SURFACIANT SENSITISED COLORIMETRIC REACTIONS IN INORGANIC ANALYSIS.

A thesis submitted to the School of Chemical Sciences, N.I.H.E., Dublin.

by

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September 1988.

DECLARATION.

I hereby declare that:

The contents of this thesis, except where otherwise stated, are entirely my own work, based on research carried out in the School of Chemical Sciences, National Institute for Higher Education, Dublin.

Grace Hanley.

Darioush Dadgar.

(Supervisor)

To my Parents.

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ACKNOWLEDGEMENTS.

My sincere thanks and appreciation are accorded to Dr. Darioush Dadgar of N.I.H.E., Dublin for his supervision during the course of this work and to Professor D. Thorburn Burns of Queens University, Belfast for supplying all Polyvinyl Alcohols used.

My gratitude is extended to all staff of the Chemistry Department, whose collaboration and friendship rendered this study not only a valuble extension of my education and experience, but also a very real pleasure.

My thanks are due to my fellow post-graduates Anna, Mary and Paula for their continued encouragement and good humour throughout.

Financial support during this research from Squibb Linson Ltd., is gratefully acknowledged.

I would also like to thank Ms. Clare Manning for her undying patience and kindness and the skilful typing of this thesis.

Finally, words cannot express my thanks to my parents for their understanding and unselfish support and to whom I am forever indebted.

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ABSTRACT.

SURFACTANT SENSITISED COLORIMETRIC REACTIONS IN INORGANIC ANALYSIS.

by Grace Hanley.

Highly sensitive spectrophotometric methods for selected metals, based upon the formation of a ternary complex on a micelle surface formed in the presence of a cationic, anionic or non-ionic dispersant, are proposed. The conditions under which microgram amounts of Iron, Germanium and Tin are determined, the influence of diverse ions, the composition of the complex and the role of surfactants thereon of such complexes are examined and discussed. The initial impetus to study such metals was encouraged in part by their apparent interference in the spectrophotometric determination of other ions. Attempts are thus made to modify and improve such analyses by a similar treatment, sensitivity, selectivity and reproducibility reported in each case. Limits of detection and quantitation are also presented, being of a pharmaceutical and environmental significance. The incorporation of Fluoride ion into such systems was also studied, conclusions being such that no reaction occurs in such media. Stringent pH control being necessary to avoid apparent effects.

Chapter I : Introduction.

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1.1 Preface:

Since the appearance of water on the earth, aqua complex ions of metals must have existed. The subsequent appearance of life depended on, and may even have resulted from, interaction of metal ions with organic molecules. Attempts to use consciously and to understand the metal-binding properties of what are now recognised as electron-donating molecules or anions (ligands) date from the development of analytical procedures for metals by Berzelius and his contemporaries. By the late 19th century there were numerous examples of the complexing of metal ions, and the synthesis of the great variety of metal complexes that could be isolated and crystallized was being rapidly developed by chemists such as S.M. Jørgensen in Copenhagen. Attempts to understand the 'residual affinity' of metal ions for other molecules and anions culminated in the theories of Alfred Werner, although it is salutory to remember that his views were by no means universally accepted until the mid 1920's. The progress in studies of metal complex chemistry was rapid, perhaps partly because of the utility and economic importance of metal chemistry, but also because of the intrinsic interest of many of the compounds and the intellectual challenge of the structural problems to be solved.

Presently, this treatise is an attempt to develop and evaluate optimum methods of analysis of selected metals through their co-ordination, presenting the reader with, if not an opportunity to thereafter improve, then a challenge to meet the same requirements for other systems.

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1.2 Introduction to Ultra-Violet/Visible Spectroscopy:

The work SPECTROSCOPY is widely used to mean the separation, detection and recording of energy changes involving nuclei, atoms or molecules. These changes are due to emission, absorption, or scattering of electromagnetic radiation or particles. Spectrometry is that branch of physical science that treats the measurement of spectra.

The experimental applications of spectroscopic methods are diverse, but all have in common the interaction of electromagnetic radiation with the quantized energy states of matter. A chemist may wish to determine a molecular structure or the value of an electric dipole moment. He may wish to quantify a compound in solution or to verify the presence of a chemical bond. A particular spectroscopic method is chosen, based on the possible energy states of matter in particular configurations and the particular wavelengths of electromagnetic radiation that interact with these states.

Absorption Spectrophotometry, is the science of the measurement of the amount of electromagnetic radiation absorbed at a particular wavelength or set of wavelengths. The relationship between absorbance or optical density, concentration of the absorbing species and path length of the solution is governed by the Beer-Lambert Law: where

 $A = \epsilon.c.l,$

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A being absorbance, c concentration and 1 the path length. ε is a proportionality constant known as the extinction co-efficient, this law holding for ideal systems. Deviations from ideality include concentration effects, solvent effects, pH effects, fluorescence or phosphorescence and instrumental errors.

The Spectrophotometer is an instrument that measures the amount of visible/UV and/or Infra-red radiation absorbed by a solution at a given wavelength. The basic functions are three fold:

- (a) The production of radiation of frequencies appropriate to energy changes within the sample.
- (b) Spectral examination of this radiation to facilitate qualitative analysis of the sample.
- (c) Measurement of the intensity of radiation at frequencies selected from the information obtained in (b) to facilitate quantitative analysis of the sample.

A block diagram outlining the schematics of a spectrophotometer is shown in Fig. 1.2.1.

With the advent of modern microprocessor - controlled instruments, and especially with the specific advantage of diode array instruments, many of the classical limitations on quantitation have been eliminated and a variety of new techniques have become available.

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Fig. 1.2.1. Block diagram of a basic spectrometer, including some typical devices and conditions.

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In classical quantitation methods, the wavelength of maximum absorbance is always chosen as the analytical wavelength, since this is the point which usually has the best signal/noise ratio, hence maximum sensitivity is achieved. Also, at this point, absorbance changes very little with changes in measurement wavelength.

A frequent limitation of UV/VIS spectroscopy is a lack of sensitivity, the problem being inherent to the molecular physics of the absorption of light and to the physics of the instrumentation. Techniques used to improve sensitivity include those inherent to spectrophotometer design, the ideal instrument having a minimum number of optical components, since light is lost at every optical surface. Sensitivity is further improved by averaging together data points over a wavelength range and/or time. 1.3 Metal Complexes and their Spectra:

For the most part reagents used in absorptiometric procedures are those containing both chelating and chromophoric groupings forming stable metal complexes whose favourable absorption characteristics (i.e. λ max and ε max) differ as widely as possible from those of the reagent. In the broad sense, a co-ordination complex is the product of association of a Brønsted Base with a Lewis Acid. As H₂O molecules are electron pair donors then in solution, co-ordination between metal M and ligand L is represented thus:

 $M(H_2O)_X + nL \rightleftharpoons M(H_2O)_{X-n}L_n + (x-n)H_2O$ With co-ordination numbers greater than unity the complex

formation process proceeds stepwise via:

$$M + L \implies ML \qquad K_1 = [ML]/[M].[L]$$

$$ML + L \implies ML_2 \qquad K_2 = [ML_2]/[ML].[L]$$

$$MI_{n-1} + L \implies MI_n \qquad K_n = [MI_n]/[MI_{n-1}].[L]$$

where n is the maximum co-ordination number of the complex and the overall stability constant β_n being the product of the n stepwise constants:

$$K_1.K_2...K_n = \beta_n$$

For the purpose of this research the ligands of interest are those of organic nature which show a tendency to form donor acceptor bonds with metal ions i.e. dative in nature. The chelate formation is especially favoured if 5 or 6 membered ring chelates are formed as shown in Fig. 1.3.1 - the method of presentation does not indicate inequality of the bonds of each functional group, it is merely a convenient way of assessing the charge on the complex as a whole, with only negatively charged groups compensating the charge on the metal ion. It is, however, the donor atom directly bonded with the central metal ion that plays the main role in the co-ordinate bond, rather than the functional group as a whole.



(only a single chelate ring is shown)

Fig. 1.3.1 5 and 6 membered ring chelates.

For the interpretation of electronic spectra, chromophoric groups of interest are classified thus:

- 1. <u>d-electron chromophores</u>: Characterised by a metal ion with an unfilled d-level configuration, the absorption bands being thus assigned to transitions substantially localised on the d-level denoted as d-d transitions. The splitting of the states of a transition metal ion is mainly affected by the electrostatic interaction between the d-electrons of a central metal ion and the donor atoms, hence the energy of d-d transitions is different for different complexes of a given ion, leading to the development of the spectrochemical series.
- 2. <u>d- π chromophores</u>: Characterised by ligand to metal transfer or vice versa, the electron being transferred from one component of the complex to the other, resulting in what is called a charge - transfer transition. For spin allowed transitions ϵ is in the range $10^2 - 10^4 \ 1 \ mol^{-1} \ cm^{-1}$, these intense bands usually occurring in a region where the ligand itself possesses no absorbance. Hence, research has been aimed at preparation of ligands with a d- π chromophoric group, which is only possible for those d-shell metals capable of existing in two oxidation states differing by one electron e.g. Fe(II)/Fe(III). Transitions of the metal M -> ligand L type are characterised by metals in the lower oxidation state and ligands with unfilled orbitals typified by a single or chain of double bonds.

Examples include complexes of Iron (II) with

8-hydroxyquinoline and 1,10 phenanthroline, the absorption bands found in the visible region and are assigned to the transfer of a t_{2g} electron to a free anti-bonding π orbital of the ligand. Since a substitution in the π electron system brings about a change in the relative values of energies of the molecular orbitals, the wavelength corresponding to the charge transfer band is also changed. Complexes of the L -> M type are found with d-shell metals easily reduced to a lower oxidation state, the ligand having a π electron system to which an acidic group is attached. Such groups include OH, SH, = NH, where, after deprotonation, the non-bonding electron is shifted to an anti-bonding orbital of the π electron system, and subsequently transferred to an un-filled d-orbital of the metal ion upon complex formation. Examples include complexes of Iron (III) with 8-hydroxyquinoline and sulphosalicyclic acid.

3. <u> π -electron chromophores</u>: Characterised by single or several double bonds e.g. - CH = CH -, C = 0, C = S, -N = 0 etc. Those with more double bonds include phenyl and pyridyl groups, the ethylene group - CH = CH - representing the simplest π -electron chromophore. If the mutual interaction between σ and π electrons in this entity is neglected, then two absorption bands can be ascribed to this chromophore i.e. from π bonding -> π * anti-bonding, and from σ bonding -> π * anti-bonding.

In both cases the energy of transition is high, hence corresponding bands being found in the vacuum UV. Conversely, for the carbonyl group C = 0 where electrons are differentiated as sigma σ , π and non-bonding n with transitions occurring in the UV and visible range (n -> π^* and π -> π^*) - see Fig. 1.3.2 n -> π^* transitions occur only for those π -electron chromophores with atoms with free electron pairs typified by C = S, -NO, $-NO_2$, -N = N and hetero-analogues of aromatic compounds. ε is typically 10 $- 10^2 1 \text{ mole}^{-1} \text{ cm}^{-1}$ in such cases.



Fig. 1.3.2 Relative Energy of molecular orbitals of the carbonyl group for a one electron approximation.

Sensitivity is one of the obvious demands in applications of analytical methods. In order to comply with this requirement for reactions which involve a change in colour, the complex formed or the organic reagent itself must contain chromophoric groups characterised by transitions with ϵ in the range 10^3 - $10^5 \ 1 \ mol^{-1} \ cm^{-1}$. Such chromophoric groups are found among d- π and π chromophores, complexes of the d- π type being restricted in use to the transition metals, in particular those existing in two oxidation states differing by one electron. 1.4 Surfactants and Micellar Systems in Analytical Chemistry:

A great deal of knowledge and better understanding of micellar structure and behaviour has been obtained since the pioneering work done by Hartley in 1936¹. In fact, the last ten years or so has seen considerable improvements in analytical methodologies and even in areas such as molecular absorption/luminescence and chromatography, sound theoretical bases and understanding of their particular applications are yet emerging. Aside from their intrinsic interest, micellar systems are involved in many industrial and technical applications^{2,3,4} where micellar solubilization can be of fundamental importance in e.g. altering rates of chemical or photochemical reactions of solutes⁵. They can also serve as relatively simple models for enzymatic, membrane mediated and related processes.

