{\epsilon}c$ are calculated and plotted vs concentration (c). In all cases, a linear curve is obtained, which can be expressed by

$$\bar{\epsilon}_c = \bar{\epsilon}_o - mc$$

If m and $\bar{\epsilon}_o$ are known for a method, the absorbance, (A), is measured and the corresponding concentration can be calculated by:

$$c = \pm\sqrt{(\bar{\epsilon}_o / 2m)^2 - (A / m + \bar{\epsilon}_o / 2m)}.$$

The "true Beer's law slopes" can be calculated from $\bar{\epsilon}_o$ values.

Other sources of error encountered in spectrophotometry are as follows: [1,4]

(i) Instrumental errors:-

a - Slit width

b - Multiple reflection path effect which gives a positive deviation to Beer's law. This error can be minimized by using longer cell lengths, and by avoiding measurements in the low absorbance range (less than 0.4).

c - Stray radiation, which gives a negative deviation to Beer's law. It can be minimized by avoiding measurements in the high absorbance range (i.e. 1.5).

(ii) Native errors (those having their origin in the coloured product).

a. Reproducibility of colour.

b. Stability of colour.

(iii) Interferences (those due to foreign substances which may have positive or a negative effect.

The last source of errors (interferences) is the most unpredictable and must be overcome in order to achieve selectivity of reaction.

Whereas the wavelength of the absorbed light is determined by the energy of the transition, the extinction coefficient (molar Absorptivity) is governed by the size of the absorbing species and by the probability of transition. In

order that interaction may take place, a photon must obviously strike a molecule approximately within the space of the molecular dimensions and the transition probability (P) will be the proportion of "target-hits" which lead to absorption. Consider light falling on a slice of thickness (dl) of a cell of unit area containing an absorbent at a concentration of (c) g-mols/1. Let the effective average cross-sectional-area of the molecules be (a) and let the slice be sufficiently thin so that there is no superposition of molecules in the direction of propagation of the light. Then the (loss in intensity/total intensity) will be equal to the absorbing area/total area multiplied by the probability.

Thus:

$$-dI/I = 1/3\ PcNadl/1000 \qquad (I)$$

where:

N is avogadro number.

1/3 is the statistical factor to allow for random orientation since absorption will normally be at its maximum for a particular angle of incidence. On integrating and insertion of the numerical constants equation (I) becomes:

$$\log_{10}(Io/I)/cl = \epsilon = 0.87 \times 10^{20}\ Pa \qquad (II)$$

The cross sectional target-area (a) can be estimated

from X-ray and electron-diffraction data and is of order of 10 $\mathring{A}^2$ (10^{-15} cm^2 for ordinary organic molecules) so that for a transition of unit probability ϵ is approximately 10^5.[10,11] The highest coefficients observed are of this order and generally, an absorption with ϵ values of about 10^4 or greater is referred to as a high intensity absorption and is due to transitions of high probability (allowed transition, P = 0.1-1). An absorption with values less than about 10^3 is referred to as a low intensity absorption and arises from transitions of low probability (forbidden transitions P = 0.001 or less).[11]

According to electromagnetic theory, absorption can take place only if the transition is accompanied by a polarization of the molecule. The transition probability is related to the magnitude of the resulting dipole moment (transition moment); transitions of relatively high moment are allowed, while transitions of low moment are forbidden. This often is expressed in terms of oscillator strength (f), approximately given by:

$$\epsilon = 0.464 \times 10^9 f/\Delta\nu \qquad \text{(III)}$$

where $\Delta\nu$ is the range of wave numbers (reciprocal

wavelengths) over which the electronic transition extends.[11]

A unit oscillator strength corresponds roughly to a unit probability. The oscillator strength may be regarded as a measure of the number of electrons per molecule taking part in the light absorption process.[11]

(c) SPECTROPHOTOMETRIC METHODS OF ANALYSIS

The most refined method of measuring the radiant energy transmitted by coloured solutions involves the use of a spectrophotometer, which enables the selection of any wavelength of any incident energy and to determine the characteristics spectrophotometric curves of coloured solutions.

A spectrophotometer may be defined as an instrument by means of which the absorption of a sample may be measured at any wavelength in a specified spectral range. Visual, photographic, photoelectric, or thermoelectric methods of measurements may be used; the last two may be made automatically recording. It consists essentially of:

(i) Light Source

The white light or light of restricted spectral bands are used. When several restricted spectral

bands are used, the instrument is called an abridged spectrophotometer.[6] The light source may be an incandescent filament lamp, or a mercury vapour lamp.

(ii) Optical System (Monochromator)

The optical system is used to collimate the light and to select the appropriate spectral region. (It may be a prism or a grating).

(iii) Detector

The detector consists of a photoelectric cell or cells to receive the light transmitted by the sample, together with an electric circuit to measure the response of the photoelectric cell or cells. The use of vacuum photoemission type photocells or electron multiplier phototubes, and suitable amplifiers greatly increases the sensitivity of the photometers and permits transmitted radiant energy of very low intensity to be measured. Improved sensitivity, and better conformity to Beer's law are found as the spectral band-width is decreased (optimum band-width is 1-5 mμ).

HISTORY

Absorption spectrophotometry in the ultraviolet and visible regions is among the earliest physical

methods employed in the structural analysis of organic compounds. The most elementary form of absorption spectrophotometry is the observation of the colour of a substance by the naked eye. The colour of a solid or a liquid is that of the light which is not absorbed. The colour of a compound can often provide a valuable clue to its constitution or identity, and the visual estimation of colour intensity (visual colorimetry) has been widely used to determine the concentration of coloured compounds in mixtures and solutions. In the proper sense of the word, however, absorption spectrophotometry involves the dispersion of the incident light or transmitted light and measurements at certain wavelengths. The simplest means of effecting this is to place the absorbing substance in the optical path of a spectroscope illuminated with a continuous source of light; in the resultant absorption spectrum, regions of the absorption appear as dark lines or bands. The solar spectrum itself is an absorption spectrum; it contains a series of dark lines, discovered by Wollaston in 1802 [11] and investigated in more detail by Fraunhofer. These are due to absorption by metal vapours in the chromosphere surrounding the sun. The first observation of an absorption spectrum of an organic compound was made by Sir David Brewswater [11] in 1834 with green leaf extracts described in the following words: "The

light transmitted through the fluid may be analysed by a fine prism ... we shall observe a spectrum of the most beautiful kind ... divided into several coloured bands of unequal breadth and having their colour greatly changed by absorption. More precise measurements on leaf extracts were later made by Stokes [11] who also discovered the fluorescence of chlorophyll, and by Angstrom [11] and Harting. [11] Since about 1860 qualitative absorption spectroscopy has been widely applied to the characterization of both natural and synthetic pigments and dyestuffs. The early history of the subject has been summarised in a masterly fashion by Kayser. [11]

Progress in the study of the light absorption properties of organic compounds has been closely dependent on advances in experimental techniques. The extension of absorption spectrophotometry to the ultraviolet region developed slowly from 1870 onwards through the pioneer work of Hartley, Dobbie, Baly, Hantzch, Henri and others[11] who made use of photographic plates as a means of detecting and recording

ultraviolet radiation. However, until about 1920, the subject remained primarily a specialised branch of physical chemistry and its far reaching potentialities as an analytical method were not exploited. The rapid growth of ultraviolet absorption spectrophotometry as a popular tool in organic chemistry dates from the period between 1920 and 1930 and can be traced in some considerable measure to the influence of the work of Heilborn and Morton, pupils of Hantzch and Baly respectively, on the vitamins A and D. This development was greatly assisted by the introduction of commercially manufactured photometers, i.e. optical devices for the measurement of absorption intensity permitting the rapid and accurate determination of extinction curves. The importance of quantitative intensity measurements lies in the fact that the absorption co-efficient is much more specifically related to constitution than an absorption intensity which normally bears a linear logarithmic relationship to the concentration of the absorbing species, thus affording an accurate and selective method of quantitative analysis.[11]

Photographic absorption spectrophotometry is, of course, applicable to the visible as well as the

ultraviolet region, and a vast amount of work on organic compounds in solution was carried out using this technique between 1930 and 1945. Absorption spectrophotometry played a part in, and not infrequently provided the key to the elucidation of the structure of many of the important natural products investigated during that period. It also found numerous applications in synthetic problems. [11]

In the last 25 years the international journals of analytical chemistry have seen a remarkable growth in the number of publications concerned with the determination of inorganic species and organic species in solution by absorption spectrophotometry. According to Mellon, 483 papers up to 1954, [12] 696 papers up to 1956, [13] 800 papers up to 1958, [14] 746 papers up to 1960, [15] 1,500 papers up to 1962 [16] and 1,500 also up to 1964, [17] have been published.

Although absorption spectrophotometry is classified amongst the most sensitive techniques for trace analysis, it is limited by the two factors "selectivity" and "sensitivity". The successful spectrophotometric method is the one which is capable of overcoming those two main barriers and achieves both selectivity and

sensitivity toward the desired ion to be determined.[18]

(d) SELECTIVITY AND SPECIFITY

The ideal organic reagent is one which, under given conditions, will react with a single ion or molecule. Such substances are comparatively rare. Reagents can often be made selective by the following methods:[19]

1. Masking of the diverse ions. Masking reagents exert their action in a variety of ways:

   (i) Some substances act by removing the undesired cation from the sphere of action by precipitating it as an insoluble compound. These methods involved are essentially separation methods which are tedious and time consuming.

   (ii) The masking reagent forms a stronger soluble complex with the interfering ion than that with the reagent under consideration.

   (iii) Other reagents act by reducing or oxidising a cation to another valency state, in which form it is not capable of reacting strongly with the reagent used.

(iv) Use of the hydrogen ion as a masking agent. Many cations may be masked by selective pH control.

2. The design of highly selective reagents:

(i) Using organic compounds which possess specific atomic groupings toward the metal ion under consideration, e.g. the atomic grouping p - ON - C_6H_5 - N< was reported to be specific for palladium.[20] Neocuprione was described as a specific reagent for copper (I), but West found that it was only so within the context of spectrophotometry. This reagent also forms colourless compounds with many metals on extraction, e.g. cadmium, cobalt, nickel and zinc.[21] This example illustrates that most of the selective reactions are only conditionally so, and that it is not always possible to transpose selectivity of reaction from one technique to another.[21]

(ii) Construction of a chelate cage molecule (inclusion compound or clathrate).

The construction of a chelate cage

molecule into which only ions of certain size would fit, e.g. the compound, calcichrome has been recommended by Close and West as a highly selective chromogenic reagent for calcium.[21,22,23] Calcichrome, at pH12, reacts only with calcium ion (its radius is 0.9 Å) but not with strontium (1.1 Å) or barium (1.3 Å) ions. Other ions that would normally be expected to fit into the cage are insoluble at pH12. Therefore, this chromogenic reaction is conditionally selective for calcium. However, this method is not very sensitive since the blue coloured calcium - calcichrome (1:1) complex has a molar absorptivity of only 7,600. Another similar example has also been recently reported by Dagnall, Smith and West.[24] Here the reagent NN` - bis - salicylidene - 2,3 - diaminobenzofuran forms a strongly fluorescent complex with magnesium, but not with calcium, barium or strontium. The reagent in fact only reacts with ions having an octehedral ionic radius greater than ca 1Å.

3. The formation of ternary complexes.[21]

In the formation of ternary complexes, the cation reacts not only with one ligand species, but rather with two. In this way it is possible for a much more complex absorbing organic envelope to be put around an ion than is normally possible. Consequently the selectivity and sensitivity of such a ternary system is considerably superior to that of binary-complex formation. If we have a series of divalent metals, M^1, M^2, M^3, of similar chemical nature, they are likely to react to form complexes with a ligand, H_2L of the nature of M^1L, M^2L, M^3L, etc. or $M^1L_2^{2-}$, $M^2L_2^{2-}$, etc. As a generalisation, it is often permissible to say that the absorption characteristics of most metal complexes of a reagent tend to resemble closely the next higher ionisation stage of ligand molecule considered in its reactive form as an acid. Hence if a reagent reacts in the form HL^-, its metal complexes frequently tend to have absorption spectra closely resembling that of L^{2-}. Consequently most metals form similarly coloured complexes so that selectivity is low. However, when two ligands are involved, e.g. H_2L and H_2R, the chances of duplication of ternary complexes of the nature M.L.R are much smaller, and this gives greater selectivity of reaction. [21]

Therefore, it is obvious that the utilization of the

formation of the ternary complexes to achieve selective determination of the desired cation compares favourably with the other previous methods especially as none of the existing reagents is truely specific but only "conditionally specific". In addition, although the synthesis of organic ligands possessing the so-called selective functional groups is possible, the task is a difficult one and the resultant reagent is not likely to be completely specific. [21]

(e) SENSITIVITY

The sensitivity of absorbance measurements in solution is limited by two factors, both of which suggest that there is always a lower limit of detection of about 10^{-8}M for any complex in aqueous solution.

(i) The inability of even a good spectrophotometer to measure less than 0.001 absorbance unit. According to Lambert-Bouger-Beer's law, the absorbance (p.8) for trace amounts tends to zero because $I_o \simeq I$ in this case and consequently the ratio I_o/I tends to unity. Hence the logarithmic term also tends to

zero ($\log I_o/I = \log 1 = 0$). Therefore, an increase in the intensity of the incident light will be of no benefit. Similarly, increased amplifier gain will also yield no benefit in sensitivity. [21]

(ii) The molecules have a limited capacity to absorb light. Before light is absorbed, an electronic transition must occur within the molecule. The probability of such a transition is limited by several considerations. Any molecule can be regarded as having a light capture cross section. One method of increasing this is to spread a mesh of closely spaced π orbitals in the molecule to capture photons and secure a transition. [21] The maximum molar absorptivity for any organic molecule is 10^5. [10,11,21]

Due to these limiting factors, several attempts had been reported, e.g. the use of a ternary complex formed between silver, 1,10 - phenanthroline and bromopyrogallol red reaction and

is an extremely sensitive and selective for the silver ion. This method was described by Dagnall and West. [25] Another attempt to increase the sensitivity was described by Kirkbright and West. [26] These authors applied an amplification procedure for the determination of the phosphate ion. The phosphate ion is converted to phosphomolybdate, in which 12 molybdate ions are associated with each phosphate ion. This is then separated away from the excess molybdate and 12 molybdate ligand complexes are formed and measured. The method is very sensitive and has an overall molar absorptivity of 360,000.[26]

It was considered for the purpose of this study that the use of ternary complexes was the most promising way of overcoming the main two barriers of selectivity and sensitivity. The following reports the use of ternary complexes for the determination of some of the noble metals.

PART ONE

CHAPTER ONE

SPECTROPHOTOMETRIC DETERMINATION OF SILVER

SUMMARY

Silver (I) forms a blue-coloured ternary complex with 1,10 - phenanthroline and bromophenol blue in aqueous solution at pH 7, with molar absorptivity of 12,000 at 625 mμ. This complex is extractable into nitrobenzene at pH 8 with molar absorptivity of Ca 38,000 at 605 mμ. This is a simple and rapid method for the spectrophotometric determination of small amounts of silver (I) both in aqueous solution or by selective extraction into nitrobenzene down to 0.216 and 0.27 ppm respectively.

In the developed procedure, the silver ions can be determined in the presence of aluminium (III), barium (II), calcium (II), cobalt (II), copper (II), gold (III), iron (III) mercury (II), nickel (II), palladium (II), platinum (IV), sodium, zinc (II); and acetate, chloride, fluoride, nitrate, and sulphate using EDTA as a mass-masking agent. Only cyanide interferes seriously.

Another similar method based on the formation of a mauve coloured ternary complex between silver (I), 1,10 -phenanthroline and rose bengal is also proposed.

It has a molar absorptivity of ca 40,000 at pH 7 in aqueous solution at 575 mμ. The silver complex is extractable into nitrobenzene at pH 7 with molar absorptivity of ca. 35,000 at 570 mμ. This is a simple, rapid sensitive method for the determination of trace amounts of silver (I) either in aqueous solution or by selective extraction into nitrobenzene down to 0.043 and 0.27 ppm respectively in the presence of EDTA as a mass-masking agent.

The two proposed methods provide reproducible and sensitive means for the spectrophotometric determination of trace amounts of silver (I) in aqueous solutions or by its selective extraction into nitrobenzene. They are highly, conditionally, selective towards the silver ions and allow its determination in the presence of the other coinage and noble metals such as copper (II) and gold (III), etc.

INTRODUCTION

The quantitative determination of trace amounts of silver (< 10 ppm) are of vital concern in many areas, such as effluent analysis. For the determination of such small amounts of silver there are few methods which are satisfactory, but those generally used are based on absorption spectrophotometry. These methods are based mainly on the organic reagents which possess the so-called silver binding - NH - C(=S) - groups, e.g. p-dimethylaminobenzyl-idenerhodanine (rhodanine)[1,27,28,11] diphenylthiocarbazone (dithizone)[29,30] and their derivatives,[31,32] The molar absorptivities of the silver complexes are 23,200 and 29,900 respectively.[2] The former is relatively selective,[1] but neither is specific for silver as gold and palladium react with both.[1] The rhodanine method is troublesome in many aspects, e.g. the colour system is susceptible to changes in the acidity, it is time consuming and poor reproducibility is given.[1] The dithizone method is subject to interferences from photodecomposition, oxidation, temperature changes, acidity changes, and cationic interferences from copper (I) and (II), mercury (I) and (II), polonium (II), tellurium (IV) besides gold and palladium which were

previously mentioned. All these factors combine to give a poorly reproducible colour system.[1]

Other reagents have been used for the spectrophotometric determination of silver e.g. thiourea and rebeanic acid derivatives, pyrocatechol violet,[37] and pyrogallol red.[38] Perhaps the latter reagent is the most important relatively. This method was proposed by Dagnall and West[38] who reported that the pyrogallol red method is more reproducible and reliable than the others. The same authors reported in a second paper[39] that the silver - pyrogallol red reaction can be conditionally specific for silver. Even so, this method is not as sensitive as that using dithizone and has a molar absorptivity of only 10,000. Also, the formation of the yellow coloured complex is not instantaneous and is dependent upon concentration.

From the published spectrophotometric methods for the determination of silver, which are based on the formation of binary complexes between silver and the organic reagents, it is apparent that most of them lack selectivity, and in some instances, sensitivity.

The most reliable and sensitive spectrophotometric method for the determination of silver was published in 1964 by Dagnall and West.[25] This method involves the

formation of a ternary complex between silver, 1,10-phenanthroline and bromopyrogallol red. The reaction takes place instantaneously over a wide range of pH (3 - 10) and the blue coloured complex is stable for ca 0.5 hour. The molar absorptivity is 51,000 and only gold (III) and cyanide were found to interfere. The method is quite selective especially if the complex is extracted into nitrobenzene.[40,41] Nevertheless this method involves a relatively unstable reagent (bromopyrogallol red in 1.0% w/v ammonium acetate) which must be prepared freshly about every five days. Also the blue coloured complex produced is only stable for ½ hour which adds to the difficulties of routine analyses. In addition, the method is still subject to interference from gold and cyanide in aqueous solution. The authors did not investigate the other noble metals e.g. platinum, palladium, etc. which might behave similarly to gold.

Recently, in 1967, Chung and Meloan[42] described the use of 2-amino-6-methylthio-4-pyrimidine carboxilic acid as a spectrophotometric reagent for the spectrophotometric determination of silver (I) at pH 10 ± 0.1

with molar absorptivity of ca.2.09 x 10^3 at 375 mμ. However, this method is not sensitive and is very much pH sensitive which must be closely controlled to ± 0.1 pH unit.

In view of these criticisms, it is apparent that there is a need for a more selective spectrophotometric method for the determination of silver (I) or a method which utilizes more stable reagents.

DEVELOPMENT OF THE PROCEDURE

In 1964, Dagnall and West described an extremely sensitive spectrophotometric method for the determination of trace amounts of silver (I) which was based on the formation of a ternary complex with 1,10-phenanthroline and Bromopyrogallol Red (BPR). The reaction was conditionally specific for silver via the use of EDTA plus, in some instances, hydrogen peroxide and fluoride ion.[25] An extractive system for the selective separation of the ternary complex into nitrobenzene was also described.[40]

Further investigation of this type of ternary complex system indicated that the selectivity of reaction could be improved considerably by using an anionic dyestuff other than BPR, which did not contain vic. hydroxyl groups, as counter ion for the silver (I)-phenanthrolinium cation. In the case of BPR, the complex formation occurs through the co-ordination of the phenanthroline to form a co-ordinately bonded phanthrolinium cation carrying the same charge as the central ion. This ion then associates with BPR to form a well defined ternary complex system. Since

the vic. hydroxyl groups play no co-ordinative part in binding the cation, it is apparent that their presence detracts from the inherent selectivity of this reaction because BPR may undergo colour reactions with many ions other than silver in this way. Furthermore, BPR is subject to oxidation, particularly in alkaline media, and its solutions are, therefore, somewhat unstable and according to Dagnall and West[25] the BPR solution must be prepared freshly after 5 days. In addition, the method was still subject to interferences from the other noble metals, e.g. gold (III).

A range of anionic dyestuffs which did not possess vic. hydroxyl groups was examined as substitutes for Bromopyrogallol Red. Two reagents, Bromophenol Blue, (γ - sultone), [α - α - bis(3,5 -dibromo - 4 - hydroxyl phenyl) α - hydroxyl , and Rose Bengal (Extra), C.I.45440, tetrachloro (P) tetraiodo (R) fluorescein , were found capable of forming ternary complexes with the bis-phenanthrolinium silver (I) cation.

Preliminary investigations showed that silver (I) ions alone gave no colour change with bromophenol blue, but the bis-phenanthrolinium silver (I) cation formed a blue-coloured complex cf. Fig. 1. With rose bengal,

D C B A

Fig. 1

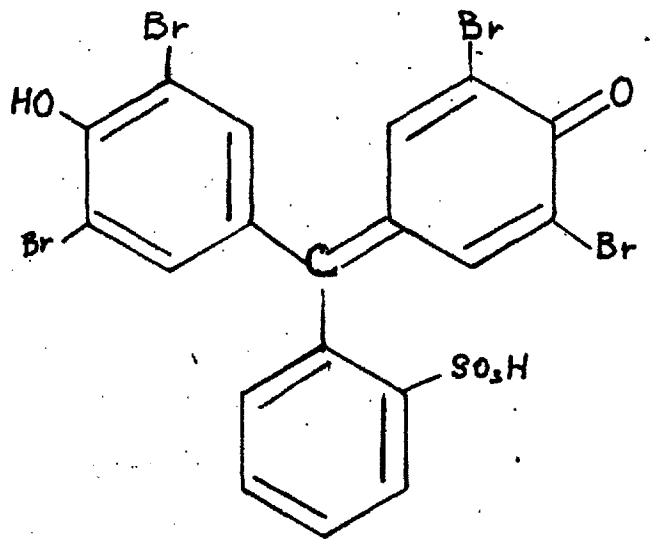
it was found that silver ions gave a very slight colour change while the bis-phenanthrolinium silver (I) cation formed a mauve coloured complex. Because the colour formation in both instances was rapid, stable, unaffected by the addition of the mass-masking agent EDTA and the utilized reagents were quite stable it was decided to investigate these two reactions and develop them for the determination of trace amounts of silver (I).

SECTION (I)

DETERMINATION OF SILVER (I) USING BROMOPHENOL BLUE

1. Preliminary investigations

1.1, Structure:



1,2 Preliminary Spectra

Because the reaction is not very sensitive in aqueous solution (ϵ = 12,000); a relatively high concentration of silver was taken e.g. 10ml - 10^{-4}M $AgNO_3$, 1ml 10^{-2}M 1,10 phenanthroline (phen), 1.4 ml 20% amonium acetate and 10 ml 10^{-4}M BPB diluted to 50 ml with distilled water. The absorption spectra of this solution was measured in a 1 cm cuvette against distilled water as blank. Fig. 2 (a). The reagent blank, carried through the same procedure, but containing no silver (b), has a peak at 585 mμ which decreases on the addition of silver. A plot of (a) against (b) gives a peak at 625 mμ.

2. Optimisation Of Conditions For Maximum Colour Development of Silver

2.1 pH

The blue-coloured complex may be formed by the addition of a solution of silver nitrate to an aqueous solution of 1,10-phenanthroline buffered to pH 7 with ammonium acetate (20% w/v) followed by addition of aqueous solution of BPB. Although the blue colour was obtained in acidic and slightly

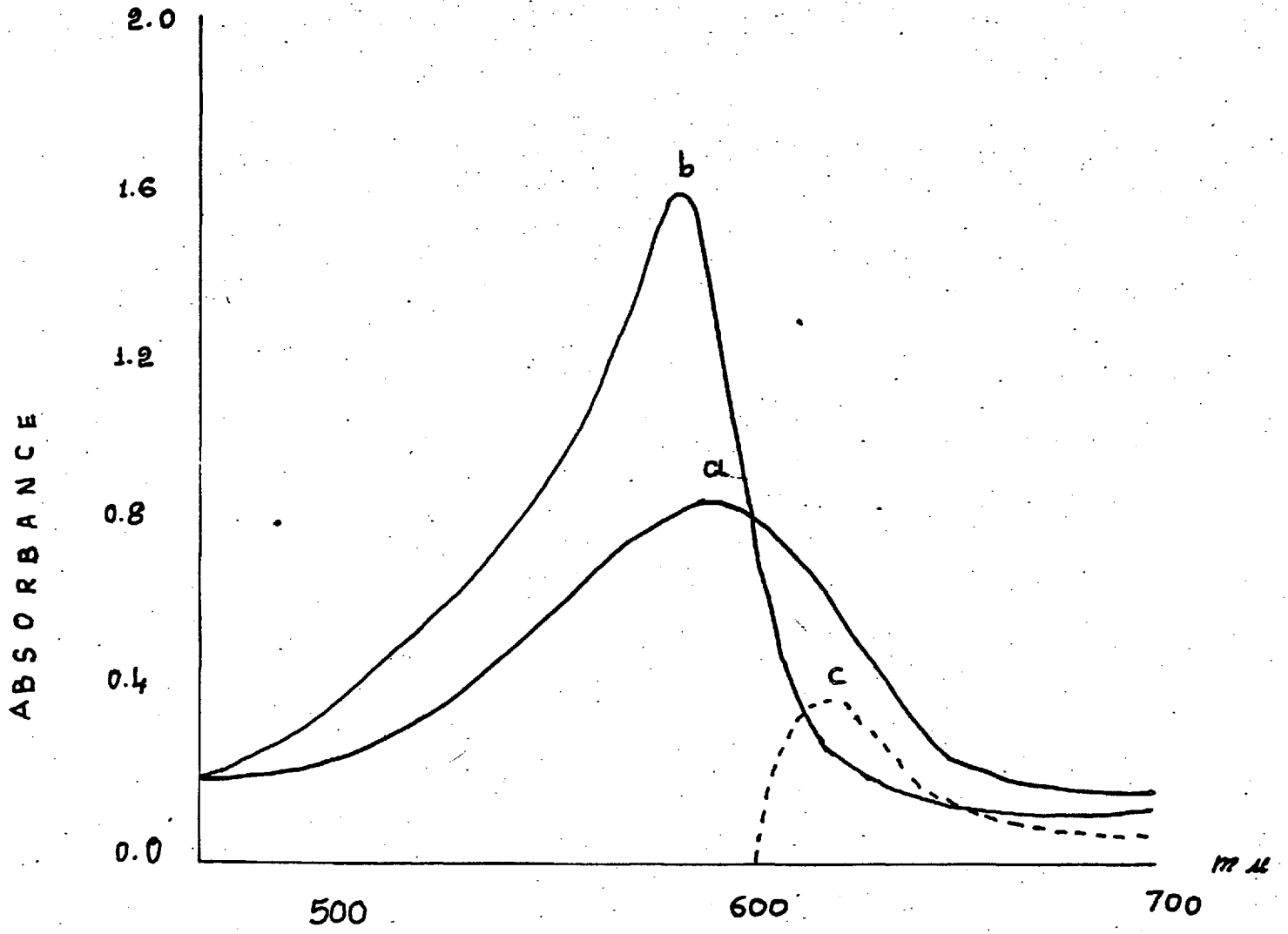


FIG. 2

alkaline media, the optimum pH was obtained over the range 4.5 - 8.5 (Fig. 3). A pH 7 was chosen for further studies because of the ease and the rapidity of the preparation of the buffer solution (20% w/v ammonium acetate). The solutions prepared for the examination of the optimum pH were prepared by pipetting 10 ml of 10^{-4}M $AgNO_3$, 1 ml 10^{-2}M phen and 20 ml of 10^{-4}M BPB and adjusting the pH using 0.1N HCl or 0.1N NH_3. The whole was then diluted to 50 ml in graduated flasks.

2.2 Development Time

The reaction between silver, phen and BPB was instantaneous and the blue colour was infinitely stable. No decrease in the absorbance were observed up to a fortnight (Fig. 4). In addition, direct sunlight or artificial light had no effect on the reaction.

2.3 Reagent Excess

The absorbancies of a series of solutions containing 10 ml 10^{-4}M silver (I) and 1 ml 10^{-2} 1,10-phenanthroline and a 1-10 fold molar excess of bromophenol blue in the presence of 1 ml 20% ammonium

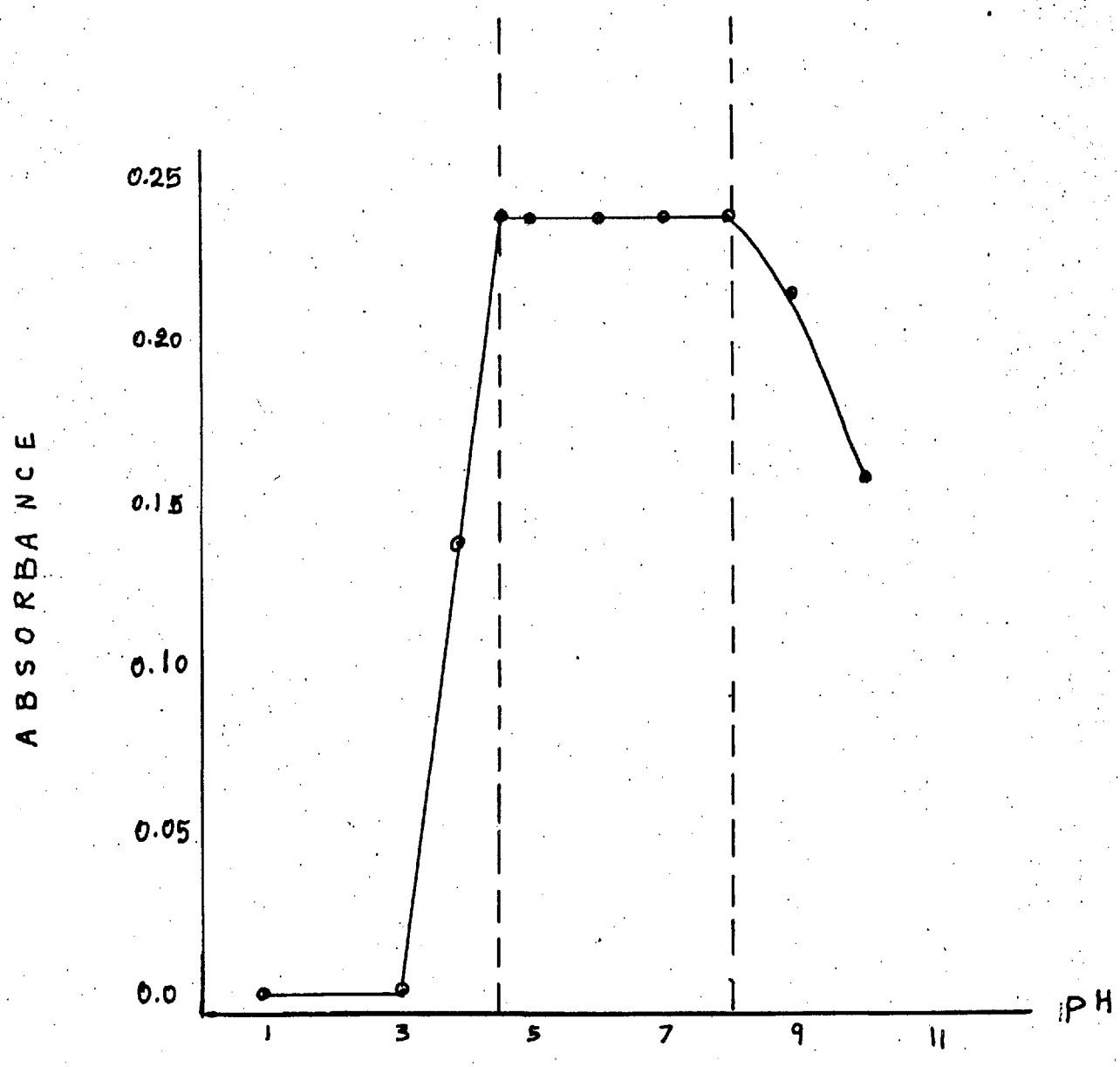


FIG. 3

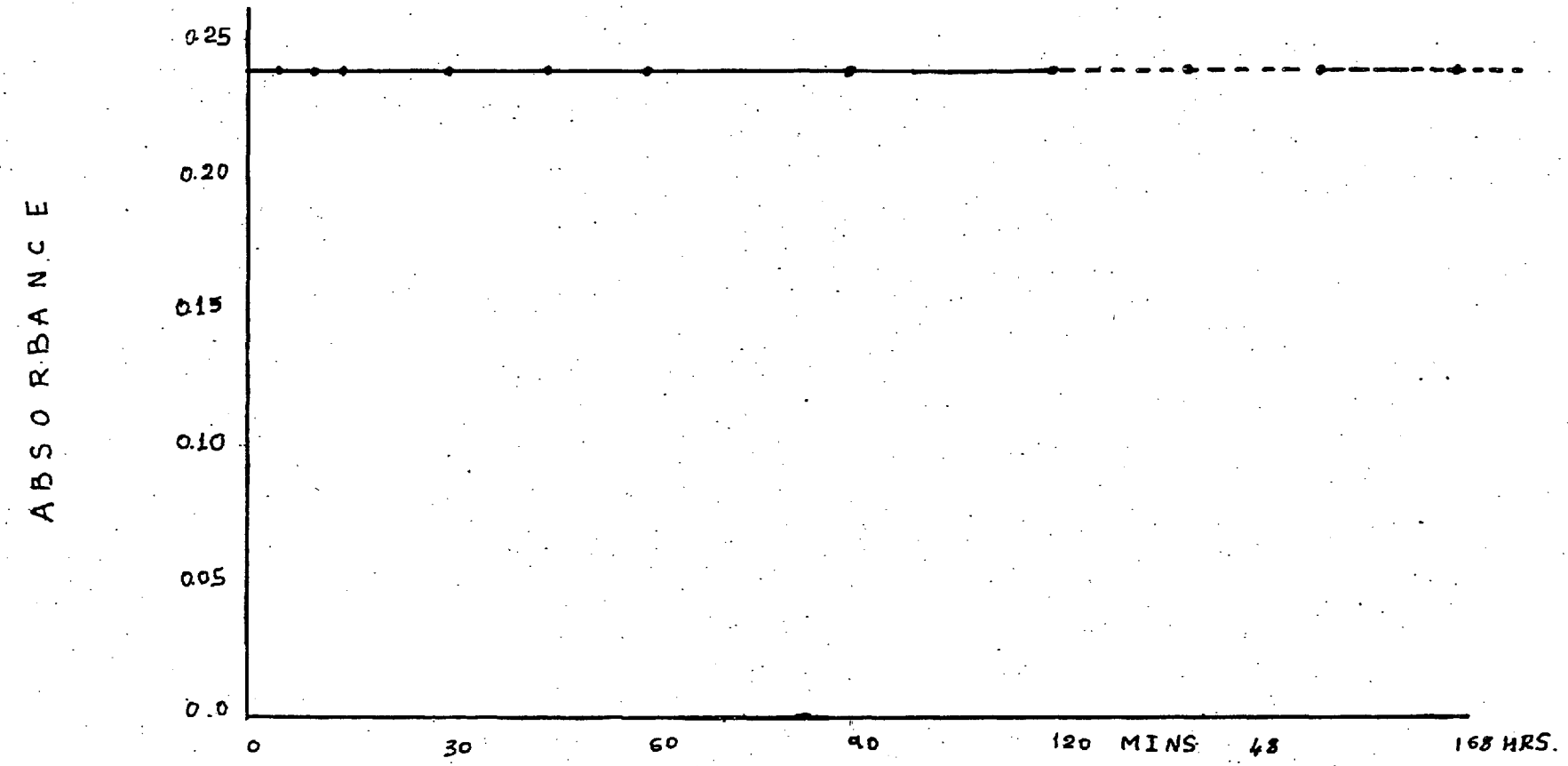


FIG 4

acetate were measured against reagent blanks containing similar amounts of BPB. Maximum absorbance at ca. a 2 - fold molar excess was given (Fig. 5). Above a 5-fold molar excess there is a gradual decrease in the absorbance with increasing reagent concentration. From investigation of the effect of the concentration of 1,10-phenanthroline, it is clear from Fig. 6 that the minimum concentration of phen with respect to silver is at least a 10 fold molar excess.

3. Lambert-Beer Law Check

With the established optimum conditions a calibration curve was prepared in the usual manner. Beer's law was obeyed between 1 - 10 ml 10^{-4}M Ag(I) per 50 ml or 10.788 - 107.88 of Ag(I) per 50 ml or 0.216 - 2.16 ppm final Ag(I) concentration giving a molecular extinction coefficient of 12,000 at 625 mμ (Fig. 7). However, smaller amounts of silver could be determined using 25 ml flasks and or using 4 cm cuvettes.

4. Interferences

The permissible level of the cation concentra-

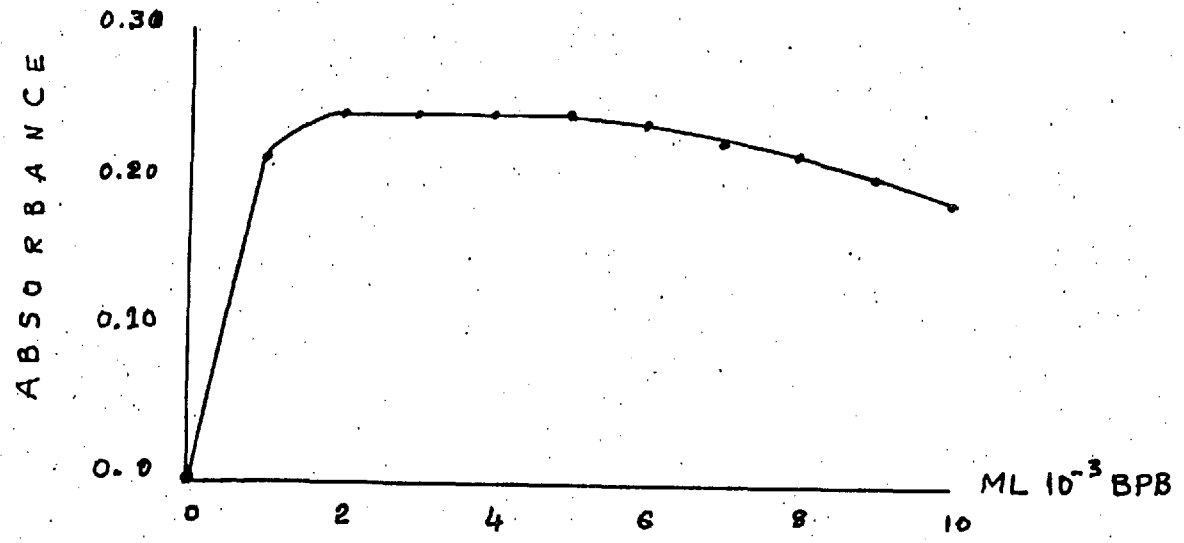

ABSORBANCE
0.30
0.20
0.10
0.0
0
2
4
6
8
10
ML 10^{-3} BPB

FIG. 5

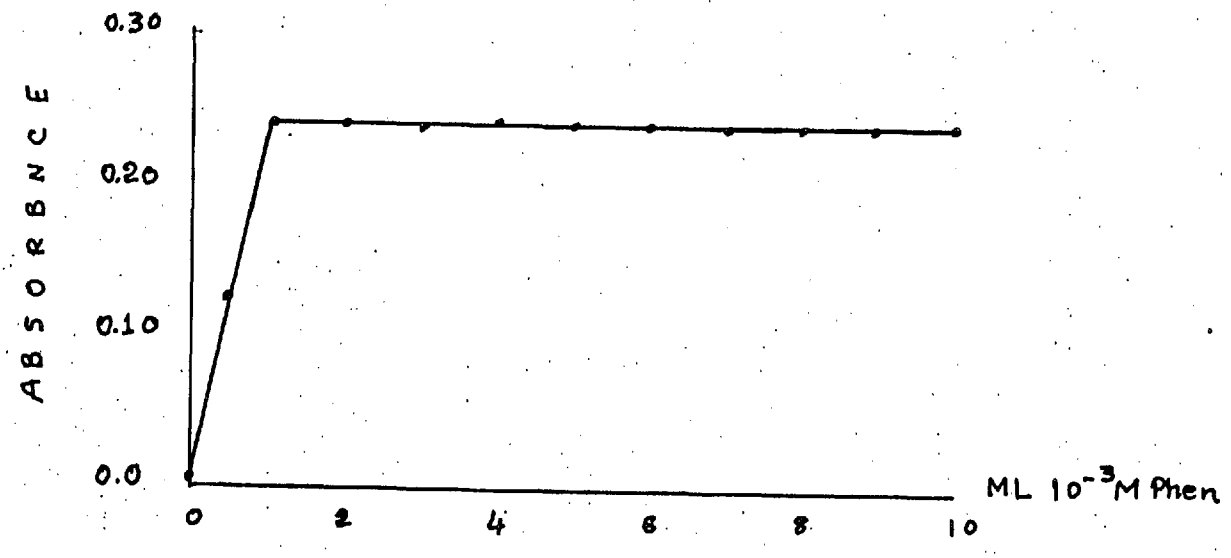

ABSORBANCE
0.30
0.20
0.10
0.0
0
2
4
6
8
10
ML 10^{-3}M Phen

FIG. 6

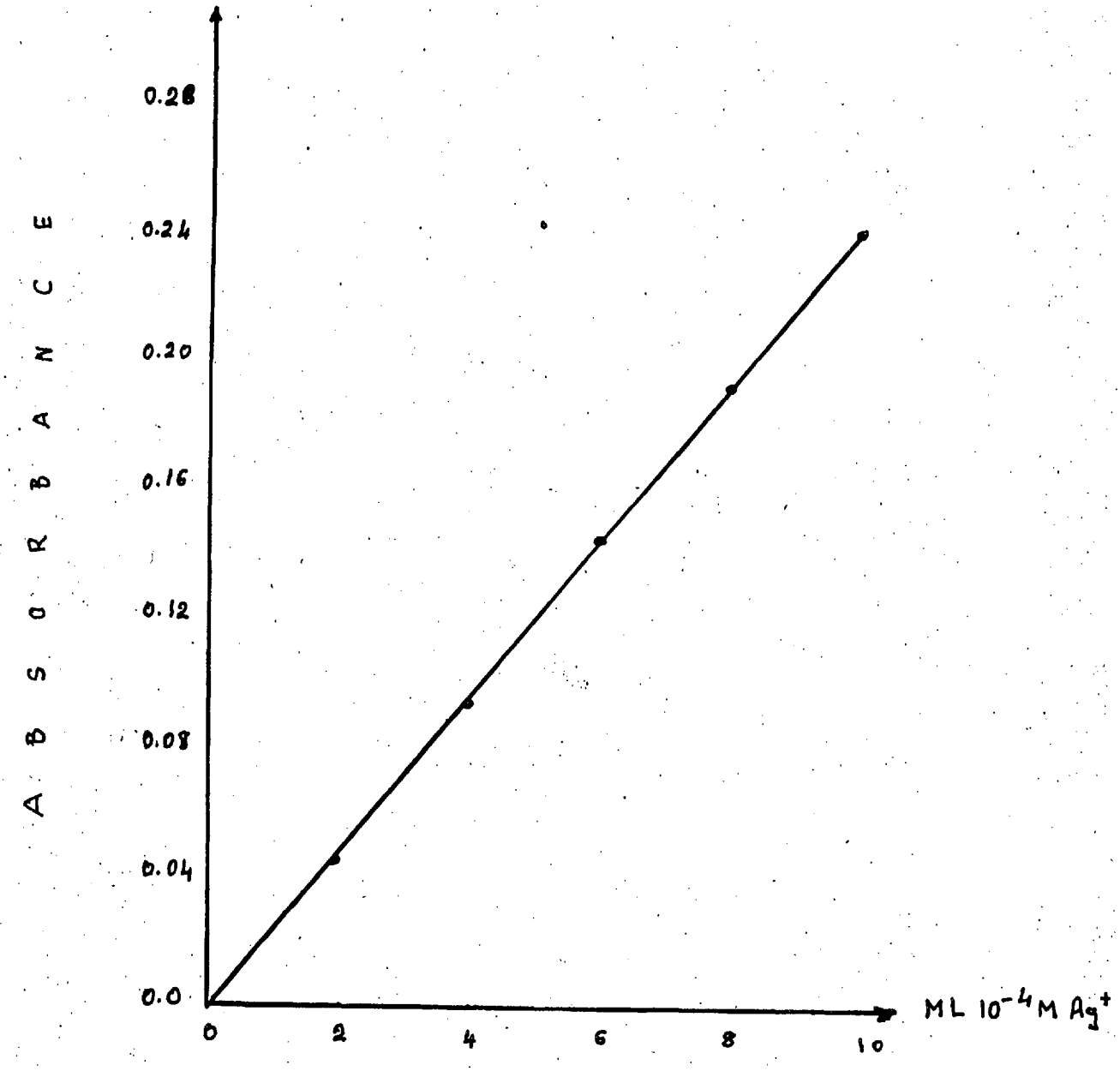


FIG 7

tion, other than silver, depends largely on the concentration of EDTA employed, because it was intended that EDTA should function as the principal masking agent. Solutions were prepared, therefore containing 1.08 ppm of Ag under the normal optimum conditions. By varying the concentration of EDTA from 10 - 1000 fold molar excess over silver, it was found that the absorbance of the solution containing 10 ml 10^{-4} Ag remained unchanged at an absorbance value of ca. 0.24 against a reagent blank containing the same amount of EDTA. Thus, the masking of 14 cations and 5 anions was examined using a 1000 fold molar excess of EDTA over silver (I). The procedure used was: Pipette 5 ml 10^{-2}M of the diverse or extraneous ion followed by 5 ml 10^{-4} M $AgNO_3$ - 5 ml 10^{-1}MEDTA, 1 ml 10^{-2}M phen, 1 ml 20% ammonium acetate and 2 ml 10^{-3}M BPB and then dilute with distilled water to 50 ml in a graduated flask. Measure the absorbance in a 1 cm cuvette against a blank carried through the same procedure, but containing no silver at 625 mμ. Compare the absorbance with a standard solution of silver carried through the same procedure, but containing no extraneous ions. Table I shows the effect and the maximum tolerance level of the

TABLE (I)

ion	Molar Fold Excess over Silver	Absorbance vs. Blank	Deviation from the Standard
Ag(I) (STANDARD)	0	0.120	-
Ag(I) + Al(III)	100	0.120	0
Ag(I) + Au(III)	100	0.115	- 0.005
Ag(I) + Ba(II)	100	0.120	0
Ag(I) + Ca(II)	100	0.120	0
Ag(I) + Co(II)	100	0.125	+ 0.005
Ag(I) + Fe(III)	100	0.128	+ 0.008
Ag(I) + Hg(II)	100	0.125	+ 0.005
Ag(I) + K^+	100	0.120	0.0
Ag(I) + Na^+	100	0.120	0.0
Ag(I) + Zn(II)	100	0.122	+ 0.002
Ag(I) + Cu(II)	50	0.128	+ 0.008
Ag(I) + Ni(II)	50	0.120	0.0
Ag(I) + Pd(II)	20	0.115	- 0.005
Ag(I) + Pt(IV)	10	0.110	- 0.01
Ag(I) + Acetate	3,000	0.120	0
Ag(I) + Cl^-	100	0.120	0
Ag(I) + F^-	100	0.120	0
Ag(I) + NO_3^-	100	0.120	0
Ag(I) + SO_4	100	1.122	+ 0.002
Ag(I) + CN^-	10	0.000	- 0.122

extraneous ions using a 1000 fold molar excess of EDTA. Palladium (II) and platinum (IV) interfere when present in large excesses because of the precipitation of their 1,10-phenanthroline complexes. However, it is obvious that this method is very selective, with the exception of cyanide which destroys the blue coloured-complex.

5. Nature of Complex

A continuous variation plot measured at 625 mu exhibited clear indication of a 2:4:1 silver: phen:BPB ratio. The Job Plots in Fig. 8 are as follows:

(i) Ag:BPB ratio (10^{-4}M) in excess of phen (10^{-2} M).

A continuous variation plot indicated a silver:reagent ratio of ~~12~~ 12.7:6.3 (i.e., (1:2), Fig. 8)

(ii) Silver:phen ratio (10^{-4} M) in excess of BPB (10 ml 10^{-3} M).

Here the Ag:phen ratio was 6.4:12.6 (ie., 2:4 1:2), Fig. 9.

(iii) BPB:Phen ratio (10^{-4} M) in excess of silver (10 ml 10^{-3} M)

In this instance a reagent ratio of 4:16

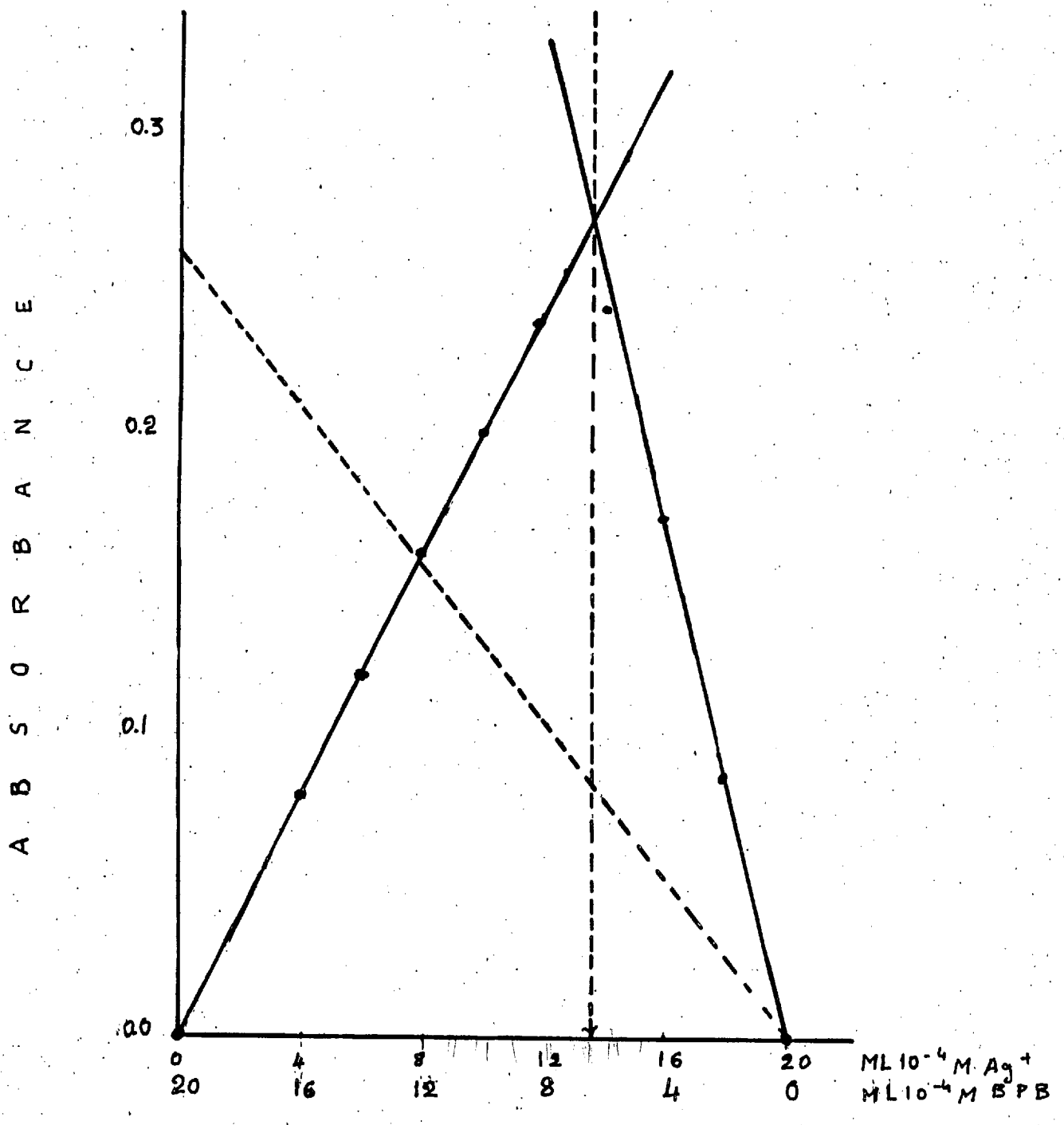

ABSORBANCE
0.3
0.2
0.1
0.0
0
20
4
16
8
12
12
8
16
4
20
0
ML 10⁻⁴ M Ag⁺
ML 10⁻⁴ M BPB

FIG. 8

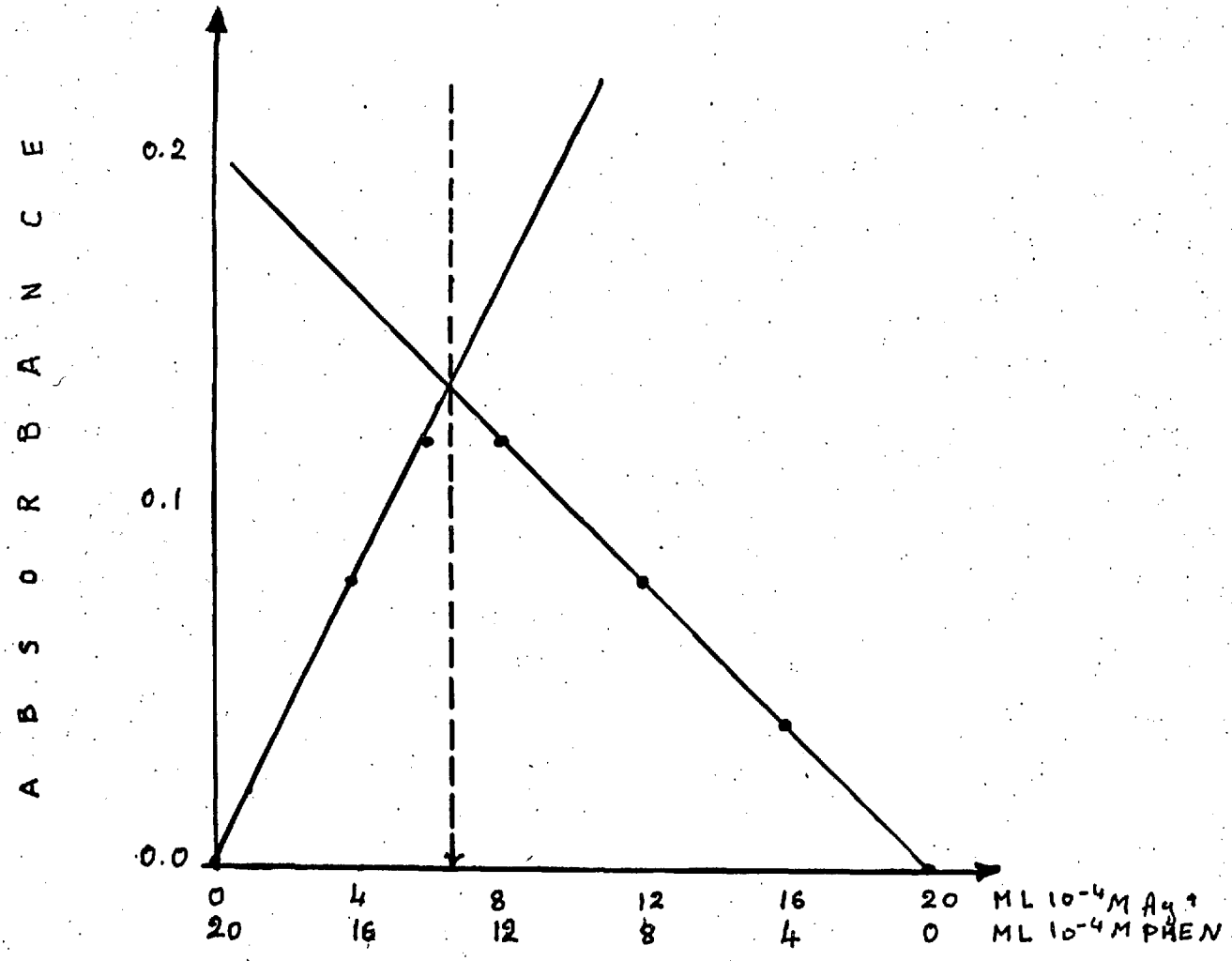
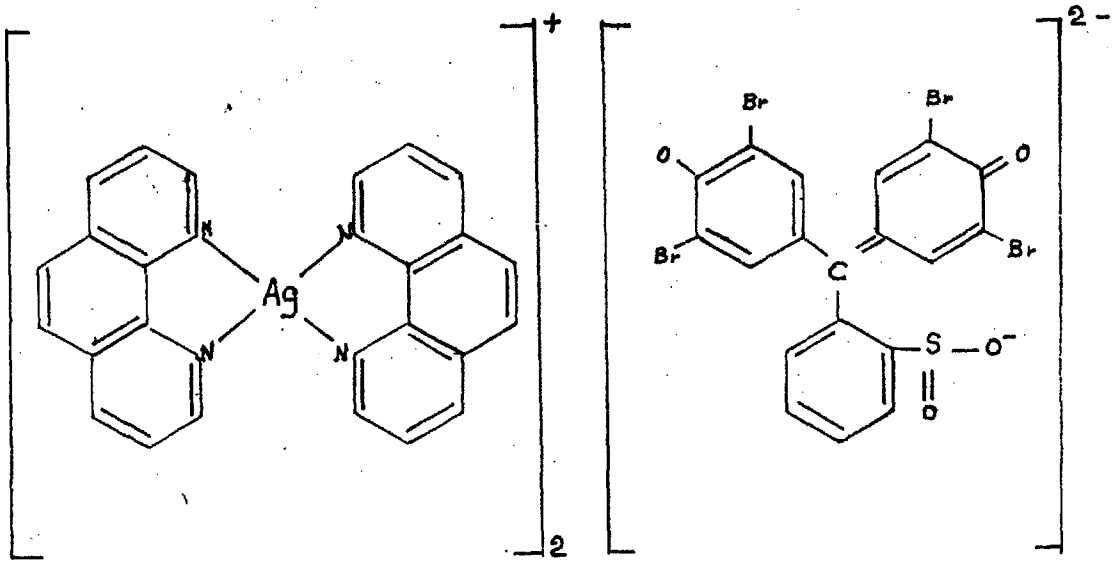

ABSORBANCE
0.2
0.1
0.0
0
20
4
16
8
12
12
8
16
4
20
0
ML 10-4 M Ag+
ML 10-4 M PHEN

FIG. 9

i.e., 1:4) was given, Fig. 10.

Thus, the over all ratio of the reagents employed is $(Silver)_2:(Phen)_4:BPB_1$.

It is well known that silver forms a co-ordinately bound complex with 1,10-phenanthroline to give the positively charged silver (I)-bis phenanthrolinium complex $(Phen - Ag - phen)^+$, BPB provides the counter ion for the silver (I) phenanthrolinium cation to form an uncharged ternary complex of the ion-association type. This complex can be formulated as $(phen - Ag - phen)^+_2$, BPB^{2-} and illustrated as follows:



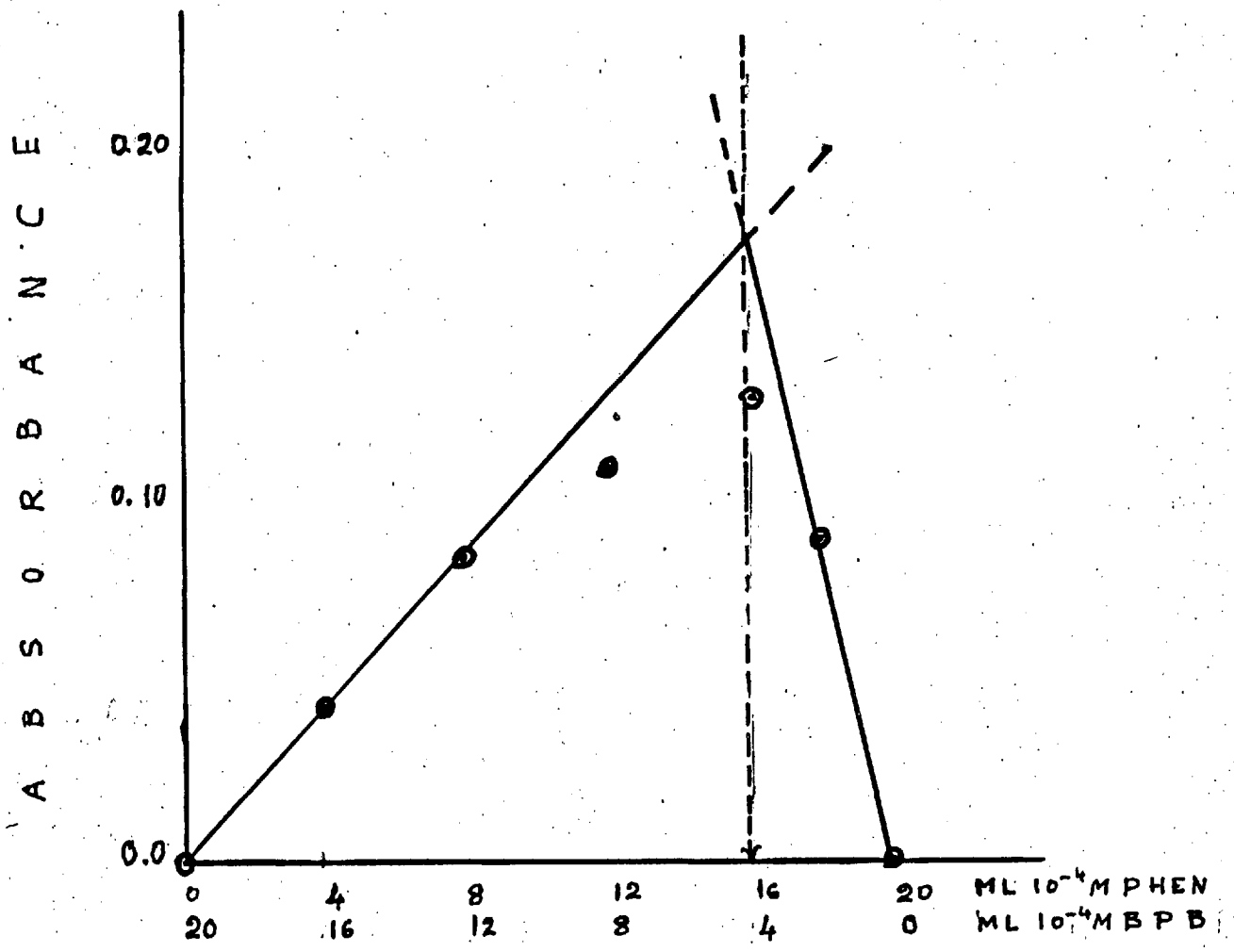

ABSORBANCE
0.20
0.10
0.0
0
20
4
16
8
12
12
8
16
4
20
0
ML 10^{-4}M PHEN
ML 10^{-4}M BPB

FIG. 10

6. Solvent Extraction

Although the reaction in aqueous media is extremely selective using EDTA as masking agent, it is not very sensitive as its molar absorptivity is only 12,000. This is, in fact, due to the high absorbance of the violet-coloured reagent blank which absorbs appreciably at 625 mμ . It was thought that by extraction into organic solvents, the absorbance of the blank might be decreased and consequently a higher sensitivity might be obtained. Actually, this was the case when nitrobenzene, which had already been found to be the best solvent capable of extracting (phen - Ag - $Phen^{+}_{2}$ BPB ternary complex, was utilised. The optimum pH was found to be about 8 and must be controlled between ± 0.5 pH/unit and using ammonium acetate/amonia as a buffer.

The absorption spectra of the extracted Ag - phen - BPB complex in nitrobenzene has a sharp peak at 605 mμ (a), while the reagent blank (b) has no significant absorbance in the range of 500 - 700 mμ (Fig. 11).

Although the green colour was obtained instantaneously, it reached a maximum only after Ca 90 mins.

Beer's law was obeyed over the range 5.393 -53.94

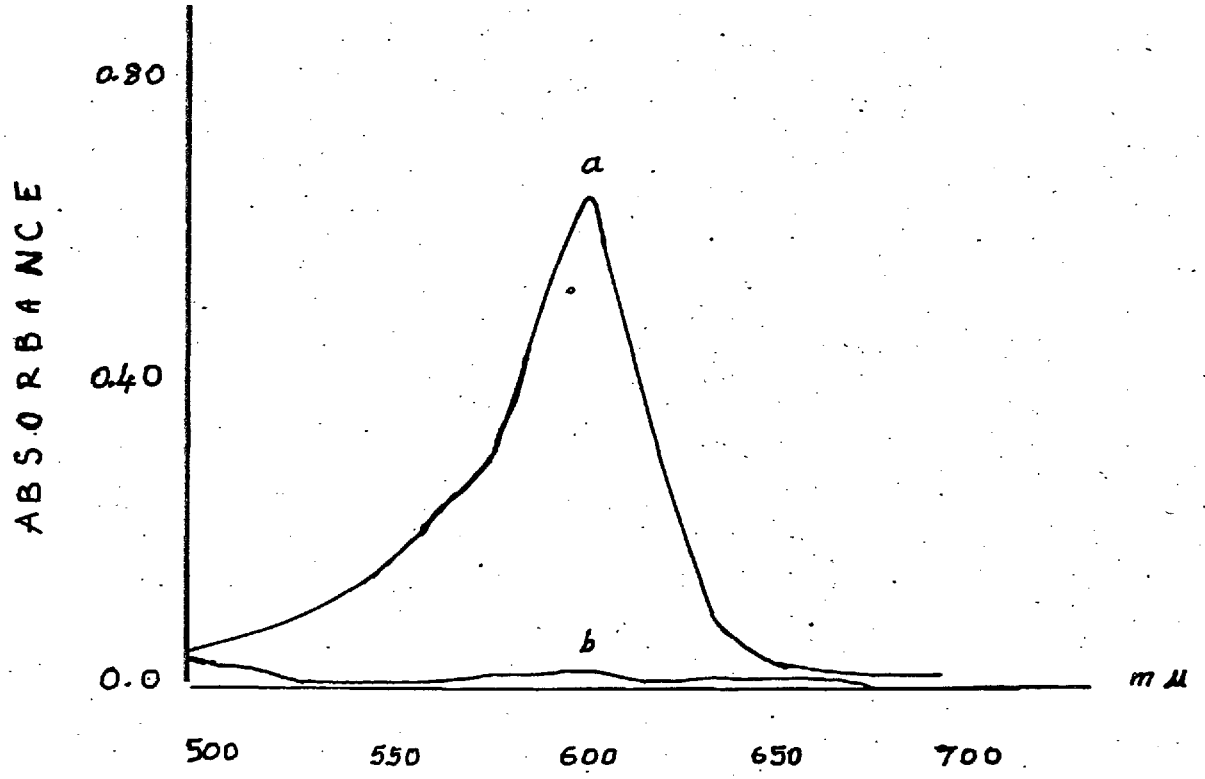


FIG. 11

µg of Ag/20 ml nitrobenzene, i.e. 0.27 - 2.7 ppm of Ag and the calibration curve obtained over that range was linear and passed through the origin. With a 200 fold molar excess of EDTA as masking agent (with respect to the upper limit of silver) a molecular extinction coefficient of 38,000 was given at 605 m µ (Fig 12).

1) Interferences in Extraction.

The permissibility of using 200 fold molar excess of EDTA, the mass masking agent, with respect to the upper limit of silver concentration i.e. 10 ml 5 x 10^{-5}M, indicates the feasibility of masking the extraneous ions prescribed in aqueous solution. Therefore, the extraction of silver-1,10-phenanthroline-bromophenol blue ternary complex into nitrobenzene is quite selective method at pH 8.

7. Precision

The precision of the method was investigated by determining the multiple analyses of a series of solutions, each contains a 5 ml of 10^{-4}M silver nitrate, a 1 ml of 10^{-1}M EDTA, 1 ml of 10^{-2}M 1,10-Phenanthroline, a 1 ml of 20% w/v ammonium acetate solution and 2 ml of 10^{-3}M bromophenol blue and diluted to 50 ml with distilled water.

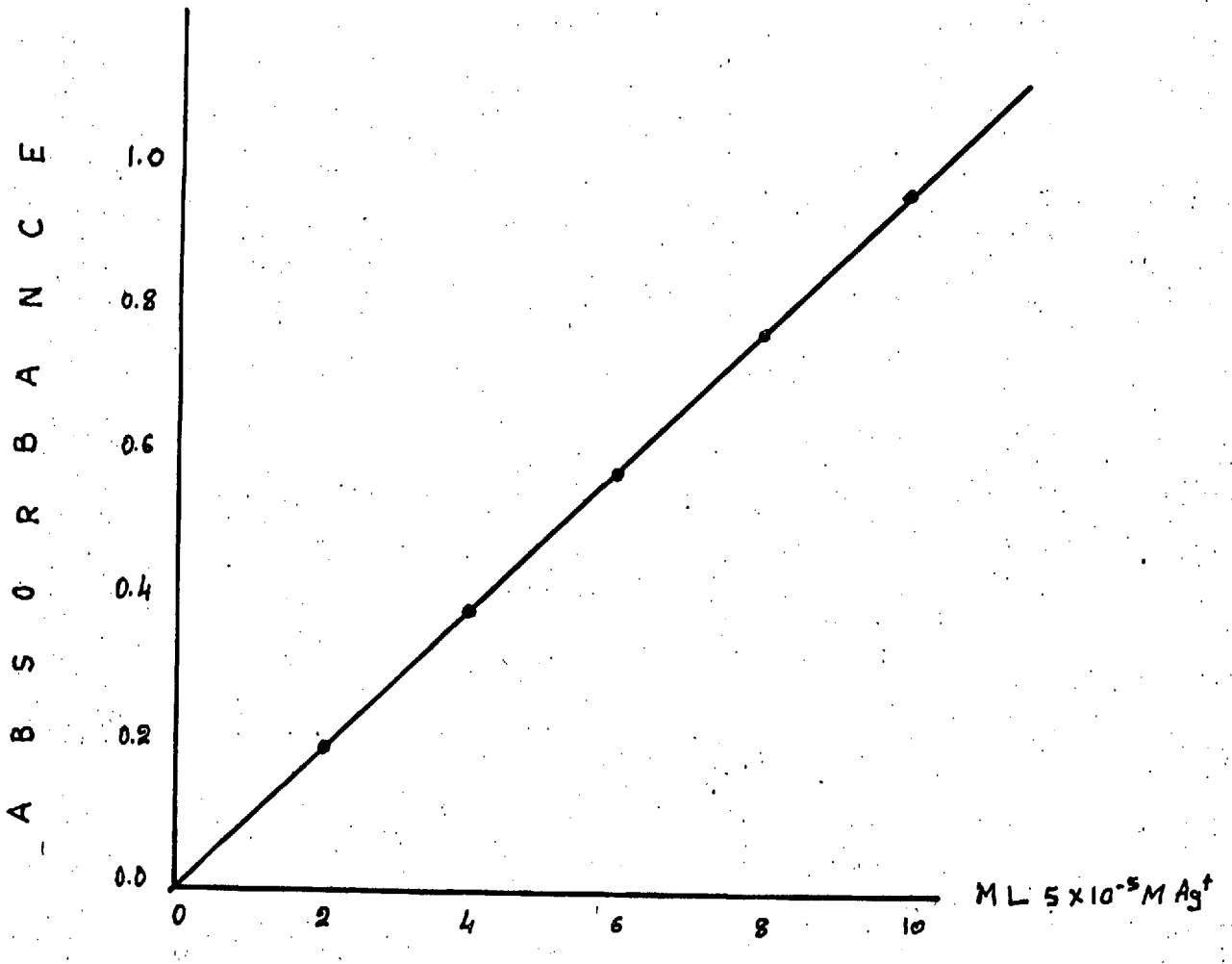


FIG. 12

The absorbance was measured against a reagent blank at 625 mμ . The results obtained are summarised in Table (II).

TABLE (II)

Number	Absorbance x 1000	Deviance D	Deviance^2 D^2
1	125	+ 5	25
2	120	0.0	0.0
3	127	+ 7	49
4	117	- 3	9
5	125	+ 5	25
6	115	- 5	25
7	122	+ 2	4
8	117	- 3	9
9	115	- 5	25
10	122	+ 2	4
11	115	- 5	25
n = 11	$\Sigma x = 1320$	$\Sigma D^2 = 200$	
	$\bar{x} = 120$		

$$\text{Standard Deviation} = S = \sqrt{\frac{\Sigma D^2}{n - 1}}$$

$$= \sqrt{\frac{200}{10}} = 4.48$$

Therefore % Standard Deviation

$$= \frac{4.48}{120} \times 100 = 3.73$$

E X P E R I M E N T A L

APPARATUS

Spectrophotometer	Unicam SP 600 with 1 cm. glass cuvettes
pH Meter	E.L.I. (Electronic Instruments Ltd.) Model 23A

REAGENTS

All reagents were of analytical grade unless otherwise stated.

Silver nitrate solutions - 10^{-1} - 2×10^{-5} M

Prepare by appropriate dilution of standard 10^{-1}M silver nitrate (B.D.H...)

1,10-Phenanthroline, 10^{-2} M

Prepare by dissolving 0.9910 g. of 1,10-phenanthroline hydrate in distilled water and dilute to 500 ml. in a graduated flask.

Bromophenol Blue, 10^{-3} - 10^{-4} M

Prepare by dissolving 0.3351 g of bromophenol blue (BPB) in distilled water and dilute to 500 ml. in a graduated flask (10^{-3} M). Then by appropriate dilution prepare a 10^{-4} solution.

Rose Bengal (Extra), 2×10^{-4} M

Prepare by dissolving 0.1018 g of Rose Bengal (Extra), (RBE) into distilled water and dilute to 500 ml. in a graduated flask.

EDTA, 10^{-1} M

Prepare by dissolving 18.6125 g of Na_2 EDTA in distilled water and dilute to 500 ml. in a graduated flask.

Ammonium Acetate, 20% W/V

Dissolve 20 g. of ammonium acetate trihydrate in distilled water and dilute to 100 ml. into a graduated flask.

Buffer Solution, pH 8

Prepare by dissolving 20g. of ammonium acetate into distilled water followed by the addition of few drops of 4 N ammonium hydroxide and adjust the pH to 8 at pH meter. Transfer the solution to 100 ml. graduated flask and dilute to the mark with distilled water.

Nitrobenzene Analar

Recommended Procedure for Silver/1,10 Phenanthroline/Bromophenol Blue

a) In Aqueous Media

Pipette 1-10 ml of a 10^{-4}M silver nitrate solution into 50 ml graduated flasks followed by 1 ml 10^{-2}M 1,10-phenanthroline (Phen), 1 ml of 20% w/v ammonium acetate after the addition of 1 ml 10^{-1}M EDTA then pipette 2.0 ml 10^{-3}M Bromophenol Blue (BPB) and then dilute with distilled water to the mark.

Then transfer an aliquot of the solution into a 1 cm glass cuvette, and measure the absorbance against a reagent blank carried through the same procedure, but containing no silver, at 625 mμ. Plot the absorbance obtained against ug of silver

1 ml of 10^{-4}M Ag NO_3 ≡ 10.787 μg of Ag^+

b) Solvent Extraction (into nitrobenzene)

Pipette 1-10 ml of 5 x 10^{-5}M Ag NO_3 solution into 100 ml separating funnels followed by 1 ml 10^{-2} Phen, 1 ml 10^{-1}M EDTA, 5 ml of a pH 8 buffer and add sufficient distilled water to give a constant volume of solution in each funnel, then

add 20 ml nitrobenzene, shake by continuous inversion for 1 minute. Allow about 10 minutes for the layers to separate, then transfer the lower organic layers to different 100 ml separating funnels and add 5 ml of pH 8 buffer and add 2.5 ml 10^{-3} of BPB and add enough distilled water to give a constant volume in each funnel. Again shake by continuous inversion for 1 minute and allow a standing time of ca. 90 minutes.

Run the lower nitrobenzene layers into clean dry 100 ml-beakers, and swirl each beaker until all cloudiness disappears (ca. 1 min.).

Finally transfer the solutions into 1-cm glass cuvettes and, as soon as possible, measure the absorbance at 605 mμ against a blank carried through the same procedure but containing no silver.

Plot the absorbance vs. μg of silver

1 ml of 5×10^{-5}M $AgNO_3$ ≡ 5.394 g of Ag

The graph of absorbance vs. micrograms of Ag^+ is a straight line from 5.394 - 53.94 μg of Ag^+ or 0.27 -2.7 ppm of final concentration of silver and passes through the origin.

CONCLUSION

The proposed method is, in many respects, superior to the existing spectrophotometric procedures for the determination of silver either in aqueous media or by extraction into water-immiscible organic solvents. It is simple and quick in operation, there is no need for a special purification of reagents and the usual disadvantages of the dithizone and p-aminobenzylidinerhodanine are, therefore, eliminated. The colour, in aqueous solution, takes place instaneously and remains stable regardless of the action of direct light or temperature fluctuations between day and night laboratory conditions. This allows the application of this method for routine analysis under any conditions.

This method is, utilising EDTA as a mass-masking agent, reliable and virtually completely free from all cationic interferences. It is one of the most selective methods for the determination of silver in the presence of the other noble and coinage metals e.g. 100-fold molar excess of gold (III) can be tolerated. Most of the published methods of determination of silver spectrophotometrically lack selectivity and always emphasise the separation of the

other noble metals e.g. gold. Even the previously most selective and sensitive method proposed by Dagnall and West in 1964 was subject to interference from gold.

The main drawback of this proposed method is that it lacks sensitivity in aqueous solution although it is extremely selective. However, this could be overcome by extracting the silver - 1,10-phenanthroline-bromophenol blue complex into nitrobenzene which yields the high sensitivity. Thus, the method, by extraction, compares favourably with the other common methods from the sensitivity point of view, cf. Table III

Table III

Method	Molar Absorptivity	
Phen/BPB	38,000	(605mμ)
Phen/BPR [40]	32,000	(590mμ)
Dithizone [2]	29,900	(462-465mμ)
p-Dimethylaminobenzyl-idenerhodanine [2]	23,200	(595mμ)

Furthermore, the phen/BPB system has some useful indicator properties, e.g. in silver/cyanide titrations, etc.

SECTION II

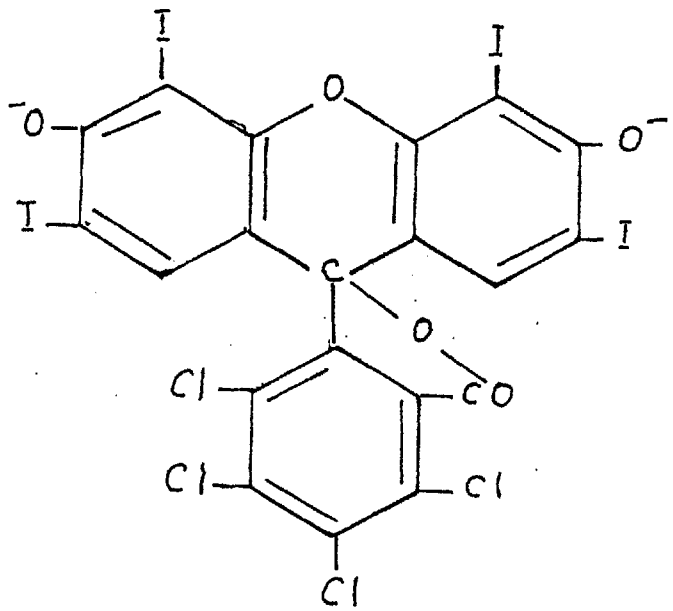
USING ROSE BENGAL (EXTRA)

DEVELOPMENT OF THE PROCEDURE

As has already been mentioned, Rose Bengal (Extra), C.I. 45440 tetrachloro (P) tetra-iodine (R) fluoriscein , (RBE), was found a suitable anionic reagent for the determination of trace amounts of silver (I). This provides a counter ion for the silver (I) bis-phenanthrolinium cation.

1. Preliminary Investigations

1.1 Structure



1.2 Preliminary Spectra

The absorption spectra of the RBE/Phen reagent blank (b) shows that it has a sharp peak at 540 mμ. The addition of silver ions to this solution shows appreciable absorbance at 575 - 580 mμ (a), at which the reagent blank (b) does not show absorbance very much. A plot of the silver/Phen/RBE solution (a) against the reagent blank (b) yields a sharp peak at 575 mμ (c)(fig. 13).

2. Optimisation of Conditions For the Development of Maximum Colour.

2.1 pH

The mauve coloured complex was formed in acidic, neutral and slightly alkaline solutions and the optimum pH range was 5 - 8. (Fig. 14). A pH of 7 was chosen because of the ease of preparation of the buffer solution (20% w/v of ammonium acetate).

2.2 Complex Development Time

The colour formation reached a maximum after 30 minutes. The colour remained stable for, as long as measurements were recorded viz 72 hours. (Fig. 15). Daylight, artificial light and the temperature fluctuations in the laboratory had no effect on the

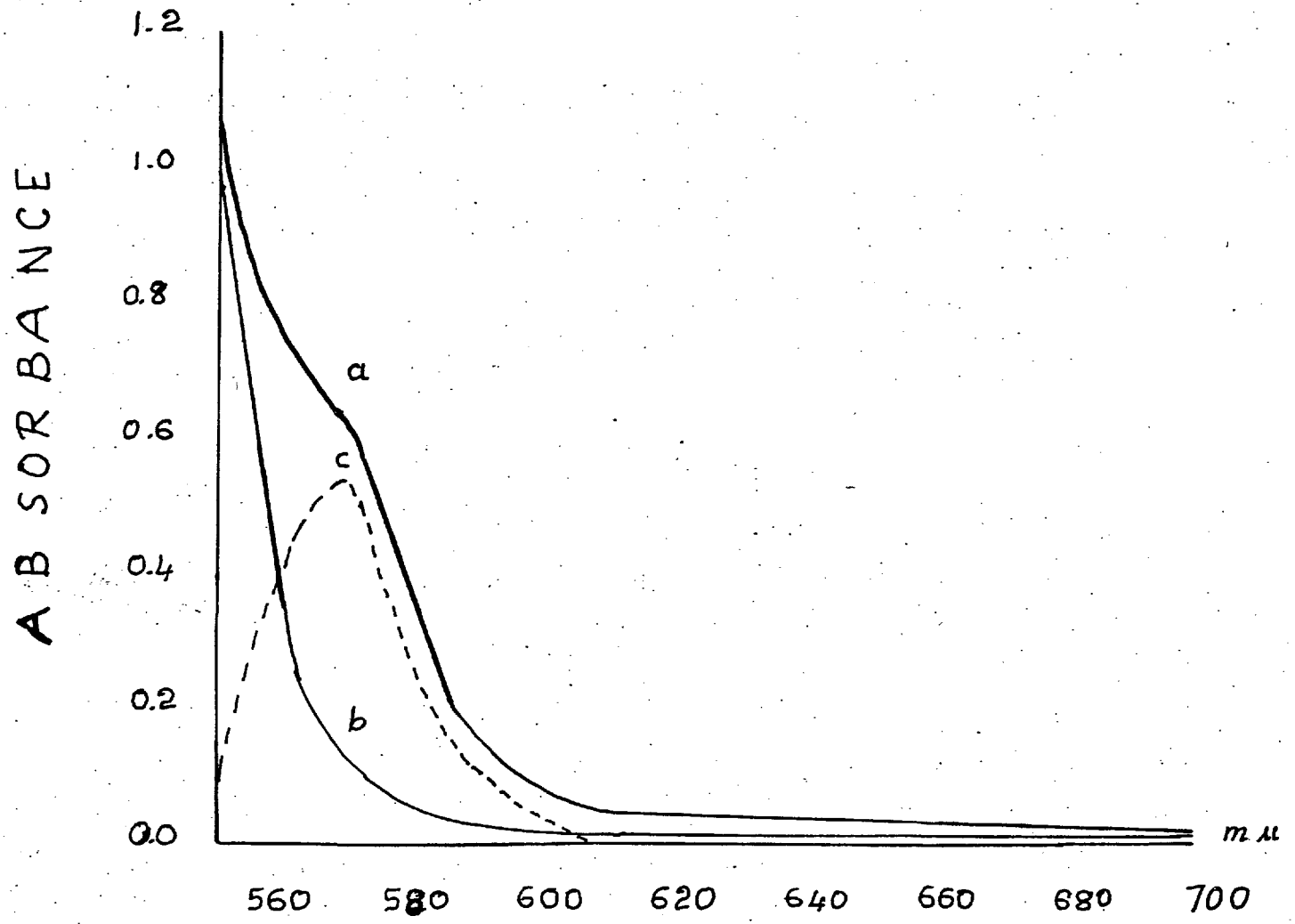

ABSORBANCE
1.2
1.0
0.8
0.6
0.4
0.2
0.0
a
b
c
mμ
560
580
600
620
640
660
680
700

FIG. 13

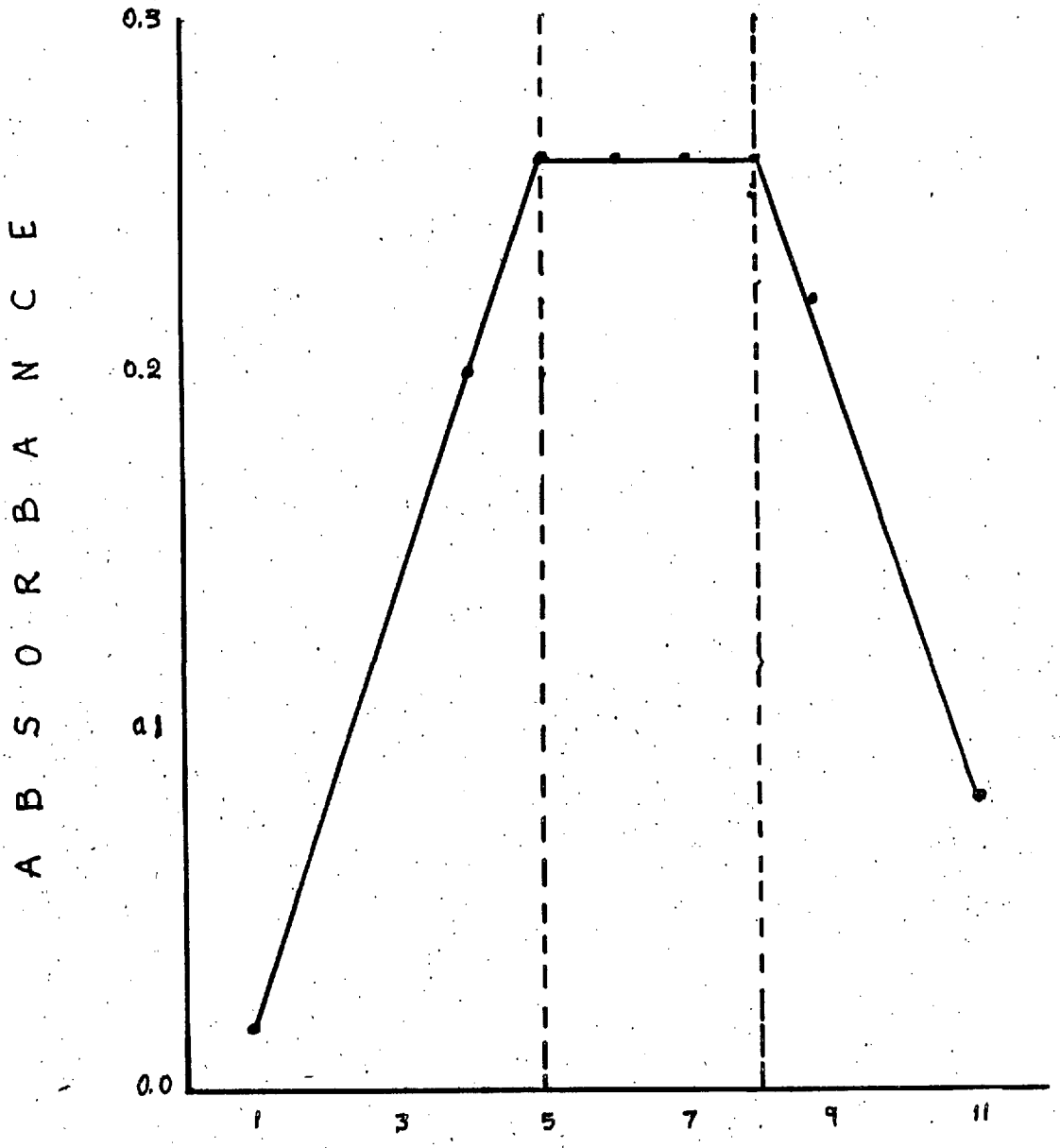


FIG. 14

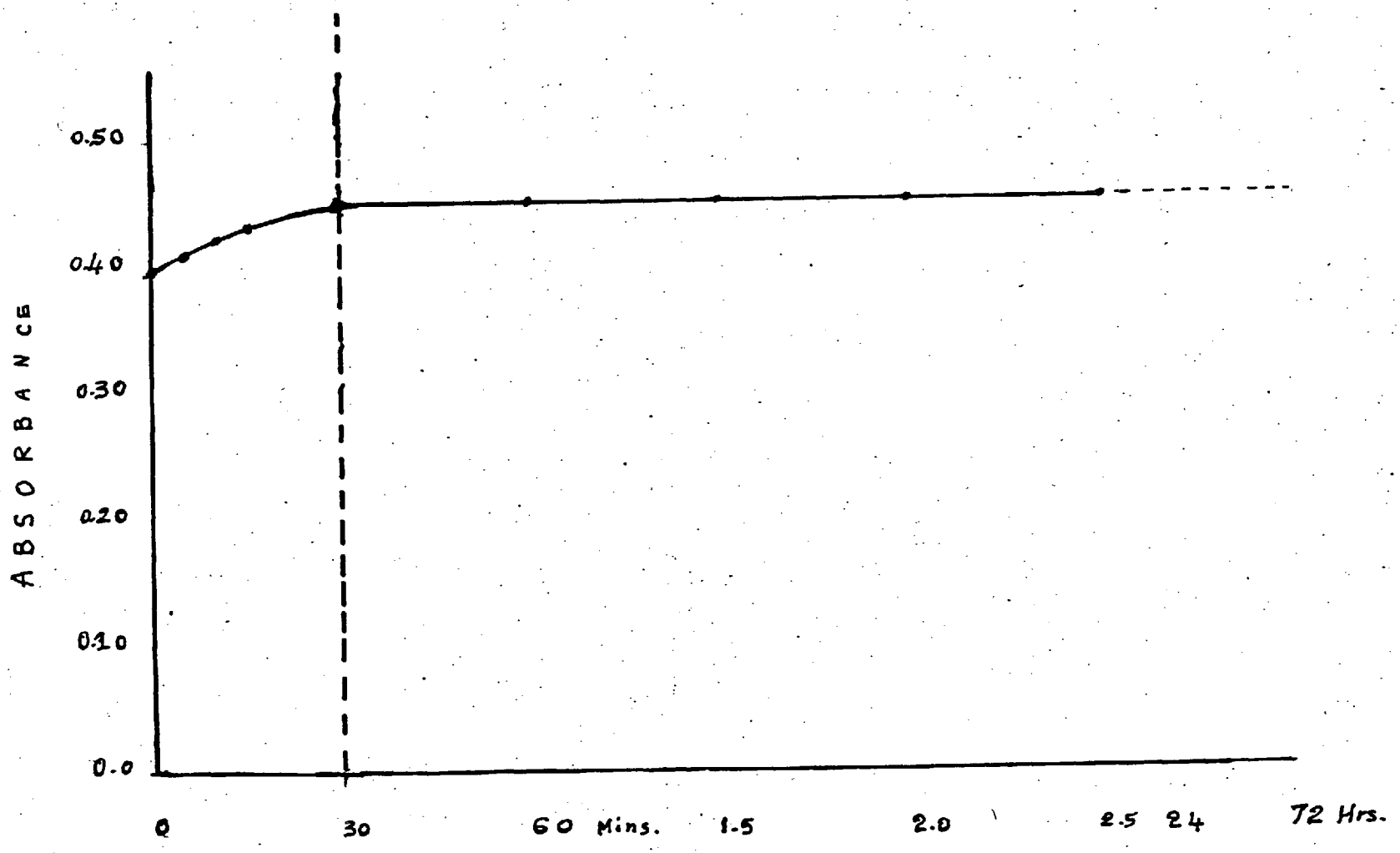


FIG. 15

stability.