Analytical work done concerned their application to ultra-violet/visible absorption spectral methods, primarily those involving metal ion determinations where they complex with chelometric indicators^{10,11}. Thus surmountable problems typically include those of solubility, rate of reaction, unfavourable equilibrium positions for methods based on the equilibrium reaction, lack of sensitivity of method, lack of selectivity due to interferences, spectral overlap and potential restraints due to buffer or pH considerations of the analytical system. In the past, the analytical chemist usually either entirely abandoned development of the potential procedure or resorted to the use of different solvent systems.

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This latter technique usually results in a loss of effective sensitivity for the particular procedure due to dilution, easily overcome upon addition of very small amounts of a surfactant.

Surfactants, a syncope of SURFace, ACTive, ageNIS, are amphiphilic molecules, composed of a hydrophobic tail joined to a hydrophilic head group, the former varying in length from 8-20 carbon atoms and the latter either a partially dissociable carboxylate (soap), a fully ionised moiety (such as anionic sulphate or cationic trimethylammonium) plus counterion, or an uncharged polar species, (e.g. polyethyleneglycol). Varying not only in their charge type (zwitterionic, cationic, anionic or neutral), the nature of the hydrophobic portion is typically single or double hydrocarbon chains, multiple bonds etc.

While dispersed mainly as monomers at low concentrations in aqueous solution, surfactants assemble in a connivent aggregate of colloidal dimensions to form what is called a MICELLE, above a certain critical concentration termed the c.m.c (critical micelle conc.). A dynamic equilibrium between monomer and micelle is then set up, having a profound impact on an analyte residing in or on the micelle and on analytical measurements centered on the associated analyte. The time frame of the analytical measurement overlays the temporal dynamics of the analyte – micelle association, and the quality of this match determines in large part whether useful analytical results can be obtained.

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At surfactant concentrations near the c.m.c., aggregation occurs to form roughly spherical or ellipsoidal shaped micelles, each composed of a certain number of surfactant molecules (termed aggregation number), Fig. 1.4.1(a) illustrates a 2-dimensional schematic representation of a typical spherical ionic micellar system⁵.

The structure is such that the hydrophilic head groups are directed towards and in contact with the aqueous solution, thus forming a polar surface while the hydrophobic tails are directed away from the water forming a central non-polar core. Such surfactant aggregation in aqueous media is referred to as a NORMAL micelle. Formation of association colloids also occurs in apolar solvents where the polar head groups and counterions orient together in an inward fashion in contact with a small water pool where they are hydrated, the aliphatic tail extending outward in contact with the apolar solvent. These surfactant aggregates are then termed REVERSED or INVERTED micelles⁵. A schematic representation of a reversed micellar system with small and relatively large aggregation numbers is shown in Fig. 1.4.1(b).



Fig. 1.4.1(a).

A two-dimensional schematic representation of the regions of an ionic spherical micelle. The counterions (X), the head groups (0), and the hydrocarbon chains $(\sim\sim\sim)$ are schematically indicated to denote their relative locations but not their number, distribution, or configuration.



Fig 1.4.1(b).

Schematic representations of reversed micelles for surfactants composed of a long-chain cation and a short-chain anion with small (on left) and relatively large (on right) aggregation numbers.

For the purpose of this investigation with metal chelation occurring in aqueous media only normal micelles are considered where formation is believed to be the result of three primary forces namely:

- 1. Hydrophobic repulsion between the hydrocarbon chains and the aqueous environment.
- 2. Charge repulsion of ionic head groups.
- 3. Van der Waals attraction between the alkyl chains.

Alkyl chain length, size of head group structure and interactions of the alkyl chains with one another and with the solvent determine the c.m.c, micelle size, aggregation number and structure.

Specific characteristics of micelles that make them attractive for analytical applications are the existence of the charged Stern Layer (in the case of ionic micelles), the orientational anisotropy (degree of ordering, an equilibrium property) of the micellar "core", the ordering of the micelle interface due to charge and solvent interactions and the unique polarity gradient going from the bulk solvent to the "core". Due to relatively high concentrations of surface charge, electrostatic interactions can be used to repel like-charged interferents in analysis. The orientational anisotropy of the core can reduce the freedom of motion, enhancing the photophysical characteristics of molecules. This, together with the available polarity gradient for the analyte to choose from, UV/VIS absorption and luminescence can successfully experience an enhanced sensitivity. To take advantage of the micelles' organising ability, the species involved must preferentially associate with the micelle over the bulk solvent. Kinetically, analyte and reagent should exhibit significantly smaller rate constants for exit from the micelle compared to entrance rate constants. Factors influencing the magnitude of the entrance/exit rate constant ratio of analytes with micelles include analyte and reagent polarity and charge type, selection of a surfactant system whose characteristics allow significant association of analyte and reagent with the micelle, pH and ionic strength. Simply by making small pH adjustments, the analyte can be converted into a form which interacts much more strongly with the micellar assemblies. Ionic strength modification can result in larger micelles due to better screening of electrostatic repulsions among head groups, causing altered residency time of the analyte in or on the micelle.

Typical chelometric indicators that have been used to determine a wide variety of metal ions using micellar modified procedures include 3,3' -dimethylfuchsone-5,5'-dicarboxylate (Chrome Blue G or CBG)¹², 3,3',4' trihydroxyfuchsone-2' -sulphonic acid (Pyrocatechol violet or PCV)^{13,14}, Pyrogallolsulphonaphthalein (Pyrogallol Red or PR)¹⁵, 4,5-dihydroxyfluorescein (Gallein or G)¹⁶, where cationic and non-ionic surfactants such as cetyltrimethylammonium bromide (CTAB), chloride (CTMAC) or iodide (CTMAI); tetradecyldimethylbenzylammonium chloride (Zephiramine or Z) and p-1,1,3,3, tetramethylbutylphenol (Triton X-100) are used.

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One improvement that has been reported for some of these procedures is due almost solely to the solubilizing ability of micellar systems, the metal complexes of oxinates¹⁷, dithizonates¹⁸, PAN¹⁹, XB¹⁸ being thus solubilized. The use of surfactants eliminates the "extraction into an organic phase" step without any apparent decrease in the effective sensitivity of the method. Non-ionic surfactants (e.g. TX-100) were typically employed here. Based on comparison with other similar systems, there are presumably two possible solubilization sites 2,3,5 , either the hydrophobic moiety extending only partly into the core region so that its hydrophilic portion is near to or adsorbed on the Stern Layer, or alternatively, the metal chelate is oriented within the polyoxyethylene shell of the TX-100 micellar core region. This latter possibility is assumed to occur in cases where the solute has phenolic hydroxy groups present, favourably interacting with the ether oxygens of the ethylene oxide groups of TX-100 or similar non-ionic surfactants via H-bond formation²⁰. Ionic micellar systems are usually not employed in these procedures using the above complexing agents, cationic surfactants sometimes promoting further dissociation of a second or third ionizable group present in the excess complexing agent. Frequently, this leads to formation of a coloured species whose absorption overlaps with that of the metal chelate, thus causing a high blank (especially true when PAN is the complexing agent).



1-(2-Pyridylazo)-2-Napthol (PAN)

Anionic surfactants, in this case, presumably impede or inhibit complex formation between an anionic chelating agent and the metal ion.

Unlike the situation just described there are many anionic chelating agents that do react with metal ions (in the absence of added surfactants) to form relatively water soluble binary metal-chelate complexes²¹. Characteristically, they absorb in the visible region i.e. 550 ± 60 rm with $\epsilon = 0.5 - 6.0 \times 10^4$ 1 mol⁻¹cm⁻¹. With pH values of 7 or greater methods are not very selective and can exhibit poor reproducibility or precision, due in part to a high background absorbance of the excess analytical chelating agent. On addition of relatively small amounts of a cationic surfactant first to the solution of dye e.g. Xylenol Orange^{10,22,23} methylthymol blue²⁴ resulted in marked colour changes corresponding to an apparent pH shift of several units^{10,22}. That acid-base indicators can change their colour in the presence of micellar forming surfactants has long been known^{5,25}.

Like many organic compounds, chelometric indicators absorb light differently depending on their particular ionization state (Eqn. 1.4.2).

 $\begin{array}{ccc} & & & K_1 & & K_2 & & K_3 \\ H_3 \text{In} & & & H_2 \text{In} \end{array} \xrightarrow{} & H \text{In}^{\equiv} \end{array} \xrightarrow{} & \text{In}^{\equiv} \dots \dots & 1.4.2. \end{array}$

Hartley²⁶ enunciated a simple sign rule based upon consideration of the valence change of the indicator and subsequent electrostatic interactions with charged surfactants in order to account for effects on equilibria. If the indicator is neutral in one form then equilibrium will be displaced to the basic side by cationic and to the acidic side by anionic micellar systems. Obviously, non-ionic micelles do not fall into this category. Additionally, if both forms of the indicator are opposite in sign to that of the micelle then displacement direction can depend on other factors such as hydrophobic and microsolvent interactions in addition to the electrostatic forces involved^{4,5}. Protolytic dissociation of the indicator is thus promoted due to favourable positive charge-dipole interactions, through being solubilized on or near to the positively charged cationic micellar surface²⁷. Reports of lower pK_a values of indicators with cationic micelles include CAS²⁸ with pK_a values of 4.92 and 4.40 in the absence and presence of CTAB respectively. The free energy difference between dye and its conjugate form is presumably reduced, with enthalpy being the predominate term. As a result a hypsochromic shift of their absorption bands towards shorter wavelength is observed.

Addition of the metal to such micellar-solubilized dye solutions exhibits spectrophotometric data different to that in the absence of micelles. This forms the basis for improvement. Table 1.4.3 shows a comparison of the spectral parameters of some of the metal chelate complexes formed in both the presence and absence of micellar systems i.e. large bathochromic shifts and a 3 to 20 fold hyperchromic shift in molar absorptivity. The improvement is a consequence of a greater wavelength separation between the excess dye's absorption (lowered pK_a and hence shorter λ) and that of the metal-chelate complex (bathochromic shift).

Increase in stability is attributable to favourable interactions between the anionic complex and positively charged head group of the surfactant. Extremely high stability constants in such cases demonstrate the advantage of a micelle. In its absence, simultaneous formation of two or more complexes between metal and indicator are possible²⁹. Preferred formation and stability of only one form in the micellar system greatly reduces this problem, hence better reproducibility and adherence to Beer's Law as a result.

Surfactant	Metal	Complexing Agent	Absence of Micelles $\lambda \max \epsilon(x10^{-4})$	Presence of <u>Micelles</u> $\lambda \max \epsilon (x \ 10^{-4})$
CPC	Fe ³⁺	BDAS	550 4.5	565 6.1
CTMAC	A1 ³⁺	Ferron	370	385
CTAB, CPB	A1 ³⁺	PCV	615 1.5	670 5.3
CTAB, CTMAC	Be ²⁺	ECR	525 3.0	590 8.6
CTMAC	Be ²⁺	CBG	610 3.1	626 9.4
2, BDHA	Be ²⁺	CAS	2.0	611, 8.8
СРВ	La ³⁺	хо	576 3.1	610 10.2
CTAB	La ³⁺	EAB	500 1.3	650 6.6
CTAB	La ³⁺	G	595 1.4	630 2.8
CTAB	¥Ъ ³⁺	GTB	600 0.5	646 3.3
CTAB	∼ γ ³⁺	EAB	500 1.3	650 6.3
СРВ	y ³⁺	хо	578 4.8	600 8.7
CTAB	Sn ⁴⁺	PCV	555 6.5	662 9.6
CPC	T1 ⁴⁺	DSPF	570 10.0	620 12.0
OTMAB	Th ²⁺	ECR	530	604
CTAB	Th ²⁺	CAS	555	635
CTAB	In	CAS	555 0.2	630 12.3

Table 1.4.3:⁴ Comparison of the Spectral Parameters of some Metal-Chelate Complexes formed in the absence and presence of micellar systems.

To date, much uncertainty surrounds the exact kinetic and mechanistic steps involved in complex formation in such a system. The hypothesis currently prevailing envisages the possibility of either step-wise or concurrent interaction between indicator, metal ion and the micellar system. Perpendicular direction of orientation of indicator to the charged micellar surface has been shown by Kohara³⁰. This would facilitate co-ordination with the incoming metal ion, two alternative modes being possible, either step-wise²⁶ reaction i.e. first co-ordination followed by re-orientation in the micellar system so that its other ionizable functional groups are now in a position to favourably interact with the positively charged head groups of neighbouring surfactant molecules or concurrent interaction of chelate both with the metal ion and surfactant³¹. To illustrate the above, the reagent Pyrocatechol Violet PCV, metal Me and cationic surfactant Co micellar system is considered (Fig. 1.4.4).