3. Lambert-Beer's Law Check

Under the established optimum conditions, a calibration curve was prepared in the usual manner. Beer's law was obeyed over the range 1-10 ml of a 2×10^{-5}M and 1-10 ml of 10^{-4}M solution of silver nitrate per 50 ml or 0.043 - 0.43 and 2.16 - 21.6 ppm of final concentration of silver (I) respectively. The molar extinction co-efficient was 40,000 at 575 mu using a 100 fold molar excess of Phen, and 4 fold molar excess of RBE with respect to the upper limit of silver (I) concentration. The calibration curves obtained were linear and passed through the origin (Fig. 16 (a) and (b)).

4. Interferences

Since EDTA is used as a mass masking agent, it should be possible to mask most other cations as in the case of bromophenol blue.

5. Complex Ratio

Because Rose Bengal (Extra) is not readily available in the pure state and it was difficult to

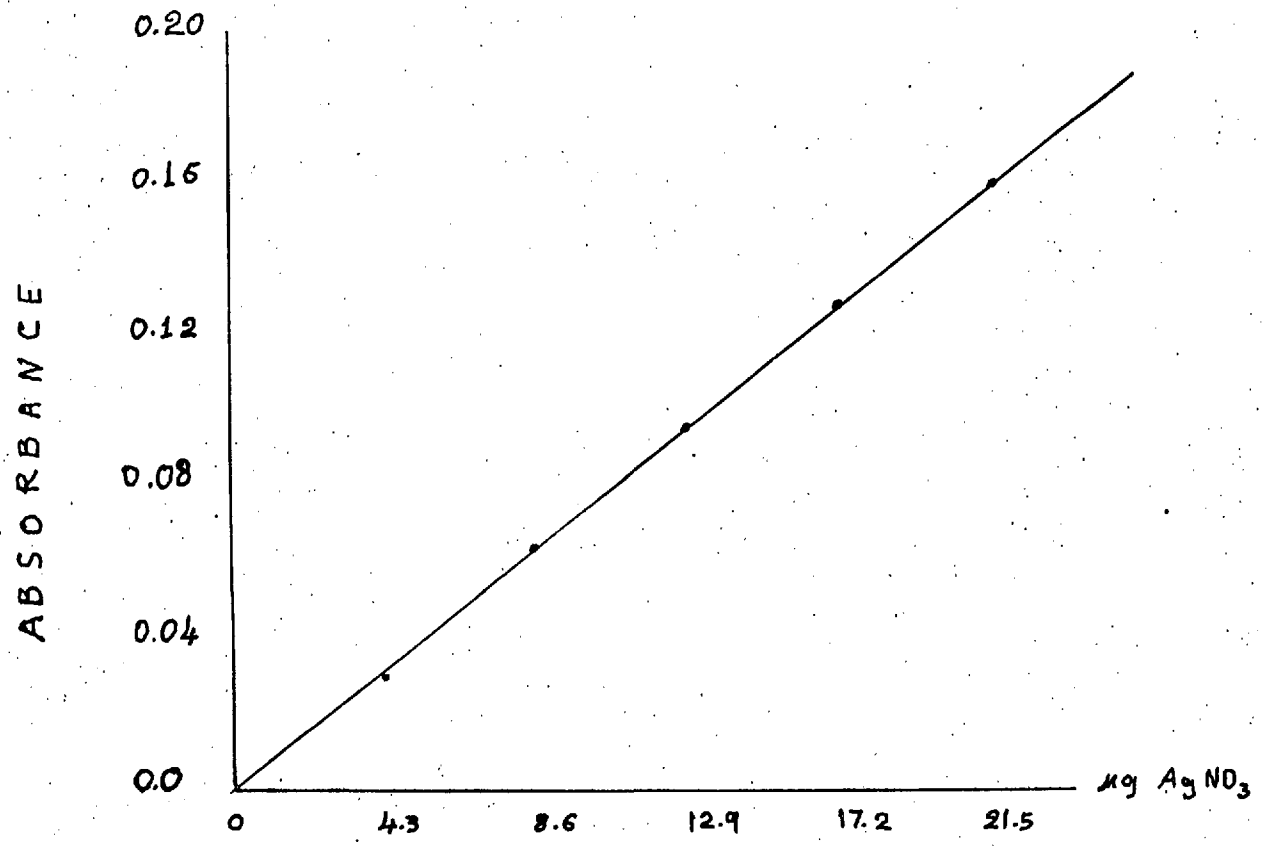


FIG. 16 (A)

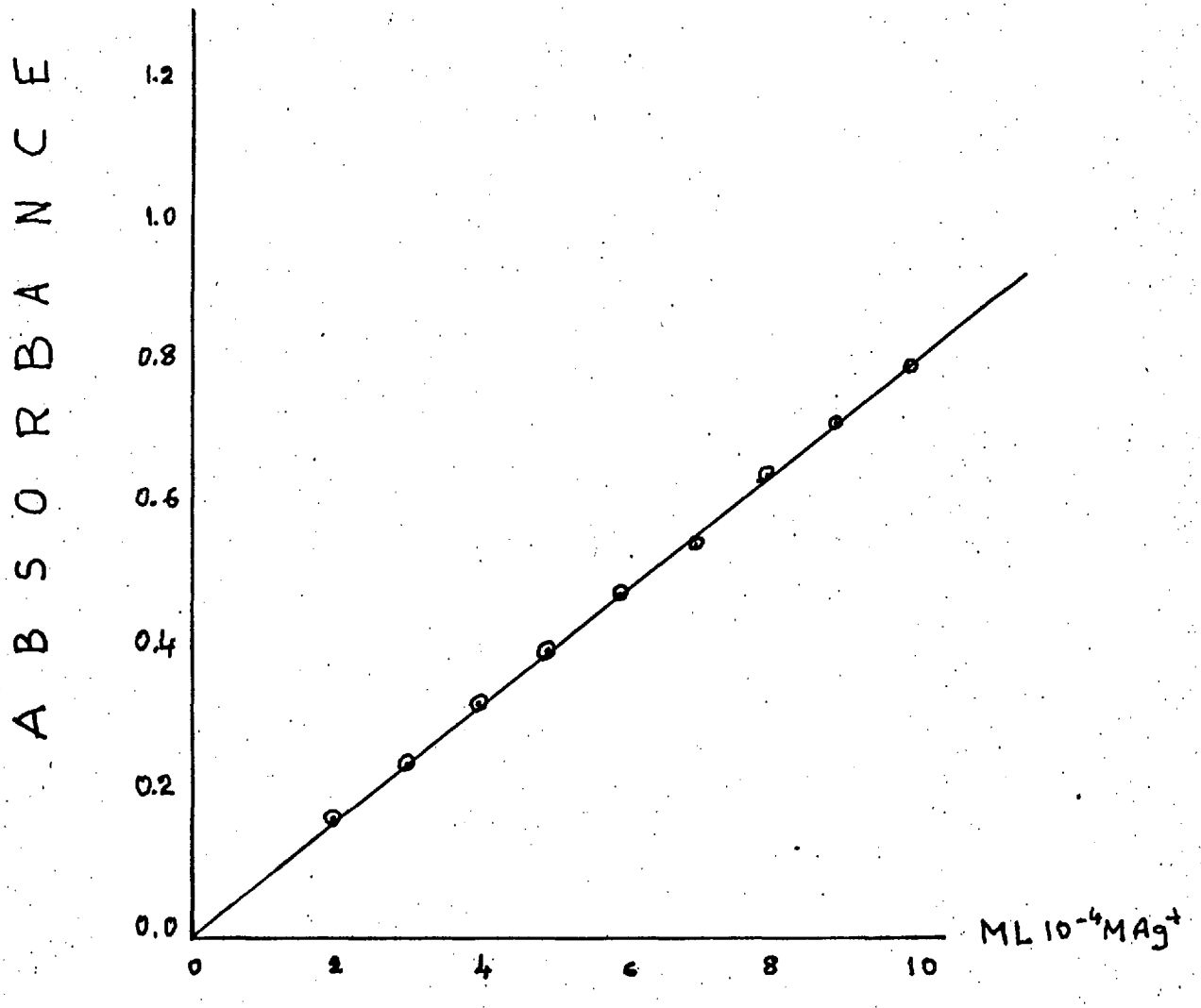


FIG. 16 (B)

purify,[43] Job's Plots and mole ratio plots were not made. However, it may be deduced, as expected theoretically , that the ternary complex formed between Ag/Phen/RBE would be ($(Phen - Ag - Phen)_2^+$), RBE^{2-} in the light of the results obtained previously using bromophenol blue.

6. Solvent Extraction

Several organic solvents have been examined for this purpose, viz. Namyl acetate, chloroform, carbon tetrachloride, chloroform, benzene, athyl acetate iso butyl methylketone and nitrobenzene. Only the latter was found capable of extracting the complex. A pH of ca. 7 was used and a standing time of 30 mins. was allowed for complete separation of the two layers before measuring the absorbance of the mauve coloured complex.

The absorption spectra of the reagent blank has a small peak at 570 mμ (b) and the ternary complex extract has a sharp peak at 570 mμ(a).The spectra in Fig 17 were obtained using a 10 fold molar excess of RBE and a 200 fold molar excess of EDTA over the silver concentration.

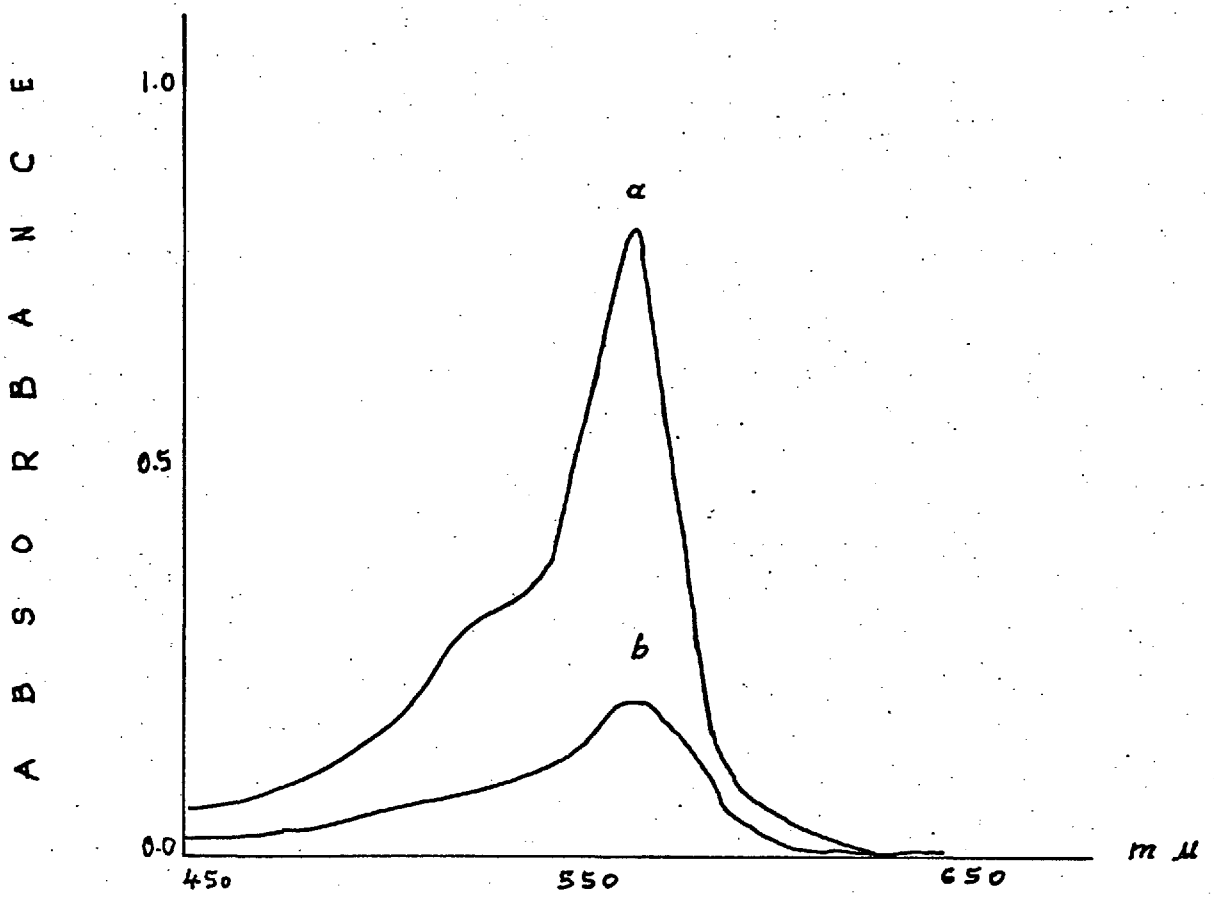


FIG. 17

Beer's law was obeyed between 1-10 ml of a 5×10^{-5}M solution of silver nitrate or 0.27 - 2.7 ppm of final concentration of silver (Fig. 18). The calibration graph was linear and passed through the origin. The molar absorptivity was 35,000 at 570 mμ .

RECOMMENDED PROCEDURE

a) In Aqueous Solution

As described for Ag/Phen/BPB, but for the calibration graph of 1-10 ml of 2×10^{-5}M silver nitrate, add 5 ml of 2×10^{-4}M Rose Bengal (Extra), (RBE), and measure the absorbance at 575 mμ . For 1-10 ml of 10^{-4}M silver nitrate, add 20 ml of 2×10^{-4}M RBE.

1 ml of 2×10^{-5}M $AgNO_3 \equiv 2.156$ μg of Ag^+

b) Solvent Extraction

As described for Ag/Phen/BPB, but add 1 ml of 20% w/v ammonium acetate solution as buffer. Also add 25 ml of 2×10^{-4}M of RBE and measure the absorbance at 570 mμ .

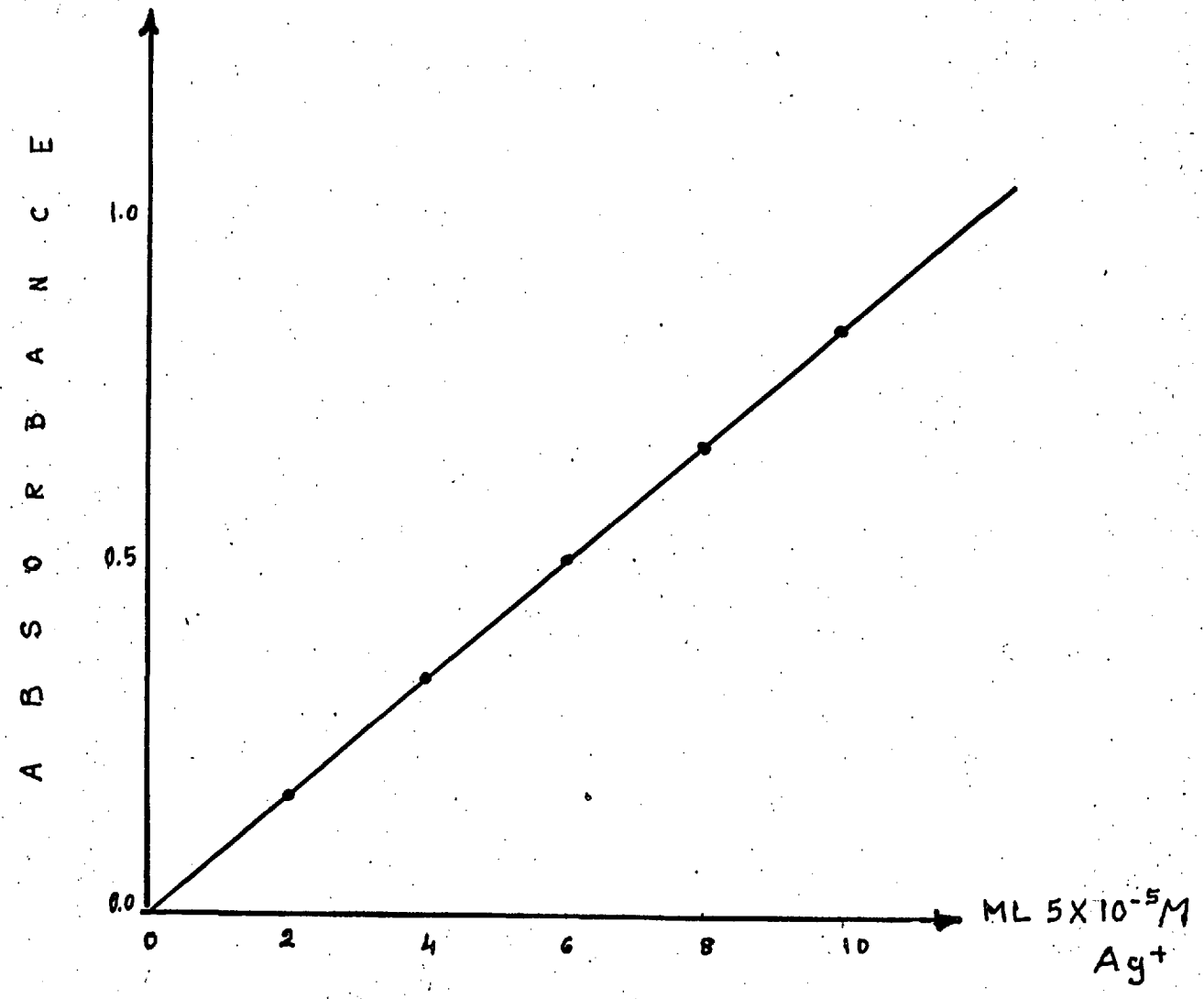


FIG. 18

CONCLUSION

The proposed method is rapid, yields a stable mauve-coloured complex which remains stable for several days under normal laboratory conditions. An important advantage is that it is applicable over a wide range of silver concentrations, i.e., 0.043 - 2.16 ppm. It is very sensitive in aqueous media, i.e. ϵ = 40,000, or after extraction into nitrobenzene, i.e., ϵ = 35,000. Another advantage is that it does not involve the utilization of unstable reagents as in other published methods, e.g. that using bromopyragallol red.[25,40]

Furthermore, the phen/RBE has some useful indicator properties such as in silver/cyanide titrations.

C H A P T E R II

SPECTROPHOTOMETRIC DETERMINATION OF CYANIDE

SUMMARY

A simple, rapid, reproducible and sensitive indirect spectrophotometric method is proposed for the determination of trace amounts of cyanides in aqueous solution. This method is based on the formation of the, silver(I)/Bromo-pyrogallol Red, blue coloured - ternary complex. The addition of cyanides to a solution containing excess of silver (I) decreases the absorbance gradually as the concentration of the cyanide increases. This method allows the determination of cyanides down to 0.0052 ppm and Beer's Law was obeyed over the range 0.26 - 26 μg of cyanides per 50 ml or 0.0052 - 0.52 ppm of final concentration of cyanides at 635 mμ.

This method is extremely conditionally selective, using EDTA as a mass-masking agent for most of the extraneous cations. Among the seventeen cations examined only mercury (II) interfered seriously and must be absent. These cations were, aluminum (III), barium (II), bismuth (III), calcium (II), cadmium (II), cobalt (II), copper (II), iron (III), lead (II), lithium, magnesium (II), manganese (II), mercury (II), nickel (II), potassium, sodium, and zinc (II). Furthermore, fourteen anions did not interfere as well.

These anions were, acetate, bromide, carbonate, chloride, chromate, fluoride, iodide, nitrate, perchlorate, persulphate, phosphate, sulphate, sulphite and thiocyanate.

Cyanides can, also be determined by selective extraction into nitrobenzene using Bromopyrogallol Red, and Bromophenol Blue as spectrophotometric reagents at 582 mμ and 605 mμ respectively. These two methods are applicable over the range of 0.13 - 1.30 ppm of cyanides.

These two methods can be classified among the sensitive and selective methods for the spectrophotometric determination of trace amounts of cyanides and are far superior, in many respects, to the other standard spectrophotometric methods such as Aldridge and Epstein methods.

INTRODUCTION

Cyanides are present in the atmosphere and effluents of many varied industries and are used in precious metal refining, antiseptics and fumigation, etc. [44] They are extremely toxic to both humans and other living creatures, so deadly are these cyanides that death may result simply from allowing the solutions to come into contact with cuts, etc. Repeated exposures to small concentrations of cyanides over long periods causes symptoms such as nausea, paralysis of limbs, psycoses, etc. [45]

Very low maximum concentrations are allowed for drinking water or in atmospheres where humans may be working e.g. water containing $\geq$ 0.01 ppm cyanide (CN^-) is unfit for public supply or domestic use, and the maximum allowable concentration of hydrogen cyanide in air is 0.005 ppm or 5 mg of hydrocyanic acid/m^3 of air. [46] Normal cyanide levels in blood are found to range from 0 - 0.1 ppm of cyanide. [47]

Since small amounts of cyanides are extremely toxic, the need for sensitive methods for their detection and determination is very important.

A - Methods of Detection of Cyanides

Cyanides may be detected down to 0.001 ppm by their

characteristic smell of bitter almonds; however, many people are relatively insensitive to this smell. [44,46] The formation of Prussian Blue, [44,48,49,50] is a means of detection of cyanide down to 1 ppm. The benzidine test [51,52] detects cyanogen ($(CN)_2$) down to 0.25 ppm; the sensitivity is increased four-fold by using 2:7 - diamino diphenylene oxide [53] instead of benzidine. The use of benzidine was prohibited recently [54] and it was replaced by copper ethyl-acetoacetate tetrabase. [55] This latter compound detects down to 1 ppm of hydrogen cyanide.

The ability of the cyanide ion to form stable complexes and cause demasking of inner complex-bonded transition metals has been used to detect cyanides, e.g. demasking of dimethylglyoxime from its palladium (II) complex. The liberated dimethylglyoxime is allowed to react then with nickel (II). [56] The bleaching of the red colour of the Cu ($Hg\ I_4$) complex by cyanide has been used to detect down to 0.2 ppm hydrogen cyanide. [57] Similar methods are reported and reviewed by Bark and Higson. [58]

A specific fluorimetric method for the direct detection of cyanides using various quinone derivatives, e.g., quinone monoxime ester, has been reported for the detection of cyanides down to 0.2 ppm. In this method, the addition of cyanide to the quinone monoxime ester gives a green fluores-

cence.[59,60]

B - Methods of Determination of Cyanides

The earliest method used was the gravimetric determination in which cyanide is precipitated with silver nitrate and weighed, after drying at 100°C, as silver cyanide. An alternative weighing form was as metallic silver after ignition.[2,44,61,62] However, the method is subject to interferences from extraneous ions, e.g., halides. Other possible methods of determination of cyanides may be classified under the general headings "non-colorimetric" and "colorimetric" methods.

I Non -Colorimetric Methods

Excluding polarographic and gas chromatographic methods, which are not commonly used, the principal non-colorimetric methods are titrimetric involving both visual and instrumental end-point detection.

a) Titrimetric Methods Involving Visual End-Point Detection

Several visual methods have been described using

different titrants. Silver nitrate was described for the argentimetric determination of cyanides more than a century ago by Liebig.[61] This was based on the appearance of an opalescence due to the formation of silver cyanide, or more precisely silver argenticyanide ($Ag(Ag(CN)_2)$).[61-64] The main practical difficulty of Liebig's method is that the silver argenticyanide produced by local excesses of the titrant redissolves with great difficulty.[61] The method is also subject to errors if carried out in alkaline solution.[65] The method was later modified by Deniges[61] who used potassium iodide as indicator in the presence of ammonia.

$$Ag(Ag(CN)_2) + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Ag(CN)_2^-$$

$$Ag(NH_3)_2^+ + I^- \rightleftharpoons AgI + 2NH_3$$

The silver iodide produced by local excesses of the titrant redissolves readily and is less soluble in the ammonical solution than silver argenticyanide.[61] This modification gives accurate results especially if the amount of ammonia is carefully controlled.[65] However, both methods are subject to interference by oxidising and reducing compounds such as ferric salts and hydrogen sulphide. In addition they are only applicable for higher concentrations of cyanide ca. 260 ppm.

Liebig's method has also been modified by Ryan and Culshaw [66] who proposed the use of p-dimethylaminobenzylidene rhodanine as an indicator. [66,67] Other indicators have also been reported, e.g. diphenyl carbazide [68] (down to ca. 52 ppm CN^-); diphenyl carbazone [69] (260 - 1,300 ppm CN^-); dithizone, [70,71] lead dithizonate, [72] ferric salt (after the transformation of cyanide to thiocyanate [73] or by back titration of excess silver with this cyanate in presence of ferric salts) [74]; p-ethoxy - 1 - naphthyl red; [75] fluorescein complexone [76] (the end point is detected by the disappearance of the fluorescence); thiofluorescein [77] (250 ppm HCN), luminol [78,79] (not specific) and calcein. [23]

A standard mercury solution has been proposed as a titrant for the visual mercurimetric titration of cyanide via formation of mercuric cyanide. Bognar [80] investigated several indicators and claimed that some 13 indicators could be used for the determination of macro amounts of cyanide (down to ca. 520 ppm). Diphenylcarbazone [81] has also been used to detect this end-point down to 2 ppm of cyanide, and also redox indicators Variamin Blue [82] and 2,5 - bis (β - hydroxyethylamino) terephthalic acid [40,83] have been used for the determination of 50 - 500 ppm

200 - 2,000 ppm of cyanide respectively. Other indicators have also been reported.[46,58,84]

A standard nickel solution, which is less expensive than silver nitrate, can be used as a titrant for the nickelometric determination of cyanide. Xylenol orange,[68] pyrocatecol violet,[85] murexide,[77,86] dimethylglyoxime and resacetophenone oxime[87] can be used as indicators.[87]

Acidic cuprous chloride has also been recommended as a titrant for determining cyanide using p-dimethylaminobenzylidenerhodanine (≥ 10 ppm CN^-)[88] or variamine blue[68] (0.5 - 1.6 ppm CN^-) as indicators. The chemiluminescent indicator luminol has also been used to detect the end point (2 - 10 ppm of cyanide).[89]

The appearance of a turbidity due to the formation of the sparingly soluble zinc cyanide has been reported for the macro-titration of cyanide. In this instance standard zinc sulphate is used as titrant.[90]

Other reported methods for the titration of hydrocyanic acid include the alkalimetric titration using standard sodium hydroxide and the iodometric titration using starch or carbon tetrachloride to

detect the end-point.[68,91,92]

From this brief survey of the published visual titrimetric methods, it may be deduced that the majority of them are applicable only in the macro-scale (ie. ca. 260 ppm) and that they lack sensitivity and specifity. The end-point detection is also rather a problem in the recommended, and widely used, Liebig's and Denigès method. The ability to detect the first appearance of a permanent turbidity in the clear solution differs from one worker to another. Also, if the solution is not perfectly clear prior to the titration, then the detection becomes even more difficult. Even many indicators, which change colour at the end-point, do not have a sharp colour change e.g. thiofluorescein. Therefore, there is a need for more sensitive and specific titrimetric methods for the determination of cyanide and for indicators which give a sharp colour change.

b - Titrimetric Methods Involving Instrumental End-Point Detection

Instrumental methods of analysis, such as the potentiometric titration of cyanide with silver nitrate[93-96]

have been frequently used and are reviewed by Bark and Higson.[58] The amperometric titration of cyanide with silver nitrate is equal in accuracy and precision to the visual Deniges method and is applicable at much higher dilutions (down to 0.01 ppm of cyanide have been determined). However, the electrode response and the sensitivity levels may change daily and must be frequently checked.[97] The coulometric generation of the mercuric ion with 100% current efficiency has been reported for the determination of cyanide solutions down to 0.052 ppm. Mercuric ions were found to be slightly superior to silver ions as a titrant for such small concentrations of cyanide.[98] The electrometric titration of cyanide by the dead-stop end point system using standard solutions of silver, mercury (I) or (II) has also been described.[99] Similarly a standard solution of iodine has been used as titrant.[58]

Cyanides can also be titrated photometrically using silver nitrate as titrant and potassium iodide as an indicator with a blue filter.[100] This method, however, is subject to interference from most other anions except chloride and phosphate, and in addition, not very sensitive (ca. 2.6 ppm CN^-). Gregorwicz[101]

has determined trace amounts of cyanide photometrically using cupric sulphate as titrant and Variamine Blue as indicator. The limit of sensitivity of this procedure is 0.03 ppm CN^-. Although photometric titration is suitable for the detection of those end-points which are not easily detected visually few photometric titration methods for cyanide have been published so far.

II COLORIMETRIC METHODS

From the literature, it is apparent that none of the colorimetric methods for cyanide is truely specific, although they are superior in sensitivity to the above mentioned methods of determination. Most of the colorimetric methods are based on the formation of metal complexes or on Konig reaction.

(a) Colorimetric Methods Involving Formation of Metal Complexes

Several colorimetric methods involving formation of metal complexes have been developed. The thiocyanate[102] and Prussian Blue[103] methods which are of ample sensitivity, have been deemed unsatisfactory due to the instability of the developed colour.[104] Phenolphthalein[104] and o-cresolphthalein[105] were recommended

for the colorimetric determination of cyanides because of their extreme sensitivity. However, neither is specific and very small amounts of oxidising compounds interfere.

The ability of the cyanide ion to form stable complexes and cause demasking of inner complex-bonded transition metals has been used for both detection and determination of cyanide, e.g. demasking of palladium complexes of dimethylglyoxime, furildioxime,[106] potassium di - (7 -iodo - 5 - sulpho oxino)[107] and 1 - nitroso -2- naphthol.[108] Small amounts of cyanide have been determined by the ability of cyanide to liberate 2 - hydroxy ethyl dithiocarbamic acid from its mercuric complex, which then reacts with copper (II) to give a yellow coloured complex.[109] In this determination thiosulphate interferes. The demasking of the mercuric complexes of p - dimethylaminobenzylidene-rhodanine,[110,111] and of diphenylcarbazone[112] in benzene have been used for the spectrophotometric determination of trace amounts of cyanide. However, both sunlight and temperature affect the absorbance of both reactions. The bleaching of the cupric ethylene-diamine sulphate complex by cyanide ions has also been

used for determining cyanide but sulphide, ferric and ferrous iron interfere and the method is not very sensitive. [113] The ability of cyanide to destroy the silver ketodithizonate complex at pH 9 has also been reported but in this instance, a deviation of 0.2 ppm unit caused considerable decrease in the absorbance values. [114] The reaction between cyanide and ferroin (tris(1,10-phenanthroline) iron (II)) to produce the neutral dicyano bis-(1,10-phenanthroline iron (II)) complex, which is extract$_a$ble into chloroform, has been used to determine down to 2 ppm of cyanide spectrophotometrically. [72] However, the pH must be carefully controlled in the range 9.2 - 9.7 and, although this method is sensitive, it is subject to interference from sulphide, copper, cobalt and iron (II) and the reaction takes some twenty hours to reach completion. Although this period can be shortened by heating at 100°C for 10 - 15 minutes, it is still tedious and time-consuming.

Fluorimetric methods for the determination of cyanide based on the demasking of the palladium - 8 - hydroxy - 5 - quinoline sulphonic acid complex have also been reported. The liberated quinoline derivative co-ordinates with magnesium to form a fluorescent com-

plex.[107] The formation of a fluorescent compound by reaction between nicotinamide and cyanogen chloride has also been used to determine cyanide.[116] This method is not widely used and is not specific.[59] A specific fluorimetric method has been described recently for the direct determination of 0.2 - 50 ppm of cyanide and involves the use of various quinone derivatives. e.g. quinone monoxime ester.[59,60]

b - Colorimetric Methods Based on the Konig" Reaction

1. Aldridge's Method:

This method has been recommended for determining small amounts of cyanide in trade effluent. Aldridge's method[117] is an example of the Konig"[118] synthesis for pyridine dyestuffs in which cyanogen bromide (CNBr) or chloride (CNCl) reacts with pyridine and aromatic amines to form a dyestuff. The cyanide is allowed to react with bromine

$$HCN + Br_2 \rightarrow CNBr + HBr$$

and the excess of bromine is removed with arsenious acid solution. The cyanogen bromide formed is then allowed to react with a mixed pyridine - bensidene reagent. The intense orange colour which

is formed, is measured immediately as it is stable for only 6 minutes after which it turns red. Later, Aldridge[119] improved his method by measuring the red colour which is stable for about 30 minutes. Down to 0.1 ppm of cyanide can be determined by this method with an error of ± 2%. Saltzman[120] reported that the final colour was unstable and that the the instability increased with temperature. Many modifications of this method have appeared in the literature.[121-130] Bark and Higson[131,132] replaced benzidine by p-phenylenediamine since it is, unlike the former, not carcinongenic. This modification increases the sensitivity of the original method and is applicable over a wider range of cyanide concentration (0.005 - 100 ppm).

2. Epstein's Method[133]

This method is similar to Aldridge's and is also based on the Konig reaction. Cyanide is oxidised to cyanogen chloride with chloramine T, and the CNCl is then allowed to react with pyridine containing 3 - methyl 1 - phenyl - 5 - pyrazolone (pyrazolone) and a small amount of bis - (3 - methyl 1 - phenyl - 5 - pyrazolone) and the blue colour

produced is measured after 20 minutes at 630 mμ. If the "bis-pyralozone" is not used a blue colour is still developed, but it is not stable. Epstein's method is sensitive down to 1.2 μg of cyanide and it may be used in acidic, neutral or slightly alkaline media, although the optimum pH was later reported to be 7.2.[134] Jørgensen[135] reported that the sensitivity could be increased about six times if his modified reagent preparation and storage was used. He was able to determine cyanide down to 0.1 ppm. Gardner et al.[136] pointed out that the limit of detection is 0.02 ppm of cyanide using Epstein's method. Malatesta and Dubin[137] replaced the pyrazolone reagent by four other reagents in order to increase the sensitivity of the method. However, this modification involves heating and cooling which is time consuming and the reagents are only stable for about 16 mins. Whiston and Cherry [138] favour Epstein's method because of the carcinogenic properties of the benzidine reagent used in Aldridge's method and obtained a calibration graph over the range 0-2 ppm of cyanide.

Although Aldridge's and Epstein's methods are

generally considered to be the best spectrophotometric methods for determining trace amounts of cyanide, each has certain disadvantages. The main disadvantage of Aldridge's method is that the amine used is a well known active carcinogen. Also there is some confusion as to the correct wavelength to use for measuring the developed colour and Beer's law is only obeyed down to concentrations of the order 1-2 ppm. The modified method of Murty and Viswanathan, [127] who used barbituric acid in place of benzidine, was claimed to be satisfactory because it was sensitive and small amounts of cyanide down to 0.01 ppm could be determined. However, it needs to be heated for a relatively long time (40 minutes at 40°C).

Although, the p-phenylenediamine method is sensitive, there is confusion as to the choice of the procedure to be utilized, which depends on the expected concentration of cyanide to be determined, the size of the sample available and the contaminants. In addition it is not relatively rapid because it involves a standing time of about 30 minutes after the colour is

developed. Also, the aromatic amine, p-phenylenediamine, which is preferred to benzidine, has dangerous physiological effects; it is a blood poison producing oedema, salivation, eczema, and exophthalmia which completely alters the eye tissues.[45]

The main disadvantage of Epstein's method is that a relatively unstable reagent is used.

In view of these criticisms, there is an obvious need for a sensitive and rapid spectrophotometric method for the determination of trace amounts of cyanide.

DEVELOPMENT OF THE PROCEDURE

As has been mentioned in Chapters (I) and (II), the spectrophotometric method for the determination of silver (I) described by Dagnall and West [25,40] and involving the ternary complex formation between silver, 1,10-phenanthroline and bromopyrogallol red provides an extremely sensitive and, conditionally, selective method for the determination of trace amounts of silver. The reaction can be carried out either in aqueous solution or by a selective extraction of the ternary complex into nitrobenzene using EDTA as masking agent. The attempts to replace BPR with other anionic reagents indicated that BPB and RBE could be used with some loss in sensitivity in aqueous media, but with a gain in sensitivity by extraction of the silver complexes into nitrobenzene: **cf. Table IV.**

Table IV

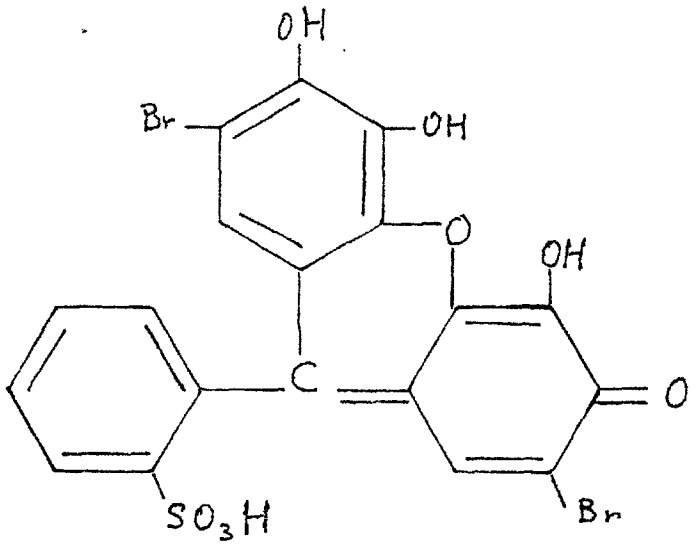
Method	Molar Absorptivity	
	Aqueous Media	Nitrobenzene
Ag/Phen/BPR	52,000	32,000
Ag/Phen/BPB	12,000	38,000
Ag/Phen/RBE	40,000	35,000

Because cyanide ions, in these three methods, prevent the formation of the coloured ternary complexes it was decided to investigate the possibility of using these methods for the indirect determination of trace amounts of cyanide in the presence of excess of silver.

As a result of the high sensitivity of the Ag/Phen/BPR method in aqueous solution, it was decided then, to investigate this reagent first. The first attempted indirect determination of cyanide using Ag/Phen/BPR was first reported by Dagnall and West in 1964.[25] They pointed out, briefly, the possibility of such a determination. Consequently, it was felt worthwhile to investigate this method in detail.

1. PRELIMINARY INVESTIGATIONS

1.1 Reagent: Bromopyrogallol Red (Dibromopyrogallol Sulphonephthalein)



1.2 PRELIMINARY SPECTRA

The absorption spectra of the scarlet-red-coloured BPR/Phen, the reagent blank, has an absorbance peak at 570 mμ Fig. 17 (c). The blue coloured ternary complex (Ag/Phen/BPR) has an absorbance peak at 635 mμ at the expense of the peak at 570 mμ Fig. 19 (a) The

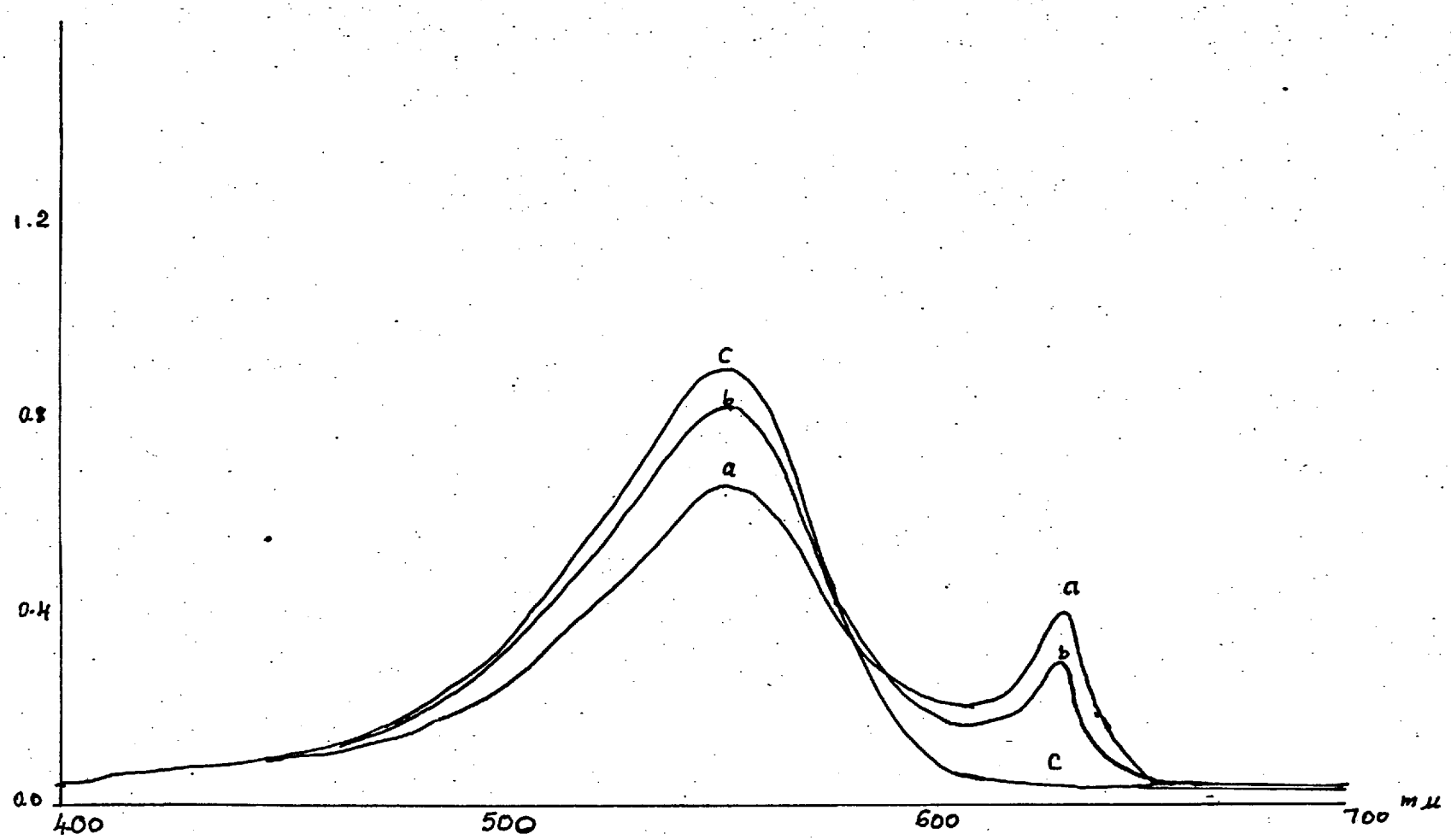


FIG. 19

addition of cyanide ions to the silver solution results in a decrease in the absorbance peak at 635 mμ and an increase at 570 mμ (b). The solutions used in this experiment were: (a) 3 ml of 10^{-4}M $AgNO_3$ 1 ml 10^{-2}M phen, 1 ml of ammonium acetate (20% W/V) and 10ml 10^{-4}M BPR and diluted with distilled water to 50 ml; (b) was prepared similarly except 2 ml 10^{-4}M of KCN were added before the addition of silver; (c) prepared in the same way but containing neither silver nor cyanide ions. The absorbance was plotted against wavelength using distilled water as a blank. The absorption spectra obtained indicates that the maximum decrease in absorbance is obtained at 635 mμ.