Fig. 1.4.4.

Me co-ordinates through the ortho-hydroxy quinone group. Additionally the sulphonate and hydroxyl groups symmetrical to the carbonyl group can become favourably orientated to interact with the positively charged head group of the tetra alkylammonium surfactant molecules comprising the micellar system. This association leads to the production of a new metal-chelate structure, equalization of the bonds, maximum delocalization of the conjugated π -electron system and hence modification of the absorption spectrum of the complex³¹. Kohara has shown that the $\pi \rightarrow \pi^*$ electronic transitions represent an excited state stabilized relative to the ground state in such a micellar system³². Additionally, for the formation of such ternary complexes evidence³¹ indicates that it is the surfactant C_{c} molecules of the micellar aggregate that interact with the metal chelate complex formed on the micellar surface and not the monomer C_S molecules in the bulk solution, which are in dynamic equilibrium with each other. Therefore, no 'new' complex forms at concentrations below the c.m.c. or in the presence of other tetra alkylammonium compounds incapable of micelle formation³¹ e.g. tetra alkylammonium bromide.

Finally, other applications of micellar systems to UV/VIS spectroscopy include catalysis of analytical reactions⁵ where, typically equilibria are incomplete and lie towards the reactant side. Cationic micellar systems in nucleophilic equilibria reactions, can favour solubilization of the product and hence catalyse the reaction.

Micellar systems as Spectral Shift reagents are yet another application where absorption changes of specific solubilized probe molecules are utilized. Depending upon the site of solubilization and type of interaction present within the micelle system, the spectral parameters of the solubilized solute can be altered due to the 'new' local microenvironment that is now present.

The effective local microscopic polarity, acidity, viscosity and dielectric constant of the surfactant – entrapped solute can thus be substantially different from that observed in the bulk solvent. Compounds such as methyl, ethyl or butyl orange have been used as probes of micellar microenvironments as well as for the determination of microscopic properties such as polarity, viscosity etc.. Bibliography:

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Chapter II : Iron.

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2.1 Occurrence, Importance and Utilisation of Iron:.

The impetus for the research on Fe(III) has in the main been <u>environmental</u> and to a lesser extent <u>pharmaceutical</u>, both areas widely employing spectrophotometric techniques in its determination^{1,2}.

Being the fourth most abundant element in the earths' crust, Iron occurs to the extent of some 5.1%, and is used on the largest scale of any metal. It forms three oxides FeO, Fe_2O_3 (Hematite) and Fe_3O_4 (Magnetite) occurring naturally, the carbonate ores associated with clay or coal being called ironstones. Environmentally, Iron is determined in ores, rocks and water while technologically manifesting itself in the steel industry.

Iron occurs in a number of important biological compounds including myoglobin - used to store oxygen in the muscles and in various cytochrome pigments. In the latter, a chain of transfers occurs which link dehydrogenation of alcohols or fatty acids with the conversion of O_2 to H_2O via a series of oxidation reduction steps involving Fe(II)/Fe(III) conversions in various cytochromes. Iron also occurs in the protein ferritin believed to be present as Fe(III) hydroxide micelles or clusters.

2.2 Structural Chemistry of Iron:

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The structural chemistry of Fe(III) is largely that of octahedral co-ordination in crystalline halides, Fe_2O_3 and in numerous finite complexes e.g. $Fe(en)_3^{3+}$ (en = ethylenediamine $H_2NCH_2CH_2NH_2$), $Fe(acac)_3$ (acac = acetylacetone $CH_3C(OH)=CHCOCH_3$), and $Fe(C_2O_4)_3^{3-}$ (C_2O_4 = oxalate ion), tetrahedral co-ordination being less common. Thus, there is octahedral co-ordination for the metal in crystalline $Fecl_3$, but tetrahedral co-ordination in the vapour dimer Fe_2Cl_6 and in the $Fecl_4^-$ ion, with both modes occurring in Fe_3O_4 and also in the complex $Fecl_3L_2$ (L = ligand). This compound consists of equal numbers of tetrahedral ($Fecl_4$)⁻ ions (where Fe-Cl 2.16 Å) and octahedral trans ($Fecl_2L_4$)⁺ ions (where Fe-Cl 2.34 Å, Fe-O 2.01Å).

The magnetic moments of Fe(III) compounds correspond to high spin (d⁵, 5.9 B.M), except for complexes such as $[Fe(CN)_6]^{3-}$ and $[Fe (dipy)_3]$ (where $CN^-=$ cyanide dipy = 2,2'-dipyridyl) containing strong field ligands capable of being polarised and thus promoting its tendency to form covalent bonds. For octahedral complexes, overall complete spherical symmetry can be expected for high spin d⁵ (Fe(III)). There is therefore a direct correlation between acceptor ability of the cation, or the thermodynamic stability of the resulting complex in solution and the crystal field determined occupancy of d-orbitals. Some properties of $Iron^{26}$ are given in Table 2.2.1

Electronic Structure	M. P.	Ionisation		Potential/eV		Electronegativity	Ionic Radius/p.m.	
		1st	2nd	3rd	4th			
(Ar) 3d ⁶ 4s ²	1528 ⁰	7.87	16.20	30.7	54.8	1.83	92	

Table 2.2.1 Physico Chemical Properties of Iron.

2.3 Solution Chemistry of Iron:

Iron (Fe atomic weight 55.847g) occurs in solution in the +II and +III oxidation states, compounds of the latter being generally the more stable. It occurs in salts with most anions (except those that are incompatible with it because of their character as reducing agents e.g. FeI₃). Examples obtained as pale pink to nearly white hydrates from aqueous solutions are $Fe(ClO_4)_3.10H_2O$, $Fe(NO_3)_3.9$ or $6 H_2O$ and $Fe_2(SO_4)_3.10H_2O$. The hydrolysis (equivalent in the first stage to acid dissociation of the aquo ion) is governed in its initial stages by the following equilibrium constants:

$$[Fe(H_{2}O)_{6}]^{3+} = [Fe(H_{2}O)_{5}(OH)]^{2+} + H^{+}$$

$$[Fe(H_{2}O)_{5}(OH)]^{2+} = [Fe(H_{2}O)_{4}(OH)_{2}]^{+} + H^{+}$$

$$K = 10^{-3 \cdot 26}$$

$$2[Fe(H_{2}O)_{6}]^{3+} = [Fe(H_{2}O)_{4}(OH)_{2} Fe(H_{2}O)_{4}]^{4+} + 2H^{+}$$

$$K = 10^{-2 \cdot 91}$$

which is believed to have the structure²⁷



From the constants for these equilibria it is evident that even at the rather acid pH's of 2-3, the extent of hydrolysis is very great and in order to have solutions containing Fe(III) mainly (say ~99%) in the form of the pale purple hexaquo ion, the pH must be around zero. As the pH is raised above 2-3, more highly condensed species than the dinuclear one noted above are formed, attainment of equilibrium becomes sluggish, colloidal gels are formed and ultimately, hydrous ferric oxide is precipitated as a red-brown gelatinous mass.

2.4 Analytical Chemistry of Iron:

The analytical chemistry of Iron has, to date, been the subject of several reviews and papers³⁻¹⁰, colorimetry being an area widely explored. The advent of micellar chemistry further widened this field with scope for potential development and improvement of methods hitherto proposed for the spectrophotometric determination of Iron.

The basic criteria for a good colorimetric technique are that it be sensitive, reproducible and selective. A <u>sensitive</u> technique being one where the coloured complex has a molar absorptivity large enough that the metal is determinable in the concentration range of the actual sample, <u>reproducible</u> when a C.V. of < 1% is calculated, and <u>selective</u> in determining the metal in question with reasonable precision in the presence of interferents.

Most of the potential organic reactants used in the spectrophotometric determination of Iron belong to the family of ligands with oxygen and nitrogen donor atoms which possess some of the following configurations of reactive groupings (a) - ().



(a)



(c)



(d)



(c)





- он

(g)





The derivatives of alizarin, polyphenols, aromatic hydroxy acids and nitrogen containing bases possessing configurations as above have all been proposed as suitable chelates for Fe(III), namely Xylenol Orange¹⁴, thiocyanate⁶, Chromal Blue G¹², Chromazurol S⁹, Chromazol KS¹¹, 2-(phenoxyacetyl) acetophenone¹⁰, Alizarin green⁸, Eriochrome cyanine R¹³ to name but a few. Literature investigations however revealed little work done with Xanthene dyes such as Pyrogallol Red and Bromopyrogallol Red, both of which are extensions of the reactive groupings (a) and (b) above. In fact Bromopyrogallol Red has been proposed as a successful chromophoric reagent for Uranium¹⁵, Silver¹⁶, Niobium¹⁷, Lanthanum¹⁸, Scandium¹⁹ and Germanium²⁰. When combined with quarternary ammonium salts, mixed ligand complexes with aluminium²¹, Zirconium²², Molybderum²³, and Tungsten²⁴ are formed.

This chapter therefore evaluates Bromopyrogallol red as a suitable chelate in the spectrophotometric determination of Fe(III). The awareness of a scarcity of information on the Fe(III)-BPR complex and the role of surfactants thereon of such complexes also rendered such studies desirable. 2.5 Experimental:

Reagents:

All solutions were prepared with de-ionised water and analytical reagent grade materials unless otherwise stated.

<u>Standard Fe(III) Stock Solution, 100 p.p.m.</u>: Prepared by dissolving 0.3580 g of Ferric Sulphate $Fe_2(SO_4)_3$ (99.9% Purity) BDH. Chemicals, in 1 litre de-aerated 1 M Sulphuric Acid.

Fe(III) Solution, 10 p.p.m: Prepared by diluting 10 mls of the stock 100 p.p.m. solution to 100 mls.

<u>Bromopyrogallol Red Solution (BPR) 0.03</u>⁸: Prepared by dissolving 150 mg BPR (dibromopyrogallolsulphophthalein). - Riedel de Haën, in 500 mls of 50% (v/v) aqueous ethanol. (Pre-mixing of EtOH and H₂O is necessary here).

Sodium Dodecyl Sulphate (SDS) Solution 1.0%: Prepared by dissolving 1 g SDS. (BDH Chemicals - special grade), in ~50 mls H_2O , heating to effect dissolution and upon cooling, transferred quantitatively to a 100 ml calibrated flask and diluted to the mark.

<u>Oetyltrimethylammonium Bromide (CTAB) Solution 0.5%</u>: Prepared as for SDS using 0.5 g CTAB in 100 mls H_2O .

<u>Gelatine, Gum Arabic, Polyvinyl alcohol Solutions 0.5%</u>: Prepared as for SDS, constant agitation being necessary to effect dissolution.

<u>Britton-Robinson Buffer:</u> Prepared by dissolving 2.4732 g Boric Acid, 3.9200 g Orthophosphoric Acid (BDH Chemicals - laboratory grade) and 2.29 mls of Glacial Acetic Acid in 1 litre H_2O , adjusted to the required pH using 1M and 0.2M NaOH.

Sulphuric Acid 0.1M: AnalaR Grade.

Final Procedure:

Place an aliquot of Fe(III) solution containing 50 µg Fe(III) in a 50 ml calibrated flask. Add 2 mls 0.5% CTAB (5 mls 0.5% Gelatine), and 10 mls BPR solution. Dilute to mark with B.R buffer, mix well and measure the absorbance at 650 nm (630 nm) in a 1 cm silica cell against a reagent blank. Determine the concentration from a calibration graph prepared using the same procedure. <u>Note</u> Apply ultrasonication (for no longer than 1 minute, due to possible temperature effects).

Apparatus:

Absorption spectra and single wavelength spectrophotometric measurements were made using a Shimadzu UV 240 recording spectrophotometer, using 1 cm silica cells at ambient temperature (about 22° C).

A Philips PW 9410 digital pH meter was used to record pH measurements.

2.6 Results and Discussion:

Bromopyrogallol Red (Fig 2.6.1) which is (3', 3''-dibromopyrogallol - sulphophthalein) has the molecular weight of 576.18 g and is a reddish brown powder.



(Fig. 2.6.1)

It possesses acid - base indicator properties, is coloured orange-yellow in strongly acidic solution, claret red when nearly neutral and violet to blue in basic solution.

The reacting ratio of Iron with BPR has been determined. As shown by Wen and Poe²⁵, the stoichimetric ratio in the complex in solution is 1Fe : 3BPR and it seems reasonable to believe²⁵ that the chelate (Fig. 2.6.2) is formed, where R_4N^+ is a quaternary ammonium ion.



(Fig. 2.6.2)

Preliminary Studies:

For the purpose of this investigation the method first examined was that of Burns and Dadgar $(1980)^{20}$, who reported considerable interference in the analysis of Germanium with BPR from Fe(III). A ratio of 1 : 10 Germanium : Iron (III) was found to exceed the tolerance limit by contributing an error of 9.5% to the apparent absorbance of Germanium.

Initial spectrophotometric examination of the Fe-BPR binary complex showed a light absorption maxium at 650 nm and that of the reagent vs. water at 580 nm. Hence, superposition of the light absorption curves of BPR and the complex was not a cause for concern (Fig. 2.6.3).



Fig. 2.6.4 Absorbance vs. time profile for 1 p.p.m. Fe^{3+} and 10^{-5} M BPR reagent at pH 1.75

The main difficulty however encountered was the slow attairment of equilibrium (at least 40 mins elapsed before stable colour development was achieved). For absorbance vs.tume profile see Fig. 2.6.4. In this case, a medium of pH 1.75 (achieved with addition of just Fe stock and BPR) limited the resultant stability to 10 minutes. Therefore, the aim of the subsequent study was to find the conditions under which a more sensitive and stable Fe-BPR complex forms rapidly in solution.

Effect of Various Dispersing Agents:

The slight bathochromic shift and sensitivity enhancement achieved when the anionic surfactant SDS was applied was the initial step towards method improvement. The structure of SDS is such that, when applied, a more soluble entity or micelle is formed creating a micro-environment for the metal ion, different to that in the absence of SDS. Most evidence points to the existence of a normal anionic micelle²⁵ due to the structure of SDS. An extensive pH study with SDS proved optimum conditions are achieved at pH 3.15 see Fig. 2.6.5. The resultant sensitivity is such that a 60% improvement is achieved relative to that in its absence with definite complex formation after 10 minutes.

The cationic surfactant CTAB, similarly employed, again gave an optimum pH of 3.15 demonstrating even more enhanced sensitivity (86% enhancement relative to that in its absence), and very stable after 10 minutes. Fig 2.6.6 illustrates such findings.



Fig 2.6.5 (a) pH profile with SDS as surfactant.



Fig 2.6.5 (b) Absorbance spectrum for Fe^{3+} -BPR-SDS micellar system (Fe³⁺ 1 p.p.m., BPR 10⁻⁵ M) pH 3.15

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Fig. 2.6.6 (a) pH profile with CTAB as surfactant.



Fig 2.6.6 (b) Absorbance spectrum for Fe^{3+} -BPR-CIAB micellar system (Fe^{3+} 1 p.p.m., BPR 10⁻⁵ M) pH 3.15.

A series of non-ionic polyvinyl alcohols of varying molecular weights were next employed. A systematic approach with a pH study on that of highest molecular weight, the optimum pH subsequently applied to the others in the series, showed that the polyvinyl alcohol of molecular weight 49,000 in a medium of pH 3.15 yielded maximum absorbance enhancement (71%) with rapid colour development after 10 - 15 minutes. All polyvinyl alcohols showed similar trends in stability. Thus, the difference in chain length and hence molecular weight manifests itself in varying degrees of enhancement attributed to a critical micelle size with a characteristic solubilising power. Figs. 2.6.7 and 2.6.8 illustrate the above.

Gelatine and Gum Arabic, being non-ionic exhibited similar trends to those of the PVA's, however Gelatine proving more sensitive again at pH 3.15. - See Fig. 2.6.9 . For % enhancement and absorbance maxima of each system at pH 3.15 see Fig. 2.6.10.



Fig 2.6.7 (a) pH profile with PVA 100,000 as surfactant.



Fig. 2.6.7 (b) Absorbance spectrum for Fe³⁺-BPR-PVA 100,000 micellar system (Fe³⁺ 1 p.p.m., BPR 10⁻⁵ M) pH 3.15.



Fig. 2.6.8 Effect of molecular weight of surfactant on the absorbance of 1 p.p.m. Fe^{3+} and 10^{-5} M BPR as a function of time at pH 3.15.



Fig 2.6.9 (a) Absorbance vs. time profiles with Gelatine and Gum Arabic as surfactants at pH 3.15.



Fig. 2.6.9 (b) Absorbance spectra for Fe³⁺-BPR-Gelatine and Fe³⁺-BPR-Gum Arabic micellar systems (Fe³⁺ 1 p.p.m., BPR 10⁻⁵ M) pH 3.15.

1			[∧] max∕rm		
	Surfactant	<pre>% Enhancement *</pre>			
			· · · · · · · · · · · · · · · · · · ·		
	SDS	61	630		
	CTAB	86	650		
	PVA 22,000	63	625		
	PVA 49,000	71	620		
	PVA 72,000	66	622		
	PVA 100,000	67	620		
	Gelatine	82	630		
	Gum Arabic	60	635		

* Enhancement calculated relative to that in the absence of surfactant.

Fig. 2.6.10 (a).

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Fig. 2.6.10 (b) Absorbance vs. time profiles with the 4 most effective surfactants at pH 3.15

Variation of Concentration of Surfactant:

Different volumes of each surfactant were added to 50 µg Fe, a maximum absorbance obtained for each volume and the optimum concentration noted. Results are such that optimum concentrations appear to depend on surfactant charge and hence its solubilizing efficacy. This, in turn determines the c.m.c and charge plays a major role on whether or not any excess reagent is complexed and subsequently contributes to absorbance. The anionic SDS promotes maximum absorbance at concentrations of 1 ml of a 2% solution in the final 50 mls, with a 12.6% variation between it and that in its absence. Cationic CTAB gives an optimum concentration of 1 ml of a 1% solution.

Non-ionic surfactants were different in that, an optimum concentration was reached, beyond which no significant difference in absorbance was observed (see Fig. 2.6.11). Hence it would seem logical to suggest that the neutral entity does not interact with the reagent (or not significantly so) either before or after complex formation. The presence of Fe (III) is the determining factor. Fig. 2.6.11 presents such results graphically.



Fig. 2.6.11 Variation of concentration of surfactant.

Adherence to Beer's Law:

Plots of absorbance vs. concentration of Fe(III) at the respective wavelength for each surfactant were drawn up each exhibiting a linear range of 0 - 1 p.p.m. Fe(III) i.e. $0 - 50 \mu$ g Fe(III). Molar absorptivities are as tabulated in Fig. 2.6.12 with corresponding statistically determined correlation co-efficients for the experimentally determined best linear range. Calibration curves are as depicted in Fig. 2.6.13.

Surfactant	€/1 mol ⁻¹ cm ⁻¹	Correlation Coefficients		
CTAB	29255	0.99950		
SDS	8075	0.99810		
Gelatine	19566	0.99737		
PVA 49,000	10932	0.99804		

Fig. 2.6.12

Conclusions are such that the most effective surfactant is CTAB, the exact mechanism of interaction is required to successfully predict such a result. Chain length and hence micelle size, pH and reagent composition are all contributors. Linearity appears to be consistent for each with most marked deviations (comparatively only occurring for the sensitive 0.1 p.p.m. Fe^{3+} , hence, being effective at low concentrations (< 1 p.p.m), our choice of optimum surfactants sensitise complex formation sufficiently with concurrent limitations of deviations from linearity.

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Fig. 2.6.13. Calibration curves for the 4 experimentally found, most effective micellar systems.

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Reproducibility Tests.

Reproducibility tests for each surfactant at 3 different concentrations along the linear portion of the calibration curve showed relative standard deviations as in Fig. 2.6.14 based on 5 replicate absorbance readings for each concentration. CTAB appears most reliable and reproducible in such cases with maximum co-efficient of variation of 1.63% at the sensitive end of the range.

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NO. OF MEASUREMENTS	1	2	3	4	5	MEAN	STANDARD DEVIATION	RELATIVE. STANDARD DEVIATION
Absorbance of 0.1 p.p.m	0.068	0.071	0.070	0.069	0.070	0.070	0.001	1.63%
Absorbance of 0.5 p.p.m.	0.288	0.288	0.291	0.287	0.285	0.288	0.002	0.75%
Absorbance of 1.0 p.p.m.	0.543	0.541	0.541	0.539	0.545	0.542	0.002	0.42%
<u>GELATINE (B)</u>								
Absorbance of 0.1 p.p.m.	0.020	0.024	0.021	0.025	0.022	0.022	0.002	9.43X
Absorbance of 0.5 p.p.m.	0.192	0.196	0.185	0.187	0.195	0.191	0.005	2.54%
Absorbance of 1.0 p.p.m.	0.345	0.349	0.350	0.345	0.350	0.348	0.003	0.74%
<u>PVA 49,000 (C)</u>								
Absorbance of 0.1 p.p.m.	0.029	0.026	0.030	0.031	0.029	0.029	0.002	6.45X
Absorbance of 0.5 p.p.m.	0.112	0.115	0.110	0.115	0.116	0.114	0.003	2.20%
Absorbance of 1.0 p.p.m.	0.201	0.205	0.206	0.210	0.205	0.205	0.003	1.57%
<u>\$D\$ (D)</u>								
Absorbance of 0.1 p.p.m.	0.021	0.019	0.021	0.020	0.021	0.020	0.001	4.47%
Absorbance of 0.5 p.p.m.	0.068	0.073	0.071	0.069	0.072	0.071	0.002	2.92%
Absorbance of 1.0 p.p.m.	0.151	0.148	0.149	0.153	0.151	0.150	0.002	1.30%

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Fig. 2.6.14 Reproducibility data using CTAB (A), Gelatine (B), PVA 49,000 (C) and SDS (D)

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Chapter III : Germanium.

3.1 Occurrence, Importance and Utilisation of Germanium.

The existence of Germanium was first suspected by Newlands (1864) as the missing number of the triad Si, Ge, Sn. Mendeleeff (1871) recognised it as a missing element in his periodic table and predicted its general chemical properties from its relationship to Sn and Si. It was first isolated as the sulphide GeS₂ from the rare mineral argyrodite 4 AgS.GeS₂ (Winkler, 1887). The development of its chemistry has been slow compared to its neighbours; this may be ascribed to its comparative rarity and high price and because early studies established that its properties seemed to fit so clearly between those of Silicon and Tin that its chemistry appeared to lack novelty. Germanium metal, the dioxide and tetrahalides are now commercially available in quantity.

During the last 20 years Germanium has gained wide acceptance and various applications in technology. The most important commercial outlet is based on the semi-conductor properties of the metal, where, in radioelectronics, it is used in the preparation of rectifier crystals (diodes and amplifiers) and transistors (triodes).

Other fields of application include pellicular resistors (up to a few megohms); Germanium dosimeters for measuring biological doses of fast neutrons; coating of reflectometers by a Germanium film with a high reflection capacity; Germanium counters; highly sensitive thermometers for measuring temperatures close to absolute zero; infra-red detectors of radar instruments and special alloys. GeO₂ is used in the preparation of optical glass with a high refractive index and as a catalyst in oxidation reactions. Organogermanium compounds are used in the production of lubricating oils.

Being an ubiquitous component of living organisms Germanium has however, no structural function nor is it a proven required trace element for plants or animals. Having a low order of toxicity (Germanium compounds in general are much less poisonous than those of Tin and Lead), Germanium is of some interest in two widely separated areas of biology and physiology: its erythropoietic effect and the possible bacteriocidal or fungicidal effect of organogermanium compounds. Stimulation of the formation of red blod cells (erythrocytes) by injections of GeO2 was first reported in 1922 and caused a flurry of activity aimed towards the treatment of anemias. While results proved inconsistent, the marginal toxicity of most Germanium compounds leads to the recurrent hope that some rather particular organogermanium structures will be found to be effective against invading micro-organisms or may restore balance to a pathogenic condition. without being dangerously toxic to a human host. So far, however, any such chemotherapeutic acitivity of Germanium remains in the realm of hopeful speculation.

3.2 Structural Chemistry of Germanium.

Germanium, like Silicon, crystallises in the diamond lattice. It is brittle with a bright lustre and is stable to H_2O , 50% NaOH, conc.HCl and H_2SO_4 . The metal is tarnished by aqueous caustic soda or conc. HNO_3 ; it dissolves in 3% H_2O_2 with precipitation of the dioxide.