2. OPTIMISATION OF CONDITIONS FOR COLOUR DEVELOPMENT

2.1 pH

According to Dagnall and West, [25] the blue colour of the Ag/Phen/BPR complex was obtained over pHrange 3-10. With cyanide, operation in an acidic media is impossible because of the evolution of hydrogen cyanide which is extremely toxic. On the other hand, the BPR reagent is subject to oxidation

at high pH. Consequently pH 7 was chosen as being the most suitable one.

2.2. Development Time

According to Dagnall and West, [25] the reaction is instantaneous and the blue colour obtained was stable for 30 minutes. The results obtained were in agreement with this statement.

2.3. Reagent Excess

The results obtained were in agreement with those obtained by Dagnall and West [25] which indicated that 1,10-phenanthroline should be present in at least a 10 fold molar excess and bromopyrogallol red in at least a 4 fold molar excess.

2.4. Masking Agents

EDTA was examined as a convenient masking agent and it was found that it could be used in the range of 10 - 10,000 fold molar excess over the upper limit of cyanide (ca. 10 ml 10^{-5}M KCN).

3. Lambert-Beer's law check

A calibration curve was prepared in the usual way, using 1000 fold molar excess of EDTA over the

upper limit of cyanide. Beer's law was obeyed between 1-10 ml of 10^{-5}M CN^- and 1-10 ml of 10 ml 10^{-4}M CN^- e.g. 0.262 - 2.62 µg of CN^- and 2.62 - 26.2 µg of CN^-or 0.524 - 5.24 and 5.24 -52.4 x 10^{-2} ppm of final concentration of cyanide respectively. The absorbance decreases as the concentration of cyanide increases. (Fig. 20)

4. INTERFERENCES

4.1 Cationic Interferences

The presence of EDTA up to 10,000 fold molar excess over cyanide or silver without any alteration in the absorbance, enables its utilization as a mass-masking agent for the extraneous cations which may react with cyanide or with the other reagents.

Seventeen cations have been examined in the presence of a 500 fold molar excess of EDTA, in combination with 500 fold molar excess of 1,10-phenanthroline in case of iron (III), over cyanide or silver. The deviation of the absorbance of these cations solutions from a standard solution containing no extraneous cations are summarised in Table V.

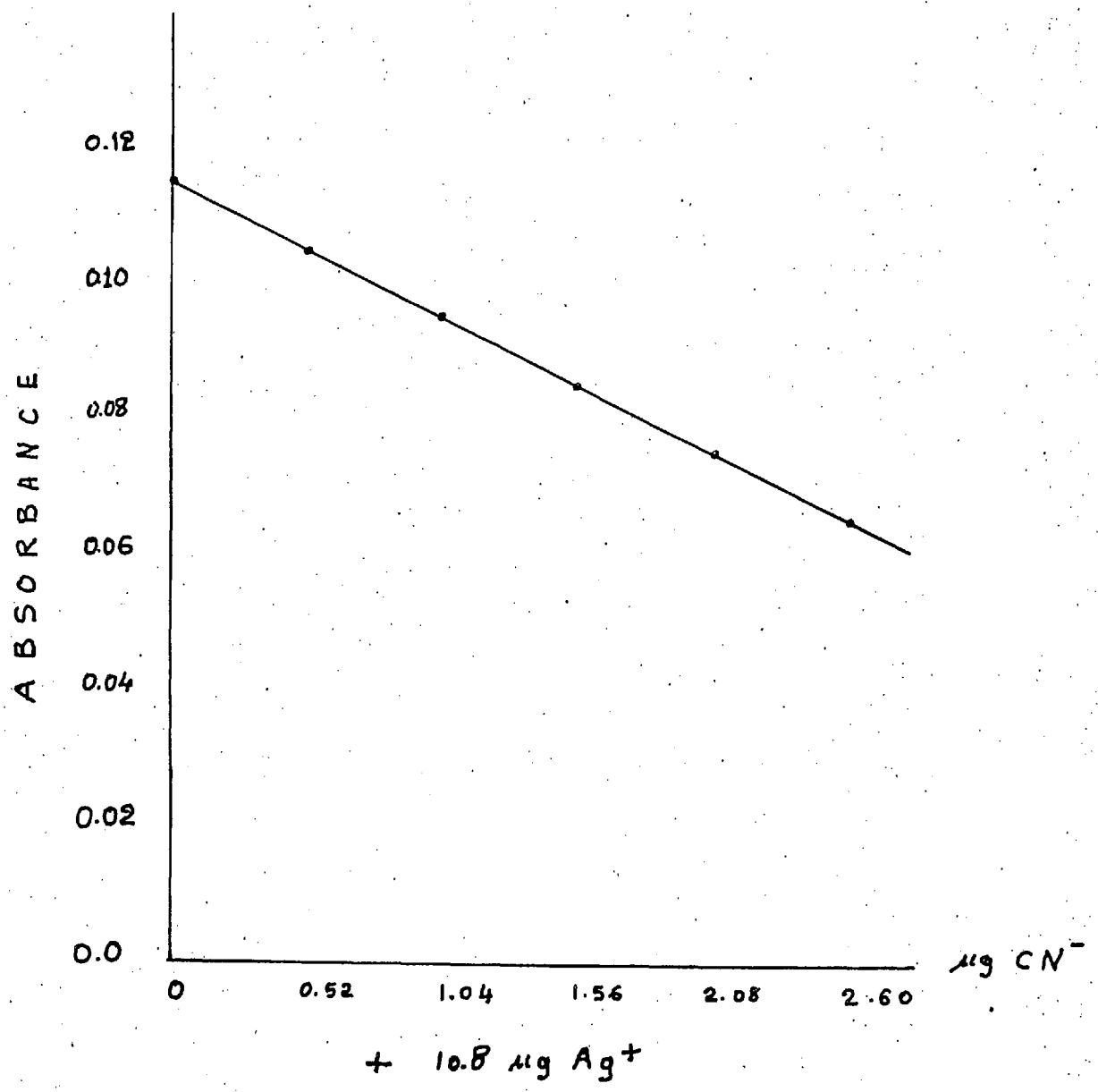

ABSORBANCE
0.12
0.10
0.08
0.06
0.04
0.02
0.0
0
0.52
1.04
1.56
2.08
2.60
μg CN⁻
+ 10.8 μg Ag⁺

Fig. 20.

Table V

Ions	Fold-Molar Excess over Cyanide	Absorbance Against a Reagent Blank	Deviation From The Standard
$CN^- + Ag^+$(standard)	0	0.120	0
$CN^- + Al^{3+} + Ag^+$	100	0.120	0.0
$CN^- + Ba^{2+} + Ag^+$	100	0.120	0.0
$CN^- + Bi^{3+} + Ag^+$	100	0.120	0.0
$CN^- + Ca^{2+} + Ag^+$	100	0.120	0.0
$CN^- + Cd^{2+} + Ag^+$	100	0.145	+ 0.025
$CN^- + Co^{2+} + Ag^+$	100	0.155	+ 0.035
$CN^- + Cu^{2+} + Ag^+$	100	0.127	+ 0.007
$CN^- + Fe^{3+} + Ag^+$	100	0.125	+ 0.005
$CN^- + Hg^{2+} + Ag^+$	100	0.245	+ 0.125
$CN^- + K^+ + Ag^+$	100	0.120	0.0
$CN^- + Li^+ + Ag^+$	100	0.120	0.0
$CN^- + Mg^{2+} + Ag^+$	100	0.122	+ 0.002
$CN^- + Mn^{2+} + Ag^+$	100	0.125	+ 0.005
$CN^- + Na^+ + Ag^+$	100	0.120	0.0
$CN^- + Ni^{2+} + Ag^+$	100	0.130	+ 0.010
$CN^- + Pb^{2+} + Ag^+$	100	0.120	0.0
$CN^- + Zn^{2+} + Ag^+$	100	0.135	+ 0.015

The order of addition was as follows:
Pipette 2 ml of 10^{-4}M KCN into 50 ml volumetric flask, followed by 2 ml of 10^{-2}M interferentent cation, 2 ml 10^{-4}M of $AgNO_3$, 1 ml of 10^{-1}M EDTA, 1 ml 10^{-2}M of Phen, 1 ml of ammonium acetate (20% W/V) 10 ml of 10^{-4}M BPR and diluted with distilled water to the mark. The pH must be checked and adjusted to 7 either with 0.1N ammonia or 0,1N hydrochloric acid if the solution of the inter extraneous ion cation was very acidic or alkaline. The absorbance of the solution was measured at 635 mμ in a 1 cm glass cuvette against a reagent blank carried through the same procedure but containing no silver or cyanide or foreign cations. The absorbances obtained were compared with that of standard solution prepared similarly but containing no extraneous cation.

Table V indicates that cadmium (II), cobalt (II), mercury (II) and zinc (II) interfere. It was found that cadmium (II), cobalt (II) and zinc(II) did not interfere if they were present in the level 10, 1 and 50 fold molar excess respectively. Only mercury (II) was found interfering seriously at the equimolar level, which increased the absorbance nearly twice (e.g. 0.235), in the presence of

500fold molar excess of EDTA, with respect to cyanide or silver concentration. This interference arises because of the high stability constant of mercury (II) - cyanide complex compared with that of the silver (I) - cyanide complex and the mercury (II) - EDTA complex.[139] Consequently all the cyanide ions are completely complexed and all the silver ions are free to react with 1,10-phenanthroline and bromopyrogallol red and give an absorbance value approximately equal to that of silver solution containing neither mercury (II) nor cyanide ions.[140]

4,2 Anionic Interferences

Fourteen anions have been investigated for their interference with cyanide. These anions were acetate, bromide, carbonate, chloride, chromate, fluoride, iodide, nitrate, perchlorate, persulphate, phosphate, sulphate, sulphite and thiocyanate.

By following the same procedure as that used in the cationic interference investigation, it was found that up to 15,000 fold molar excess of acetate, 1000 fold molar excess of fluoride and nitrate, and 100 fold molar excess

of carbonate, chloride, perchlorate and sulphate, over cyanide, did not interfere.

Sulphate could be tolerated up to 1000 fold molar excess over cyanide by following the previous procedure, but only after adding barium nitrate as a precipitant followed by centrifuging or filtration and measuring the absorbance of the clear solution against a reagent blank at 635 mμ. Chromate persulphate, phosphate and sulphite could also be tolerated up to 1000 fold molar excess over cyanide in this way. Only bromide, iodide and thiocyanate still interfered seriously at the equimolar level.

Attempts to mask these three anions (Br^-, I^- and SCN^-) by removing them from the sphere of the reaction indicated that lead nitrate may be used as an effective precipitant. The lead nitrate was added in excess, with respect to the three anion concentrations, and the excess of lead nitrate was then masked. An attempt to mask the excess of lead nitrate with EDTA was unsuccessful because of the high stability constant of the Pb(II) - EDTA complex. Under these conditions all the lead was complexed by the EDTA.

The only successful method that could be devised was

as follows:

Sulphate ions were added to precipitate first the excess of lead as lead sulphate. The excess of sulphate was then removed by precipitation with excess barium nitrate. This procedure, although somewhat involved, was found to be an effective means of determining cyanide in the presence of 1000 fold molar excess of halides such as bromide and iodide or pseudohalides such as thiocyanate.

5. NATURE OF COMPLEX

According to Dagnall and West, silver forms a ternary complex with 1,10-phenanthroline and bromopyrogallol red of the ratio 2:4:1 respectively.

Cyanide ions react with silver to form the dicyano-argentate complex, potassium argentocyanide as follows:

$$Ag^{+} + 2CN^{-} \rightleftharpoons Ag(CN)_2^{-}$$

Hence the ratio between silver and cyanide is 1:2. Since the argentocyanide, complex is a quite stable complex and is stronger than that between silver and the Phen/ BPR reagent, the cyanide in solution reacts with an equivalent amount of silver and the free silver ions then

forms the usual ternary complex.

6. SOLVENT EXTRACTION

6.1 Using Bromopyrogallol Red

According to Dagnall and West,[40] the silver/1,10-phenanthroline/Bromopyrogallol Red ternary complex is extracted into nitrobenzene at pH 7 with a maximum wavelength of absorbance at 585 mμ. This method has been applied to the indirect spectrophotometric determination of trace amounts of cyanide. The absorption spectra of a 10 ml 10^{-4}M silver nitrate, a 1 ml of 10^{-1}M EDTA, a 1 ml of 10^{-2}M 1,10-phenanthroline and 25 ml of 10^{-4}M Bromopyrogallol Red extracted into 25 ml of nitrobenzene, has an absorbance peak at 582 mμ, Fig. 21 (a). The addition of 8 ml 10^{-4}M of potassium cyanide to this solution decreases this absorbance peak, Fig. 21 (b). The optimum conditions obtained were in agreement with those obtained by Dagnall and West.[40] The absorbance of the silver ternary complex extract was found to decrease gradually with increasing amounts of cyanide. The calibration curve obtained over the range of 1 - 10 ml of 10^{-4}M cyanide in the presence of a 10 ml of 10^{-4}M silver nitrate, and 100-fold molar excess of EDTA over silver or the upper limit of cyanide (i.e.,

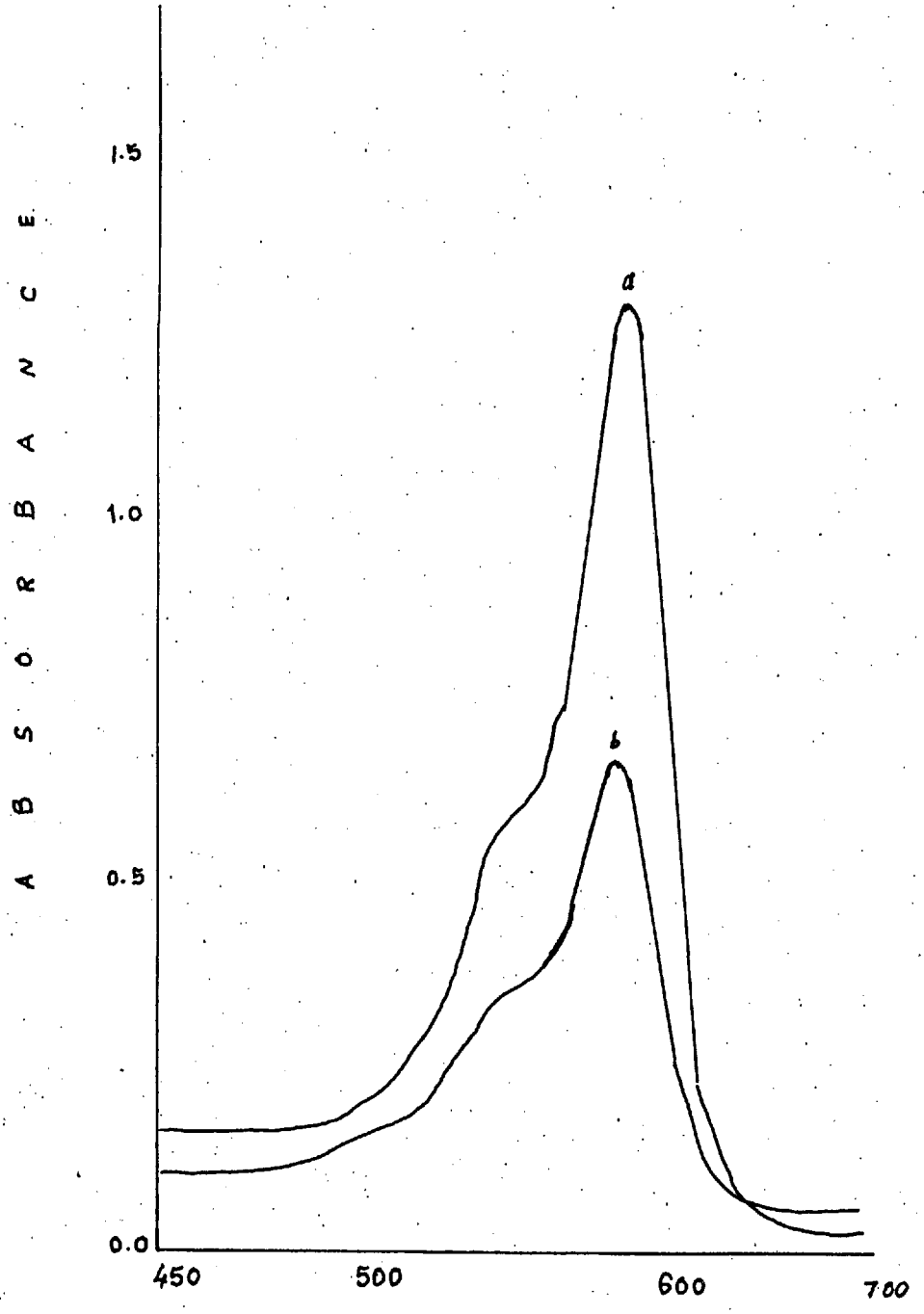


Fig. 21.

10 ml 10^{-4}M) was linear at 582 mμ (Fig. 22).

6.2 Using Bromophenol Blue

Under the established optimum conditions for the colour development of the Ag/Phen/BPB ternary complex extracted into nitrobenzene which were discussed in Chapter (I), a gradual decrease in the absorbance (at 605 mμ)was found with increasing amounts of cyanide. The calibration graph obtained over the range of 1 - 10 ml of 5 x 10^{-5}M cyanide, in the presence of 10 ml of 5 x 10^{-5}M silver nitrate and 200 fold molar excess of EDTA over silver or over the upper limit of cyanide concentration (i.e., 10 ml of 5 x 10^{-5}M) was linear (Fig. 23).

Extraneous cations can be masked with EDTA as in aqueous solution. Similarly, the fourteen anions examined previously in aqueous solution will not interfere if masked as indicated above.

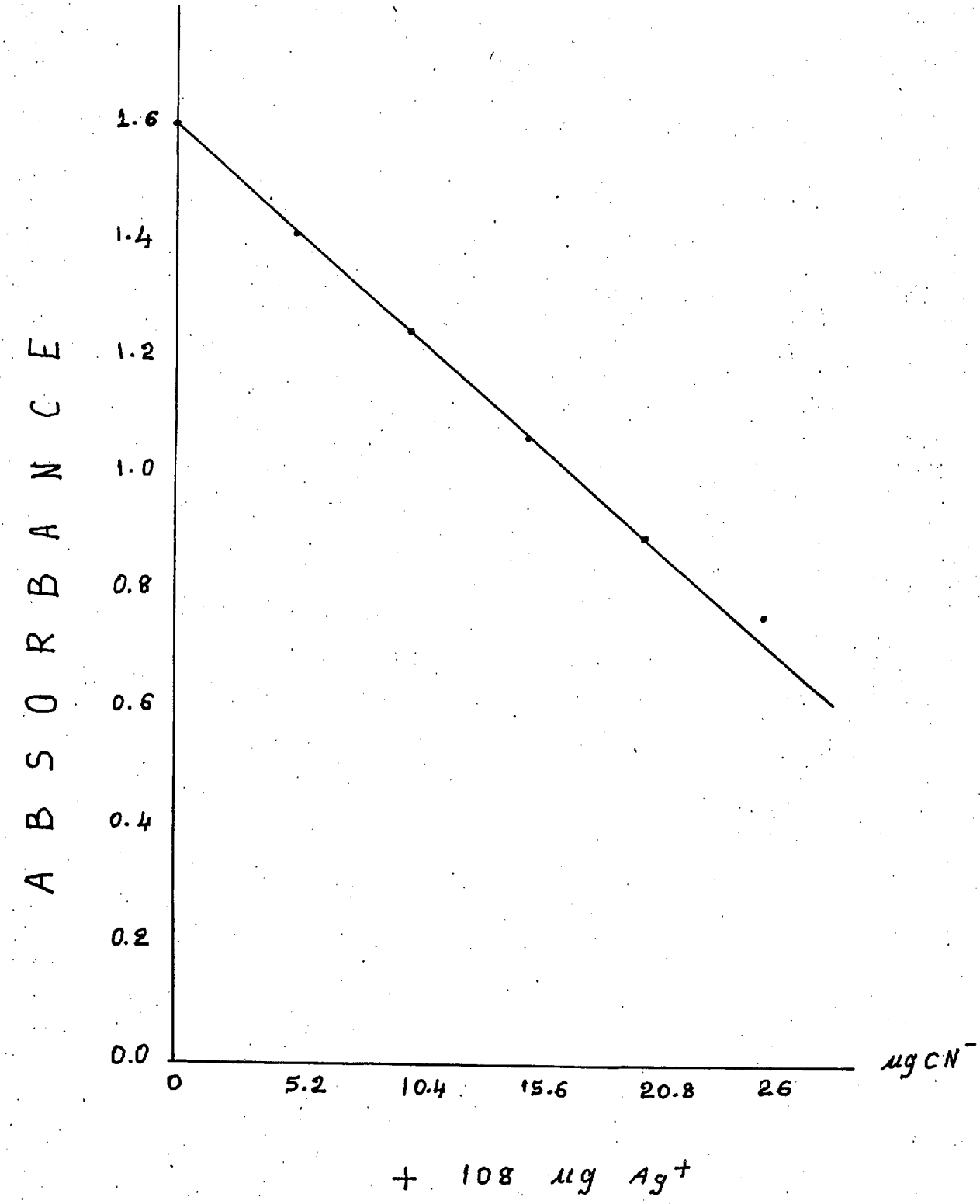

ABSORBANCE
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5.2
10.4
15.6
20.8
26
μg CN⁻
+ 108 μg Ag⁺

Fig. 22.

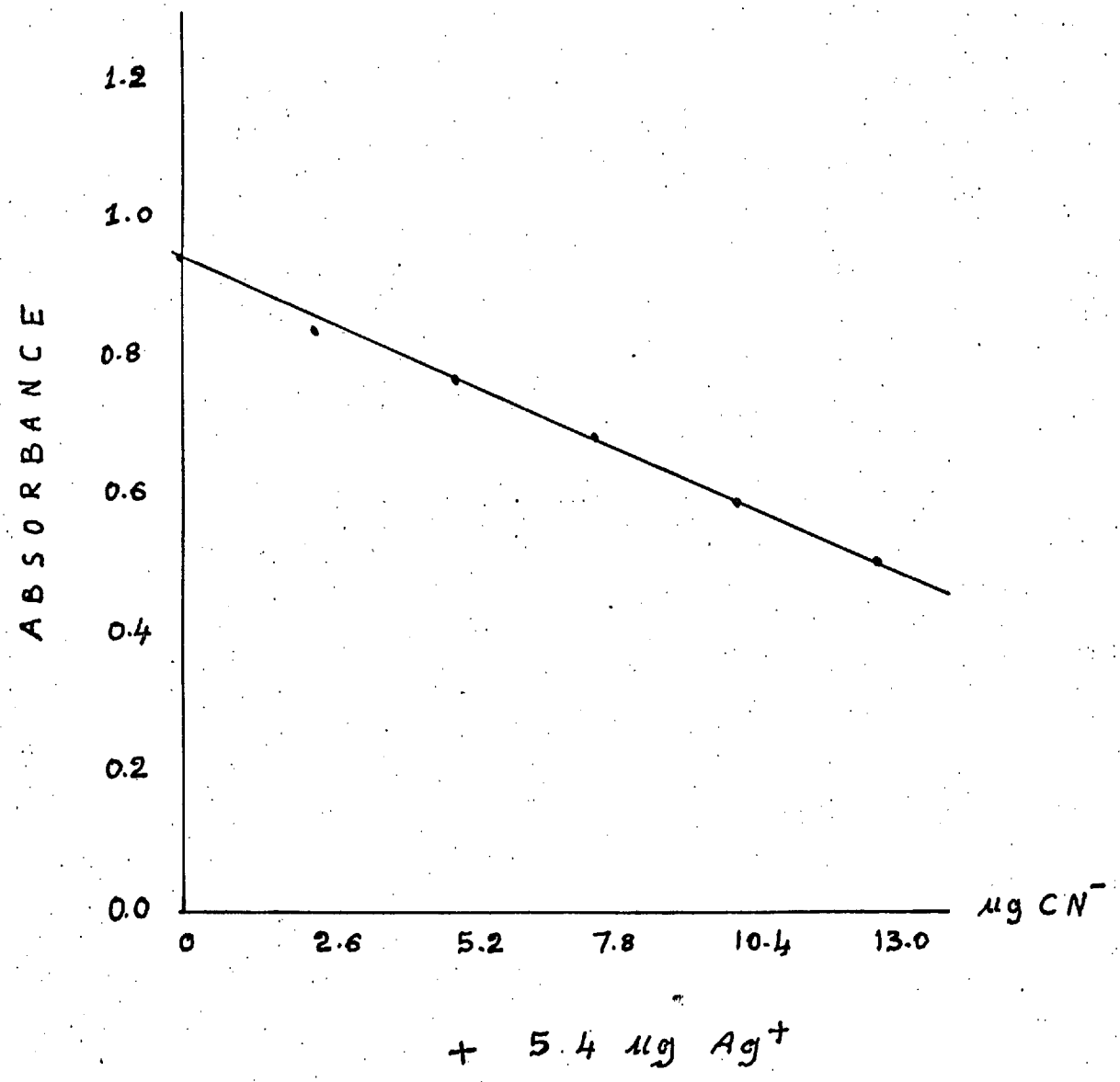


Fig. 23.

7. STANDARD DEVIATION

Number	Absorbance x 1000	Deviance D	Deviance^2 D^2
1	125	+ 5	25
2	115	- 5	25
3	117	- 3	9
4	122	+ 2	4
5	117	- 3	9
6	120	0.0	0.0
7	115	+ 5	25
8	130	+10	100
9	120	0.0	0.0
10	125	+ 5	25
11	125	- 5	25
ΣX =	1,321	ΣD^2 =	247
$\bar{x}$ =	120		

$\therefore$ Standard Deviation (S) $= \sqrt{\frac{\Sigma D^2}{n-1}}$

Therefore, $S = \sqrt{\frac{247}{10}} = 4.97$

$\bar{S} = \frac{4.97}{120} = 0.0414$

Hence, % Standard Deviation = 0.0414 x 100

= 4.14

E X P E R I M E N T A L

APPARATUS

Spectrophotometer, Unicam 600 Sp. and 1 cm glass cuvette.

pH Meter Model 23A (Electronic Instruments Ltd)

REAGENTS

All reagents were of analytical grade unless otherwise stated.

Potassium cyanide solutions, 10^{-4} - 10^{-5}M

Prepare by appropriate dilution of 10^{-1}M potassium cyanide solution standardised against standard silver nitrate solution by the Liebig - Deniges method.

Silver Nitrate, 10^{-4} - 10^{-5}M,

Prepare by appropriate dilution of 10^{-1}M silver nitrate (B.D.H.

1,10-Phenanthroline, 10^{-2}M (B.D.H.)

Prepare by dissolving 0.99115 g of 1,10-phenanthroline hydrate into 500 ml of distilled water.

Bromopyrogallol Red Solution, 10^{-4}M (B.D.H.)

Prepare by dissolving 0.00558 g of BPR and 1 g of ammonium acetate into 100 ml of distilled water. This solution must be freshly prepared every 5 days.

Bromophenol Blue (BPB), 10^{-3}M (Hopkins and Williams)

Dissolve 0.3351 g of BPB into 500 ml of distilled water.

Ammonium Acetate 20% W/V solution

Dissolve 20 g of ammonium acetate into 100 ml distilled water.

Buffer Solution pH 8

Prepare by dissolving 50 g of ammonium acetate into distilled water in 250 - ml beaker. Add few drops of 4N ammonia and adjust the pH to pH 8 under a pH meter. Transfer the solution to a 250 ml graduated flask and dilute to the mark with distilled water.

Nitrobenzene Analar

RECOMMENDED PROCEDURE

(a) AQUEOUS SOLUTION USING BROMOPYROGALLOL RED (BPR)

Pipette 1 - 10 ml of a 10^{-5}M solution of potassium cyanide into 50 ml volumetric flasks followed by 10 ml of a 10^{-5}M solution of silver nitrate, 1 ml of a 10^{-1}M solution of EDTA, 1 ml of a 20% W/V solution of ammonium acetate trihydrate 1 ml of a 10^{-3}M solution of 1,10-phenanthroline and 4 ml of a 10^{-4}M bromopyrogallol red solution. Dilute the solution to 50 ml with distilled water and measure the absorbance immediately, or within 30 minutes in a 1 cm cuvette at 635 mμ against a reagent blank containing all the reagents except cyanide and silver.

A plot of absorbance against cyanide in micrograms gives a linear graph over the range 0.26 - 2.6 μg of cyanide, or 0.0052 - 0.052 ppm of final concentration of cyanide.

1 ml of 10^{-5}M KCN ≡ 0.26 μg of CN^-

(b) SOLVENT EXTRACTION

(i) USING BROMOPYROGALLOL RED

Pipette 1 - 10 ml of 10^{-4}M cyanide into 100 - ml separating funnels followed by 10 ml of 10^{-4}M silver nitrate, 1 ml of 10^{-1}M EDTA, 1 ml of 10^{-2}M 1,10-phenanthroline and 1 ml of 20% W/V ammonium acetate. Add sufficient distilled water to give a constant volume of solution in each funnel, then add 20 ml of nitrobenzene and shake by continuous inversion for 1 minute. Allow about 10 minutes for the layers to separate, then transfer the lower organic layers to different 100 ml separating funnels and add to the latter 25 ml of a 10^{-4}M bromopyrogallol red solution. Again shake by continuous inversion for 1 minute and allow about 30 minutes for the layers to separate. Run the lower nitrobenzene layers into 100 ml beakers and swirl each beaker until all cloudiness disappears (ca. 1 min.). Finally transfer the solutions to a 1 cm glass cuvette and, as soon as possible, measure the absorbance at 582 mμ against a reagent blank carried through the same

procedure, but containing neither cyanide nor silver.

1 ml of 10^{-4}M KCN $\equiv$ 2.6 µg of CN^-

The graph of absorbance vs. cyanide in micrograms is a straight line over the range of 2.6 - 26 µg of cyanide or 0.15 - 1.5 ppm of final concentration of cyanide.

(ii) USING BROMOPHENOL BLUE

The same procedure prescribed in (i), but add 5.0 ml of pH 8 buffer instead of 1.0 ml of 20% W/V ammonium acetate and add 20 ml of 10^{-4} bromophenol blue solution instead of bromopyrogallol red. Also, allow the solutions to stand for 90 minutes before measuring the absorbance at 605 mµ instead of 582 mµ.

CONCLUSION

The proposed spectrophotometric methods for the indirect spectrophotometric determination of trace amounts of cyanide provide simple, rapid, extremely sensitive and selective methods which are superior to most of the previously published. The standard methods are mainly based on the Konig reaction, i.e., Aldridge and Epstein methods and the former involves the use of cariconogenic reagent such as benzidine, and the latter involves the use of unstable reagent such as (bis-pyralozone).

The BPR method is applicable over a wide range of cyanide concentration in aqueous media, e.g. 0.26 - 26 µg of cyanide per 50 ml or 0.0052 - 0.52 ppm of final concentration of cyanide with a percentage standard deviation of 4·14

The methods are also extremely selective since among the fourteen anions and seventeen cations examined, only mercury (II) interfered. The use of BPB increases the selectivity of the method because of the less interference of cations.

CHAPTER THREE

TITRIMITRIC DETERMINATION OF CYANIDES

S U M M A R Y

The use of a 1,10- phenanthroline/Bromopyrogallol Red indicator system is proposed for the visual and photometric titration of cyanide with silver nitrate in the range 10^{-1} - 10^{-4}M and 10^{-4} - 10^{-5}M respectively. Sharp, well defined end-points are observed and the titration succeeds at low concentrations where the standard Liebig - Déniges method is inapplicable. The results obtained agree well with those of the conventional method. EDTA may be used as a mass-masking agent for most cations.

SECTION ONE. VISUAL TITRATION OF CYANIDES

The previously mentioned method described by Dagnall and West[25] provide an extremely sensitive and selective colour reaction for silver ion, ϵ_{635} mu = 51,000, based on the formation of a ternary complex with 1,10-phenanthroline and Bromopyrogallol Red (BPR). This reaction was made virtually specific for silver by the use of EDTA plus, in some instances hydrogen peroxide and fluoride ions as masking agents. It was shown that complex formation in this system occurs through co-ordination of the silver cations bonded with the nitrogen atoms of the phenanthroline to form a phenanthrolinium cation carrying the same charge as the silver ion. This then forms a well-defined ternary complex with BPR by ion-association. Subsequent studies involved the use of anionic dyestuffs other than BPR which do not contain vic. hydroxyl groups e.g. Rose Bengal Extra, C.I. 45440 (tetrachloro (P) tetraiodo (R) fluorescein), (RBE).

Because cyanide is virtually the only anion which prevents the formation of the bis(1,10-phenanthroline)-silver (I) complex, it was considered that these ternary systems would offer an excellent means of indic-

ating the equivalence point in the argentometric titration of cyanide ions with silver nitrate. The silver ions would only react to form the colour body beyond the eqivalence point, according to the following reactions:

$$Ag^{+} + 2CN^{-} \rightleftharpoons Ag(CN)_2^{-} \qquad (I)$$

Silver ions react with cyanide to form the water-soluble argentocyanide complex. Hence no precipitate is formed when silver nitrate is added to a solution of cyanide since the latter is in excess. When all the cyanide has reacted the next drop of titrant ($AgNO_3$) reacts with a portion of the anionic complex ($Ag(CN)_2^{-}$) forming the sparingly soluble argento cyanide as follows:

$$Ag^{+} + Ag(CN)_2^{-} \rightleftharpoons Ag(Ag(CN)_2) \qquad (2)$$

Therefore, the first appearance of the responsible colour of Ag/Phen/R (where R is BPR, BPB or RBE) marks the end-point. The three reagents Bromopyrogallol Red (BPR), Rose Bengal (Extra) (RBE) and Bromophenol Blue (BPB) in combination with 1,10-phenanthroline (Phen) have been applied as indicator systems to detect the end-point of the argentometric

titration of cyanide. This study reports the results obtained by titrating cyanide in concentration of 10^{-1} - 10^{-4}M visually in near neutral solution.

1. Bromopyrogallol Red

The addition of a 1 ml of 0.2% 1,10-phenanthroline, a 5 ml of 20% W/V ammonium acetate solution, a 1 ml of 10^{-1}M EDTA, and a 1 ml of 0.006% bromopyrogallol red to a 25 ml of cyanide solution ca. 10^{-3}M into a 250 ml conical flask, diluted to 100 ml with distilled water, gave a scarlet red colour. By the dropwise addition of silver nitrate (ca. 10^{-3}M), the colour changes sharply from red to blue via a violet colour prior to the end-point. The absorption maxima being at 560 and 635 mμ respectively (Fig. 24). According to Dagnall, El-Ghamry and West[141] this method is applicable over the range if 10^{-2} - 10^{-4}M cyanide. This is because the blue coloured ternary complex of Ag/Phen/BPR involves very sensitive reaction of molar absorptivity ca. 51,000 in aqueous solution. Consequently down to 12.48 μg of cyanide/100 ml or 0.1250 ppm could be determined visually. The results obtained are summarised in Table VI

Fig. 24

TABLE VI

VISUAL TITRATION OF CYANIDE USING BPR AS INDICATOR

KCN, M	Volume of KCN ml	$AgNO_3$, M	Volume of $AgNO_3$ Required ml				
			Total Volume	Reagent Blank		Corrected Titre	Liebig and Deniges
				Experimental	Theoretical		
9.72×10^{-2}	25	10^{-1}	12.15	1 drop	0.002	12.148	12.15
9.72×10^{-3}	25	10^{-2}	12.17	1 drop	0.02	12.15	12.10
9.72×10^{-4}	25	10^{-3}	12.35	0.2	0.2	12.15	Not Possible
9.72×10^{-5}	25	10^{-4}	14.11	1.9	2.0	12.21	Not Possible

Each result in columns 4 and 8 represent the mean of three titrations.

2. Rose Bengal (Extra)

In this case, the colour changed sharply from red salmon pink to mauve sharply at the end-point. According to Dagnall, El-Ghamry and West [141] this method is applicable over the range of 10^{-1} - 10^{-3}M cyanide. This is because the colour reaction of Ag/Phen/RBE has molar absorptivity of ca. 40,000 only. Therefore in this case down to 124.8 µg of cyanide/100 ml or 1.248 ppm of final concentration of cyanide could be easily determined. The results obtained are summarised in table VII.

TABLE VII

VISUAL TITRATION OF CYANIDE USING RBE AS INDICATOR

KCN, M	Volume of KCN, ml	$AgNO_3$, M	Volume of $AgNO_3$ Required, ml				
			Total Volume	Indicator Blank		Corrected Titre	Liebig and Deniges
				Experimental	Theoretical		
9.72×10^{-2}	25	10^{-1}	12.15	1 drop	0.002	12.148	12.15
9.72×10^{-3}	25	10^{-2}	12.14	1 drop	0.02	12.12	12.10
9.72×10^{-4}	25	10^{-3}	12.32	0.2	0.2	12.12	Not Possible

Each result in columns 4 and 8 represent the mean of three titrations.

3. Bromophenol Blue

In case of using BPB, the colour change was from violet to blue at the end-point (absorption maxima at 585 to 625 mμ respectively). This reagent is only applicable over the range 10^{-1} - 10^{-2}M of potassium cyanide, because of the lower sensitivity of the silver/Phen/BPB colour reaction (molar absorptivity of only 12,000 at 625 mμ). The results obtained are summarised in Table VIII.

TABLE VIII

VISUAL TITRATION OF CYANIDE USING BPB AS INDICATOR

KCN, M	Volume of KCN	$AgNO_3$, M	Volume of $AgNO_3$ Required, ml				
			Total Volume	Indicator Blank		Corrected Titre	Liebig and Deniges
				Experimental	Theoretical		
9.72×10^{-2}	25	10^{-1}	12.15	1 drop	0.002	12.148	12.15
9.72×10^{-3}	25	10^{-2}	12.15	1 drop	0.02	12.13	12.10

Each result in columns 4 and 8 represents the mean of three titrations.

INTERFERENCES

It has already shown that in the presence of EDTA, in some instances, fluoride and hydrogen peroxide there is no interference from 24 cations and 11 anions in the spectrophotometric determination of silver.[25] Only gold (III), thiosulphate and of course cyanide were found to interfere.[25] In the present determination interferences would be expected only from those cations which form more stable complexes with cyanide than with EDTA. However, the only metals which form more firmly bound cyanide complexes than silver are iron (II) and (III), cobalt (III), copper (I) and (II), mercury (II), and platinum (II). Thus, in the presence of EDTA small amounts of zinc (II) might be expected to react:

$$Zn(CN)_4^{2-} + 2Ag^+ \rightleftharpoons 2Ag(CN)_2^- + Zn^{2+}$$

Interaction of zinc (II) with BPR indicator would be prevented by subsequent complexation with the excess of EDTA. Indeed, the latter reaction should enhance the exchange reaction with silver. In view of the previous findings and the above argument, we have only examined the interference of those cations which form stable cyanide complexes, viz. cadmium (II),

cobalt (II), copper (II), iron (III), mercury (II), manganese (II), nickel (II) and zinc (II). Cobalt (III), gold (I) and platinum (II) were not investigated.

Titrations were carried out under the usual conditions with 25 ml of 10^{-2}M potassium cyanide solution in the presence of equimolar amounts of these ions. No interference was observed for cadmium (II), manganese (II) or zinc (II). The exchange reaction between the nickel cyanide complex and silver ions was slow and the usual colour change could only be obtained when the solution was warmed and cooled again a few ml before the end-point was reached. The reason for the slow exchange is not immediately obvious, but it would appear that the nickel and silver cyanide complexes are of nearly equal stability. Widely differing values for the tetracyanonickelate (II) stability constant have been reported.[139] The slowness of this reaction is exaggerated with equimolar amounts of nickel because a large proportion of the nickel existed as precipitated nickel cyanide.

As expected, iron (III), cobalt (II), copper (II) and mercury (II) did not interfere when their

concentration was one hundredth of it. As with nickel, these exchange reactions were slow, but the usual colour change could again be obtained by warming and cooling the solution just before the end-point. [141]

The apparent difference in the results obtained in this case from those obtained in the case of spectrophotometric determination (Chapter II) is due to the small concentration of EDTA (1 ml 10^{-1}M) with respect to that of cyanide or the interferent cation (25 ml 10^{-2}M), which favoured the formation of the interferent cation-cyanide complex to that with EDTA in case of the equal stability constants of both complexes. Because in the case of spectrophotometric determination of cyanide, those cations were masked with EDTA, which was utilized in larger excess with respect to both cyanide and the extraneous cation, i.e., 1000 and 10 fold molar excesses respectively. Consequently, it was possible to mask all the 16 previously mentioned, cations, with the exception of mercury (II), using large excess of EDTA as a mass-masking agent.

The anions examined for interference were phosphate, sulphate, carbonate, fluoride, chloride, bromide, iodide, thiocyanate and thiosulphate. In the presence of equimolar amounts of these ions interference was observed

only from the thiosulphate, thiocyanate and iodide. The amounts of these anions that could be tolerated was not examined.

However, the methods prescribed for masking the anions such as, bromide, iodide and thiocyanate, in the spectrophotometric determination (Chapter II), can be applied here to achieve the selective visual determination of cyanide in the presence of the fourteen anions mentioned previously.

E X P E R I M E N T A L

REAGENTS

All reagents were of analytical grade unless otherwise stated.

Potassium Cyanide Solutions, 10^{-1} - 10^{-4}M

Dissolve 0.3275 g of potassium cyanide into distilled water and dilute to 500ml in a volumetric flask. By appropriate dilution of this solution (10^{-1}M), prepare the other solutions. This solution was standardised against silver nitrate by the Liebig-Déniges method during this work.

Silver Nitrate, 10^{-1} - 10^{-4}M (B.D.H. ampoules)

Prepare by appropriate dilution of 10^{-1}M silver nitrate.

1,10-Phenanthroline Solution, 0.2%

Dissolve 0.5 g of 1,10-phenanthroline hydrate in 250 ml of distilled water.

Bromopyrogallol Red Solution, 0.006%

Dissolve 3 mg of Bromopyrogallol Red and 0.5 g of ammonium acetate in 50ml distilled water. This solution should not be kept for longer than 5 days.

Rose Bengal Extra Solution, 0.04%

Dissolve 20 mg of Rose Bengal Extra, C.I. 45440, (B.D.H. Ltd) in 50 ml of distilled water.

Bromophenol Blue, 0.0067%

Dissolve 3.35 mg of Bromophenol Blue (Hopkins and Williams) in 50 ml of distilled water.

Ammonium Acetate Solution, 20% W/V

Dissolve 20 g of ammonium acetate into distilled water and dilute to 100 ml in a volumetric flask.

EDTA Solution, ca. 10^{-1}M

Dissolve 3 g of EDTA (disodium salt) in distilled water and dilute to 100 ml.

RECOMMENDED PROCEDURE

Transfer 25 ml aliquots of potassium cyanide solution (10^{-1} - 10^{-4}M) into 250 ml conical flasks and add 1 ml of 0.2% 1,10-phenanthroline solution, 5 ml of 20% W/V ammonium acetate solution, 1 ml of the 10^{-1}M EDTA solution and 1 ml of indicator solution (BPR, RBE or BPB) to each. Titrate with the appropriate silver nitrate solution to the end-point.

The indicator blank should be determined experimentally or theoretically, as in Tables VI, VII and VIII and deducted from the observed titration value. This is essential for titrations with titrants more diluted than 10^{-1}M.

CONCLUSION

The three proposed methods for the visual argentometric titration of cyanides provide simple, rapid and sensitive methods for the sharp detection of the end-point using BPR, RBE and BPB as indicators. The three indicators indicate the same equivalence point as the classical Liebig-Deniges titration, and there is complete agreement

between the methods after deduction of the indicator blank. The blank values only become appreciable with titrants that were $< 10^{-2}$M. The blanks shown in TableIV agree very closely with the theoritical values calculated from the stoichiometry of the ternary complex. It would seem an obvious advantage to be able to calculate the blank value simply from the concentrations of the solutions used (equal to 2(BPR)/ ($AgNO_3$))although it can equally well be determined experimentally.

BPR is applicable over a wide range of concentrations of cyanide i.e. 10^{-1} -10^{-4}M, because of its high sensitivity of, i.e. ϵ = 51,000 at 635 mμ, with sharp colour change at the equivalence-point from red to blue via violet colour prior to the equivalence-point.

Because the molar absorptivity of RBE is only 40.000 at 570 mu, it is applicable only over the range, 10^{-1} - 10^{-3}M of potassium cyanide with a sharp colour change from salmon pink to mauve at the end-point.

BPB is the least sensitive reagent, in aqueous solution with a molar absorptivity of ca. 12,000. Consequently, it is applicable only over the range of 10^{-1} - 10^{-2}M potassium cyanide, with a colour change from violet to blue at the

equivalence-point.

The three methods compare favourably with most of the published methods, even with the standard method of Liebig and Deniges. In this method the equivalence point is detected by the first appearance of permanent opalescence in the clear solution, which is not easy. Also, the standard Liebig and Dénigès method is not sensitive, and is only applicable over a narrow concentration range, i.e., 10^{-1} - 10^{-2}M of potassium cyanide. All the proposed methods indicate the end point by a colour-change and not by the appearance of a slight permanent turbidity. Therefore, these methods are more convenient and, for an inexperienced operator it is easier to observe a colour change than the first appearance of a turbidity.

S E C T I O N T W O

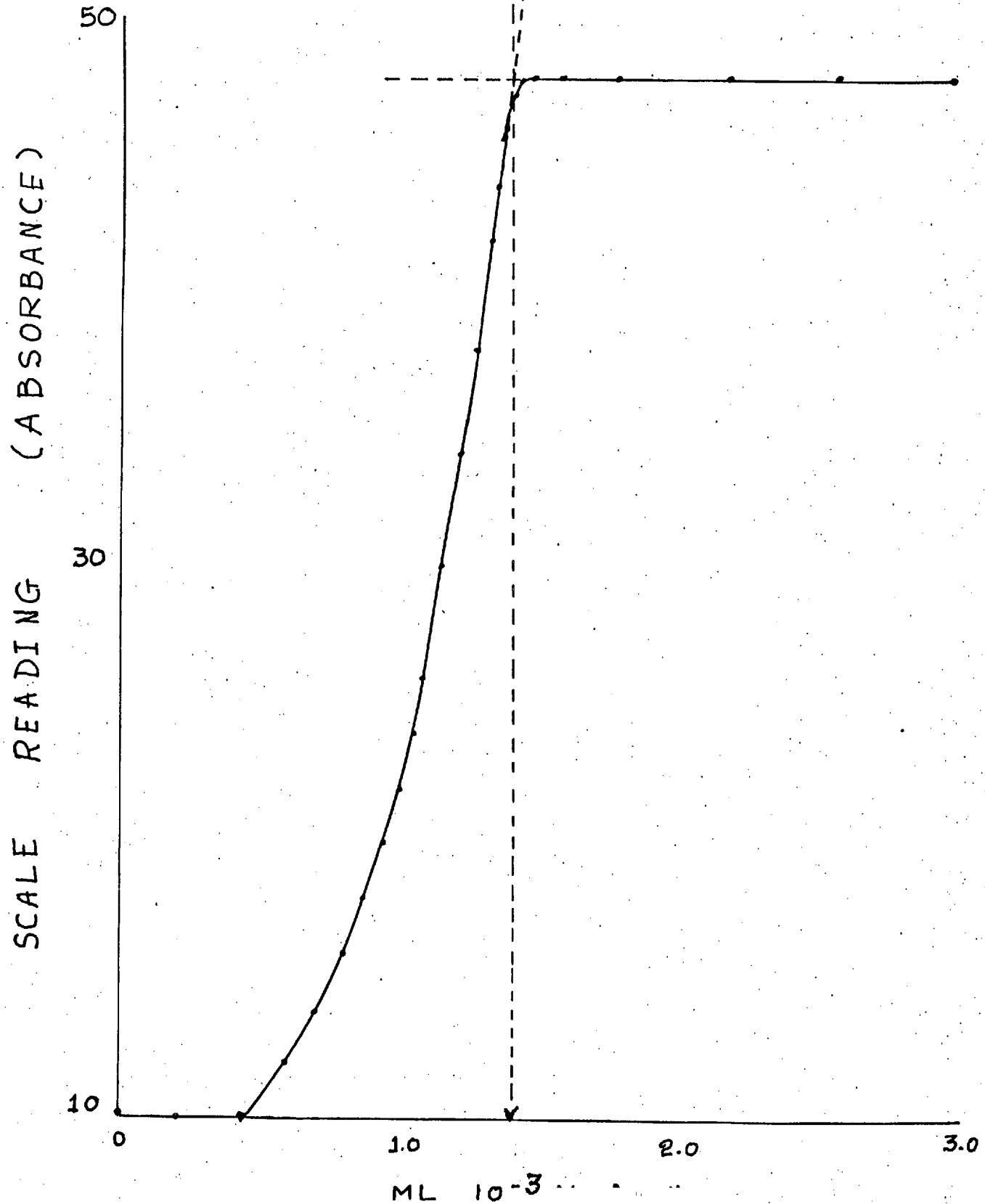
PHOTOMETRIC TITRATIONS

Since BPR, was found to be the most sensitive indicator for the argentometric visual titration of cyanide (down to ca. 1.25 ppm), it was decided to apply this indicator system for lower concentrations of cyanide utilising photometric titration. The suitable filter was found to be the orange one (bandpass maximum at 600 mu) number 607. The end-point was obtained by the intersection of the two straight lines of the titration curve. According to Dagnall, West and the author, [141] this method is applicable down to 1.248 ug of cyanide in 30 ml or, down to 1.0 ppm of cyanide using 4,000 fold molar excess of EDTA over cyanide as mass masking agent. The titration curves obtained over the range of 10^{-4}-10^{-5}M cyanide using 10^{-3}M and 10^{-4}M silver nitrate as titrant respectively (Fig. 25, 27) and the indicator blank are shown in Fig. 26 & 28.

The results obtained are summarised in Table IX.

In case of titrating 10^{-5}M potassium cyanide solution, the volume of the indicator blank could be cut down by half by utilising the half volume of the BPR indicator solution

FIG. 25



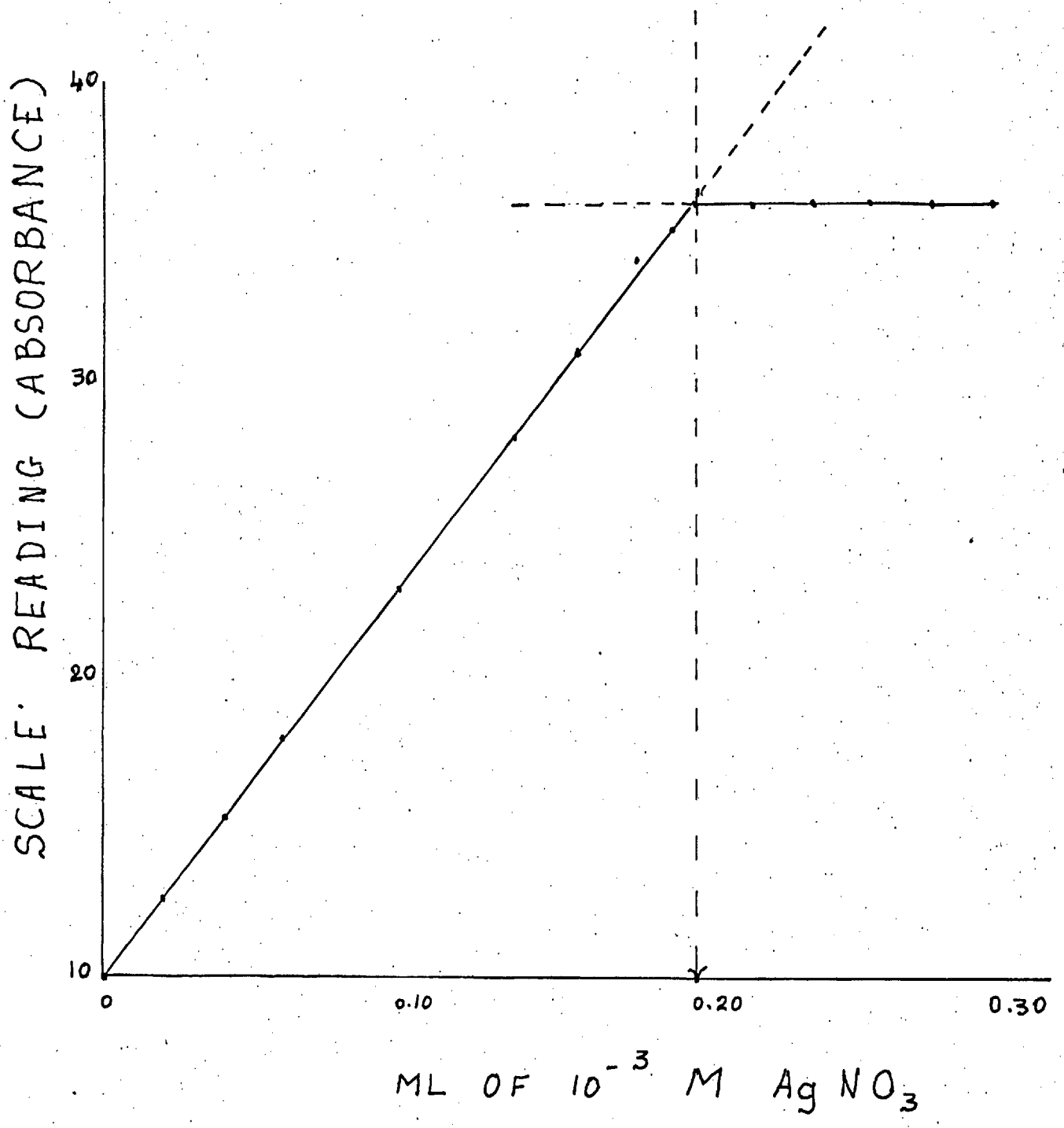

SCALE READING (ABSORBANCE)
40
30
20
10
0
0.10
0.20
0.30
ML OF 10^{-3} M $AgNO_3$

FIG. 26

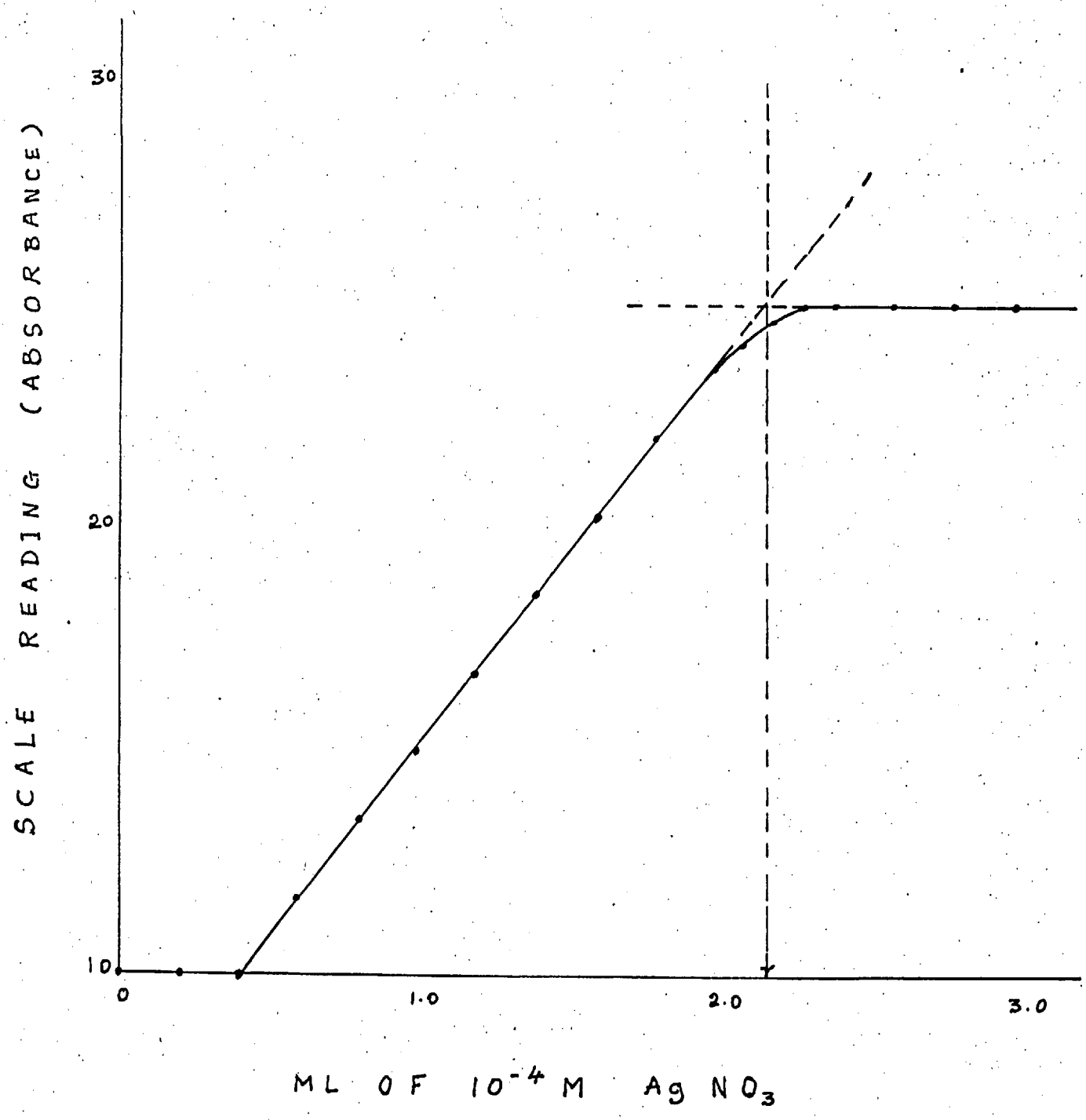


FIG. 27

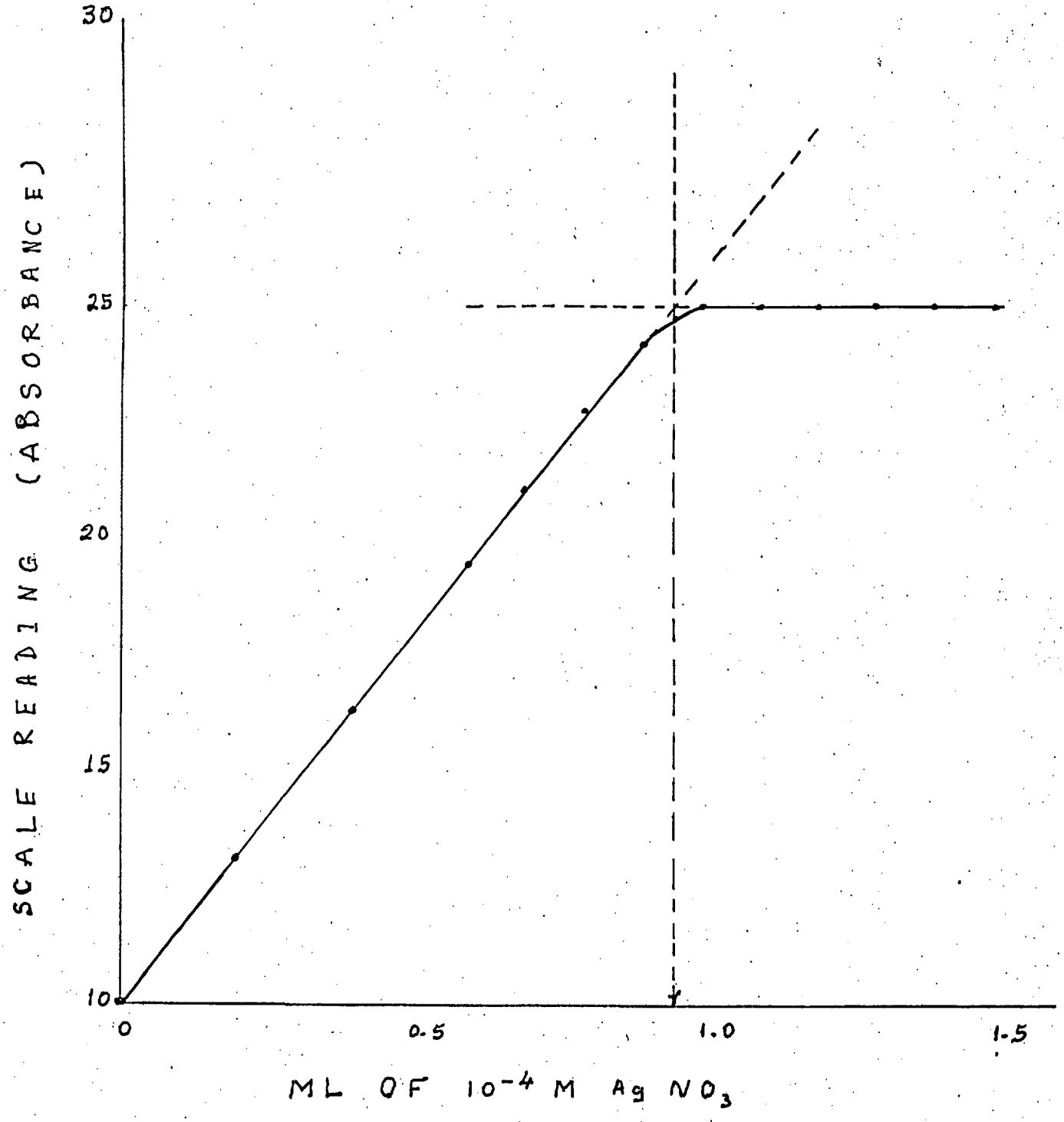

30
25
20
15
10
SCALE READING (ABSORBANCE)
0
0.5
1.0
1.5
ML OF 10^{-4} M $AgNO_3$

FIG. 28

TABLE IX

PHOTOMETRIC TITRATION OF 10^{-4} - 10^{-5}M POTASSIUM CYANIDE

USING 1 ML OF 0.2% 1,10-Phen and 1 ML OF BPR SOLUTION

KCN, M	Volume of KCN ml	$AgNO_3$, M	Volume of $AgNO_3$ Required, ml				
			Total	Indicator Blank		Corrected Titre	Mean Volume, $\bar{x}$
				Experimental	Theoritical		
9.72×10^{-5}	25	10^{-3}	1.42	0.18	0.20	1.24	
9.72×10^{-5}	25	10^{-3}	1.44	0.20	0.20	1.24	1.24
9.72×10^{-5}	25	10^{-3}	1.41	0.19	0.20	1.22	
9.72×10^{-6}	25	10^{-4}	3.22	2.03	2.00	1.19	
9.72×10^{-6}	25	10^{-4}	3.16	1.94	2.00	1.22	1.21
9.72×10^{-6}	25	10^{-4}	3.18	1.96	2.0	1.22	

i.e. adding only 0.5 ml of the indicator solution yields in indicator blank equivalent to 1 ml of 10^{-4}M silver nitrate instead of 2 ml, which is the case by adding 1 ml of the BPR indicator solution, (Table IX and Fig. 27, 28).

TABLE X

TITRATION OF 9.72×10^{-6} M POTASSIUM CYANIDE USING 0.5 ML OF 0.2%

1,10-PHENANTHROLINE AND 0.5 ML OF 0.006% BPR SOLUTION

KCN M	Volume of KCN, ml	$AgNO_3$, M	Volume of $AgNO_3$ Required, ml				
			Total	Indicator Blank		Corrected Titre	Mean Volume $\bar{x}$
				Experimental	Theoritical		
9.72×10^{-6}	25	10^{-4}	2.18	0.95	1.0	1.23	
9.72×10^{-6}	25	10^{-4}	2.22	1.0	1.0	1.22	1.22
9.72×10^{-6}	25	10^{-4}	2.17	0.95	1.0	1.22	

S T A N D A R D D E V I A T I O N

Number	Volume of 10^{-4} M KCN ml	Volume of $AgNO_3$ x 100			D	D^2
		Total ml	Experimental Blank ml	Equivalent Volume ml		
1	25	142	18	124	+ 0.10	0.01
2	25	144	20	124	+ 0.10	0.01
3	25	142	19	123	- 0.90	0.81
4	25	144	20	124	+ 0.10	0.01
5	25	141	18	123	- 0.90	0.81
6	25	145	20	125	+ 1.10	1.21
7	25	141	18	123	- 0.90	0.81
8	25	143	19	124	+ 0.10	0.01
9	25	145	20	125	+ 1.10	1.21
10	25	143	19	124	+ 0.10	0.01
			ΣX	= 1239	ΣD^2	=4.90
			$\bar{x}$	= 123.9		

$$S = \sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{4.9}{9}}$$

$$= \frac{2.2}{3} = 0.73$$

Whence, $\bar{s} = \frac{0.73}{123.9} = 0.00589$

Therefore Standard Deviation per cent

$$= \frac{0.00589}{100} = 0.589\ \%$$

E X P E R I M E N T A L

REAGENTS:

As for visual titrations, plus 10^{-5}M potassium cyanide solution.

APPARATUS:

Titrator:

An EEL photometric titrator (Evans Electro Selenium Ltd.) with an orange filter No. 607 (bandpass at 600 mu) and a 50 ml cylindrical titration cell.

R E C O M M E N D E D P R O C E D U R E

Transfer 25 ml aliquots of potassium cyanide solution (10^{-4}M) into the titration cell and add 1 ml of 0.2% 1,10-phenanthroline solution, 5 ml of ammonium acetate solution, 1 ml of 10^{-1}M EDTA solution and 1 ml of the BPR indicator solution. Titrate the solution, with continuous stirring, with 10^{-3}M silver nitrate and plot the galvanometer readings against the volume of titrant used.

In case of titrating 10^{-5}M potassium cyanide solution, the same procedure is followed but utilising

0.5 ml of 0.2% 1,10-phenanthroline and 0.5 ml of the BPR solution. Titrate against 10^{-4}M silver nitrate.

C O N C L U S I O N

By utilising photometric titration, the sensitivity of the proposed visual method, using BPR/Phen as an indicator system, is improved and the method becomes applicable down to 10^{-5}M of potassium cyanide.

The end-point of the titration is obtained from the intersection of the curve and corresponds to the attainment of maximum absorbance. At these concentrations the blank value, i.e., the amount of silver required to produce a colour transition of the indicator system, becomes significant and must be subtracted. This value can be obtained as before by calculation from the concentration of BPR and silver nitrate. Alternatively, the blank value may be obtained by carrying out a similar titration in the absence of potassium cyanide.

The proposed method is easy to carry out, it is rapid, sensitive and is generally superior to other photometric titration methods for cyanide. It is

applicable down to 10^{-5}M of potassium cyanide and allows the determination of 1-100 ppm of cyanide with standard deviation of 0.589.

The use of a 400 fold molar excess of EDTA over cyanide, renders the method conditionally selective and free from the interference of those metals which can be masked by EDTA, as it was mentioned in Chapter (II).

P A R T T W O

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM AND GOLD

C H A P T E R F O U R

SPECTROPHOTOMETRIC DETERMINATION OF THE PALLADIUM/1,10-PHENANTHROLINE/ ROSE BENGAL EXTRA IN AQUEOUS SOLUTION

S U M M A R Y

A simple, rapid, easily operated, reproducible and sensitive method is proposed for the direct spectrophotometric determination of trace amounts of palladium in aqueous solution. This method is based on the formation of a mauve coloured ternary complex between palladium (II), 1,10-phenanthroline and rose bengal at pH 6. This complex is formed instantaneously and remains stable for over 48 hours. It is applicable over a wide range of palladium concentration, i.e., 0.02128 - 0.4256 ppm could be determined and the molar absorptivity is ca. 50,000 at 575 mμ.

The use of EDTA as a mass masking agent renders the method highly selective towards palladium (II) ions and allows its determination in the presence of the other noble metals such as gold (III) or platinum (IV).

I N T R O D U C T I O N

From an examination of the published methods for the separation and determination of palladium it appears that most of them are quite unselective, e.g. gold interferes in the use of dimethylglyoxime as a precipitant for palladium.[1] Perhaps, the most selective method is that proposed by Wilson and Magee[142] involving the formation of the pyridine-thiocyanate complex. Pontani[143] reported that using palladium complexes of pyridine allowed the determination of palladium (II) in the presence of gold (III), platinum (IV), and iridium (IV).

In view of the importance for the determination of trace amounts of palladium, analytical chemists have shown a special interest during the last two decades in spectrophotometric methods of determination. The number of methods proposed during this period probably exceeds all other reported quantitative methods for this element. Up to 1953, nine spectrophotometric methods had been published,[144] a further seven chromogenic reagents were described up to 1958[145] and up to 1965, fifty more reagents were reported.[146]

Popa et al.[147] investigated twenty-two organic compounds as reagents for palladium and pointed out that the functional groupings characteristic for reacting with palladium (II) were "4 - x C_6 H_5 N N =" (where x is NO or N:NO) and "2 - Y C_6 H_5 N = N C_6 H_5" (where Y is OH or COOH). These authors recommended methyl red as being the most sensitive reagent. In a second paper, Popa [148] added tropaeolin O and tropaeolin OO and applied the later to the determination of palladium in the ranges 0.63 - 9.83, and 2.46 - 39.3 ppm.[149]

The feasability of determining trace amounts of palladium with organic reagents possessing the functional grouping p-nitrosophenylamino (p-NO C_6 H_4 N) has been known for about twenty years. The simplest reagent of this series, p-nitroso diphenylamine, has been used for the spectrophotometric determination of palladium via extraction of the complex into immiscible organic solvents; Ryan [150] used chloroform and Sandell[151] used diethyl oxalate as extraetants. Prozhevalskii etal.[152] reported that the complex was more stable after extraction into butanol than in aqueous media and a procedure was developed at pH 1.8 for the

determination of 0.05 - 0.5 ppm of palladium.

Although the p-nitrosodiphenylamine method is the most sensitive (the molar absorptivity is ca. 6.5×10^4), it suffers interference from oxidising agents, gold (III), small amounts of platinum metals, cyanide and iodide. The method also involves a colour development time of 0.5 hrs.

A similar reagent, p-dimethyl-aniline, has also been used for the spectrophotometric determination of palladium.[153] It is preferable to p-nitroso diphenylamine in pure solution because the colour development is rapid. However, in practice, the former is preferable because it can be used over a relatively wider concentration range. The p-nitroso aniline method is subject to the same interferences.

A more selective but less sensitive method, with a molar absorptivity of 1.8×10^4,[2] involves the use of 2-nitroso-1-naphthol and extraction of the complex into benzene in the presence of EDTA as masking agent was reported.[154,155]

2-nitroso-1-naphthol-4-sulphonic acid has also been described for the determination of trace amounts of palladium (II), but the noble metals, nickel(II), cobalt (II), cyanide and iodide interfere.[156]

Another insensitive method (molar absorptivity = 1.2×10^4) involves the use of nitroso-R. salt. In this instance the pH must be closely controlled at 2.6. [157-160]

The palladium (II) dithizonate complex was claimed to have molar absorptivities of ca. 6.3×10^4 and 5.7×10^4 at 450 and 650 mμ respectively using chloroform as extractant. [161]

P-dimethylaminobenzylidenerhodanine has also been reported as chromogenic reagent for palladium.[162,163] The molar absorptivity of thepalladium (II) complex is ca. 2.5×10^4 and the method is applicable over the concentration range 0.4 - 2.5 ppm of palladium (II). At higher concentrations of palladium a violet-red precipitate is formed. [163] The method is subject to interference from all noble metals, iron (III), cobalt (II), nickel (II), and chromium (III).

Palladium (II) has been determined spectrophotometrically using oximes as reagents. [164-171] The dimethylglyoxime - palladium (II) complex has a molar absorptivity of ca. 1.6×10^3, [164] 1-benzoyl-2-methylglyoxal dioxime is more sensitive,[165] its molar absorp-

tivity is ca. 1.4 x 10^4, and 4-methyl-1,2, cyclohexanedione dioxime [166] and furyldioxime [167,168] have molar absorptivities of ca. 1.51 x 10^4 and 2.38 x 10^4 respectively.

Another class of reagent frequently reported for the determination of palladium is 8-hydroxyquinoline and its derivatives. [172-179] The 8-hydroxyquinoline complex has a molar absorptivity of ca. 1.08 x 10^4 and the dibromo-substituted derivative has one of ca. 1.23 x 10^4. [174-176] These two methods employ chloroform as extractant, but both involve heating at 100°C for ca. 15 minutes.

The interaction of palladium and iodide gives a molar absorptivity of ca. 9.9 x 10^3 and has been reported for the spectrophotometric determination of palladium. [180,181]

Tin (II)-bromide, [182] chloride [183] and phosphate [183] form complexes with palladium and have been used for the determination of 1-10, 8-32, and 0.5-2.5 ppm of palladium respectively. Tin (II) phosphate was reported to be the most sensitive. However, gold (III) interferes in all three instances and the methods are not very sensitive relatively.

A further reported method utilizes the formation of the complex between palladium and thiocyanate. The molar absorptivity of this method is ca. 2.4×10^4 and a ten-fold molar excess of platinum (IV) can be tolerated.[184,185]

Many other miscellaneous methods have been reported.[186-224] One of the more sensitive is that using didodecyldithoxamamide,[202]

$(CH_3-(CH_2)_{11}-NH-\overset{\overset{S}{\|}}{C}-\overset{\overset{S}{\|}}{C}-NH-(CH_2)_{11}-CH_3)$, as reagent. This reagent forms a yellow water-insoluble complex with palladium (II), is extractable into chloroform and gives a sensitivity of ca. 0.005 $\mu g/cm^2$. The colour is stable for 48 hours, rhodium and iridium can be tolerated, but gold interferes.[202]

However, most of these methods are not very sensitive or selective, and most of them involve heating which is undesirable and time-consuming.

Recently, in 1967, Sen Gupta,[225] described the use of arsenazo (III) as a chromogenic reagent for the spectrophotometric determination of palladium and claimed a molar absorptivity of ca. 1.26×10^5. This is the most sensitive method to date, but it involves

evaporation to dryness on a steam bath and redissolution of the residue. Also, the colour development takes about one hour. These disadvantages make the method tedious and time-consuming.

Bustmante and Marti,[226] also in 1967, reported that the molar absorptivities of the palladium (II) - arsenazo (III) complex were only ca. 4.2×10^4 and 1.6×10^4 at 630 and 620 mμ respectively. The method was also found to be subject to interferences due to copper (II), cobalt (II), nickel (II), thorium (IV), uranium (VI) and the rare earth metals. These authors proposed at the same time a new chromogenic reagent called "palladiazo".[227] The molar absorptivities of the palladium (II) - palladiazo complex were ca. 3.3×10^4 and 1.7×10^4 at 540 and 635 mμ respectively. The method was applicable over a concentration range of 0.2 - 5 ppm of palladium (II), but lead (II), bismuth (III), cerium (III), and the rare earth elements interfered.

From this brief survey, it is obvious that most of the reported methods are not very sensitive and they lack selectivity. In addition, most of them involve heating and cooling, evaporation to dryness and then re-dissolution steps. This results in a loss of

constituent and renders the method tedious and time-consuming. In consequence, it was felt worthwhile to attempt to develop a spectrophotometric method for palladium which did not involve these undesirable steps and would allow the determination of palladium in the presence of other noble metals such as platinum (IV).

1 - DEVELOPMENT OF PROCEDURE

The ability of palladium ions to form a co-ordinately bonded complex with 1,10-phenanthroline via co-ordination of the central ion with the nitrogen atoms of the 1,10-phenanthroline is well known,[228,230] This positively charged bis-phenanthrolinium-palladium (II) ion, may associate then with an anionic dyestuff to form a coloured ternary complex.

A series of reagents have been examined for this purpose and three of them have been found capable of acting as the counter ion. These reagents were, Bromopyrogallol Red, Bromophenol Blue and Rose Bengal (Extra). Bromopyrogallol Red formed a violet coloured complex with the palladium (II)-bis-phenanthrolinium cation at pH 4. The reagent blank, (Bromopyrogallol Red and 1,10-Phenanthroline) has an absorption peak at 560 mμ (Fig. 29b). The addition of palladium ions gives a bathochromic shift, and the absorption peak is now found at ca. 590 mμ (a). A plot of (a) vs. (b) indicates that the maximum absorption is at 605 mμ (c). Preliminary experiments showed that this colour reaction was not sensitive and its molar absorptivity was

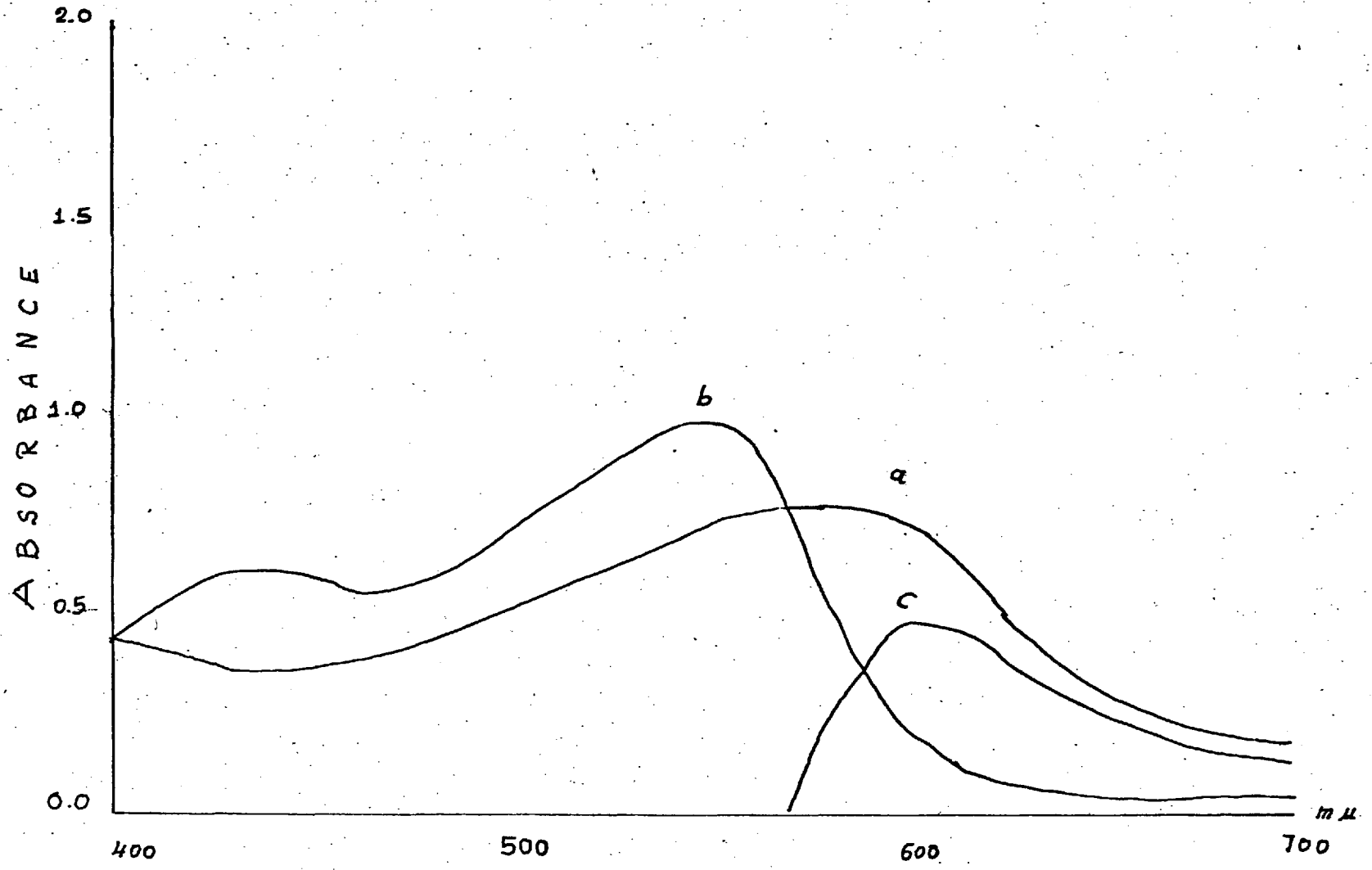


FIG. 29

only ca. 12,500 at 605 mμ.

With Bromophenol Blue, the absorption spectra obtained (Fig. 30) indicates that both the reagent blank (b) and the palladium complex (a) have maximum absorption peaks at the same wavelength, i.e. ca. 585 mμ. A plot of (a) vs. (b) shows that the maximum wavelength is, in fact, at 585 mμ (c). Because of the high absorbance of the reagent blank itself at this wavelength, this reaction is also not very sensitive.

On the other hand, by utilising Rose Bengal as a reagent, the reagent blank (Rose Bengal/1,10-phenanthroline) has a sharp absorbance peak at 535 mμ, Fig. 31 (b). This absorbance peak is decreased by the addition of palladium ions and another absorbance peak is established at 575 mμ, Fig. 31 (a). A plot of (a) vs. (b) (using 2 ml of 10^{-4}M palladium solution, 1 ml of 10^{-2}M 1,10-phenanthroline, 10 ml of 2 x 10^{-4}M Rose Bengal Solution and diluted to 50 ml with distilled water) gives a maximum wavelength at 575 mμ, Fig. 31 (c).

With Rose Bengal as a reagent, without the addition of 1,10-phenanthroline, the addition of palladium

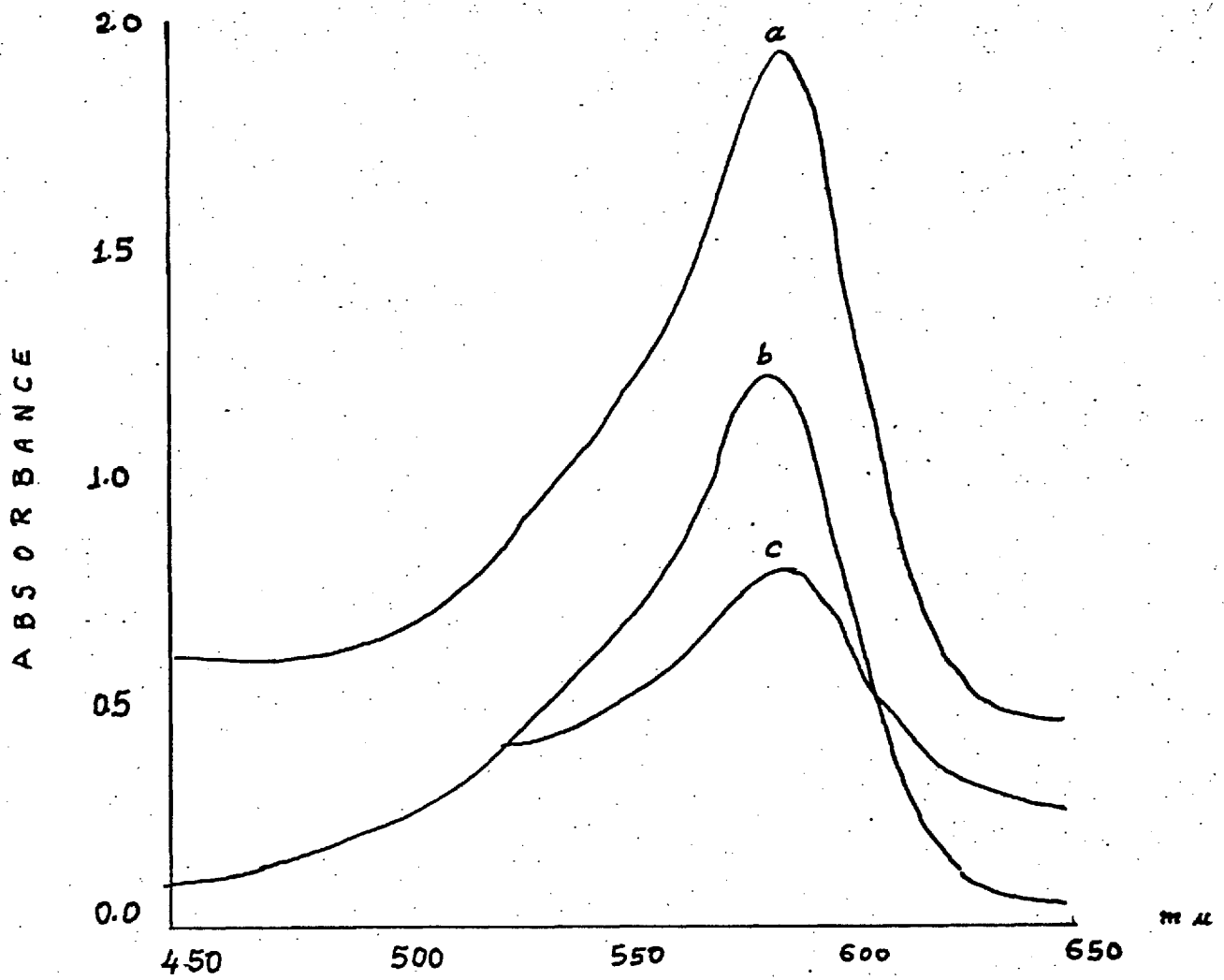


FIG. 30

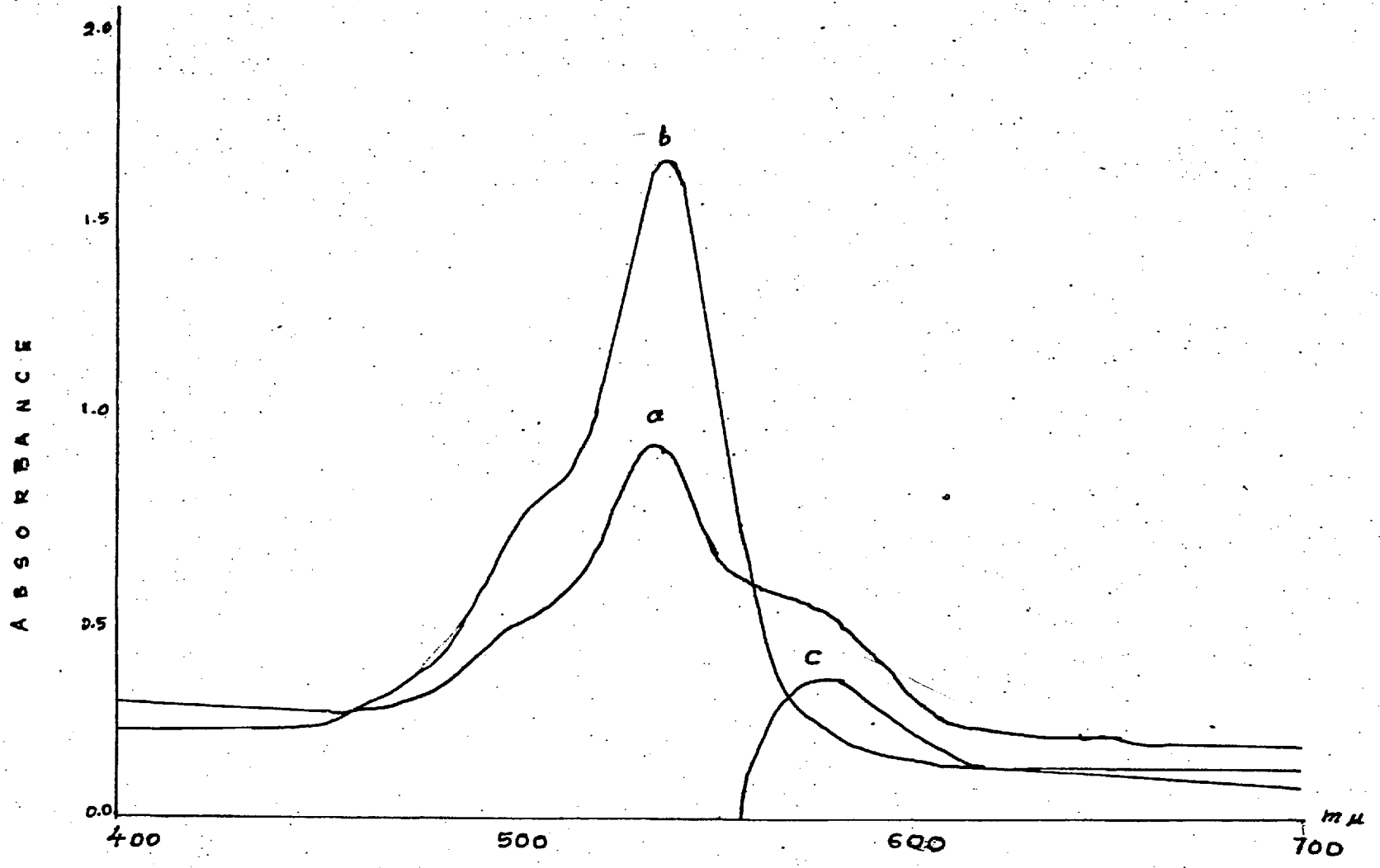


FIG. 31

solution to the reagent blank does not alter its absorbance at all. The various colours obtained are depicted in Fig. 32. The mauve coloured ternary complex formed was quite stable (for as long as required, i.e., 48 hours) and was the most sensitive reaction (ϵ = 50.000 at 575 mμ) with respect to the other reagents. Consequently, Rose Bengal Extra was selected for development as a reagent for the spectrophotometric determination of trace amounts of palladium.