Germanium forms compounds or eutectics with a wide range of metals or metalloids. All of the alkali metals form compounds M-Ge. Sodium germanide is a hard, dense, pyrophoric material which is monoclinic whereas Potassium, Rubidium and Cesium germanide are cubic. RbGe forms bronze crystals and CsGe is black (Schaefer and Klemm, 1961; Busmann, 1961). The Mg-Ge system shows two eutetics and Ca and Ge react at a red heat forming a dark grey crystalline powder.

The addition of small amounts of Ge to aluminium alloys improves hardness and rolling properties. Ge and Si are evidently completely miscible in solid solution whereas Ge and Pb only so in the liquid state (Briggs and Benedict, 1930). The resemblance of Ge(IV) to Si is very marked¹. The elementary forms of Ge and Si, some halides, many oxy compounds and analogues of all the major types of silicates and aluminosilicates are isostructural. There is however, a greater tendency of Ge(IV) to form 6 bonds e.g. 6 co-ordination in the stable tetragonal form of GeO_2 in contrast to 4 co-ordination in the soluble form. Formation of salts e.g. $Ge(SO_4)_2$, $Ge(ClO_4)_4$ and $GeH_2(C_2H_4)_3$ by Ge(IV) is more applicable to Germanium than any of the other triad members.

Elements of the carbon group are also characterised by their tendency to catenation and chains of GeCl_4 and Ge_2Cl_2 are commonly found. Being a metalloid Germanium also forms strong and durable bonds to carbon with bond dissociation energies² of 59.1, 56.7 and 56.8 kcal/mole for Ge-CH₃(methyl), Ge-C₂H₅ (ethyl) and Ge-C₃H₇ (propyl) respectively. Bonds to hydrogen, oxygen and the halogens are also considered strong. Hence there are many varieties of organogermanium compounds, the roster of individual compounds reaching 2,300 by 1967³.

The concept of π bonding involving unoccupied 4d orbitals has passed through a controversial stage. There is scarcely an anomoly in Germanium chemistry that has not been ascribed to π bonding. In most of its compounds Ge forms four sp³ tetrahedrally disposed σ bonds to other elements. When bonded to electronegative elements the co-ordination number can increase to six as in $(Me_3N)_2GeF_4$. These are octahedral d^2sp^3 complexes in which all of the bonds to Ge have σ symmetry. In its divalent state Ge has not yielded stable monomeric compounds and the dihalides e.g. GeF₂ are associated by bridging fluorine groups. Germanium Dioxide GeO_2 exists in four forms, the hexagonal "soluble" form ($\alpha - \text{GeO}_2$), the tetragonal "insoluble" form ($\beta - \text{GeO}_2$), the cubic (β -cristobalite forms) and the amorphous vitreous form. α -GeO₂ is obtained by the hydrolysis of Germanium tetrahalides or alkali metal germanates. The insoluble $\hat{\beta}$ -GeO₂ is formed by heating Germanium dioxide containing small amounts of alkali metal salts or hydroxides at 200 - 500°C. α and β forms are enantiotropic, the transition point being at 1033 + 10°C.

The cubic form arises on heating ammonium-germanic zeolite to about 300° C. The amorphous vitreous form appears when fused GeO₂ is rapidly cooled. It devitrifies to the soluble hexagonal form.

The properties of Germanium dioxide are shown in Fig. 3.2.14.

	Form							
Parameter	soluble	insoluble	vitreous (amorphous)					
Crystallographic form	Hexagonal, low- temperature quartz type	Tetragonal, rutile type	-					
Density, g/cm ³ , 25°C	6.239	4.228	3.637					
Melting point, °C	$1116 \pm 4^{\circ}$ (1112 ± 4° (1585))	1086 ± 5°	-					
Boiling point, °C	1870 [202]	-	-					
Solubility, mg/100 g	453 (25°C)	0.25 (25°C)	518.4 (30°C)					
Action of HF	Dissolves	Practically no action	Readily dissolves					
Action of HCl	44	As above	As above					
Action of 5 N NaOH	64	Dissolves very slowly	-					

3.3 Solution Chemistry of Germanium.

Divalent Ge compounds are unstable in solution and the existence of Ge^{2+} cations in aqueous solution has not been established. Because they are readily hydrolysable and tend to form complexes, they probably appear only as an intermediate stage in oxidation/reduction reactions⁶. Complex anions $GeHfI_3^$ exist in solutions of hydrohalic acids. Solutions of $Ge(OH)_2$ and sodium hydroxide have a colloidal character. Tetravalent Ge compounds also readily undergo hydrolysis. Germanium is present in aqueous solutions of GeO_2 in the form of anionic, cationic and neutral hydroxo complexes depending on the concentration of hydrogen ions. The first and slowest stage of the dissolution of GeO_2 in water is said to be the formation of $H_2GeO_3^{-7}$.

 $GeO_2 + aq. \longrightarrow [GeO_2.aq] \longrightarrow GeO(OH)_2 + aq.$ In the presence of H⁺ or OH⁻ ions, parallel reactions are possible:-

 $GeO_2 + H_3O^+ ---> Ge(OH)_3^+$ $GeO_2 + OH^- ---> HGeO_3^-$

The hydroxo complexes of Ge tend to polymerize, the ratio between monomeric and polymeric forms being determined by the overall concentration of Ge and hydrogen ions.

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In concentrated solutions ($[GeO_2] > 0.01$ M and a pH of 6.9 - 9.4) penta - $(H_2Ge_5O_{11})^8$, hepta - $(H_4Ge_7O_{16})^8$ and octa - germanic acids are formed⁹.

Above and below these pH values, metagermanic acid is formed by depolymerization:-

$$2 \text{ HGeO}_3^- + 3 \text{ H}_2\text{GeO}_3 < ---> \text{Ge}_5\text{O}_{11}^{2-} + 4 \text{ H}_2\text{O}_3$$

with an equilibrium constant of 4.55×10^{-9} ¹⁰.

The distribution of the different monomeric forms of Germanium at $[GeO_2] \ll 0.01$ M as a function of the pH is shown in Fig. 3.3.1.



Fig. 3.3.1 Dependence of distribution (A) of Ge(IV) hydroxo complexes on pH ([GeO₂] < 0.01 M):

1) Ge^{4+} ; 2) $GeOH^{3+}$; 3) $Ge(OH)_2^{2+}$; 4) $Ge(OH)_3^+$; 5) $Ge(OH)_4$.

3.4 Analytical Chemistry of Germanium:

Because Germanium is a metalloid it forms two types of complexes⁴. Germanium, like Silicon in the same group, forms complexes with oxygen containing ligands and easily forms heteropolyacids with Molybdenum and Tungsten. However, like Tin, also in the same group, Germanium forms sulphide complexes, which, although weaker than the Tin complexes, still place Germanium in the hydrogen sulphide analytical group. Both form complexes with nitrogen containing ligands, e.g. 8-hydroxyquinoline¹¹ and EDTA¹² but Silicon does not.

For the purpose of this research only complexes of organic reagents are of interest, namely complexes of oxalates, hydroxycarboxylic acids, glycols, polyhydric alcohols, ortho-diphenols and ortho-hydroxycarbonyls. Hydroxazo compounds and derivatives are also successful chromophoric reagents for Germanium.

The complexes of Germanium with the following acids have been described: tartaric¹³, citric¹⁴, lactic¹³, dihydroxymaleic¹⁵ aliphatic α -hydroxyacids with carbon chain lengths from C₆ to C₁₆¹⁶ and others. The composition of the majority of such complexes corresponds to the ratio Ge:L of 1:2, in the case of tartrate complexes, the compositions GeT, GeT₂ and Ge₂T₃ have been found.

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Addition of a di - or polyhydric alcohol to a solution of GeO_2 causes an appreciable drop in pH due to the formation of a complex acid stronger than Germanic acid¹⁷, the stability and acidity of the complexes increasing with increase in the carbon chain length, and the number of hydroxy groups in the ligand. Spatial arrangement of the hydroxy groups and the conformation of the ligand also affect these properties. It was found that the stability of the Germanium complexes with hexitols increases in the order d-mannitol-d-dulcitol- d-sorbitol.

Ge(IV) forms two types of compounds with simple orthodiphenols (pyrocatechol, pyrogallol, 2,3, -dihydroxynaphthalene, etc). The first consists of neutral complexes which dissolve with difficulty having a ratio Ge : L = 1 : 2; these are the so-called Germanium diphenols. The second type are the acidic soluble complexes having a ratio Ge : L = 1 : 3; these are the phenolgermanic or tridiphenolgermanic acids¹⁸. Fig 3.4.1 depicts the structure of each complex, confirmed by IR-spectral data.



Fig. 3.4.1: Germanium diphenol (I), Phenolgermanic Acid (II).

Phenolgermanic acids are more stable than polyologermanic acids, conversion occurring in solution with changes in concentration of the reagent.

The presence of acid substituents in the molecule of ortho-diphenol does not interfere with the formation of tridiphenolgermanic acids e.g. 2,3,-dihydroxynaphthalene-6-sulphonic acid¹⁹ and pyrocatechol-3,5-disulphonic acid¹⁸, the complexes formed being ionised completely to the first two stages.

Ortho-hydroxy carbonyl compounds, as depicted in chapter 2 (a) - (j) are widely employed in spectrophotometric determination of Germanium. The hypothesis that the ortho-hydroxy carbonyl grouping is the ring-forming group in a reagent of this type²⁰ was first rejected and the chemical reaction with Germanium was regarded merely as the formation of phenolgermanic acids having the composition H_2GeL_2 , as in the case of simple orthodiphenols. Subsequent research on the composition and properties of the complexes formed, taking into account the state of Ge in the solutions and reagents, has established that in an acidic medium the complex formation takes place with the participation of the hydroxycarbonyl grouping, even if an ortho diphenol group is present in the ligand molecule at the same time. Moreover, if the reagent of an ortho-diphenol type is capable of undergoing a tautomeric ortho-diphenol - ortho-hydroxyquinone rearrangement, then in acid media it reacts with Germanium as ortho-hydroxy quinone.

Of the many compounds of ortho-hydroxycarbonyl derivatives of triphenylmethane, Pyrocatechol violet (PCV) is most widely used for the photometric determination of Ge(IV). Reaction of PCV with Ge has been observed in a wide range of hydrogen ion concentrations.

In the absence of Gelatine^{21,22} at pH 4.8, Ge forms a purple complex with PCV having a maximum absorbance at 555 nm. At pH 3.4 -3.6 and in the presence of Gelatine, the complex is green with λ max at 650 nm.

A ternary complex between Ge, PCV and CTAB²³ has also been proposed, which, in terms of sensitivity appears to be similar to the Phenylfluorone and Gum Arabic method²⁴, Phenylfluorone being an hydroxycarbonyl compound of the Xanthene series. Of this series, Pyrogallol red (PR)²⁵ and Bromopyrogallol red (BPR)²⁶ have been successfully applied in Ge determination. BPR forms two complexes with Ge, a slightly stable complex at pH 8 - 12 and a more stable one at pH 0.5 - 4.5, where the complex composition is GeL₃. GeOH³⁺ is the co-ordinating cation and the anion of the reagent, the singly charged hydroxy group, is co-ordinated. The red-violet complex has a λ max at 550 nm with an extinction co-efficient $\varepsilon = 2.05 \times 10^4$. The binary complex of BPR with Ge forms an associate ternary complex with diphenylguanidine²⁷, extractable by higher alcohols. Campe and Hoste²⁸ have found p-dimethylamino phenylfluorone in alcoholic solutions, a sensitive method in Ge determination. A 1:4 complex is formed and Beer's Law is obeyed for concentrations up to 0.24 μ g Ge/ml. However, in this case, stability and intensity of the colour produced are dependent upon temperature and the amount of H₂O in solution.

Hematein (a derivative of γ -pyrone) with Germanium in a weakly acidic medium forms a slightly soluble purple complex, solubilized with gelatine or gum arabic ²⁹ and obeys Beer's Law in the concentration range 0.08 - 1.6 µg Ge/ml.

Literature investigations on hydroxazo reagents described Stilbazo as a suitable chromophoric entity. At pH 6 Beer's Law holds for 5 - 73 µg Ge with $\varepsilon = 1.78 \times 10^4$ 1 mol⁻¹ cm^{-1 30}.