D C B A

Fig. 32

2. OPTIMISATION OF CONDITIONS FOR MAXIMUM COLOUR DEVELOPMENT

2.1 pH

A series of solutions were prepared containing 2 ml of a 10^{-4}M solution of palladium (II), 1 ml of a 10^{-2}M 1,10-phenanthroline solution, and 5 ml of a 2 x 10^{-4}M and RBE, and the pH was adjusted by the addition of 0.1N ammonium hydroxide under a pH meter over the range 1 - 10. The solutions were then diluted to 50 ml with distilled water and the absorbance was measured against a reagent blank at 575 mμ prepared in the same manner but containing no palladium. It was found from this study that maximum colour development was obtained over the pH range 5-6.5 (Fig. 33).

2.2 DEVELOPMENT TIME

The colour formation is instantaneous and remains stable for over 48 hours under normal laboratory conditions (Fig. 34). The solution used in this experiment contained 2 ml of a 10^{-4}M palladium (II) solution, 1 ml of a 10^{-2}M solution of 1,10-phenanthroline, 2 ml of pH 6

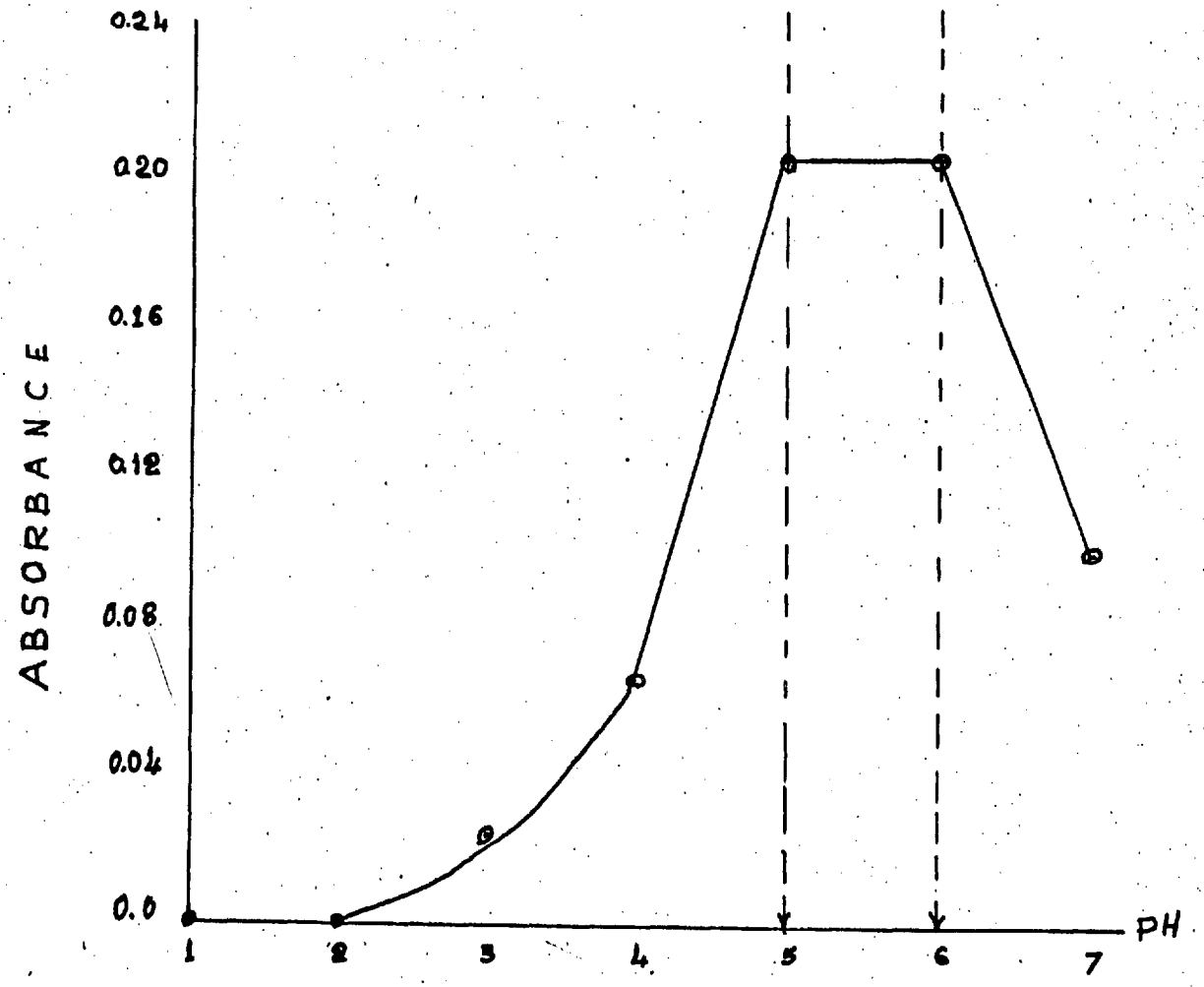


Fig. 33.

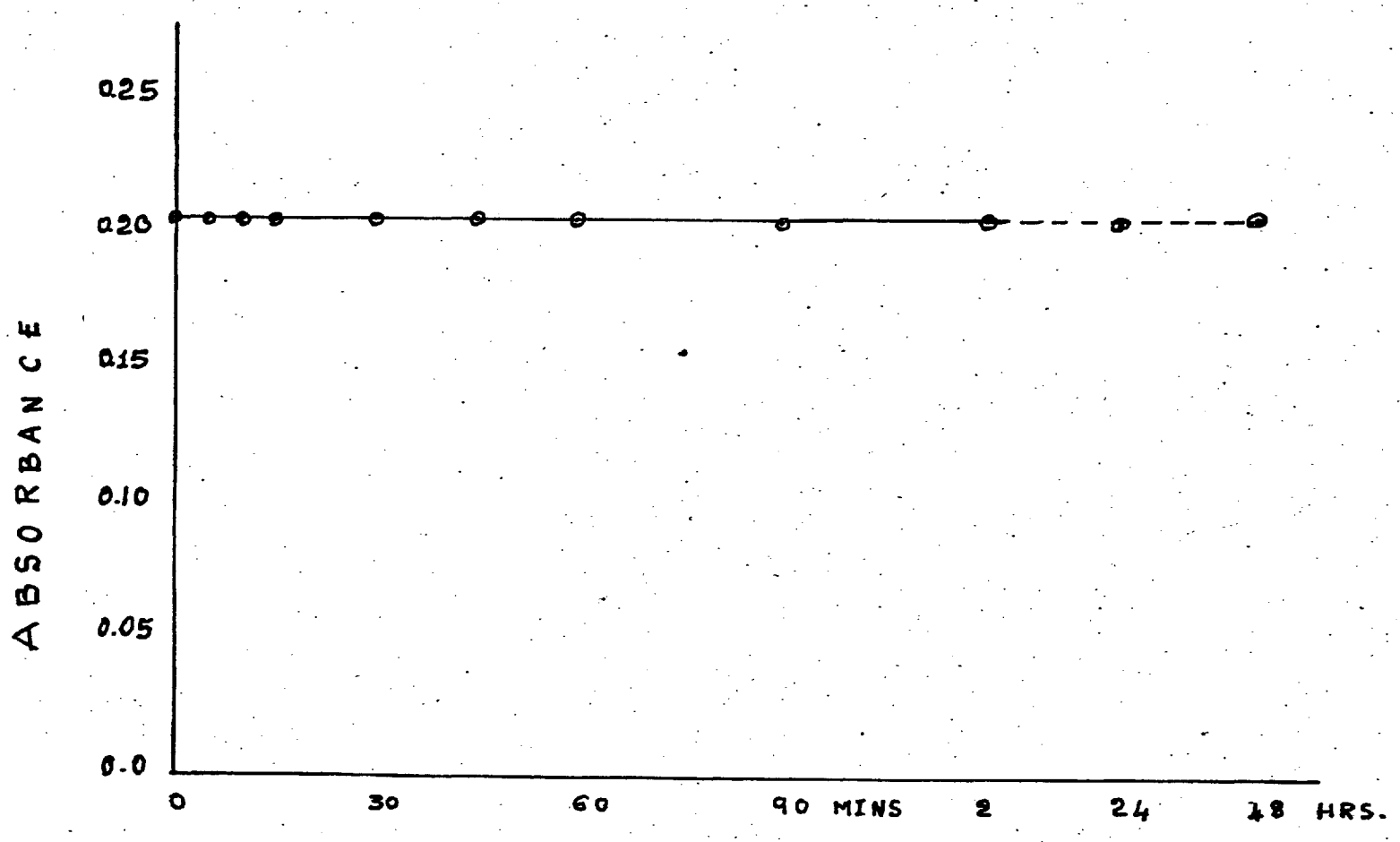


FIG. 34

buffer solution and 5 ml of a 2 x 10^{-4}M solution of Rose Bengal Extra. The whole was then diluted to 50 ml with distilled water. The absorbance was measured at 575 mμ against a reagent blank carried through the same procedure, but containing no palladium.

2.3 MASKING AGENTS

EDTA has been examined as a convenient mass masking agent. The method involved pipetting a 1 ml of a 10^{-1}M EDTA solution into a 50 ml volumetric flask followed by 1 ml of a 10^{-4}M palladium (II) solution, 1 ml of a 10^{-2}M solution of 1,10-phenanthroline, 2 ml of pH 6 buffer solution and 5 ml of a 2 x 10^{-4}M Rose Bengal Extra solution. The whole was diluted to the mark with distilled water. It was found that the absorbance of this solution when measured against a reagent blank exactly similar to that of a solution containing all the above reagents except EDTA measured in the same way (i.e., a value of 0.105 was given). Thus, EDTA may be used as a masking agent, and may be present in a 1000-fold molar excess over palladium.

3. LAMBERT-BEER'S LAW CHECK

Under the above established optimum conditions a calibration curve was prepared as described in the recommended procedure (page 176).

The curve obtained was a straight line and passed through the origin. Beer's law was obeyed over the range 1 - 20 ml of 10^{-5}M palladium (II), that is 1.064-21.28 µg of palladium (II) or 0.021 - 0.42 ppm of final concentration of palladium (II). The molar absorptivity was ca. 50,000 at 575 mµ (Fig. 35).

4. NATURE OF COMPLEX

Because of the low purity of the reagent, Rose Bengal Extra (B.D.H.) and the many difficulties associated with its purification, the Job plots, mole ratio or slope ratio studies will not provide the correct reacting ratio of the reagents involved.[43]

5. INTERFERENCES

The use of EDTA as a general masking agent for most of the more common cations has been well demonstrated

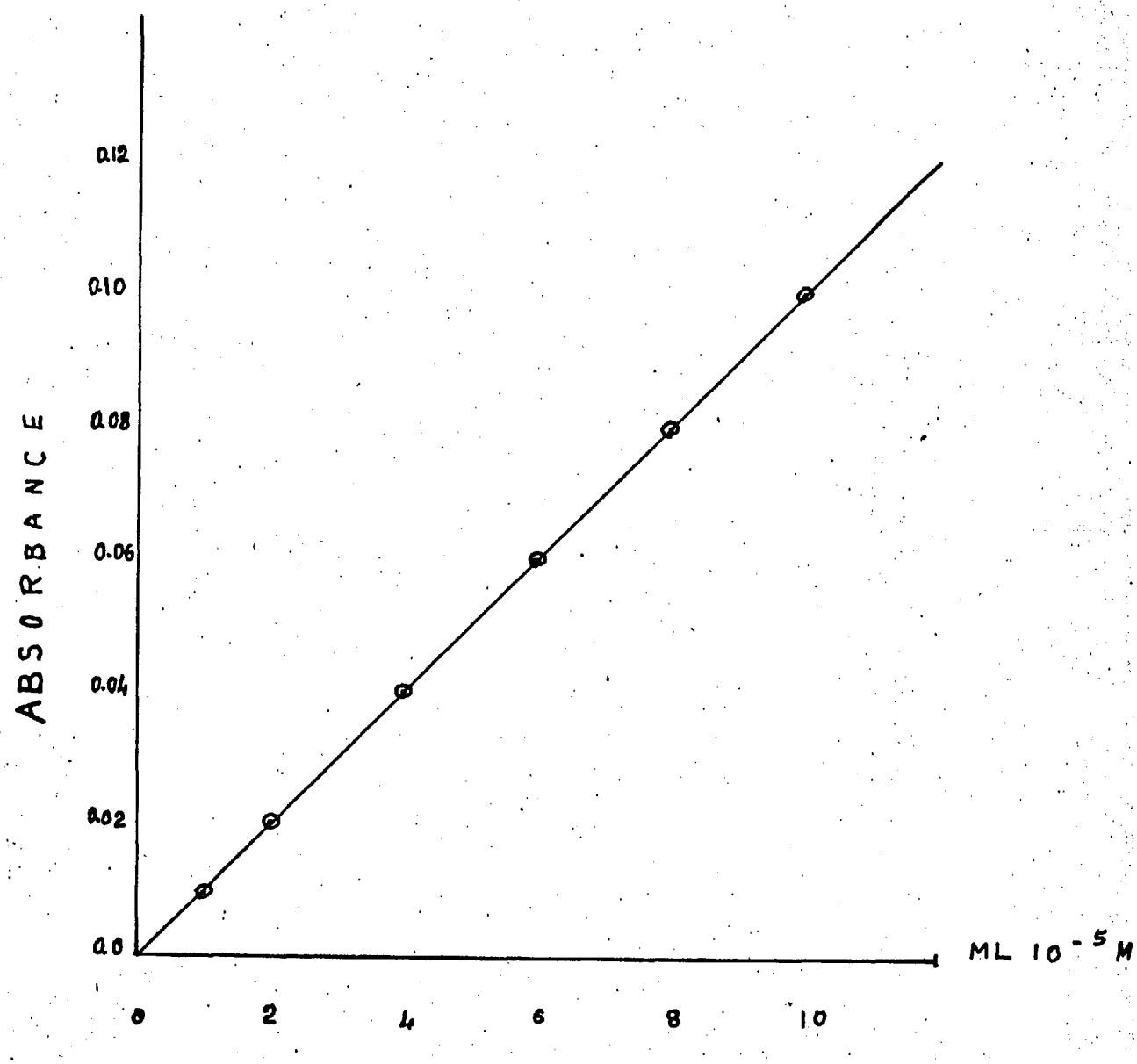


FIG. 35

with a similar system involving silver, 1,10-phenanthroline and Bromopyrogallol Red by Dagnall and West.[25] Hence, in this instance attention was paid primarily to the effect on the other noble metals e.g. gold (III) and platinum (IV).

It was found that platinum (IV) and gold (III) could be tolerated up to 10-fold molar excess over palladium (II) using a 1000-fold molar excess of EDTA, a 100-fold molar excess of 1,10-phenanthroline and a 10-fold molar excess of Rose Bengal Extra over palladium.

6. SOLVENT EXTRACTION

A wide range of water-immiscible solvents has been investigated to extract the palladium/1,10-phenanthroline/Rose Bengal Extra Complex, which included, benzine, carbon tetrachloride, chloroform, ethyl acetate, iso-butyl methyl ketone (hexone) and nitrobenzene. Unfortunately, the palladium complex was not extracted into those organic solvents, and a mauve coloured precipitate was found at the interphase in the case of nitrobenzene. Therefore, the palladium/1,10-phenanthroline/Rose Bengal Extra complex is not extractable in the above mentioned six organic solvents. However, attempts have been made to

extract the palladium complex by replacing 1,10-phenanthroline with pyridine (see Chapter V).

7. PRECISION

The precision of the method was investigated by determining the percentage standard deviation from the multiple analyses of a series of solutions, each containing, 2 ml of a 10^{-4}M palladium (II) solution, 1 ml of a 10^{-1}M solution of EDTA, 1 ml of a 10^{-2}M solution of 1,10-phenanthroline, 2 ml of pH 6 buffer solution and 10 ml of a 2 x 10^{-4}M Rose Bengal Extra solution and diluted to 50 ml with distilled water. The absorbance was measured against a reagent blank at 575 mμ. The results obtained are summarised in Table XI.

Table XI

Number (n)	Absorbance x 1000 (x)	Deviance D	D^2
1	205	+ 3.0	9
2	200	- 2.0	4
3	202	0.0	0
4	205	+ 3.0	9
5	202	0.0	0
6	197	- 5.0	25
7	200	- 2.0	4
8	205	+ 3.0	9
9	200	- 2.0	4
10	207	+ 5.0	25
	$\Sigma X = 2020$		$\Sigma D^2 = 89$
	$\bar{x} = 202$		

$$\text{Standard Deviation} = \sqrt{\frac{\Sigma D^2}{n-1}}$$

$$(S) \qquad (S) = \sqrt{\frac{89}{9}} = 3.1$$

$$\therefore \quad S^- = \frac{3.1}{202} = 0.014$$

Whence, the Standard Deviation per cent

$$= 0.014 \times 100 = 1.4$$

E X P E R I M E N T A L

APPARATUS:

Spectrophotometer: Unicam Sp 600 Spectrophotometer and 1 cm glass cuvette.

pH Meter E.L.I. (Electronic Instruments Ltd.), Model 23A

REAGENTS:

Unless otherwise stated all the reagents used in this study were of analytical grade.

Palladium Chloride, 10^{-2} - 10^{-5}M

Dissolve 0.8805 g of palladium chloride in 10 ml of concentrated hydrochloric acid and dilute to 500 ml with distilled water. Standardise this solution by adding excess of EDTA and back titrate with standard zinc solution using xylenol orange as indicator. Dilute this solution as required.

1,10-Phenanthroline hydrate, 10^{-2}M

Dissolve 0.991 g of 1,10-phenanthroline hydrate into 500 ml of distilled water.

Rose Bengal (Extra), 2×10^{-4}M

Prepare by dissolving 0.1018 g of Rose Bengal (Extra) into 500 ml of distilled water.

Buffering Agent pH 6

Prepare by adding 2.5 ml of 4 N acetic acid to 47.5 ml of 4N sodium acetate and diluted to 250 ml with distilled water.

R E C O M M E N D E D P R O C E D U R E

Pipette 1 - 20 ml of 10^{-5}M palladium solution into a series of 50 ml volumetric flasks, followed by the addition of a 1 ml of 10^{-2}M 1,10-phenanthroline solution, after adding a 1 ml of 10^{-1}M EDTA solution, 2 ml of buffering agent pH 6, 5 ml of 2 x 10^{-4}M Rose Bengal solution and dilute with distilled water up to the mark.

Transfer a portion of the solution into 1 cm cuvette and measure the absorbance in a spectrophotometer against a reagent blank, carried throughout the same procedure, but containing no palladium, at 575 mμ.

Plot the absorbance obtained against micrograms of palladium.

1 ml of 10^{-5}M palladium ≅ 1.064 μg of palladium

The obtained graph was a straight line over the range of 1.064 - 21.28 μg of palladium or 0.0212 - 0.4256 ppm of final concentration of palladium.

C O N C L U S I O N

The method as developed for the direct spectrophotometric determination of trace amounts of palladium in aqueous solution is a simple, rapid, easily operated, reproducible and sensitive method. It compares very favourably with most of the publiched methods for the determination of palladium in aqueous solution and it can certainly be classified amongst the most sensitive methods cf. (Table XII).

Table XII

Method	Molar Absorptivity x 1000	max mμ
Bromide [231]	0.267	505
Thioglycolic Acid [231]	5.3	Not Available
Iodide [2,231]	9.29	408
Rose Bengal Extra/ 1,10-Phenanthroline	50.0	575
Nitrosodimethylaniline [231]	65.0	500

The nitrosodimethylaniline method suffers interferences from cobalt (II), gold (III), iron (III), iridium (IV), nickel (II), platinum (IV) and rhodium (III), neutral salts and oxidising and reducing agents. [231] In the proposed method the colour formation is instantaneous and can tolerate small amounts of gold (III) and platinum (IV), i.e. up to 10-fold molar excess over palladium (II) using EDTA as a masking agent. There is no reason to suspect that most other cationic interferences can be eliminated in this manner.

Finally, the proposed method, because of its simplicity and the high stability of the mauve-coloured complex, can be used in routine analysis.

C H A P T E R F I V E

SELECTIVE EXTRACTION OF THE PALLADIUM/PYRIDINE/ROSE BENGAL EXTRA COMPLEX

S U M M A R Y

An extremely sensitive and conditionally selective method is proposed for the spectrophotometric determination of trace amounts of palladium in an organic medium. The method is based on the formation of a ternary complex system between palladium(II), pyridine and Rose Bengal Extra. This complex is extractable into chloroform at pH 8. Beer's law is obeyed over the range 1 - 10 ml of 2 x 10^{-5}M palladium per 25 ml (or 2.128 - 21.28 µg palladium/ 25 ml or 0.085 - 0.85 ppm of palladium in the final concentration) with a molar absorptivity of 125,000 at 570 mµ. This method is selective towards palladium ions by using EDTA as a mass-masking agent for most of the common extraneous cations. Silver (I), gold (III) and platinum (IV) do not interfere up to 100-fold molar excess over palladium using EDTA as a masking agent. Furthermore, another 19 cations and seven anions do not interfere as well. The proposed method is rapid and the reaction takes place instantaneously and the mauve colour developed is stable for at least five hours.

1. DEVELOPMENT OF THE PROCEDURE

As was mentioned in Chapter (IV), the ternary complex formed between palladium (II), 1,10-phenanthroline and Rose Bengal Extra, was found to be non-extractable in several water-immiscible organic solvents. It was then thought worthwhile to try to replace the phenanthroline molecule by other similar ligands containing the same tertiary amine $\geq N-$ functional grouping, e.g. pyridine, dipyridyl, etc. Preliminary investigations showed that pyridine offered many advantages. In this case an extractable complex was obtained using nitrobenzene or chloroform as solvents because (i) the colour development takes place instantaneously, (ii) remains stable for a long time, (iii) has a high sensitivity (molar absorptivity of ca. 125,000), (iv) EDTA has no effect on the colour.

1.1 Preliminary Spectra

Using nitrobenzene as extractant, the pyridine/Rose Bengal Extra, reagent blank shows only a small absorbance peak at 570 mu (Fig. 36 (b)). The addition

of palladium to this solution, produces a very sharp maximum at the same wavelength (570 mμ) (Fig. 36 a).

With chloroform as extractant, the reagent blank shows no absorbance at all (Fig. 37 b) while the mauve coloured extract with palladium shows a very sharp absorbance peak at 570 mμ (Fig. 37 a).

In view of these findings and the unpleasant nature of nitrobenzene, chloroform was selected as the better solvent.

2. OPTIMISATION OF CONDITIONS FOR MAXIMUM COLOUR DEVELOPMENT

2.1. pH

Preliminary investigations showed that the reaction is pH sensitive. By investigating the colour formation over the pH range 3 - 11, e.g., 3, 5, 7, 9 and 11, it was observed that colour development was obtained only at pH 7. It was subsequently found that maximum colour formation occurred over the range pH 7.5 - 8 (Fig 38). It was found that maximum colour formation was given using a phosphate buffer consisting

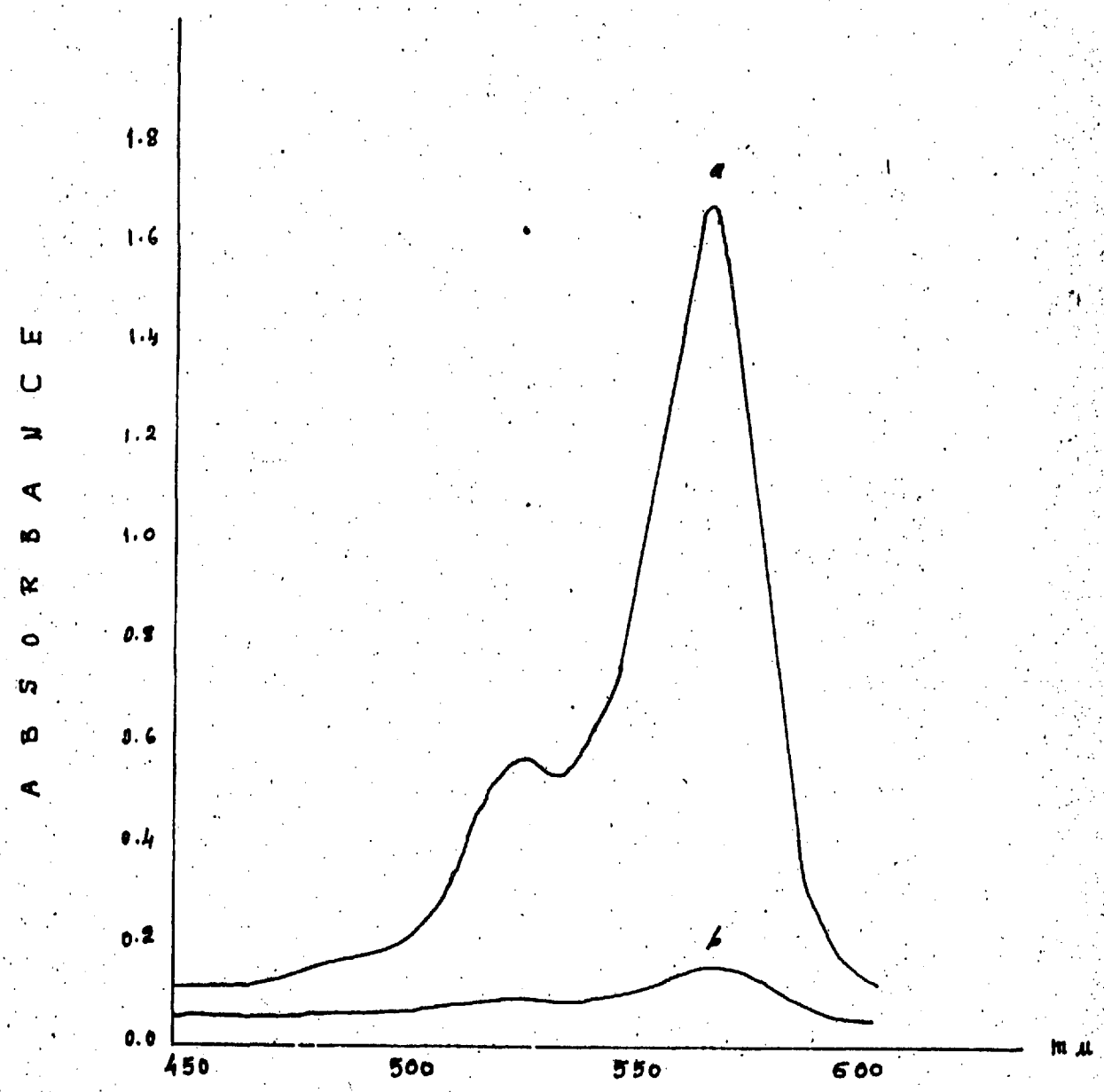


FIG. 36

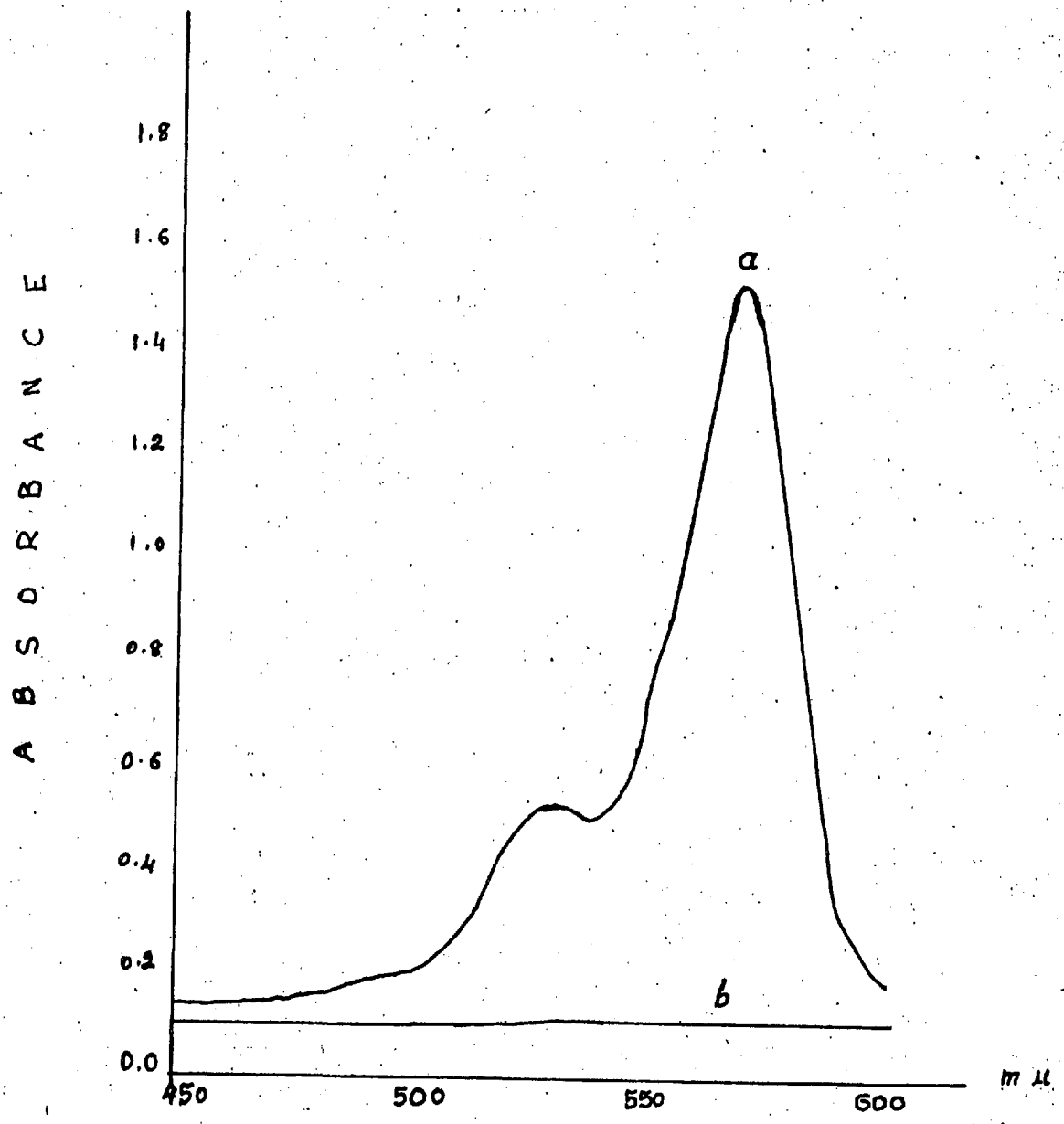


FIG. 37

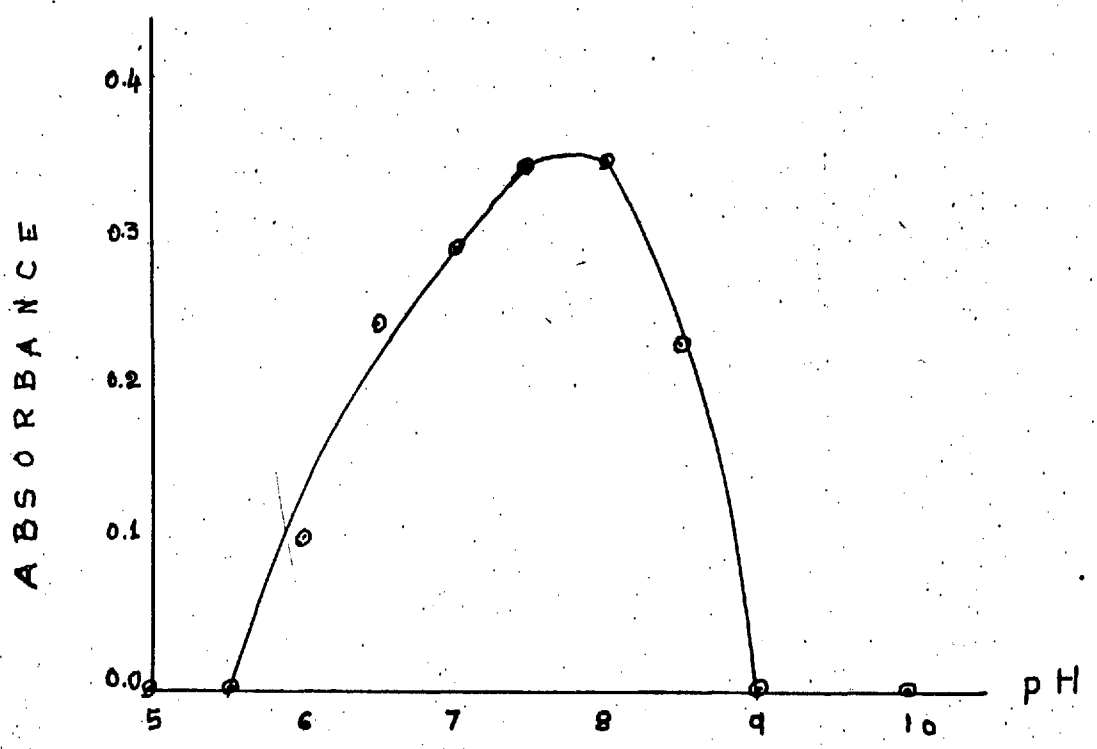

ABSORBANCE
0.4
0.3
0.2
0.1
0.0
5
6
7
8
9
10
pH

FIG. 38

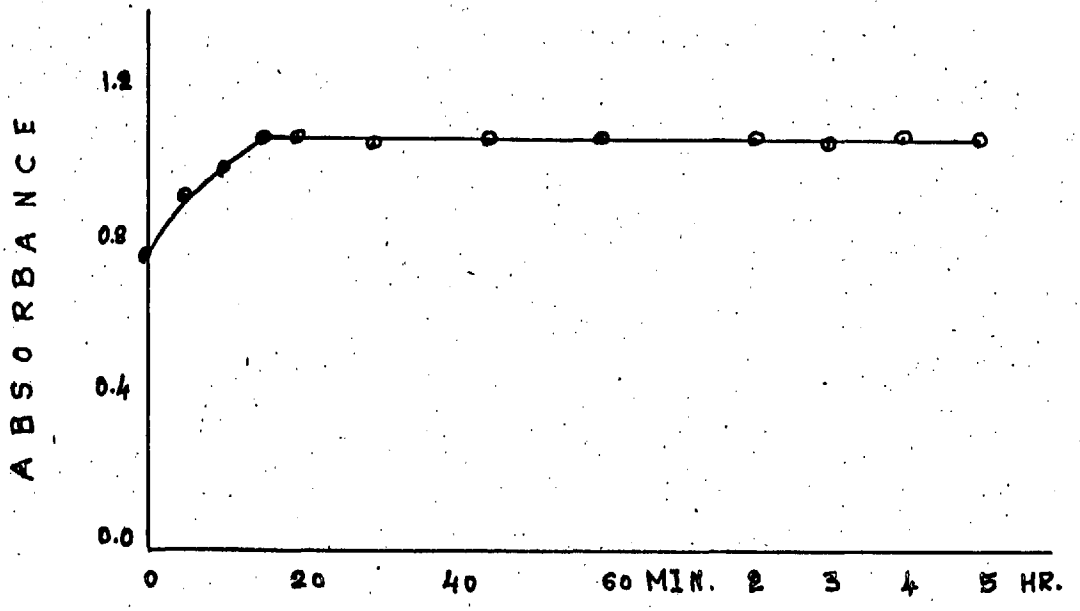

ABSORBANCE
1.2
0.8
0.4
0.0
0
20
40
60 MIN.
2
3
4
5 HR.

FIG. 39

of disodium hydrogen phosphate.

2.2 Optimum Time for Colour Formation

Although the reaction takes place instantaneously, it reaches a maximum after ca. 15 minutes and remains stable for at least 5 hours (Fig. 39).

2.3 Masking Agents

The addition of a 1000 fold molar excess of EDTA over palladium did not alter the absorbance. Consequently it was decided to utilise EDTA as a mass-masking agent for most of the common extraneous cations.

2.4 Order of Addition

It was found that by pipetting palladium solution into a separatory funnel containing 1 ml of a 10% w/v pyridine, followed by a solution of EDTA, buffer solution, Rose Bengal Extra and then the solvent. A slightly higher absorbance was obtained if the chloroform was added in two separate portions. This yielded a more complete and rapid extraction of the complex.

Also no precipitate was observed at the interphase as was the case if the whole solvent was added at once. Hence, it was decided to add the solvent as follows: Add 15 ml of the solvent and mix the contents thoroughly. After phase separation (ca. 1 minute) add a further 10 ml and again shake the separating funnel (ca, 1 min).

3. BEER'S LAW CHECK

Under the above established optimum conditions, a calibration curve was prepared. It was found that Beer's law was obeyed over the range 1 - 10 ml of a 2×10^{-5}M palladium solution per 25 ml or 2.128 - 21.28 µg of palladium per 25 ml or 0.085 - 0.85 ppm of palladium in the final concentration. The graph was a straight line passing through the origin and gave a molar absorptivity of 125,000 at 570 mµ. This was obtained in the presence of a 500 molar excess of EDTA with respect to the upper limit of palladium (Fig. 40).

4. INTERFERENCES

The use of EDTA as a masking agent for most of

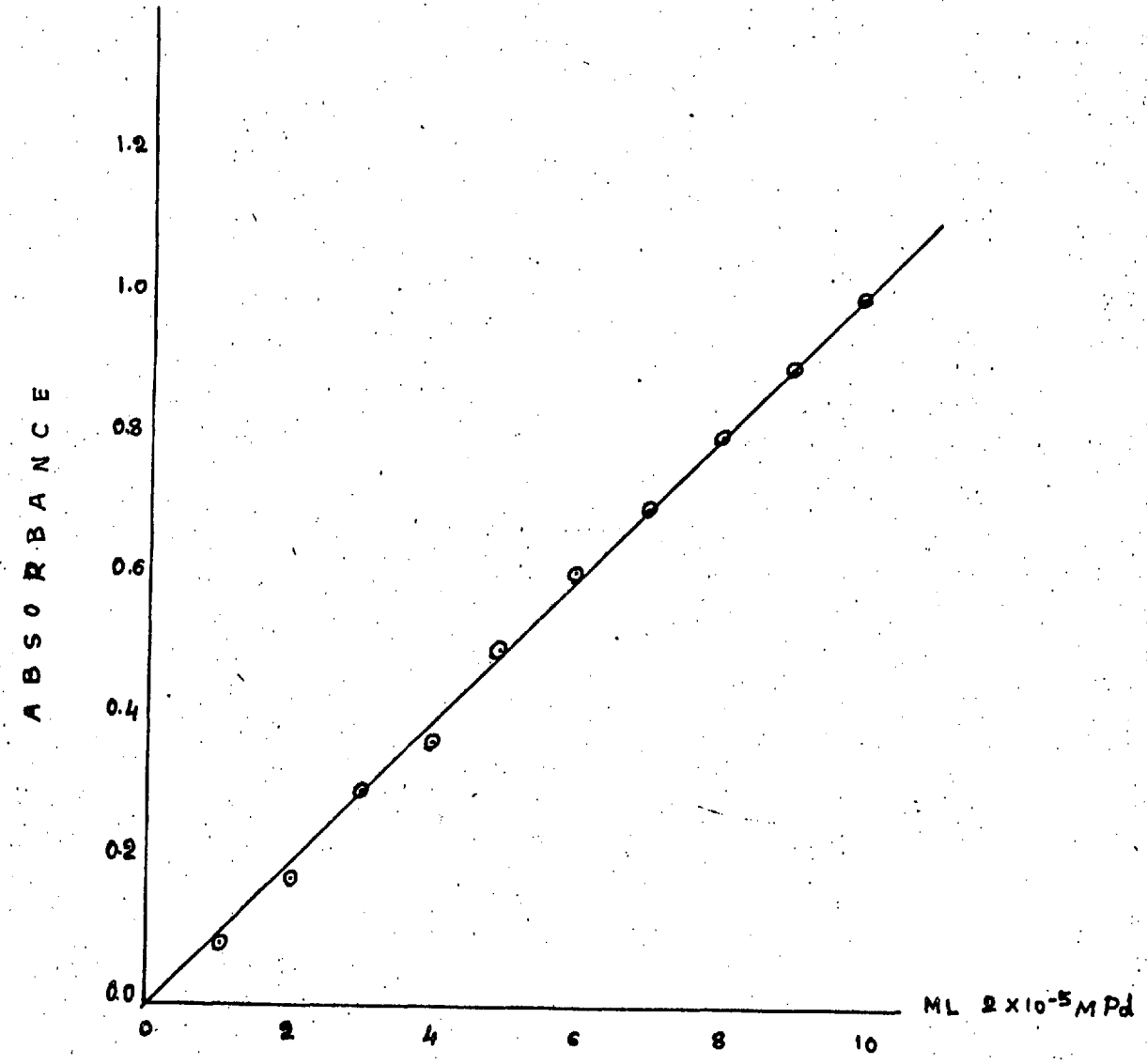


FIG. 40

the common cations which may interfere by reacting with pyridine such as cobalt (II), copper (II), or nickel (II), etc., allows a very selective method for the determination of palladium. In this study, twenty two cations and seven anions were investigated for their interferences. The results obtained are summarised in Table XIII. The solutions prepared for this experiment were containing 1 ml of a 10^{-2}M of the extraneous ion solution, 1 ml of a 10^{-4}M palladium solution, 1 ml of 10^{-1}M EDTA solution, 2 ml of the phosphate buffer, 15 ml of 2 x 10^{-4}M Rose Bengal Extra solution and 25 ml of chloroform. The pH was checked and brought to 8 in case of strong acidity of the extraneous metal ion solution, such as mercuric nitrate or niobium solution, with 0.1N ammonia solution. The absorbance was then measured against a reagent blank which contains all the reagents but containing neither extraneous ions nor palladium at 570 mμ. The readings obtained were then compared against a standard solution containing all reagents except the extraneous ions.

Table XIII

Ions	Fold Molar Excess over Palladium	Absorbance against Blank	Deviation From the Standard
Pd^{2+} (standard)		0.505	
$Pd^{2+} + Ag^{+}$	100	0.535	+ 0.030
$Pd^{2+} + Al^{3+}$	100	0.500	- 0.005
$Pd^{2+} + Au^{2+}$	100	0.540	+ 0.035
$Pd^{2+} + Ba^{2+}$	100	0.515	+ 0.010
$Pd^{2+} + Ca^{2+}$	100	0.500	- 0.005
$Pd^{2+} + Cd^{3+}$	100	0.510	+ 0.005
$Pd^{2+} + Co^{2+}$	100	0.520	+ 0.015
$Pd^{2+} + Cu^{3+}$	100	0.495	- 0.010
$Pd^{2+} + Fe^{2+}$	100	0.495	- 0.010
$Pd^{2+} + Hg^{+}$	100	0.53	+ 0.025
$Pd^{2+} + K^{+}$	1000	0.502	- 0.003
$Pd^{2+} + La^{3+}$	100	0.500	- 0.005
$Pd^{2+} + Li^{+}$	100	0.510	+ 0.005
$Pd^{2+} + Mg^{2+}$	100	0.502	- 0.003
$Pd^{2+} + Mn^{+}$	100	0.510	+ 0.005
$Pd^{2+} + Na^{+}$	1,000	0.500	- 0.005
$Pd^{2+} + Nb^{5+}$	100	0.485	- 0.020
$Pd^{2+} + Ni^{2+}$	100	0.52	+ 0.015
$Pd^{2+} + Pb^{4+}$	100	0.517	+ 0.012
$Pd^{2+} + Pt^{5+}$	100	0.492	- 0.013
$Pd^{2+} + V^{2+}$	100	0.495	- 0.010
$Pd^{2+} + Zn^{2+}$	100	0.490	- 0.015
$Pd^{2+} + Cl^{-}$	1,000	0.502	- 0.003
$Pd^{2+} + ClO_4^{-}$	100	0.510	+ 0.005
$Pd^{2+} + CO_3^{2-}$	100	0.500	- 0.005
$Pd^{2+} + F^{-}$	1,000	0.500	- 0.005
$Pd^{2+} + HPO_4^{2-}$	10,000	0.505	0.00
$Pd^{2+} + NO_3^{-}$	100	0.530	+ 0.025
$Pd^{2+} + SO_4^{2-}$	100	0.490	- 0.010

From Table XIII, it is obvious that none of the 22 cations or the 7 anions interfere in the presence of 100 fold molar excess of EDTA over palladium. However, the masking of the silver ions is due to the precipitation of silver as silver chloride, which is already present in the solution, and not due to the presence of EDTA, because after the addition of palladium solution to the silver nitrate solution, a precipitate of silver chloride was observed.

Consequently, the proposed method becomes very selective for the palladium ions employing EDTA as a masking agent.

5. NATURE OF THE COMPLEX

Because of the difficulties associated with purifying Rose Bengal Extra to its theoretical composition,[43] Job's Plots or slope-ratio methods will not provide the correct complex ratio. However, in view of the results obtained in Chapter (I) and the results obtained by Dagnall and West[25,40] it can be deduced that the complex ratio palladium:pyridine:Rose Bengal Extra is 1:4:1.

However, it may be possible to obtain the actual complex ratio by replacing Rose Bengal Extra with some other related dyestuff which can be obtained in a known state of purity such as erythrosin (see future work).

6. PRECISION

The precision of the method was investigated by determining the percentage standard deviation from the multiple analyses of a series of solutions each containing 2 ml of a 10^{-4}M solution of palladium (II), 1 ml of a 10% w/v pyridine solution, 1 ml of a 10^{-1}M EDTA solution, 2 ml of a 10% phosphate buffer, 15 ml of a 2×10^{-4}M Rose Bengal Extra solution and extracted into 25 ml of chloroform. The results obtained are summarised in Table XIV.

Table XIV

Number	Absorbance x 100	Deviance D	Deviance^2 D^2
1	102	+ 2	4
2	100	0	0
3	98	- 2	4
4	104	+ 4	16
5	96	- 4	16
6	100	0	0
7	97	- 3	9
8	99	- 1	1
9	101	+ 1	1
10	102	+ 2	4
11	101	+ 1	1
ΣX =	1100	ΣD^2 =	56
$\therefore \bar{x}$ =	100		

$$\text{Standard Deviation} = \sqrt{\frac{\Sigma D^2}{n-1}}$$

$$= \sqrt{\frac{56}{10}} = 2.37$$

Whence, Percentage Standard Deviation

$$= \frac{2.37}{100} \times 100 = 2.37$$

E X P E R I M E N T A L

APPARATUS:

Spectrophotometer	A Unicam SP. 600 Spectrophotometer with 2 matched 1 cm glass cuvettes.
pH Meter	E.I.L. (Electronic Instruments Ltd) Model 23 A.

REAGENTS:

All reagents were of analytical grade unless otherwise stated.

Palladium Chloride, 2×10^{-5}M

Prepare by appropriate dilution of a standardised 10^{-4}M palladium chloride (see page 174). The final acidity of the solution is 0,1N in hydrochloric acid.

Rose Bengal Extra, 2 x 10^{-4}M

See Chapter IV.

Pyridine, 10% w/v

Prepare by pipetting 25 ml of pyridine (Analar Grade) into a 250 ml graduated flask and diluted to the mark with distilled water.

Buffer Solution, pH 8

Prepare by dissolving 10 g of disodium hydrogen phosphate in distilled water and dilute to 100 ml.

EDTA, 10^{-1}M

Prepare by dissolving 18.6125 g of Na_2EDTA in distilled water and dilute to 500 ml in a graduated flask.

Chloroform Analar Grade.

R E C O M M E N D E D P R O C E D U R E

Pipette 1 ml of a 10% w/v solution of pyridine into a series of 100 ml separatory funnels, followed by 1 - 10 ml of a 2 x 10^{-5}M palladium chloride solution. Add 1 ml of a 10^{-1}M EDTA solution, 2 ml of phosphate buffer, 15 ml of a 2 x 10^{-4}M Rose Bengal Extra solution and dilute with distilled water to give a constant volume in each funnel. Add 15 ml of chloroform solution and shake the funnels for ca. 1 minute, and then add another 10 ml of chloroform and shake by continuous inversion for a further 1 minute. After ca. 15 minutes run a small portion of the organic layer into clean and dry 1 cm cuvettes. Measure the absorbance of the extracts against a reagent blank, carried through the same procedure containing all reagents except palladium, at 570 mμ.

Plot the absorbance vs. micrograms of palladium.

1 ml of 2 x 10^{-5}M Pd $Cl_2 \equiv$ 2.128 μg Pd

C O N C L U S I O N

The proposed method for the spectrophotometric determination of trace amounts of palladium is extremely sensitive, rapid, reproducible and easily operated. Consequently it compares very favourably with all the published methods for the determination of palladium in organic media, cf. Table XV.

Table XV shows that the proposed method is the most sensitive. Furthermore, the method is highly selective since palladium ions can be determined in the presence of the other noble metals such as gold (III) and platinum (IV) up to 100 fold molar excess, using EDTA as a masking agent.

In view of the simplicity, rapidity, good reproducibility, extreme sensitivity and selectivity, and the stability of the developed colour, the proposed method can be used for routine analysis.

Table XV

Method	Solvent	Molar Absorptivity x 1000	λ max mu
Dimethylglyoxime[231]	Chloroform	1.6	383
Salycylaldoxime[231]	Chloroform	6.6	376
Diethyldithiocarbamate[231]	Carbon-tetrachloride	7.13	305
β-Nitroso-α-Naphthol[231]	Tuluene	18.0	370
Furildioxime[231]	Chloroform	23.8	380
Salycylaldoxime[231]	Chloroform	26.0	275
Dithizone[231]	Carbon-Tetrachloride	28.8	640
Dithizone[231]	Carbon-Tetrachloride	34.4	450
Dithizone[231]	Carbon-Tetrachloride	38.4	280
Pyridine/Rose Bengal Extra	Chloroform	125.0	570

C H A P T E R S I X

SPECTROPHOTOMETRIC DETERMINATION OF GOLD

S U M M A R Y

A simple, rapid, reproducible and sensitive method is proposed for the direct spectrophotometric determination of gold (III) in aqueous solution. This method is based on the formation of a mauve-coloured ternary complex between gold (III), 1,10-phenanthroline and Rose Bengal Extra (tetrachloro (P) tetraiodo (R) fluorescein) at pH 5 with a molar absorptivity of ca.31,000 at 575 mμ. This method allows the determination of gold (III) down to ca. 0.2 ppm of gold (III) Beer's law is obeyed over the range 0.2 - 2.0 ppm of gold (III).

I N T R O D U C T I O N

In view of the wide industrial and scientific uses for gold and its alloys, several methods for its determination have been reported. For fairly large amounts of gold both gravimetric methods, for example reduction of gold to the metallic state using a reductant such as hydroquinone, and titrimetric methods, for example iodometric have been recommended.[232,233] Belcher [3] has pointed out that gravimetric methods give the more accurate results. In addition to these, many other gravimetric and titrimetric methods have been reported in the literature.[2,232-234]

Spectrophotometric methods are amongst the most sensitive for determining microgram or trace amounts of gold. Such measurements are of concern in medicine due to the theraputic use of gold, and in some natural sources, e.g., sea water (in which gold's concentration is ca. 0.0005 ppm).[235] However, despite the general industrial importance of gold and the resulting need for its analysis the reported spectrophotometric methods are only applicable under specially controlled conditions. Beamish [233] stated in 1961 that no aqueous

coloured gold-complex, except the bromo aurate complex,[261,262] had been used as the basis for the spectrophotometric determination of gold. The first reagent to be effectively used in aqeous media was o-tolidine (3,3̄ dimethylbenzidine).

This reagent was proposed by Pollard[237] in 1919 for the detection of concentrations of gold down to 0.05 ppm. gold reacts with o-tolidine to give a yellow coloured soluble compound due to the oxidation of o-tolidine.[236] The developed colour is stable for 10-30 minutes, if the reagent is recrystallised three times from hot 2N sulphuric acid.[1] The molar absorptivity of this method is ca. 5×10^4, and according to Sandell,[1] 0.04 - 0.16 ppm of gold (III) can be determined with an average deviation of 4%. Pugh and Tucker[238] later reported that the accuracy was only 10%. However, the method is subject to interference from copper (II), palladium (II), ruthenium (III), osmium (VIII) , vanadate (V), tungstate (V) and nitrite.[1]

The high sensitivity of the o-tolidine method encouraged the development of its derivatives. Daier and Jordanov in 1965[239] described the use of tetron

(N,N'-tetramethyl-o-tolidine) and claimed a sensitivity of 0.004 $\mu g/cm^2$. The orange-yellow colour developed was stable for 20-25 minutes and the range of application was from 0.1-0.8 ppm of gold. This reagent did not provide any real advantage over the well-tried tolidine method.[236]

o-Dianisidine, like o-tolidine, was used by Pollard[240] in 1937 as an indicator for the titrimetric analysis of gold. He reported that this reagent was more sensitive than o-tolidine. Block and Buchman[241] subsequently applied it to the determination of 0.5-30 ppm of gold in urine (94.2 - 100% recovery) and 5-30 ppm of gold in blood plasma (84.2-100% recovery). According to Beamish,[236] the data obtained from these samples scarcely supports the authors accuracy claim. The dianisidine method is not specific[236] and excess of acid and oxidising agents interfere.[1]

p-Anisidine was described for the determination of tervalent gold by Checneva.[242] The author reported the possibility of detecting 1 ppm of gold (III) in 5 minutes. Similar indicators of the dianisidine type, which may be used as spectrophotometric reagents, have been described by Belcher and Nutten.[243] These

authors proposed four further indicators: 2:7-diamino-fluoronene, benzidine, 3-methyl benzidine, and 3:3 diethylbenzidine. They recommended the use of the latter two as being preferable to o-tolidine or o-dianisidine.[243] Peshkov [244] recommended otolidine as it gave a sharper end-point than benzidine or dianisidine in the titration of small amounts of gold (III).

The leuco compound of malachite green, which in the presence of gold (III) turns from colourless to blue-green, has been used for the determination of trace amounts of gold.[1,236] Although this method is sensitive and can be used down to 0.3 ppm of gold (III), it is subject to interference from the other noble metals and oxidising substances associated with the dissolution of gold.[235] Lapin and Gein[245] described the use of the brilliant green. In this reagent the methyl groups of malachite green are replaced by ethyl groups. Iodine and bromine were found to interfere in this method. The authors provided no detailed procedure and from the analytical point of view the report is of little value.[236] Ducret and Maurel [246] reported the use of the gold-methyl violet complex after extraction into trichloro ethylene. The molar

absorptivity, as reported by the authors, was 1.15 x 10^5 and is the most sensitive method to date. Platinum (IV) interferes in the normal method and its removal results in a lower sensitivity. [246] A further disadvantage is that the method was applicable over a narrow range of gold (III) concentrations (0.01 - 0.015 ppm). Tsai et al.[247] applied the same reagent, but used tuluene as extractant. They reported that Beer's law was obeyed only for concentrations below 5 ppm of gold (III). The absorbance of A solution containing 4.6 ppm of gold (III) gave an absorbance reading of 0.60 and on this basis gives a molar absorptivity of 2.7 x 10^4. This latter procedure is tedious and time consuming because it involves evaporation and cooling stages. Chow and Beamish[233] examined the method using methyl violet as described by Ducret and Maurel.[246] They obtained unreproducible results and hence modified the method and pointed out that Beer's law was obeyed over the range 0-1.50 ppm of gold (III). The resulting molar absorptivity was ca. 2.79 x 10^4 following the modification. Other triphenylmethane derivatives have also been reported as chromogenic reagents. Crystal violet[248] has been used for the

determination of 0.1-1.0 ppm of gold (III) after extraction of the ternary complex (crystal violet-chloroaurate). Recently, the use of ethyl violet[249] has been reported coupled with extraction into benzene. The resulting complex has maximum absorbance peaks at 551 and 606 mμ. The molar absorptivities were found to be ca. 5.04×10^4 and 7.03×10^4 respectively. Although this method is more sensitive than crystal violet, it is not specific and iron (III), cobalt (II), chromium (III), mercury (II), antimony (III), and thallium (III) interfere.

McNulty and Woolard [250] applied rhodamine B as reagent and used iso propyl ether to extract the complex formed. Onishi[251] used benzene and obtained a molar absorptivity of ca. 9.7×10^4. Dancheva and Belva [252] used this latter procedure and stated that the minimum detectable concentration of gold was 0.2 ppm. The sensitivity of this method was reported to be at least twice that of the p-dimethyl-amino-benzylidene-rhodanine method. However, the use of rhodamine B requires a precise technique and a high reagent purity.[236]

One of the most widely described methods is that

using p-dimethylaminobenzylidenerhodanine. Sandell[1] was able to determine monovalent gold down to 0.1 ppm by measuring the resulting suspension at 500 mμ. The molar absorptivity of this method was ca. 2.0×10^4.[2] Hard[253] used the same reagent for the determination of 0.03-0.3 ppm of gold. Cotton and Woolf[254] recorded a modified rhodanine method for the determination of gold by extracting the complex into iso amyl acetate. They rejected the o-tolidine method because of its low sensitivity and the dithizone method as lacking in precision. They also considered the p-dimethylamino-benzylidenerhodanine method to be inaccurate and Sandell's method, in their estimation, failed to provide the necessary precision. Beamish[236] recommended the iso amyl acetate modification because it provided greater precision.

Erdey and Rady[255] proposed the use of dithizone as reagent. Later, Kahawata et al.[256] reported that the molar absorptivity was only 2.6×10^4. Recently, Beardsley, Briscoe et al.[257] recommended the use of p-amino dimethyl benzylidinerhodanine in preference to dithizone as a spectrophotometric reagent for gold because the

dithizone complex was unstable and was subject to interference from copper (II).

More recently, Nassouri, Shahine and Magee[258] used ferroin for the titrimetric determination of gold. In addition they proposed ferroin as a spectrophotometric reagent by extracting the tetra halogeno aurate ferroin complex into chloroform and measuring the absorbance at 510 mμ. This method is rapid and gives reproducible results. In addition, there is no interference due to cobalt (II), calcium, nickel (II), iron (III), manganese (II), and chromium (III). However, it is subject to interference from more than equimolar amounts of palladium (II), mercury (II), iridium (IV), and osmium (IV).

In 1967 Holland and Bozie [259] reported that 2,2-dipyridil Ketoxime forms a water-soluble chelate with gold III, which is extractable into dichloromethane. The molar absorptivity of the gold chelate in dichloromethane was 2.0×10^4. However, this method is not very sensitive.

Many other miscellaneous methods have been reported.[260-280] The most important of those is the bromo-

aurate method described by McBryrde and Yoe[261] ~~and~~ and recommended by Monk and Herrington.[281] This method is applicable over the range 0-40 ppm of gold. The procedure involves the preparation of bromoaurate followed by extraction into iso propyl ether and then back extracting into aqueous phase. However, the method has failed to provide consistent results when applied by various operators.[233] Chow and Beamish[233,282,283] modified this method by using ethyl acetate as an extractant. The modified method is applicable to concentrations of gold greater than 3.0 ppm in aqueous media and 60 ppm after extraction. A disadvantage of the method is that it lacks sensitivity.

From this brief survey of the more important published spectrophotometric methods, it is obvious that aqueous soluble complexes of gold have scarcely been utilised. Beamish [233] in 1961 made this same point and Wilson and Lister[272] in response to this statement published a direct spectrophotometric method using Wood's reagent. This method, however, was subject to interference from the platinum metals, uranium (VI) and oxalate. In addition it was not very sensitive

(molar absorptivity was ca. 3×10^3). In consequence, it was felt worthwhile to attempt to develop spectrophotometric methods for gold capable of operating in aqueous solution.

1 - DEVELOPMENT OF PROCEDURE

According to Dagnall and West,[25] gold was the only cation which interfered with the determination of silver bis-phenanthrolinium using Bromopyrogallol Red as reagent and EDTA as masking agent. Because gold ions form a co-ordinately-bonded complex with 1,10-phenanthroline which has the same charge as that of the central metal ion,[229,230] it was thought that Bromopyrogallol Red may be used as a spectrophotometric reagent for the determination of gold in a similar manner to silver.

Preliminary investigations indicated that gold (III) forms an orange colour with bromopyrogallol red in acid, neutral and alkaline media, which turns to yellow after ca. 15 minutes. The absorption spectra of the gold (III). - Bromopyrogallol Red solution (Fig.[41]) shows that it has a maximum absorbance at ca. 400 mμ ($\bar{a}$) while the reagent blank (b) itself has a sharp absorption peak at ca. 560 mμ. A plot of ($\bar{a}$) vs. ($\bar{b}$) shows an absorbance maximum at 400 mμ, $\bar{c}$. In the presence of a 10 fold molar excess of 1,10-phenanthroline

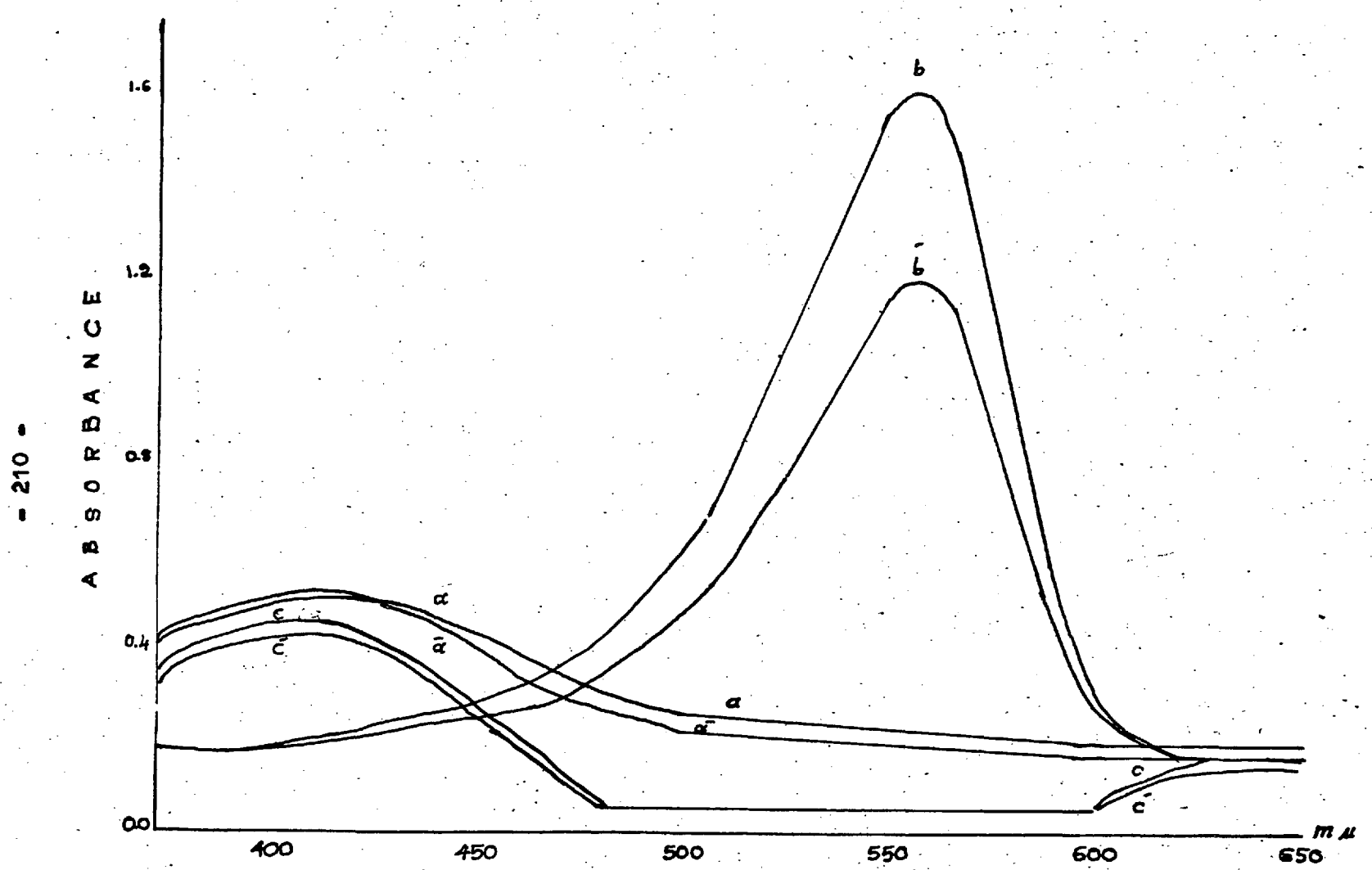


FIG. 41

over gold (III) (2 ml 10^{-3}M), the yellow colour developed immediately and remained stable for over 24 hours. The gold/Phen/BPR solution shows maximum absorption at ca. 400 mμ (a) while the reagent blank (BPR/Phen) solution has an absorption peak at 560 mμ (b). A plot of (a) vs. (b) shows maximum absorption at 400 mμ (c). This reaction is not due to complex formation between gold (III) or gold (III)/Phen, and BPR, but more likely is due to the oxidation of the reagent (BPR) with the subsequent reduction of gold (III). This reaction is not very sensitive and has molar absorptivities of 7,875 for gold/BPR and 8,250 for the gold/Phen/BPR at 400 mμ.

The addition of Bromopyrogallol Red to a gold (I) solution obtained by reducing gold (III) with ascorbic acid shows no colour change. On the other hand the addition of 1,10-phenanthroline to this solution produces at ca. pH 7 a blue colour. The absorption spectra of the reagent blank, Bromopyrogallol Red/1,10-phenanthroline solution, in the presence of ascorbic acid indicates a sharp absorption peak at 560 mμ, Fig. 42 (c). This peak decreases on addition of 10 ml of a 2.5 x 10^{-3}M gold solution and another absorbance peak

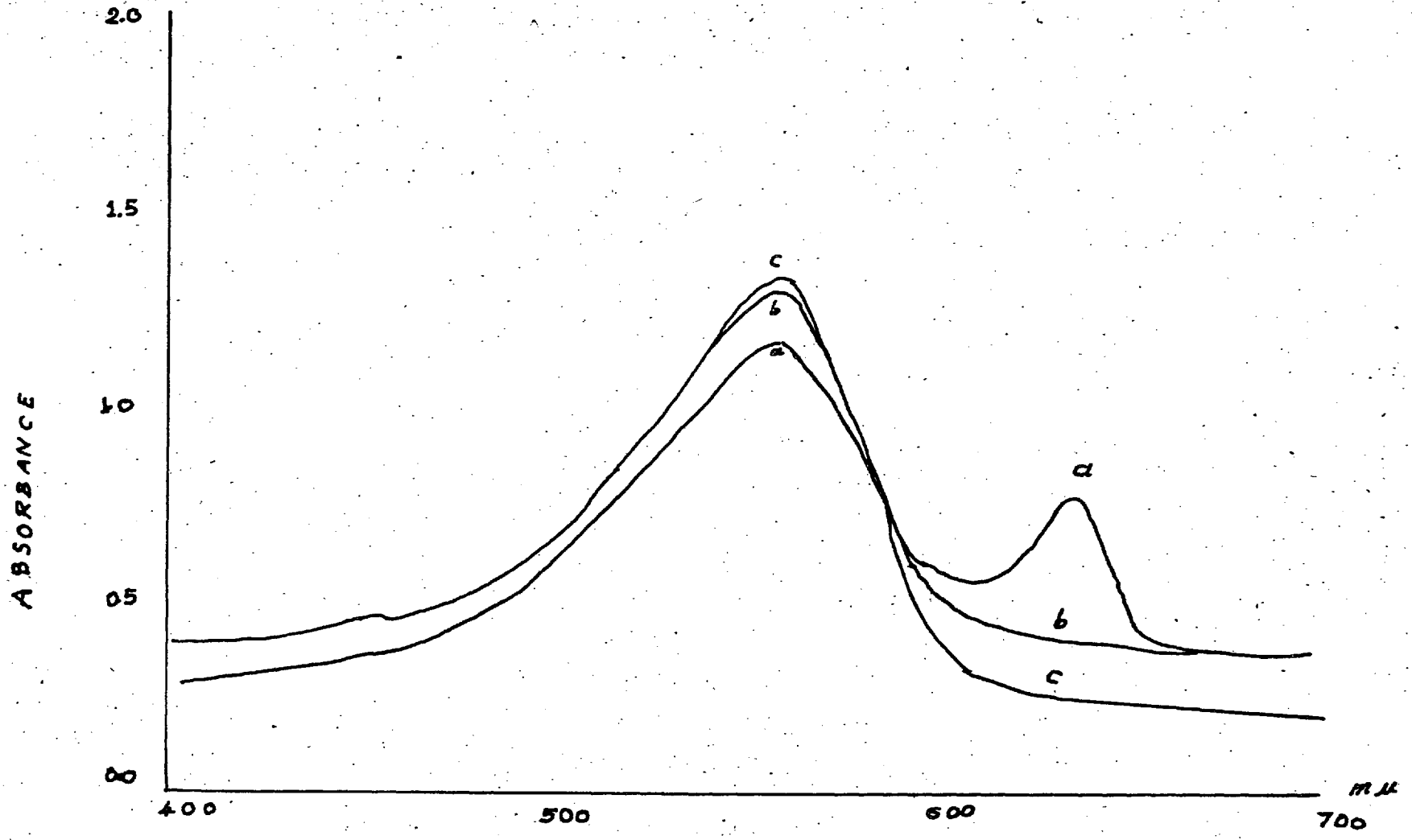


Fig. 42

is established at 635 mμ, Fig. 42 (a). In the absence of 1,10-phenanthroline no peak at all is given at 635 mμ (Fig.42 (b)).

However, this blue-colour is only stable for ca. 5 minutes, after which it turns to violet. Also, this reaction is not very sensitive and has a molar absorptivity of only ca. 10,000.

In view of these disadvantages attempts were made to replace Bromopyrogallol Red by other more suitable dyestuffs such as Bromophenol Blue and Rose Bengal Extra, etc.

With Bromophenol Blue both gold (I) and (III)/ 1,10-phenanthroline form bluish-violet coloured complexes at pH 7. The absorption spectra of the reagent blank, in the absence of ascorbic acid, shows a sharp absorbance peak at 585 mμ Fig.43 (b). The addition of gold (III) solution slightly decreases, this peak Fig. 43 (a) and a plot of (a)vs. (b) shows an absorption maxima at 625 mμ, Fig. 43 (c). In the presence of ascorbic acid, the reagent blank shows an absorbance peak at 560 mμ Fig. 43($\bar{b}$), which is decreased to a greater extent by the addition of gold (I) solution ($\bar{a}$). A plot of ($\bar{a}$) vs. ($\bar{b}$) shows an absorption

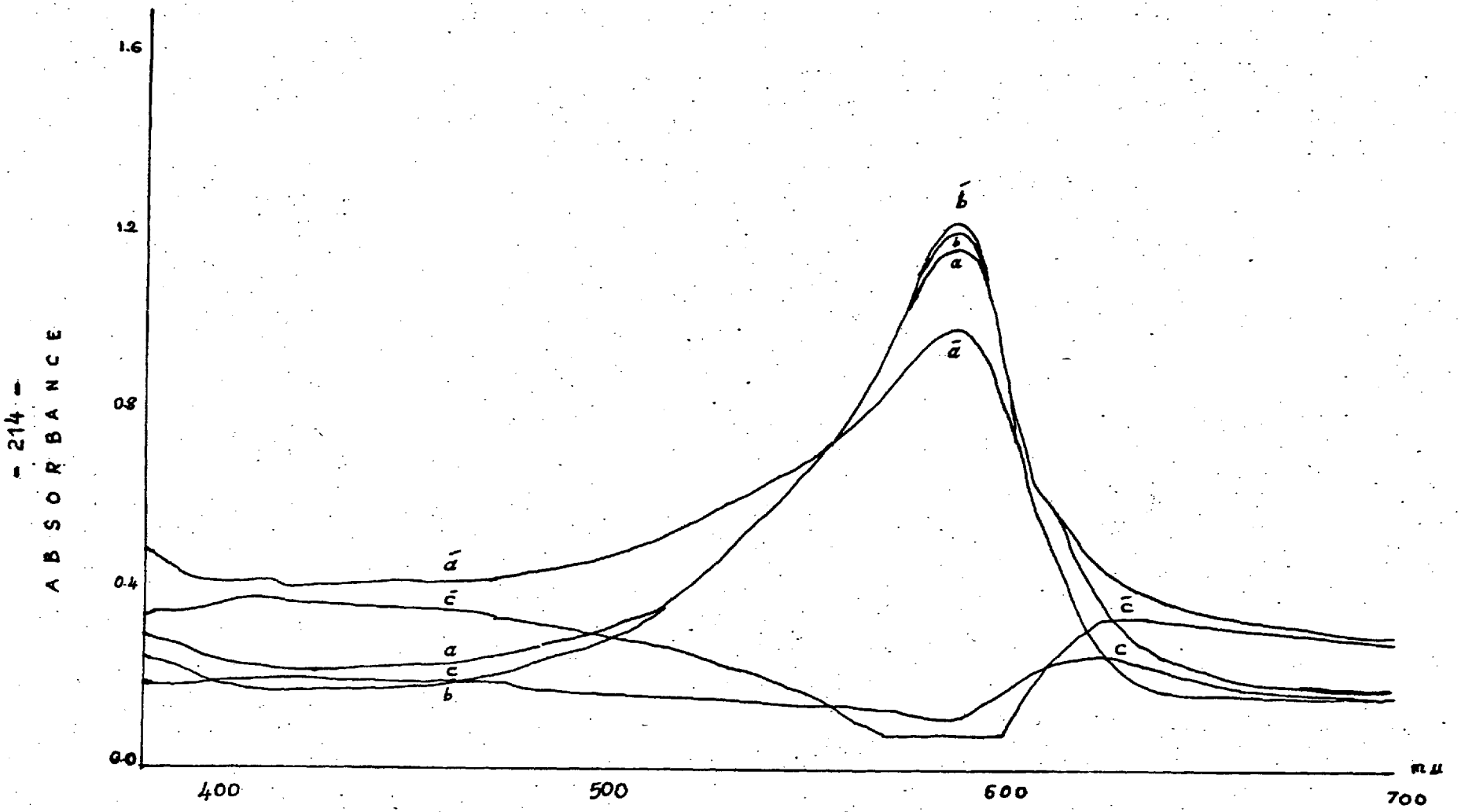


FIG. 43

maxima at 625 mμ.

From these results, it can be deduced that the reactions of bromophenol blue with both gold (I) and (III)/1,10-phenanthroline are not sensitive (molar absorptivities of ca. 6,500 and 3.500 respectively at 625 mμ).

With Rose Bengal (Extra), it was found that, in the absence of 1,10-phenanthroline, the addition of gold (III) caused no colour change Fig. 44 (b) and was similar to that of the reagent blank (a), in slightly acidic media. In the presence of 1,10-phenanthroline at the same acidity (pH 5) the colour of the reagent blank remained pink Fig. 44 (c), while the colour of the gold (III)/Phen/RBE solution turned mauve Fig. 44 (d).

Because this mauve colour was quite stable and sensitive (ϵ = 31,000) it was decided to study this reaction as a possible spectrophotometric determination of gold (III) in aqueous solution.

1.1 PRELIMINARY SPECTRA

The absorption spectra of Rose Bengal/1,10-phenanthroline, the reagent blank, shows that it

D C B A

Fig. 44

has a sharp peak at 535 mμ (Fig.45 b). The addition of 5 ml of a 10^{-4}M gold (III) solution decreases this peak while another peak is established at 575 mμ (Fig.45 a). A plot of (a) vs. (b) shows that the maximum wavelength is at 575 mμ (Fig.45 c).

2. OPTIMISATION OF CONDITIONS FOR MAXIMUM COLOUR DEVELOPMENT

2.1 pH

Fig. 46 shows that the optimum pH is 4.5 - 5.5. The solutions used in this experiment contained 1 ml of a 10^{-2}M 1,10-phenanthroline solution and 2 ml of 10^{-4}M of gold (III) solution. The pH was adjusted with 0.1N hydrochloric acid or 0.1N ammonium hydroxide at a pH meter. The solutions were then transferred to 50 ml volumetric flasks and diluted to the mark with distilled water after the addition of 5 ml of a 2 x 10^{-4}M Rose Bengal Extra solution.

2.2 Development Time

The colour formation was instantaneous and remained stable for a long time i.e. over 48 hours (Fig.47).

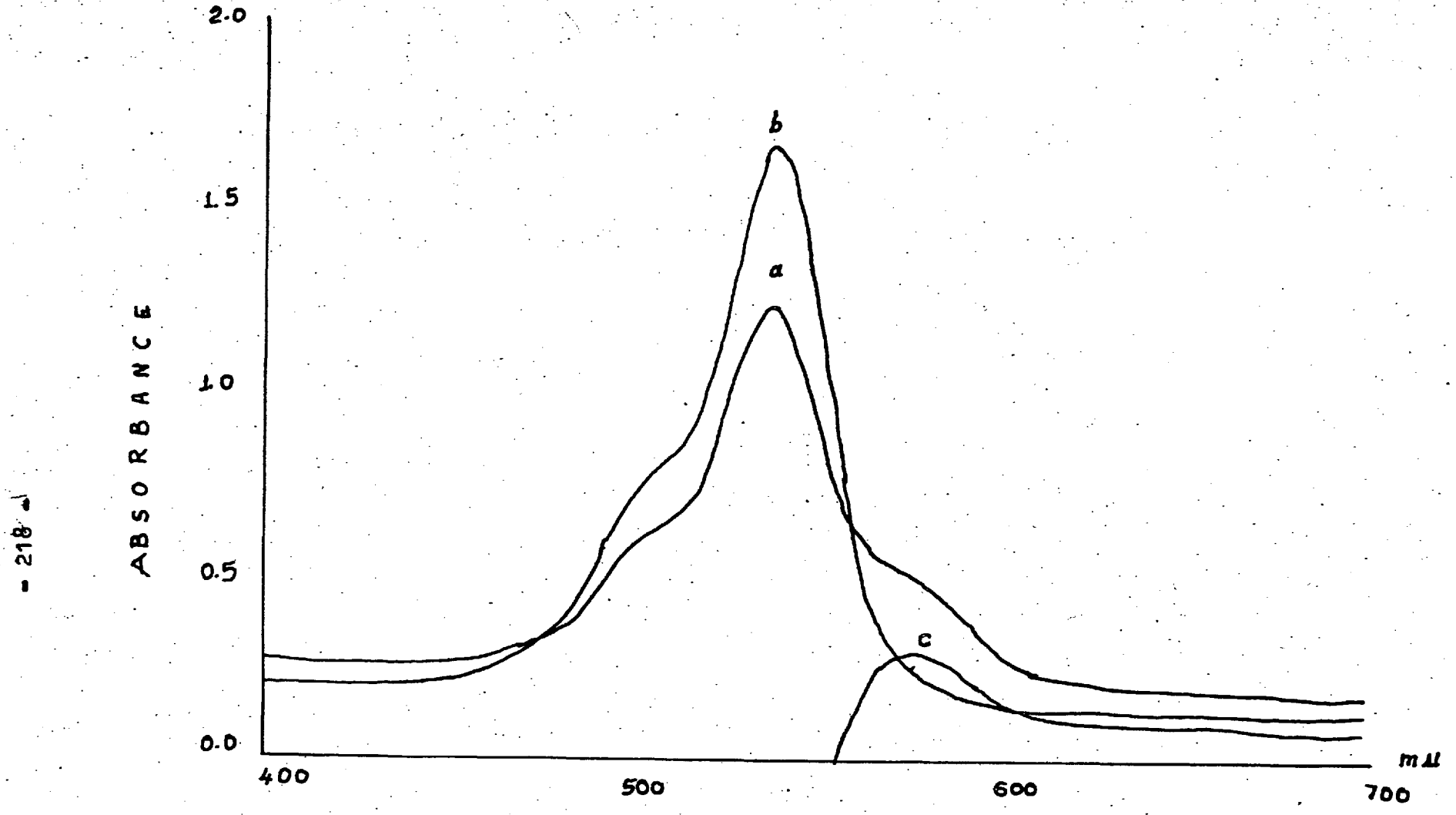


FIG. 45

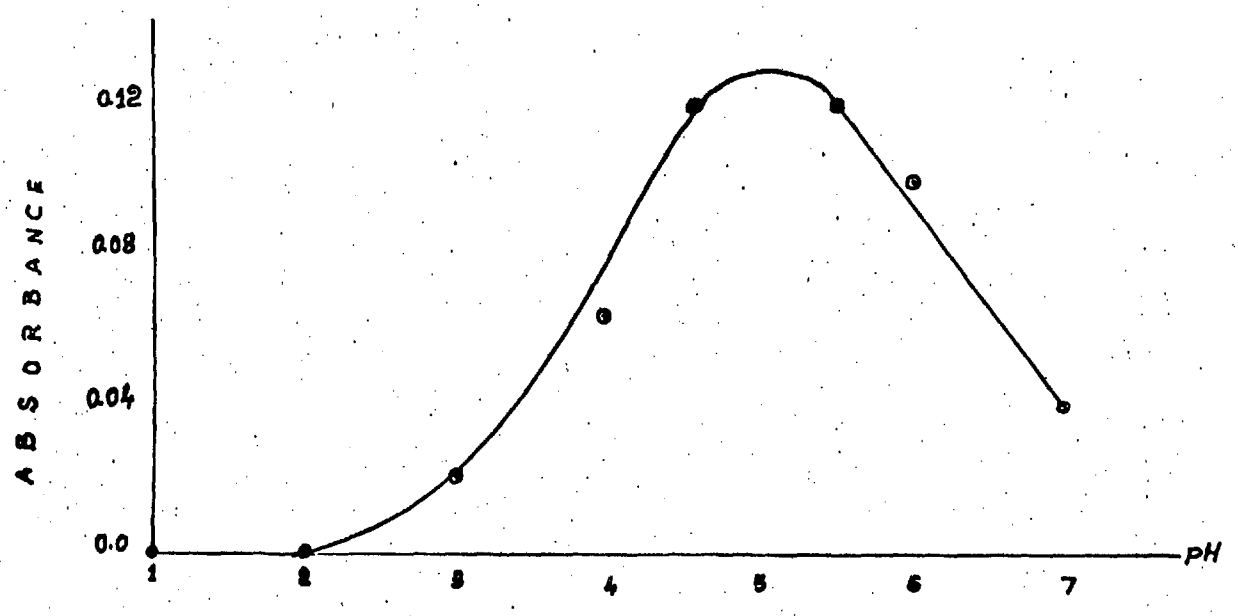

ABSORBANCE
0.12
0.08
0.04
0.0
1
2
3
4
5
6
7
pH

FIG. 46.

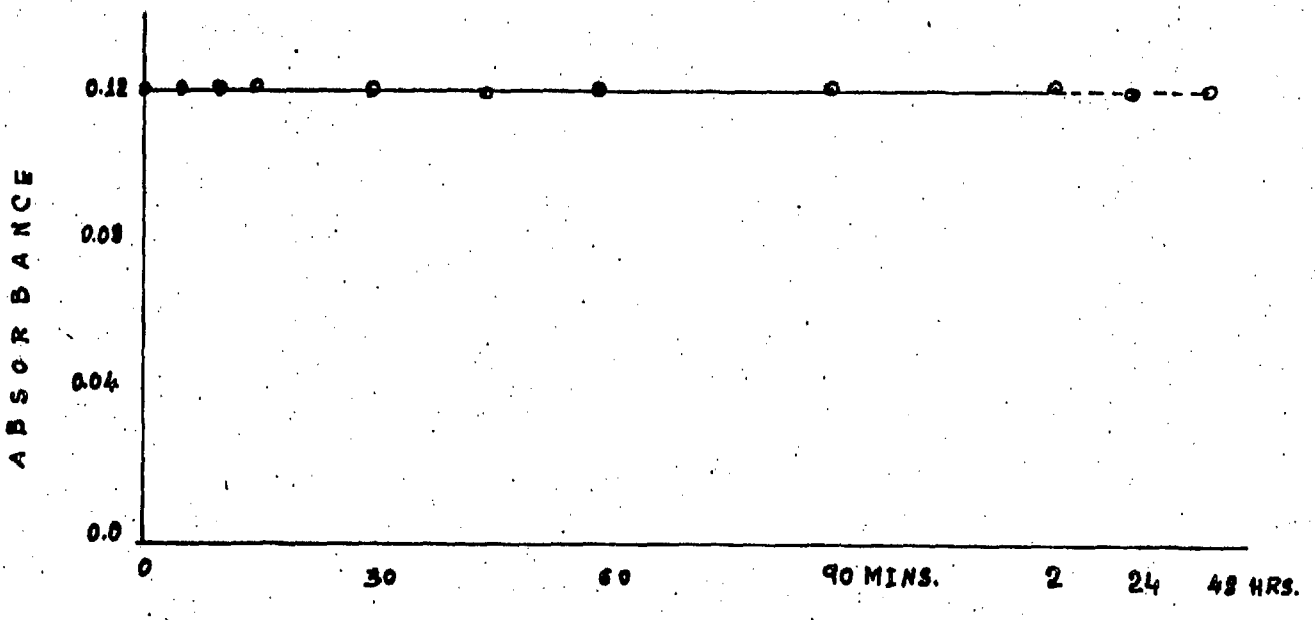

ABSORBANCE
0.12
0.08
0.04
0.0
0
30
60
90 MINS.
2
24
48 HRS.

FIG. 47

The solution utulised in this experiment contained 2 ml of a 10^{-4}M gold (III) solution, 1 ml of a 10^{-2}M 1,10-phenanthroline solution, 2 ml of pH 5 buffer solution, 5 ml of a 2 x 10^{-4}M Rose Bengal Extra solution diluted to 50 ml. The absorbance was measured at 575 mμ against a reagent blank containing all the reagents except gold.

3. LAMBERT BEER'S LAW CHECK

Using the established optimum conditions a calibration curve was prepared by pipetting 1 - 10 ml of a 5 x 10^{-5}M gold III solution into a series of 50 ml volumetric flask followed by 1 ml of a 10^{-2}M 1,10-phenanthroline solution, 2 ml of pH 5 buffer solution and 10 ml of a 2 x 10^{-4}M Rose Bengal Extra solution and diluting to the mark with distilled water. The absorbance was measured at 575 mμ against a reagent blank carried through the same procedure but containing no gold. The absorbance obtained was plotted against micrograms of gold (III).

1 ml of 5 x 10^{-5}M gold ≡ 9.94 μg of gold (III)

The calibration graph obtained was linear and

passed through the origin. Beer's law was obeyed over the range 9.86 - 98.6 μg of gold (III) or 0.1972 - 1.972 ppm of gold (III) in the final concentration. The molar absorptivity at 575 mμ was ca. 31,000 (Fig. 48).

4. NATURE OF COMPLEX

Because of the difficulty in purifying Rose Bengal to its theoretical composition [43] the usual methods of deducing reacting ratios, such as Job's method, mole ratio etc. will not provide accurate results.

Theoretically gold III may co-ordinate with 2 1,10-phenanthroline molecules, through the nitrogen atoms, forming the tri-positive charged co-ordinated complex, Bis-phenanthrolinium gold (III).[229,230] 2 molecules of this cation will react with 3 molecules of Rose Bengal Extra to form the mauve-coloured ternary complex, $(Au(Phen)_2)^{3+}$, $3(RBE)^{2-}$ and the overall ratio between gold (III), 1,10-phenanthroline and Rose Bengal should be 2:4:3 respectively.