An attempt to improve the 'Burns and Dadgar'²⁴ method for Germanium determination with Phenylfluorone is the subject of this chapter. Like other reagents of oxygen co-ordinating groups, Phenylfluorone reacts sensitively in acid solution with oxyphilic elements of higher valence⁵ such as Molybdenum(VI), Titanium(IV), Tin(IV), Zirconium Nicbium and Tantalum.

For Ge, a series of polyvinyl alcohols of varying molecular weight are examined as potential dispersing agents yielding interesting conclusions on dependence of reagent size, weight, structure and charge on such parameters as c.m.c., micelle size and hence sensitivity and selectivity. 3.5 Experimental

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Reagents:

All solutions were prepared with de-ionised water and analytical reagent grade materials unless otherwise stated.

Standard Ge(IV) Stock Solution, 100 p.p.m: Prepared by dissolving 14.41 mgs of pure Germanium dioxide GeO₂ in 100 mls H_2O . Gentle heat may be necessary to effect dissolution.

<u>Ge(IV) Solution, 10 p.p.m.</u>: Prepared by diluting 10 mls of the stock 100 p.p.m solution to 100 mls with H_2O .

<u>Phenylfluorone Solution (PF) 0.036</u>; Prepared by dissolving 0.36 g Phenylfluorone in 800 mls of ethanol, then adding 40 mls of 20% v/v H_2SO_4 and diluting to 1 litre with H_2O_4 .

<u>Polyvinyl Alcohol Solution (PVA) 0.30</u>; Prepared by dissolving 0.30 g Polyvinyl alcohol in 100 mls hot H_2O , frequent stirring necessary to effect dissolution.

<u>Hydrochloric Acid Solution:</u> Prepared by diluting 250 mls conc.HCl (analar grade) to 1 litre with H_2O .

Final Procedure:

Place an aliquot of Ge(IV) solution containing 50 ug Ge(IV) in a 50 ml calibrated flask. Add 20 mls of HCl solution, 5 mls PVA 49,000 or 0.5% Gum Arabic and 12.5 mls Phenylfluorone solution. Dilute to mark, mix well and measure the absorbance at 502 nm or 505 nm in a 1 cm silica cell against a reagent blank. Determine the concentration from a calibration graph prepared using the same procedure.

Note: Apply ultrasonication (for no longer than 1 minute, due to possible temperature effects).

Apparatus:

Absorption spectra and single wavelength spectrophotometric measurements were made using a Shimadzu UV 240 recording spectrophotometer, using 1 cm silica cells at ambient temperature (about 22^oC).

A Philips PW 9410 digital pH meter was used to record pH measurements.

3.6 Results and Discussion:

Phenylfluorone (Fig. 3.6.1) which is (2,6,7 - trihydroxy-9 phenylfluorone) has the molecular weight of 320.3 g and is an orange powder.



Fig. 3.6.1

The reacting ratio of Germanium with Phenylfluorone has been determined. As shown by Schneider³¹ the stoichometric ratio in the complex in solution is 1 Ge : 2 PF and it seems reasonable to believe 5 that the chelate (Fig 3.6.2) is formed.



Fig. 3.6.2

Preliminary Studies:

For the purpose of this investigation, the method first examined was that of R.F. Tivnann, Universal-Matthey Products Ltd., Middlesex, England - a proposed improvement to the 'Burns and Dadgar' method²⁴. A series of polyvinyl alcohols of varying molecular weight (22,000, 49,000, 72,000 and 100,000) and varying degrees of hydrolysis (75% and 100%) was examined, the required negative pH's achieved for sample and blank solutions upon addition of 20 mls HCl solution in the final 50 ml volume (see experimental section). Two recently acquired PVA's (A) and (B) (varying degrees of polymerisation :- 1600 \pm 100), ex Matheson Coleman, Bell of Cleveland, U.S.A., were also examined. Observations were such that PVA of molecular weight 49,000 at a maximum wavelength of 502 nm best sensitised the reaction (stable colour development after 10 minutes). Results are as presented in Fig. 3.6.3.

Surfactant	T	t≓0	t=10	t=20	t=30	t=40	t=50
	1						
No. PVA	ļ	0.972	0.946	0.928	0.907	0.901	0.890
PVA (A)	1	0.929	0.934	0.934	0.934	0.932	0.930
PVA (B)	I	1.052	1.032	1.010	0.998	0.982	0.978
PVA (75%)	I	1.125	1.122	1.118	1.110	1.008	1.001
PVA (100%)	1	1.036	1.098	0.946	0.908	0.901	0.891
PVA (22,000)	1	1.024	1.002	0.974	0.912	0.888	0.852
PVA (49,000)	I	1.012	1.024	1.024	1.024	1.024	1.024
PVA (72,000)	I	1.029	1.032	1.016	1.006	0.996	0.988
PVA (100,000)	1	1.029	1.022	1.019	1.018	1.016	1.010
			1	1	1	1	

Fig. 3.6.3 Absorbance vs. time data for a series of PVA's as surfactants in the Ge^{4+} -PF-PVA micellar system (applying method 2 :- R.F. Tivnann, England).

For PVA 49,000, (A) and (B), both methods as above were compared. Results (Fig. 3.6.4) again indicate that with method 2 (R.F. Tivnann) and using PVA 49,000, maximum sensitivity and stability is achieved. In the absence of any surfactant however, observations were such that method 1 (Burns and Dadgar) gave stable colour formation after 40 minutes, (λ max at 520 mm) whereas method 2 exhibits a steady decrease in absorbance over 60 minutes (λ max at 510 nm). It was also interesting to note the broader and less well defined profile with method 1 and the sharper and more sensitive (albeit decreasing) absorption profile of method 2. Hence, the potential for development (micelle formation with a suitable dispersant) using method 2 was realised from the outset. pH and reagent concentration are obviously critical in such analyses (Fig. 3.6.5). In an effort to improve method 1, increasing the PVA concentration threefold only served to decrease the absorbance by 4.8%, (Fig. 3.6.6). Additionally, for both methods, it was observed that no turbidity was produced after 48 hours indicating stable complex and micelle formation in acidic media.

Conclusions at this point were such that the proposed improved method was certainly worth pursuing, hence a complete study of anionic, cationic and non-ionic dispersants was undertaken. PVA (B) exhibited un-interesting data (steady decrease in absorbance observed). Triton X-100, Gelatine, SDS and CTAB although proving sensitive and relatively stable (compared to that in the absence of surfactant) did not sensitise the reaction sufficiently effectively as did Gum Arabic (Fig. 3.6.7). A slight bathochromic shift of 5 nm was observed - 505 nm, all others - 510 nm. Stability was reached after 10 minutes with very slight decrease in absorbance (0.9%) after 55 minutes.



Fig. 3.6.4 (a) Absorbance vs. time profiles for various PVA's comparing Method 1 (Burns & Dadgar²⁴) and Method 2 (R.F. Tivnann, England).



Fig. 3.6.4 (b) Absorbance spectrum for Ge⁴⁺-PF-PVA 49,000 micellar system, applying Method 2 (R.F. Tivnann, England).



Fig. 3.6.5 Comparison of absorbance spectra for Ge⁴⁺-PF binary system applying Method 1 (Burns & Dadgar²⁴) and Method 2 (R.F. Tivnann, England).

550.0

350 0

300.0

450 0

-650.0

 λ / nm

750 0



Fig. 3.6.6 Effect of increased PVA concentration on the absorbance vs. time profile of 1 p.p.m Ge^{4+} , 2.8 x 10⁻⁴ M PF solution.



Fig. 3.6.7 (a) Effect of different surfactants on the absorbance vs. time profiles of Ge^{4+} applying Method 2 (R.F. Tivnann, England).



Fig. 3.6.7 (b) Absorbance spectrum for the Ge⁴⁺-PF-Gum Arabic micellar system with Method 2 (R.F. Tivnann, England).

Adherence to Beer's Law:

Calibration curves applying PVA 49,000 and Gum Arabic as dispersants yielded extinction co-efficients of 70708 and 74119 1 mol^{-1} cm⁻¹. Experimentally determined linear ranges of 1.5 p.p.m. i.e. 75 µg Ge in the final 50 ml volume were confirmed statistically by correlation coefficients of 0.999964 and 0.9982336 respectively. These are considerable improvements to the linear ranges of 10 and 30 µg Ge established by Burns and Dadgar using both Phenylfluorone and Bromopyrogallol red respectively. Fig. 3.6.8 illustrates such findings.

Reproducibility Tests:

Reproducibility tests for the above 2 most effective surfactants i.e PVA 49,000 and Gum Arabic at three different concentrations along the linear portion of the calibration curve show mean, standard deviation and relative standard deviation as in Fig. 3.6.9. Both dispersants exhibit similiar trends in reproducing data at different concentrations.



Fig. 3.6.8 Calibration curves for Ge^{4+} -PF-PVA 49,000 (502 nm) and Ge^{4+} -PF-Gum Arabic (505 nm) micellar systems applying Method 2 (R.F. Tivnann, England).

NO. OF MEASUREMENTS	1	2	3	4	5	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION.
Absorbance of 0.2 ppm Ge	0.204	0.206	0.203	0.206	0.203	0.204	0.002	0.74%
Absorbance of 1.0 ppm Ge	0.972	0.978	0.969	0.976	0.972	0.973	0.004	0.37%
Absorbance of 1.5 ppm Ge	1.460	1.456	1.455	1.463	1.467	1.460	0.005	0.34%

(A)

NO OF MEASUREMENTS	1	2	3	4	5	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION
Absorbance of 0.2 ppm Ge	0.140	0.139	0.142	0.143	0.142	0.141	0.002	1.17%
Absorbance of 1.0 ppm Ge	0.940	0.938	0.943	0.943	0.937	0.940	0.003	0.30%
Absorbance of 1.5 ppm Ge	1.530	1.526	1.528	1.526	1.525	1.527	0.002	0.13%

Fig. 3.6.9 Reproducibility Data using PVA 49,000 (A) and Gum Arabic (B)

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2

Chapter IV : Tin.

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4.1 Occurrence, Importance and Utilisation of Tin:

Tin is found in nature almost exclusively as the Tin(IV) oxide known as Cassiterite or Tinstone. Small quantities of stannite, Cu₂S. FeS.SnS₂, are known and occasionally small amounts of Tin metal are found in nature along with gold.

Cassiterite is found as primary deposits interspersed in other rocks particularly as "reef-tin" in granite, or alternatively in secondary deposits as "stream-tin", mixed with large quantities of clay and sand.

Despite the 78.6% of Tin in pure SnO₂ the Tin ores for extraction of the metal often contain only a few percent of Tin. Initial concentration is carried out by floation removal of lighter rocks, such as silica and magnetic removal of certain impurities such as tungsten materials.

Cassiterite is reduced by carbon in a blast or reverberatory furnace, the crude molten Tin usually contaminated with Iron, which is then removed by oxidation. Tin is extensively recovered from Tin plate scrap either by electrolysis, whereby the scrap is made the anode in a caustic soda cell, or by detinning with chlorine to produce Tin(IV) chloride. Iron, unlike Tin is not readily attacked by dry chlorine. The primary Tin consumption for the U.S.A, Japan, U.K., Germany and France for 1970 totalled over 120,000 tons. This was utilised as timplace (47%), solder (21%), bronze (8%), babbitt (6%) and timning (5%), the remaining 13% utilized for a wide miscellany of alloys and chemicals.

Applications in industry and commerce include use of Tin(IV) oxide as an opacifier for vitreous enamels, in ceramic glazes and as a polishing powder. Tin chlorides are used to weight natural silk, stabilize soap perfumes, silver glass mirrors and as chemical reducing agents. Tin(II) fluoride finds extensive use as an additive to dentifrices.

Monobutyltin compounds stabilize plastic films, and dibutyl and other organotins are present in up to 1% by weight of Tin in polyvinyl chloride, as a stabilizer. Tributyltin compounds are used in industrial fungicides, insecticides, anti-fouling paints and disinfectants and triphenyltin derivatives are now manufactured in hundreds of tons for agricultural pesticide purposes.

Tin is also one of the very important alloying metals where small changes in composition are made to suit specific purposes. Approximately 20% of the world Tin production goes to make solders of different types, the Tin present conferring the ability of the solder to stick metals together. True bronzes are copper based Tin alloys with a good combination of chemical resistance, mechanical strength and ease of manufacture.

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Tin rich babbitt alloys find very extensive use as bearing metals in marine and automobile engines. Table 4.1.1 lists representative compositions of some Tin alloys.

Alloy	₿ Sn	% Q 1	₹ Pb	∜ Sb	% bi
Tin foil	88	3	8	1	-
Babbitt	90	4	-	6	-
Soft Solder	50	-	-	-	50

Table 4.1.1 Representative compositions of some Tin alloys.

4.2 Structural Chemistry of Tin.

Tin has two crystalline forms. Above 18° the stable form is the so-called β or white Tin and below this the stable form is α - or grey Tin. Carbon, Silicon, Germanium and grey Tin all occur with the diamond structure, the valency electrons becoming increasingly mobile with increasing atomic weight so that Si, Ge and Sn(α) have conductivities increasing in that order. The conductivities are much higher than those of insulators e.g. diamond, but many times less than those of true metals. Hence, like Ge, Sn is a semi-conductor.

 β -or white tin has the atoms in a distorted octahedral configuration with 4 nearest neighbours at 3.016 Å in the form of a very flattened tetrahedron and 2 further neighbours at 3.175 Å. Thus, the element represents a further step away from the covalent low co-ordinate structure towards the high co-ordinate structures with close-packing, typical of metals. Once started, at low temperatures, the conversion of β -(normally utilised) to the α - Sn form proceeds quite rapidly, however, due to the very different crystalline forms and densities of the two allotropes this conversion causes the Tin to completely crumble and powder.

4.3 Physical and Chemical Properties.

Sn is more reactive than C, Ge or Si and is attacked by halogens, alkalis, oxidising and non-oxidising acids. Burning Tin at white heat produces Tin(II) oxide. Dilute acids only attack Tin slowly to give Tin(II) salts and hydrogen. Concentrated nitric acid produces the hydrated Tin(IV) oxide sometimes called metastannic acid. Tin evolves hydrogen with hot alkali solutions to form alkali stannates.

Some physical properties of Tin are outlined in Table 4.3.1.

States II and IV for Tin are both reasonably stable and interconverted by moderately active reagents. With a ground state configuration of $5s^2$ $5p^2$ it can form covalent Sn(II) compounds with use of two unpaired p-electrons. Incorporated into an sp^2 or sp^3 hybridized bond situation, the former results in a bond angle of about 120° in an SnX₂ molecule, where the latter presents a directional lone pair which can behave as a donor ligand to metal etc. In such cases it is possible for the Tin atom to act simultaneously as a π electron acceptor, thus increasing the overall strength of the Tin-acceptor atom bond. The large size of the Sn^{2+} ion gives it usually an octahedral environment in materials containing smaller ions such as fluoride or oxide; maximum distortion to be expected in such compounds of Tin(II). The extra stabilization and hence the extent of distortion will however fall rapidly with increasing Tin-anion distances.

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| Configuration | Ionization Energies /e.V. | | | | | Electronegativity | Ionic radii/A | |
|-------------------------------------------------------|---------------------------|------------------|------------------|------------------|------------------|-------------------|------------------|------------------|
| | Sn ⁺ | sn ²⁺ | sn ³⁺ | Sn ⁴⁺ | Sn ⁵⁺ | | Sn ²⁺ | Sn ⁴⁺ |
| (Kr) 4d ¹⁰ 5s ² 5p ² | 7.34 | 14.6 | 30.5 | 40.7 | 72.3 | 1.8 | 1.02 | 0.71 |



Tin(IV) compounds, unlike Tin(II), make extensive use of the 5d orbitals. Thus, for example in complexes such as $(CH_3)_3SnCl.C_5H_5N$ the 5-co-ordinate Sn atom is $Sp^{3}d$ hybridized in a trigonal bipyramidal environment. Similarly, in octahedral molecules or ions such as L_2SnCl_4 (where L represents lone pair donors such as amines, ethers or phosphines) and $SnCl_6^{2-}$ the 5d orbitals are utilised to form $Sp^{3}d^{2}$ hybrid orbitals for largely covalent bonds. 7-co-ordination is found in $Me_2Sn(NCS)_2(terpy)$ where the three N of the terpy and the two NCS groups form an almost regular pentagon with the methyls on the axis completing a pentagonal bipyramid.

The elements of group IV have an extensive organometallic chemistry² and a wide variety of MR_4 and M_2R_6 compounds exist, with σ metal-carbon bonds conferring considerable stability. Organotin compounds have been studied for their pharmaceutical and biocidal properties. Tetra-alkyl and tetra-aryl tins are either colourless liquids or white crystalline solids stable to air and water; many of them now available in commercial quantities.

The tendency to catenation (typical of Group IV elements and previously discussed for Ge) is manifested in such compounds as Sn_2H_6 and ring compounds of the formula $(MR_2)_n$ where M = metal, n = 4, 5 or 6 and R = phenyl, methyl are known for Sn. The chemistry of the Tin compounds is particularly well explored and both CIS and TRANS compounds are known. There are also a limited number of penta-substituted complex ions including MF_5^- having a CIS fluorine-bridged polymeric structure.

 SnF_2 has a tetrameric structure based on an Sn_4F_4 puckered 8-membered ring. The Sn-F-Sn bridge angles are 135° , the SnF distances average 215 pm and each Tin also carries external F with a 207 pm bond length. The Sn atom is thus at the apex of a triganol pyramid with FSnF angles of 84° . Much longer Sn-Fbridges of about 290 pm link these 8-membered rings together.

Although not directly related, the structural chemistry of Tin and its compounds (including physical and chemical properties) and its analytical chemistry (of more interest for this thesis) are necessarily discussed in unison to enable one to postulate intelligently the formation of a complex and rationally discuss its composition and reactivity/stability in various media.

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4.4. Solution Chemistry of Tin.

Tin(II) hydroxide is not known. The hydrolysis of Tin(II) salt solutions under controlled conditions indicates the presence of the ions SnOH^+ , $\text{Sn}_2(\text{OH})_2^{2+}$ and $\text{Sn}_3(\text{OH})_4^{2+}$ via :-

 $\text{Sn}^{2+} + 2\text{H}_2\text{O} = \text{SnOH}^+ + \text{H}_3\text{O}^+$

and it has been $proposed^1$ that this has a ring structure as in Fig 4.4.1.

(2))



Fig. 4.4.1 Structure of $Sn_3(OH)_4^{2+}$.

Single crystals of the Tin(II) oxide-hydroxide compound $3SnO.H_2O$ are obtained by the very slow hydrolysis of Tin(II) perchlorate solution.

It is interesting to note that the structure of the only well-characterised solid hydroxide phase $Sn_6O_8H_4$ can be derived by the condensation and deprotonation of two of the cyclic ions $Sn_3(OH)_4^{2+}$ which are believed to predominate in solution. Tin(II) oxide dissolves in alkalis to form the hydroxy-stannate(II) ion $Sn(OH)_3^{-}$, many salts of which have

been isolated.

Additionally, the oxotetrahydroxyditin anions (Fig 4.4.2)



Fig. 4.4.2 $(Sn_2O(OH)_4)^{2-}$.

are known and are partial dehydration products of the $Sn(OH)_3^$ anions. Thus, whereas Ba $(Sn(OH)_3)_2$ is the product of the interaction of barium hydroxide solution and $NaSn(OH)_3$ solution at $35^{\circ}C$, at higher temperatures the salt Ba $(Sn_2O(OH_4) of$ the dehydrated anion is formed⁴. Tin(IV) hydroxide is not known. Hydrolysis of Tin(IV) salt solutions produces a white voluminous precipitate, which is not detectably crystalline and may contain bonded water in a tin oxide gel. The freshly prepared material is called α - stannic acid and is easily soluble in acid. Ageing produces β - stannic acid (or metastannic acid), which is more inert in acids and which can be obtained directly from Tin and concentrated nitric acid.

The drying of Tin(IV) oxide gel at 110° gives a reproducible product $SnO_{3}H_{2}$, which loses water stepwise between 110° and 600° to produce crystalline cassiterite⁵.

Fusion of β - stannic acid with excess of alkaline hydroxide produces the crystalline salts $M_2' \operatorname{Sn}(OH)_6$; and $\operatorname{Sn}(OH)_6^{2^-}$ ions are also well characterised in many other salts⁶. The hexahydroxytin(IV) anions have the octahedral structure shown in Fig. 4.4.3.



Fig. 4.4.3. Structure of the hexahydroxytin(IV) anion $Sn(OH)_6^{2^-}$.

The hydrolysis of organotin halides gives rise to organotin hydroxides of different types many of which, however, show a marked tendency to condense with loss of water. In analogy to Germanium, Tin is bi- and quadrivalent in its complexes, the co-ordination number of Sn(IV) most frequently being 6 and complexes mainly formed with ligands containing oxygen fluorine or sulphur as donor atoms. Sn(II) usually has co-ordination number 3 or 4 the latter forming planar species and exhibiting a prevailing affinity for oxygen as donor atom. Common organic reagents for spectrophotometric determination of Tin include EDTA, 8-hydroxyquinoline, lumogallion, phenylfluorone and pyrocatechol violet to name but a few. In fact, chelometric determination of Tin, using the above mentioned, has been extensively reviewed by Pribil⁷.

Rhodamine B^8 (an Xanthene derivative) as is Bromopyrogallol Red⁹ have both been used in Tin determination, the latter more recently (1980) in an attempt to improve the Dagnall, West and Young method¹⁰ using Catechol violet. In such a case sensitivity was reported as $\varepsilon = 30,000 \ 1 \ mol^{-1} cm^{-1}$ which fails to achieve the desired improvement (compare $\varepsilon = 95,600$ $1 \ mol^{-1} cm^{-1}$ using Catechol violet). Both methods make use of the surfactant CTAB, however, Catechol violet is reported to have the added advantage over BPR in that a considerable bathochromic shift (107 mµ) of the wavelength of maximum absorption is observed, thereby improving sensitivity.

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Phenylfluorone and Dithiol (toluene - 3,4 - dithiol) were previously recommended by Sandell³. Unlike Catechol violet with such reagents the Tin complex has to be held in colloidal solution by means of a dispersing agent such as Gelatine. Sensitivities of Catechol violet and Phenylfluorone were not dissimiliar however, when compared by Ross and White¹¹ ($\varepsilon_{555nm} = 6.5 \times 10^4$ l mol⁻¹cm⁻¹ and $\varepsilon_{530} = 4.0 \times 10^4$ l mol⁻¹cm⁻¹ respectively). Dagnall, West and Young¹⁰ since claim to have improved the former as discussed above. Dithiol, however, is much less sensitive with $\varepsilon_{530nm} = 0.58 \times 10^3$ l mol⁻¹cm⁻¹.

While recognising the advantages of Catechol violet complexation over most methods, current efforts in our laboratory have been focused on further improvement using this reaction through optimization with various surfactants. Additionally, since Pyrocatechol violet has been successfully applied as a colorimetric reagent for several metals¹², its specificity being largely dependent upon acidity, this investigation was undertaken to confirm its applicability as a colorimetric reagent for Tin.

On the basis of this study, a colorimetric method is proposed that is as sensitive as and less subject to error than those based on reagents currently in use. 4.6. Experimental.

Reagents:

All solutions were prepared with de-ionised water and analytical reagent grade materials unless otherwise stated.

Standard Sn(IV) Stock Solution, 100 p.p.m.: Prepared by dissolving 29.54 mgs of $SnCl_4$. 5H₂O in 100 mls 1N HCl.

<u>Sn(IV) Solution, 10 p.p.m</u>: Prepared by diluting 10 mls of the stock 100 p.p.m solution to 100 mls with 1N HCl. (Prepared fresh daily).

<u>Standard Sn(II) Stock Solution, 100 p.p.m</u>: Prepared by diluting 10 mls of 1000 p.p.m atomic absorption grade SnCl₂ to 100 mls in 1N HCl, or,

prepared by dissolving 15.97 mgs SnCl₂ anhydrous in 100 mls 1N HCl.

<u>Sn(II)</u> Solution, 10 p.p.m: Prepared by diluting 10 mls of the stock 100 p.p.m solution to 100 mls with 1N HCl. (Prepared fresh daily).

<u>Pyrocatechol Violet Solution (PCV) 0.1%</u>: Prepared by dissolving 250 mgs Pyrocatechol Violet in 250 mls H_2O .

<u>Triton X-100 Solution 18</u>: Prepared by diluting 1 ml Triton X-100 to 100 mls with H_2O . All other dispersants were similarly prepared.