5. INTERFERENCES

Only EDTA have so far been examined as a

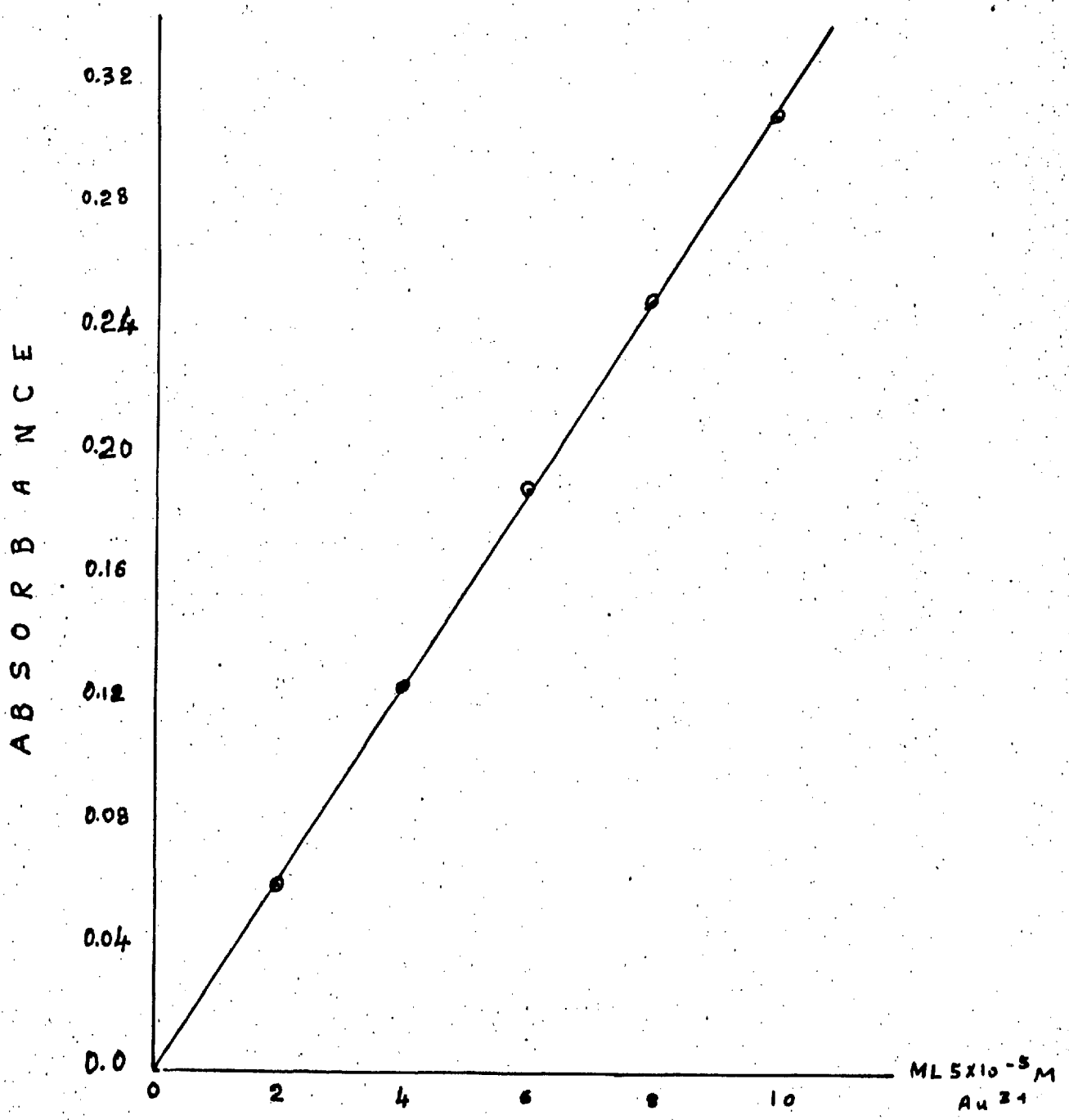

ABSORBANCE
0.32
0.28
0.24
0.20
0.16
0.12
0.08
0.04
0.0
0
2
4
6
8
10
ML 5x10 -5 M
Au 24

FIG. 48

convenient masking agent for other extraneous ions, but it was found that it decreased the absorbance. A 500 fold molar excess of EDTA decreased the absorbance by ca. 50% .

6. PRECISION

The precision of the method was investigated by determining the percentage standard deviation from the multiple analyses of a series of solutions, each containing 5 ml of a 10^{-4}M solution of gold (III), 1 ml of a 10^{-2}M solution of 1,10-phenanthroline hydrate, 2 ml of pH 5 buffer solution and 10 ml of a 2×10^{-4}M Rose Bengal Extra solution and diluted to volume with distilled water. The absorbance was measured against a reagent blank at 575 mμ. The results obtained are summarised in Table XVI .

Table XVI

Number n	Absorbance x 1000	Deviance D	Deviance^2 D^2
1	310	+ 0.20	0.04
2	315	+ 5.20	27.04
3	312	+ 2.20	4.84
4	307	- 2.80	7.48
5	315	+ 5.20	27.04
6	305	- 4.80	23.04
7	310	+ 0.20	0.04
8	307	- 2.80	7.48
9	312	+ 2.20	4.84
10	305	- 4.80	23.04
ΣX	= 3098		ΣD^2 =
$\bar{x}$	= 309.8		124.88

$$S = \sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{124.88}{9}} = 3.72$$

$$\therefore \bar{S} = \frac{3.72}{349.8} = 0.0106$$

Hence, Standard Deviation Per Cent = 0.106 x 100
= 1.06

E X P E R I M E N T A L

APPARATUS:

Spectrophotometer: A Unicam SP 600 with 2 matched 1 cm glass cuvettes.

pH Meter: E.I.L(Electronic Instruments Ltd) Model 23 A.

REAGENTS:

All reagents were of analytical grade unless otherwise stated.

Chloroauric Acid solution, 10^{-3} - 5 x 10^{-5}M

Prepare by pipetting 40 ml of a 0.5% w/v chloroauric acid trihydrate (B.D.H.) into a 250 ml graduated flask followed by 25 ml of 2N hydrochloric acid and diluting to the mark with distilled water. The resulting solution is 10^{-3}M. By appropriate dilution, 10^{-4} and 5 x 10^{-5}M solutions were prepared.

1,10-Phenanthroline Solution, 10^{-2}M

Prepare by dissolving 0.991 g of 1,10-phenan-

throline hydrate (B.D.H) in distilled water and diluting to 500 ml.

Rose Bengal (Extra) Solution, 2×10^{-4} M

Prepare by dissolving 0.1018 g of Rose Bengal (B.D.H.) in distilled water and diluting to 500 ml.

Buffer Solution pH 5

Prepare by dissolving 34.021 g of sodium acetate trihydrate in distilled water followed by 5 ml of glacial acetic acid and dilute with distilled water to 250 ml.

Hydrochloric Acid, 2 N

Prepare by pipetting 44.5 ml of hydrochloric acid (Specific Gravity = 1.18) into a 250 ml graduated flask and dilute to the mark with distilled water.

RECOMMENDED PROCEDURE

Pipette 1 - 10 ml of a 5×10^{-5}M gold solution into a series of 50 ml graduated flasks followed by 1 ml of a 5×10^{-3}M 1,10-phenanthroline solution and 2 ml of pH 5 buffer solution. Then add 10 ml of 2×10^{-4}M of Rose Bengal Extra solution and dilute to the mark with distilled water. Measure the absorbance against a reagent blank, containing all the reagents except gold, at 575 mμ in 1 cm cuvettes. Plot the absorbances obtained against micrograms of gold (III) present.

1 ml of $HAuCl_4 \cdot 3\,H_2O \equiv 9.86\ \mu g\ Au^{3+}$

CONCLUSION

The proposed method is far superior to the published methods for the direct spectrophotometric determination of gold in aqueous solution. Most of the other methods are based on the oxidation of the reagent by tervalent gold ions, e.g., o-tolidine, malachite green, etc. In 1961 Beamish stated that aqueous soluble complexes of gold have scarcely been

utilised. However, this may be because the very few methods based on the formation of aqueous usual soluble gold complexes are not very sensitive cf. Table XVII.

Table XVII

Method	Molar Absorptivity	Wavelength
Wood's Reagent[41]	3,000	535
Bromoaurate [2]	4,367 *	380
2,2-Dipyridil Ketoxime[28]	20,000	495
RBE/Phen	31,000	575

* The molar absorptivity is calsulated from the published data of the absorbance values.

From Table XVII it is obvious that the proposed method is the most sensitive in aqueous solution. In addition it has the advantage of great stability (over 48 hours under normal laboratory conditions).

SUGGESTIONS FOR FUTURE WORK

1. Spectrophotometric Determination of Silver/1,10-phenanthroline/Erythrosin. By replacing Rose Bengal Extra with a similar reagent of known purity, the complex ratio can be studied thoroughly.

2. Use of Pyridine and Substituted Phenanthrolines in place of 1,10-phenanthroline for greater selectivity.

3. Fluorescence Properties of Some Ternary Systems, e.g., silver/pyridine/Rose Bengal Extra, hence more sensitivity may be obtained.

4. Indirect Spectrophotometric Determination of Thiocyanate using the silver/1,10-phenanthroline/Bromopyrogallol Red System.

5. Spectrophotometric Determination of Gold and Palladium using Erythrosin.in place of Rose Bengal Extra.

6. Sequential Determination of Gold and Palladium in aqueous solution using Rose Bengal Extra or Erythrosin. Gold can be masked with EDTA, while the palladium is unaffected by the addition of EDTA.

7. Analytical Applications of the Ternary Complex Systems to the other Noble Metals, e.g. iridium, osmium, platinum, rhodium and ruthenium.

8. Spectrophotometric Determination of Niobium using 1,10-phenanthroline/Rose Bengal Extra. Preliminary investigations indicated that niobium (V), gives a mauve colour with 1,10-phenanthroline and Rose Bengal Extra. No colour was obtained in the absence of 1,10-phenanthroline and furthermore, EDTA does not affect the developed colour.

REFERENCES

REFERENCES

1. Sandell, E.B., "Colorimetric Determination of Traces of Metals", Interscience, London, (1959).

2. Charlot, G., "Les Methodes de la Chemie Analytique", 5th ed., Masson et CIE., Paris (1963)

3. Cook, G.F., Crespie, M.B.A., and Minczewski, J., Talanta, 10, 917 - 29, (1963).

4. Boltz, D.V., "Colorimetric Determination of Non-metals", Interscience, London, (1958)

5. Gilman, H., "Organic Chemistry, An Advanced Treatise", Vol. III, Chapman and Hall Ltd., London, (1953).

6. Strouts, C.R.N., Wilson, H.N. and Parry-Jones, R.T., "Chemical Analysis", Vol. II p. 154 et seq., Clarendon Press, Oxford, England, (1962).

7. Meites, L. and Thomas, H.C., "Advanced Analytical Chemistry", Mc.Grow-Hill Company Inc., London, (1958).

8. Kirkbright, G.F. Talanta, 13, 1 - 14, (1966).

9. Holzapfel, H., J. Prakt. Chem., 14, 323-36, (1961); C.A., 56, 9381b, (1962).

10. Braude, E.A., J. Chem. Soc., Part IX, 379-84, (1950).

11. Ibid "Determination of Organic Structures by Physical Methods", Vol. (I), p. 131 et seq Academic Press Inc., N.Y., (1955).

12. Mellon, M.G., Anal. Chem, 26, 2-11, (1954)

13. Mellon, M.G., and Boltz, D.F., Anal. Chem., 28, 559-76, (1956).

14. Idem 30, 554-69, (1958).

15. Idem 32, 194R-210R, (1960).

16. Idem 34, 232R-42R, (1962).

17. Idem 36, 256R-66R, (1964).

18. West, T.S., Analyst, 87, 630-6, (1962).

19. West, T.S., and Sykes, , "Analytical Applications of EDTA", p. 47 et seq., BDH Ltd., Poole, England, (1959).

20. Welcher, F.J. "Specific and Selective Organic Reagents", Proceedings of the International Symposium on Michrochemistry,

held at Birm. Univ., 6-21, Pergamon Press, London, (1960).

21. West, T.S., Analyst, 91, 69-77, (1966).

22. Close, R.A. and West, T.S., Talanta, 5, 221-30, (1960).

23. Belcher, R. and Wilson, C.L., in association with West, T.S., "New Methods of Analytical Chemistry", Chapman and Hall, London, (1964).

24. Dagnall, R.M., Smith, R., and West, T.S., J. Chem. Soc., (Section A). 1595-8, (1966).

25. Dagnall, R.M. and West, T.S., Talanta, 11, 1533-41, (1964)

26. Djunkin, V. Kirkbright, G.F., and West, T.S., Analyst, 91, 89-93, (1966)

27. Struszynski, M., Nowicka, T., and Marczen, Z., Pyrzemyst Chem., 9, 574 - 8 (1953) (English Summary); C.A., 51, 3360a, (1957).

28. Sostanga, M. and Chanvera, J., Bull. Sec. Chem. France, 70, 1165-70 (1961); C.A. 55, 2435 h (1961).

29. Hera, S., Bunseki Kagaku, 7, 142-7 (1958); C.A., 45, 1175 e, (1960).

30. Erdey, L., Rady, G. and Felps, V., Acta Chim. Acad. Sci. Hung., 5, 133-41 (1954); C.A., 49 8 733 G (1955).

31. Kioke, H., Ohashi, K., Matsue, M., and Kinoshita, Y., Bunseki Kagaku, 14, 610-14 (1955), (Japan); C.A. 64, 5725 G, (1966).

32. Takei, S., ibid, 9, 409-15, (1960); C.A. 56 10883 C, (1962).

33. Nadkanni, R.A. and Haldan, B.C., G. Indian Chem. S.O.C., 42, 473-8 (1965); C.A., 63,

34. Xavien, G. and Ray, P., Science and Culture (India) 20. 2556 (1955); C.A., 49, 11488 d, (1955).

35. Ibid, G. Indian Chem. Soc., 35, 430-44, (1958); C.A., 53, 16815 D, (1954).

36. Ibid, Science and Culture (Calcutta), 21, 694-5, (1956); C.A., 52, 15326 F, (1958).

37. Iasinskiene, E. Birmantas, I. and Reklyte, V., Lieturos Tsrmoskslu and Akad. Darabi: Ser. B, 3 8-81-90 (1964) (Russ), C.A. 62;

38. Dagnall, R.M. and West, T.S. Talanta, 8, 711-19, (1961)

39. Ibid, Anal. Chim. Acta., 27, 9-14, (1962).

40. Ibid, Talanta, 11, 1627-31, (1964)

41. Dagnall, R.M. Thesis, Ph.D., Birm. Univ., (1963).

42. Chung, O.K. and Meloan, C.E., Anal. Chem., 39, 383-5, (1967).

43. Bailey, B.W., Dagnall, R.M. and West, T.S., Talanta, 13, 753-61, (1966).

44. Williams, H.E. "Cyanogen Compounds", 2nd ed. Edward Arnold Co., London, (1948).

45. Jacob, M.B. "The Analytical Chemistry of Industrial Poisons Hazards and Solvents", Interscience, N. York (1949).

46. Clark, L.S., Industrial Chemist, 38, 325-28 (1962).

47. Feldstein, M. and Klendshoj, Can. Med. Technol., 17, 29-32 (1955); C.A. 49, 11055 h (1955)

48. Viehover, A. and Johns, C.O., J. Amer. Chem. Soc., 37, 601-607 (1915).

49. Gettler, A.C. and Goldbaum, L., Anal. Chem. 19, 270-1 (1947).

50. Garside, J.E., and Phillips, R.F., "Pure and Applied Chemistry", 2nd ed. 839, Sir Isaac Pitman and Sons, Ltd., London (1961).

51. Feigl, F. "Spot Tests in Inorganic Analysis", 5th Ed., 276-280. Elsevien Pub. Co., London, (1958).

52. Feigl, F. and Gentil, V., Mikrochem. Acta (1), 44-6 (1959) and 47-50 (1959) (Eng.)

53. Cullinane, N.M. and Chard, S.J., Analyst, 73, 95-7 (1948).

54. Proc. Soc. Anal. Chem., 2, 69, (1965).

55. Feigl, F. and Anger, V., Analyst, 91, 282 (1966).

56. Feigl, F. and Feigl, H.E., Anal. Chim. Acta, 3, 300-8 (1949).

57. Sa, A. and Mestarini, Pub. Inst. Invest. Microquim. Univ. NaCl., Litoral (Rosanio, Ang.), 26, 147-50 (1965), C.A. 64 5754a, (1966).

58. Bark, L.S. and Higson, H.G., Analyst 88, 751-60 (1963).

59. Guiblault, G.G. and Kramer, D.N., Anal. Chem. 37, 918 (1965).

60. Idem 37,1395-9 (1965).

61. Belcher, R. and Nutten, A.J. "Quantitative Inorg. Analysis", 2nd ed., p. 69, Butterworth, London, (1960).

62. Vogel, A.I. "Quantitative Inorg. Analysis", 3rd ed. Longmans, London, (1961).

63. Kolthoff, I. M. and Belcher, R. "Volumetric Analysis" Vol. III, Interscience, London, (1957).

64. Smith, J.B. "Analytical Processes" , 2nd ed., E.Arnold Pub. Ltd. (1957).

65. Kolchoff, I.M. and Sandell, E.B. "Textbook of Quantitation Inorganic Analysis". The Macmillan Co., N. York (1943).

66. Ryan, J.A. and Culshaw, G.W., Analyst, 69, 370-1 (1944).

67. Mentens, W., Gas Wasserfach. 106 (43), 1193-4(1965), C.A. 64, 485 (1966).

68. Sutton F., "A Systematic Handbook of Volumetric Analysis", 13th Ed., Butterworth, London, 1955.

69. Ripan-Tibici, R. Z. anal. chem., 118, 305-7, (1939), C.A., 34, 2281^{9}, (1940).

70. Archer, E.E., Analyst, 83, 571-9 (1958); C.A. 53, 5975 d (1959).

71. Higashiura, M., Kagaka To Koggo, 37 (7), 292-6 (1963); C.A., 63, 6312f (1965).

72. Johnson, W.C. (editor) "Organic Reagents For Metals" Vol. II, Hopkin and Williams Ltd., Chadwell Heath, Essex, England (1964).

73. Saredo, J.F., Anales Soc. Quim. Farm. Urgway. 42, 36-46 (1939), C.A. 35, 4074, (1941).

74. Gupta, R.C. Proc. Can. Soc. Forensic Sci. 4 241-7 (1965) (Eng); C.A.63 10306e (1965).

75. Legrandi, L., Magy. Kem. Folyoirat. 70 (9), 404-10 (1964), C.A. 61, 15321c (1964).

76. Vydra, F., Matrykova, V. and Pribid, B., Collec. Czech. Chem. Commun., 26, 2449-52 (1961) (Ger.), C.A. 57, 15802h (1962).

77. Wronski, M., Analyst, 84, 668 (1959).

78. Erdey, L., Magyan Kem. Lapja 13, 7-12 (1958);

79. Musha, S. Nippon Kagaka Zasshi, 79 647-8 (1958); C.A. 53, 6905d (1959).

80. Bognar, J., Magyan Kem. Folyoviot 64, 37-40 (1958); C.A. 52, 19677 g, (1958).

81. Hoffman, E., Z. Anal. Chem., 169, 258-63 (1959); C.A., 54, 2079b, (1960).

82. Gregorwicz, Z. and Buhl, F., Z. anal. Chem., 173, 115-21 (1960) (Ger.); C.A., 54, 16279f, (1960).

83. Uhlig, E., and Berndt, H., Z. Anal. Chem., 203, (4) 241-52 (1964); C.A., 61, 8889g, (1964).

84. Plalte, J.A., C.A., 63, 7655a (1965).

85. Vrestal, J. and Havi, J., Chem. Listy. 50, 1321-3, (1956); C.A., 50, 13661g, (1956).

86. de Soussa, A., Talanta, 8, 782-4 (1961).

87. Bhatki, K.S., Analyst, 82, 24-6 (1957).

88. Joint Committee of the Association of British Chemical Manufacturers and the Society for Analytical Chemistry, "Recommended Methods for the Analysis of Trade Effluents", W. Heffer and Sons, Ltd., Cambridge (1958) p. 87-9.

89. M sha, S., Yamamoto, N.Y. and Inamori, Y., Nippon Kagaku Zasshi, 80, 1285-8 (1959); C.A. 55, 5228b, (1961).

90. Nolke, F., Z.Anal. Chem., 122, 6-11 (1941); C.A. 36; 4441[1], (1942).

91. Cihalik, J. and Terebova, K., Chem. Listy 50, 1761-7 (1956); C.A. 51, 2470i, (1957).

92. Santibanez, M.O., Tesir Quim. Faru. 5, 336-50, (1953); C.A. 49, 13835f (1955).

93. Weiner, R. and Schmidt, S., Z. Elektrochem., 46, 249-52 (1940); C.A. 35, 2442[1] (1941).

94. Muraca, R.F., Plating 41, 1018-26 (1954); C.A. 49, 3727b, (1955).

95. Ewing, G.W. "Instrumental Methods of Analysis" 2nd ed., p. 182-3, Mc Grow-Hill Book Co. Inc., N. York - London (1960).

96. Bombi, G., Fiorani, M. and Mazzocchiu, G.A., J. Electroanal. Chem. 9, (5-6), 457-67 (1965), (Eng.); C.A. 63, 10660e, (1965).

97. McCloskey, J.A., Anal. Chem. 33, 1842 (1961).

98. Perzybylowicz, E.P. and Rogers, L.B., Anal. Chem. 30, 65-9 (1958).

99. Kies, H.L., Anal. Chim. Acta, 12, 280-4 (1955) (Germ.), C.A., 49, 10113b (1955).

100. Braudstetr and Kotrly, Chem. Listry, 50, 1316 (1956); Headridge, J.B., "Photometric Titration", p.91, Pergamon Press, London (1961).

101. Gregorowicz, Z. and Buhl, F., Tech. Intern., Symp., I, 507-10 (1961), (published 1963); C.A. 60, 15140a (1964).

102. Johnson, M.O. J. Amer. Chem. Soc., 38, 1230-5 (1916).

103. Nicholson, R.I., Analyst, 66, 89-92 (1941).

104. Fisher, F.B. and Brown, S.S., Anal Chem. 24, 1440-4 (1952).

105. Fulton, R.A. and Van Dyke, M.J., Anal. Chem. 19, 9222-3 (1947).

106. Brooke, M., Anal. Chem. 24, 583-4 (1952).

107. Hanker, J.S. Gelberg, A., and Witten, B., Anal. Chem., 30, 93-5 (1958)

108. Fato, T. and Shirro, K. Nippon Kagaku, Zasshi, 77, 885-8 (1956); C.A. 52, 978c, (1958).

109. Hikime, S. and Yoshida, H., Bunseki Kagaku, 10 832-7 (1961); C.A. 56, 6659h (1962).

110. Ohwiller, O.A. and Meditsch, J.O., Anal. Chim. Acta, 11, 111-19 (1954), (Fr.) (English Summary) C.A. 49, 6783c, (1955).

111. Ibid, Anal. Chem., 30, 450-1 (1958) (Eng.)

112. Tomonari, A., Nippon Kagaku Zasshi, 83, 455-8 (1962), C.A. 57, 10529f, (1962).

113. Meditsch, J.O. and Castiel, V., Eng. Quim., 14 No. 4, 7-8 (1962), C.A. 58, 931d, (1963).

114. Miller, A.D. and Arunovich, M.J., Zarodskaya Lab., 26 426-9 (1960), C.A. 54, 15066i, (1960).

115. Schilt, A.A. Anal. Chem. 30, 1409-11 (1958).

116. Hanker, J.S., Gamson, R.M. and Klapper, H., Anal. Chem. 29, 879-81 (1957).

117. Aldridge, W.N., Analyst, 69, 262-5 (1944).

118. Fieser, L. and Fieser, M., "Topics in Organic Chemistry", p. 89-90, Reinhold Publishing Corporation, N. York (1963).

119. Aldridge, W.N., Analyst, 70, 474-5 (1945).

120. Saltzman, B.E., Anal. Chem., 33, 1100-1112 (1961).

121. Bruce, R.B., Howard, J.W. and Hanzal, R.F., Anal. Chem. 27, 1346-7 (1955).

122. Nusbaum, I. and Skupeko, P., Sewage Works and Industrial Wastes, 23, No. 7, 875-9 (1951); C.A. 45, 10443e (1951).

123. Christ, W., Wasserwirtsch - Wassertech. 4, 369-71, (1954), C.A. 49, 5211i, (1955).

124. Baker, M.O., Foster, R.A., Post, Beno, G. and and Heit, T.A. Anal. Chem., 27, 448-9 (1955).

125. Lnr'e, Y.Y. and Panova, V.A., Zavodskagu Lab., 21, 672-5 (1955), C.A. 49, 13835d, 1955.

126. Hudson, J.R. and Pollock, J.R.A., Analyst, 82, 374 (1957).

127. Murty, G.U.L.N. and Viswanathan, T.S., Anal. Chim. Acta, 25, 293-5, (1961).

128. Conter, O.E., Schmitt, J.W., Am. Chem. Soc. Div. Waste Water Chem. Prints, 17020 Sept. 1963, C.A. 63 2736g. (1965).

129. Effenberger, M., Fenowe Odpani Vody, 56-7 (1962) (Czech.) C.A. 62, 8387e, (1965).

130. Bark, L.S. and Higson, H.G., Analyst, 89, 338-45(1964).

131. Ibid Talanta, 11, 471-9(1964).

132. Idem 11, 621-31(1964)

133. Epstein, J., Anal. Chem. 19, 272-4 (1947).

134. Danileuko, G.J. and Zubenko, V.G., Farm. Zhur. (Kiev). 15, No. 5, 17-22 (1960), C.A. 55, 9148i (1961).

135. Jorgensen, K., Acta, Chem. Scand. 9, 548 (1955) (in English) C.A. 49, 14579g (1955).

136. Gardner, D.G., Muraca, R.F. and Serfass, E.J., Plating, 43, 1027-30 (1956), C.A., 50, 6561a (1956)

137. Malatesta, P. and Dubini, M., Ricerca Sci., 27, 3649-53 (1957), C.A., 53, 6873e, (1959).

Whitson

138. Winston, T.G. and Cherry, G.W., Analyst, 87, 819-23 (1962).

139. Stability Constants, 2nd ed., The Chemical Society Spec. Publ. No. 17, London, (1964)

140. Dagnall, R.M., El-Ghamry, M.T. and West, T.S., In Press.

141. Ibid., Talanta, 13, 1667-71, (1966).

142. Forsythe, J.H.W., Magee, R.J. and Wilson, C.L., Talanta, 3, 330-4, (1960).

143. Pontani, F., Ricerca Sci., 30, 489-54, (1960); C.A., 54, 24087g, (1960).

144. Beamish, F.E., and McBryde, W.A.E., Anal. Chim. Acta, 9, 349-67, (1953).

145. Idem. 18, 551-64, (1958).

146. Beamish, F.E., Talanta, 12, 743-72, (1965).

147. Popa, G., Negoia, D., and Baiulescu, G., Zhur. Anal. Khim., 14, 322-30, (1959); C.A., 54, 8458e, (1960).

148. Popa, G., Wiss. Z. Friedrich - Schiller - Univ., Jena, Math. - Natur - wiss. Reihe, 10, 5-10, (1961); C.A., 57, 15c, (1962).

149. Popa, G., Neqoin, D., and Baillescu, G., Acad. Rep. Populare Romaine, Studii Cercetari Chim., 7,73-8, (1959); C.A., 53, 19697e, (1959).

150. Ryan, D.E., Analyst, 76, 167-71, (1951).

151. Marheuke, E.R.R., and Sandell, E.B,, Anal. Chim. Acta, 28, 259-63, (1963).

152. Prozhevalskii, E.S., Shienskaya, V.I., and Razina, I.S., Vestnik Moskov. Univ., Scr. Mat., Mekh., Astron., Fiz. Khim., 12, 111-16, (1957); C.A. 52, 162e, (1958).

153. Yoe, J.H., and Kirkland, J.J., Anal. Chem., 26, 1335-39, (1954).

154. Cheng, K.L., Anal. Chem., 26, 1894-5 (1954).

155. Kodama, K., Nagoyashi Kogyo Kenkyujo Kenkyu Hokoku, 19, 4-7, (1958); C.A. 52, 14425g, (1958).

156. Komatsu, S. and Kamiyama, S., Nip. Kag. Zas., 81 1094-7, (1960); C.A., 55, 19608b, (1961).

157. Shamir, J., and Schwartz, A., Talanta, 8, 230-32, (1961).

158. Garica, F.C., and Garrido, M.L., Annales Real Soc. Espan, Fis. Quim. Ser., B58, 399-402, (1962); C.A., 58, 3883b, (1963).

159. Sangel, S.P. and Dey, A.K., Z. Anal. Chem., 202 348, (1964)(ENGLISH).

160. Nath, S. and Agerwal, R.P., Chim. Anal., 47, 257-61, (1965); C.A., 63, 6308g, (1965).

161. Ashizawa, T., Buns. Kag., 10, 354-8, (1961); C.A. 55, 24376a & b, (1961).

162. Pontani, F., Gazz. Chim. Ital., 90, 999-1004, (1960); C.A., 55, 21969c, (1961).

163. Ayres, G.H., and Narang, B.D., Anal. Chim. Acta, 24, 241-49, (1961).

164. Nelch, W., Z. Anal. Chem., 142, 30-5, (1954).

165. P shkova, V.M. and Shlenskaya, V.I., Vestn. Mosk. Univ., Ser. 11, Khim. 17, 598-603, (1962); C.A., 58, 1905h, (1963).

166. Banks, C.V., and Smith, R.V., Anal. Chim. Acta, 21, 308-11, (1959).

167. Menis, O. and Rains, T.C., Anal. Chem., 27, 1932-(1955).

168. Peshkova, V.M., Shlenskaya, V.I. and Sokolov, S.S., Trudy Komisii Anal. Khim., 11, 328-38, (1960): C.A., 55, 8171c, (1961).

169. Jacobs, W.D., Anal. Chem., 32, 512-13, (1960).

170. Pyle, J.T. and Jacobs, W.D., Talanta, 9, 761-67, (1962).

171. Pflaum, R.T., Wehking, M.W. and Jensem. R.E., Talanta, 11, 1193-6, (1964).

172. Ayres, G.H. and Janota, H.F., Anal. Chem., 31, 1985-7, (19[illegible]).

173. Oi, N., Nip. Kag. Zas., 80, 1151-3, (1959)., C.A., 55, 4247i, (1961).

174. Kodama, K., Nag. K.K.K. Hokuku, 24, 30-2, (1960); C.A., 63, 1209f, (1965).

175. Idem. 26, 29-31, (1961); C.A., 63, 3616d,(1965).

176. Idem. 27, 29-35, (1962); C.A., 63, 3616c,(1965).

177. Gustin, V.K. and Sweet, T.R., Anal. Chem., 35, 44-6, (1963).

178. Kammori, O., Taguchi, I., Takahashi, K., and Kioke, T., Buns. Kag., 14, 702-7, (1965); C.A., 63, 15550f, (1965).

179. Fraser, J.G., Beamish, F.E., and McBryde, W.A.F., Anal. Chem., 26, 495- 8 , (1954).

180. Mezaraups, G., Barkoviskis, J., Levins, A., and Dzintarnieks, M., Lat. Zinat. Akad. Vest., Kim. Ser., 3, 331-7, (1963); C.A., 60, 4789f, (1964).

181. Francsevich-Zabludovskaya, T.F., Kaliminova, L.P. and Sharafan, G.I., Zh. Analit., Khim., 18, 1083-9, (1963); C.A., 60, 1105f, (1964).

182 Pontani, F. and Piccardi, G., Anal. Chim. Acta, 22, 231-6, (1960).

183. Ayres, G.H. and Alsop, J.H. Anal. Chem., 31, 1135-8, (1959).

184. Shlenskaya, V.I., Khvostova, V.P. and Peshkova, V.M., Zh. Analit. Khim., 17, 598-603, (1962): C.A., 58, 1905h, (1963).

185. Ibid., Akad. Nauk. Sibirsk. Otd., Tr., 5, 57-63, (1963); C.A., 61, 4955c, (1964).

186. Zicyler, M. and Buchholz, Z. Anal. Chem., 210, 344-9, (1965); C.A., 63, 6308f, (1965).

187. Munchi, K.N., and Dey, A.K., Talanta, 11, 1265-8, (1964).

188. Sen Gupta, J.G., Talanta, 8, 785-92, (1961).

189. Idem. 8, 729-36, (1961).

190. Clem, R.G. and Huffman, E. H., Anal. Chem., 37, 86-9, (1965).

191. Pino- Perez, F., Burriel-Marti, F. and Conjero, L.M., Inform. Quim. Anal. (Madrid), 13, 38-51, (1959); C.A., 53, 18759c, (1959).

192. Ibid and Balcells, J.M., Anales Real. Soc. Espan. fis y Quim (Madrid), 55b, 579-90, (1959); C.A., 54, 30576, (1960).

193. Majumadar, A.K., and Chakrabatty, M.M., Anal. Chim. Acta, 19, 372-6, (1958).

194. Idem 482-7, (1958).

195. Idem 20, 379-85, (1959).

196. Ibid., Sci. and lture, (Calcutta), 23, 46-7, (1957); C.A., 53, 125i, (1959).

197. Eagli, R.A., Z. Anal. Chem., 194, 401-5, (1963); C.A., Vol. 59, 3310h, (1963).

198. Sangal, P. and Ki Dey, A., Icho Anal. Acta, 5-6, (1963); C.A. 60, 4789e, (1964).

199. Popa, G., Paralescu, I., and Bioulescu, Gh., Acad. Rep. Populare Romaine, Studii Cercetari Chim., 9, 85-92, (1961); C.A., 56, 13542d, (1962).

200. Popa, G., Crotiru, V., and Costache, D., Studia Univ. Babes-Bolgai, Ser. Chem., 8, 195-8, (1963) C.A., 61, 10037c, (1964).

201. Dutt, N.K. and Sen Sarma, K.P., J. Indi. Chem. Soc., 39, 20-2, (1962); C.A., 57, 35i, (1962).

202. Jacobs, W.D., Wheeler, C.M., and Waggones, W.H., Talanta, 9, 243-8, (1962).

203. Srivastava, S.C., and Good, M.L., Anal. Chim. Acta, 32, 309-16, (1965).

204. Xavier, J., Z. Anal. Chem. 164, 250-54, (1958) (in English).

205. Arita, T., and Yoe, J.H., Anal. Chim. Acta, 29, 500-4, (1963).

206. Radford, A.J., Analyst, 85, 445-8, (1960).

207. Ryan, D.E., Analyst, 76, 310-13, (1951).

208. Busev, A.I., and Kh. Vin, D., Zh. Analit. Khim., 20, 1208-13, (1965); C.A., 64, 7339e, (1966).

209. Busev, A.I. and Nacu, A., Ibid., 18, 500-6, (1963); C.A., 59, 3310f, (1963).

210. Xavier, J., and Ray, P., J. Indian Chem. Soc., 35, 432-44, (1958); C.A., 53, 16815d, (1959).

211. Ibid., Sci. and Culture Assoc. (Calcutta), 21, 294-5, (1956); C.A., 52, 15326f, (1958).

212. Popa, G., Costachu, D., and Enea, O., Analele Univ. Bucresti, Ser. Stiint. Nat. 12, 9-13, (1963); C.A., 64, 8923a, (1966).

213. Goeminne, A., Herman, M., and Eeckhaut, Z., Anal. Chim. Acta, 28, 512-18,(1963)

214. Kawase, A., Bunseki Kagaku, 12, 714-19, (1963); C.A., 59, 12168f, (1963).

215. Zeigler, M. and Pape, G , Z. Anal. Chem., 197, 354-60, (1963); C.A., 60, 16a, (1964).

216. Burke, R.W. and Yoe, J.H., Talanta, 10, 1267-72 (1963).

217. Wagner, V.L. and Yoe, J.H., Talanta, 2, 223-9, (1959).

218. Idem. 2, 239-43,(1959).

219. Dema, I. and Voicu, V., Acad. Rep. Populare Romaine, Studii Cercetari Chim. 8, 173-8, (1960); C.A., 54, 22163d, (1960).

220. Good, M.L. and Srivastava, S.C., Talanta, 12, 181-3, (1965).

221. Uno, T. and Akihana, S., Kagaku Zasshi, 80, 1021-23, (1960); C.A., 54, 22577h, (1960).

222. Senise, P., and Levi, F., Anal. Chim. Acta, 30, 509-14, (1964).

223. Rangnekar, A. and Khopkar, S.M., Bull. Chem. Soc. Japan, 38, 1696-9, C.A., 64, 7360a, (1966).

224. Otomo, M., Ibid., 36, 889-92, (1963); C.A.,59, 13340f, (1963).

225. Sen Gupta, J.G.G., Anal. Chem., 39, 18-22, (1967, Jan.).

226. Porez-Bustante, J.A., and Burriel-Marti, F., Anal. Chim. Acta, 37, 62-74, (1967, Jan).

227. Idem. 49-61, (1967, Jan.).

228. Ryan, D.E., Analyst, 77, 46-8, (1952).

229. Bobtelsky, M.M. and Cohen, M.M., Analyt. Chem. Acta, 22, 485-95, (1960).

230. Idem. 22, 532-38, (1960).

231. Commission on Spectrochemical and Other Optical Procedures For Analyses, I.U.P.A.C., "Spectrophotometric Data", 437 et seq., Butterworths, London, (1963).

232. Beamish, F.E., Talanta, 8, 85-103, (1961).

233. Ibid. 10, 883-890, (1963).

234. Belcher, R., Ind. Chemist, 38, 373-5, (1962).

235. Sneed, M.C., Maynard, S.L. and Brosted, R.C., "Comprehensive Inorganic Chemistry", Vol. II, Von Nostrand Co. Inc., N.York, London, (1954).

236. Beamish, F.E., Anal. Chem., 33, 1059-66, (1961).

237. Pollard, W.B., Analyst, 44, 94-5, (1919).

238. Pugh, C.R. and Tucker, M.T., Frankel, E., J.S. African Inst. Mining and Met., 60, No. 8, 367-70, (1960); C.A., 54, 22160h, (1960).

239. Daiev, K. and Jordanov, N., Talanta, 11, 501-6 (1964).

240. Pollard, W.B., Analyst, 62, 597-603, (1937).

241. Block, D.W. and Buchman, O.H., J. Biol. Chem., 136, 379-58, (1940).

242. Checneva, A.N., Trudy ural. Poliekh. Inst. im. S.M. Kirova, No. 96, 134-7, (1960); C.A., 55, 19604a, (1961).

243. Belcher, R. and Nutten, A.J., J. Chem. Soc., Part XII, 550-1, (1951).

244. Peshkov, I.A., Nach Trudy Tul'sk. Gorn. Inst. Shoranik, No. 1, 229-38, (1958); C.A., 55, 26951b, (1961).

245. Lapin, L.N. and Gein, V.O., Trudy Komissii Anal Khim. Akad Nank, U.S.S.R., Inst. Geokhim. i. Anal. Khim., 7, 217-22, (1956); C.A., 50, 15329b, (1956).

246. Ducret, L. and Maurel, H., Anal. Chim. Acta, 21, 74-9, (1959). (in French).

247. Tsai, I.K., Lili, H. and Tu, C.L., Wu Han Ta Hsueh, Tzu. Jan K'o Huseh Hsueh Pao, 112-17, (1959); C.A., 56, 15h, (1967).

248. Dancheva, R. and Beleva, S., Godishuik Nauchnoizsled. Procktant. Inst. Pudodobiv. Ubayatyarane, 3(3), 247-511, (1964); C.A., 64, 1340e, (1966).

249. Lin, H. and Xu, J., Hua Huseh Tuny Pao, 4, 244-6, (1965); C.A., 63, 17132c, (1965)

250. Mac Nulty, B.J. and Woolard, L.D., Anal. Chim. Acta, 13, 154-8, (1955).

251. Onishi, H., Mikrochim Acta, 1, 9-17, (1959). (in English).

252. Dancheva, R., and Beleva, S., Khim. Ind. (Sofia) 36 (3), 109-11, (1964); C.A., 62, 18h, (1965).

253. Hara, S., Bunseki Kagaku, 7, 147-51, (1958); C.A., 1170g, (1960).

254. Cotton, T.M. and Woolf, A.A., Anal. Chim. Acta, 22, 192-4, (1960).

255. Erdey, L. and Rady, G., Z. Anal. Chem., 135, 1, (1952).

256. Kawahata, M., Mochizuki, H. and Misaki, T., Buneski Kagaku, 11, 819-22, (1962); C.A., 57, 11846i, (1962).

257. Beardsley, D.A., Briscoe, G.B., Ruzicka, J., and Williams, M., Talanta, 13, 328-3, (1966).

258. Nasour, F.G., Shahine, S.A.F. and Magee, R.J., Anal. Chim. Acta, 36, 436-51, (1966).

260
~~259~~. Pantani, F. and Piccardi, G., Anal. Chim. Acta, 22, 231-6, (1960).

259
~~260~~. Holland, W.J. and Bozie, J., Anal. Chem., 39, 109-10, (Jan., 1967).

261. McByrde, W.A.E. and Yoe, J.H., Anal. Chem., 2o, 1094-9, (1948).

262. Vydra, F., and Celikovsky, J., Chem. Listy 519, 768-70, (1957); C.A., 51, 9404g, (1957).

263. Conrad, F.J., Kenna, B.T., Plating, 52, 1286-8, (1965); C.A., 64, 7355b, (1966).

264. Deshmurkh, G.S. and Tatawadi, S.V., J. Sci. Ind. Res. (India) 20B, 506-7, (1961); C.A., 56, 10899h, (1962).

265. Kralijic, I., Bull. Sci. Conseil Acad. RPF, Yougoslavia, 3, 103-4, (1957); C.A., 52, 8843c, (1958).

266. Gasparec, V.K. and Pinter, T., Croat. Chem. Acta, 33, 69-72, (1961); C.A., 56, 4090f, (1962).

267. Shani derman, S.Y., Izvest. Kiev. Politekh. Inst., 17, 204-18, (1956); C.A., 52, 18081i, (1958).

268. Popa, G., Negoin, D., and Bainlescu, G., Analel. Univ., Ser Stiint. Nat., 9, 99-102, (1960); C.A. 58, 7339b, (1963).

269. Popa, G. and Mircea, D., Z. Anal. Chem., 184, 353-5, (1961); C.A., 56, 7985f, (1962).

270. Lee, K.T., Anal. Chim. Acta, 26, 478-81, (1962).

271. Murphy, J.W. and Affsprung, H.E., Anal. Chem., 33, 1658-60, (1961).

272. Wilson, R.F. and Lester, G.W., Z. Anal. Chem., 193, 260-4, (1963).

273. Frumina, N.S., Mustafin, I.S., Agrasovskaya, L.A. and Karakhtanova, Z.G., Peredovye Metody Khim. Teknol. i Kontroly a Proizv, Sb., 193-6, (1964); C.A., 63, 13e, (1965)

274. Cheng, K.L. and Lott, P.F., Microchem. J., Symp. Ser. 2, 317-31, (1962); C.A. 58, 7359d, (1963).

275. Lakin, H.W. and Nakagawa, H.M., Eng. Mining J., 166, 108-10, (1965) (English); C.A. 64, 5740e, (1966).

276. Ibid, 11-5 Geol. Surv. Profess. Papers No. 525-c 168-71, (1965); C.A., 64, 16c, (1966).

277. Ueda, H. and Deguchi, M., Hiroshima Daigaku Kogakubu Kenkyu Horokuku, 12, 121-6, (1964); C.A., 61, 12671e, (1964).

278. Gagilardi, E. and Presinger, P., Mikrochim. Ichnoanal. Acta, 4, 791-7, (1965); C.A. 63, 17132d, (1965).

279. Popper, E., Chiorean, L. and Piteat, I., Rev. Rommaine Chim., 9, 663-5, (1964); C.A., 62, 12432c, (1965).

280. Glem, R.G. and Huffman, E.H., Anal. Chem., 37, 1155-7, (1965).

281. Mouk, R.G. and Herrington, J., Anal. Chim. Acta, 24, 481-92, (1961).

282. Chow, A., Lewis, C.L., Moddle, D.A., and Beamish, F.E., Talanta, 12, 277-80, (1965).

283. Beamish, F.E., Talanta, 12, 789-816, (1965).

P U B L I C A T I O N S

1. "Titration of Macro And Micro-Amounts of Cyanide".

   Talanta, 13, 1667-71, (1966).

2. "Spectrophotometric Determination of Trace Amounts of Cyanide"

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