<u>Britton-Robinson Buffer 0.04 M. (BR)</u>: Prepared by dissolving 2.4732 g Boric acid, 3.92 g Orthophosphoric acid, 2.29 mls Glacial acetic acid in 1 litre H_2O .

Hydrochloric Acid 1N: AnalaR grade.

Final Procedure:

Place an aliquot containing 50 µg Sn(IV) (in a volume of 0.5 mls IN HCl to achieve the correct pH) in a 50 ml calibrated flask. Add 1 ml 1% Triton X-100 and 2 mls of 0.1% Pyrocatechol Violet solution. Dilute to mark, mix well and measure the absorbance at 555 nm after 35 minutes in a 1 cm silica cell against a reagent blank, following ultrasonication (for no longer than 1 minute due to possible temperature effects). Determine the concentration from a calibration graph prepared using the same procedure.

Apparatus:

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Absorption spectra and single wavelength spectrophotometric measurements were made using a Shimadzu UV 240 recording spectrophotometer, using 1 cm silica cells at ambient temperature (about 22⁰).

A Philips FW 9410 digital pH meter was used to record pH measurements.

4.7. Results and Discussion:

Pyrocatechol Violet which is (3,3',4'-trihydroxyfuchsone-2''sulphonic acid), has a molecular weight of 386.38 g, is a reddish brown powder soluble in water and ethanol, the structure of which is depicted in Fig. 4.7.1.



Fig. 4.7.1 Pyrocatechol Violet.

Aqueous solutions of Pyrocatechol Violet (PCV) exhibit a yellow colour; at pH 1.5 the colour is red; it is yellow between pH 2 and 6 (anion H_3D^-), at pH 7 it is violet (anion H_2D^{2-}) and above pH 10 the colour is blue D^{4-} , the colour change ascribed to the progressive ionisation of the hydroxyl groups.

The blue, strongly alkaline solutions are unstable and were observed to lose their colour fairly rapidly, probably owing to atmospheric oxidation. The partial spectra of unbuffered solutions of reagent, 0.004 (w/v), at various pH levels are shown in Fig. 4.7.2. Solutions that contain Tin(IV) and excess reagent are red when strongly acidic, reddish purple between pH 2 and 4, and violet when neutral or basic.



Fig. 4.7.2. Effect of pH on the spectra of Pyrocatechol Violet. PCV, 0.05% (w/v), 2 ml; Reference, H_2O , Volume, 25 ml.

Bailey, Chester, Dagnall and West¹³ have shown that a compound of definite composition is formed in the CTAB-Sn(IV)-PCV system, the stoichiometry of the complex formed being 4 : 1 : 2. Thus the Tin is present in the complex anion SnL_2^{4-} (where PCV is H_4L having 4 ionisable protons). It is interesting to note that from a rigorous study published in 1972¹⁴ the main complex species present at the reagent concentration used for analysis is SnH_2L^{2+} . The dispersing agent appears to have a dual role:- as a counter-cation precipitating the anion and as a dispersant.

Preliminary Studies:

Initial objectives of this study were to:-

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- Investigate the effect of various surfactants on the Sn(IV) -Pyrocatechol Violet method.
- 2) Determine whether Sn(II) behaves similarly in such media,

including optimisation of the method i.e. (pH, reagent concentration, bathochromic shift variations etc.) and finally verifying the Beer-Lambert Law.

Initially, varying the concentration of reagent gave optimum concentration of 2 mls of a 0.1% PCV solution in the final 50 ml volume, in a medium of pH 2.4 at a wavelength maximum of 555 rm, this pH corresponding to a minimum reagent absorbance at that wavelength where the Sn(IV)-PCV complex absorbs (see Fig 4.7.2). The reagent concentration profile is depicted in Fig. 4.7.3.

The resulting Sn(IV) binary complex, although water soluble does not exhibit stability for longer than 20 minutes at this pH, hence to thus improve with possible enhancement in sensitivity, a range of surfactants was applied.

While recognising that both non-ionic dispersants such as Gelatine¹⁰ and cationic dispersants such as CTAB⁹ had previously sensitised such reactions, a study on the effect of the anionic dispersant sodium dodecyl sulphate (SDS) was thus instigated.



Fig. 4.7.3 Effect of reagent concentration on the absorbance vs. time profile of the Sn^{4+} -PCV binary complex. (Final 50 ml volume concs. reported).

To the binary complex solutions varying volumes of a 1% SDS solution were added. Observations were such that no bathochromic shift occurred and the absorbance of a 1 p.p.m. Sn(IV)-PCV-SDS ternary complex steadily approached that of the binary complex with a decrease in SDS concentration. A thorough pH study additionally supported such results i.e. at pH 2.4, at a maximum wavelength of 555 nm the absorbance of the Sn(IV) binary complex is comparable to that when 1 ml of a 1% SDS solution is applied. The higher the pH, the more broad the spectrum, with a bathochromic shift towards 640 nm probably due to excess reagent absorbance at this pH, and the less stable is the solution formed. Fig. 4.7.4 and 4.7.5 depict dispersant concentration profile and pH study respectively (only the range of interest i.e. pH 2.4 - 4.5).

Conclusively, for SDS, no significant improvement is achieved probably due to an unfavourable electrostatic micro-environment inhibiting micelle formation. For CTAB, under the above conditions, a broad and less defined peak is observed with the gradual appearance of a shoulder at 640 nm. No significant improvement in sensitivity resulted. Gelatine produced a similar profile although less sensitive.



Fig. 4.7.4 Effect of SDS conc. on the absorbance vs. time profile of the Sn^{4+} -PCV-SDS micellar system for 1 p.p.m Sn^{4+} , 10⁻⁵ M PCV soln. (Final 50 ml volume concs. reported).



Fig. 4.7.5 Effect of pH on the absorbance vs. time profile of the $Sn_{4^+}^{4^+}$ -PCV-SDS micellar system for 1 p.p.m. $Sn_{4^+}^{4^+}$, 10^{-5} M PCV soln.

For Triton X-100 however, which is octylphenoxy polyethoxyethanol, a bathochromic shift of 10 nm with a 30% increase in sensitivity was observed. It does however take 35 minutes to achieve stable colour development. Attempting to optimise the Triton X-100 system, buffering experiments indicated an optimum pH of 2.4 (as previously found with SDS and CTAB). A more acidic medium, although proving more sensitive is still unstable after 60 minutes. For pH profile with Triton X-100 see Fig. 4.7.6. Varying the concentration of Triton X-100 gave optimum concentration as 1 ml of a 1% solution (w/v) in the final 50 ml volume - see Fig. 4.7.7. In a medium of this pH, the dispersant Gum Arabic gave rise to a favourable bathochromic shift of 80 nm with stable colour formation after 10 minutes, however, little enhancement in sensitivity was observed. Respective spectra are depicted comparatively in Fig. 4.7.8.

Hence, from the study, Triton X-100 and Gum Arabic, both non-ionic surfactants of high molecular weight, appeared to have most potential as solubilising agents in acidic media, Triton X-100 having the advantage of a 30% enhancement in sensitivity, useful at the lower end of the concentration range.



Fig. 4.7.6 Effect of pH on the absorbance vs. time profile of the Sn^{4+} -PCV-TrX-100 micellar system for 1 p.p.m. Sn^{4+} , $10^{-5}M$ PCV soln.



Fig. 4.7.7 Effect of TrX-100 conc. on the absorbance vs. time profile of the Sn_{+}^{4+} -PCV-TrX-100 micellar system for 1 p.p.m. Sn_{+}^{4+} , 10⁻⁵M PCV soln. at pH 2.40. (Final 50 ml volume concs. reported).



Fig. 4.7.8 Comparative profile of the effect of surfactants on the absorbance spectrum of Sn(IV)-PCV complex. Sn(IV) 1 p.p.m., PCV 10⁻⁵ M.

Adherence to Beer's Law:

Attempts to draw up a calibration curve from 0-25 p.p.m. Sn(IV) using Triton X-100 gave rise to some interesting observations. For Sn(IV) concentrations exceeding 5 p.p.m. a second peak at longer wavelength (640 nm) is observed with a concurrent decrease in absorbance at 555 nm. This is in accordance with observations by Ross and White¹¹ who report two types of complex existing in solution, the predominant species formed when the mole fraction of Tin 1s low with a molar ratio of reagent to Tin of 2 and with a maximum absorbance at 555 nm. A second coloured species is formed when the mole fraction of Tin exceeds 0.5 and is postulated to have a reagent to Tin ratio of 0.5. In as much as this second complex absorbs light at 640 nm the spectra of the two species overlap to a degree dependent on the mole fraction of Tin. This overlapping is evidenced by a continual shifting of the maximum absorbance band from 555 nm towards 640 nm as the mole fraction of Tin is decreased. The shift to higher wavelengths is accompanied by a decrease in absorbance since the molar absorptivity of the second species at 640 nm is approximately half that of the primary species.

Hence, it would appear that a higher concentrations the concentrations of both reagent and dispersant need to be investigated to determine whether or not the critical micelle concentration is reached. Fig. 4.7.9 depicts the bathochromic shift observed at high mole fractions of Sn(IV).



Fig. 4.7.9 Bathochromic shift of Sn(IV)-PCV-Triton X-100 micelle absorbance with mole fraction Sn(IV) \leq 0.5.

A calibration curve ranging from 0-5 p.p.m Sn(IV) was drawn up yielding a linear range of 3 p.p.m i.e. 150 ug Sn in the final 50 ml volume, a correlation coefficient of 0.999933 thus confirming. (Compare a linear range of 80 µg Sn established by Ross and White¹¹). A molar extinction coefficient of 58762 1 mol⁻¹cm⁻¹ was calculated which is of the same order of magnitude as has previously been determined. (Fig. 4.7.10).



Fig. 4.7.10 Calibration curve for Sn⁴⁺-PCV-TrX-100 micellar system at pH 2.40 and 555 nm.

Reproducibility Tests:

Reproducibility tests for the dispersant Triton X-100 at three different concentrations along the linear portion of the calibration curve show mean, standard deviation and relative standard deviation as in Fig. 4.7.11. Conclusions are such that after 30 minutes, the stable colour produced shows a maximum variation in absorbance of 0.48%, exhibiting the precision of a sensitive technique.

NO. OF MEASUREMENTS	1	2	3	4	5	MEAN	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION
Absorbance of 0.5 ppm Sn	0.237	0.239	0.240	0.238	0.238	0.238	0.001	0.48%
Absorbance of 1.0 ppm Sn	0.471	0.474	0.472	0.471	0.472	0.472	0.001	0.26%
Absorbance of 3.0 ppm Sn	1.466	1.467	1.467	1.470	1.472	1.468	0.003	0.17%

Complex Formation with Sn(II):

When a reducing agent, such as Thioglycollic acid (Mercaptoacetic acid, $HSCH_2COOH$), is added to a solution of Sn(II) prior to the addition of Pyrocatechol Violet, no coloured complex is formed. The spectra of such solutions are identical to those of the reagent reference solution between pH 2.0 and 5.5. If solutions of Sn(II) are treated in the same manner as previously described in the procedure for Sn(IV) and in the absence of a reducing agent, coloured solutions are obtained that exhibit the same spectral characteristics as achieved with solutions of Sn(IV), the sensitivity of the Sn(II) solution being somewhat less owing to only partial oxidation to Sn(IV). Therefore, Sn(II) does not form a coloured complex with Pyrocatechol Violet under the conditions used for development of the Sn(IV) complex, but is readily oxidized to the higher oxidation state and is included in the measurement of Sn(IV).

Experimental investigations involved the preparation of 4 solutions of Tin complex:-

- 1) Sn²⁺Cl₂ (atomic absorption grade), 1 p.p.m diluted to a 2 mls 0.1% PCV solution ______ 50 ml volume.
- 2) Sn²⁺Cl₂ anhydrous, 1 p.p.m diluted to a 50 ml volume.
 2 mls 0.1% PCV solution

- 3) Sn⁴⁺Cl₄.5H₂O, 1 p.p.m. diluted to a 50 ml volume. 2 mls 0.1% PCV solution
- 4) Sn²⁺Cl₂ (atomic absorption grade), 1 p.p.m
 0.2 mls Thioglycollic acid,
 2 mls 0.1% PCV solution
 diluted to a 50 ml
 volume.

0.2 mls Thioglycollic acid is our experimentally determined optimum concentration required for 100% reduction of Sn(IV) to Sn(II). The absorption spectra of each was recorded against a reagent blank, the profiles dipicted in Fig. 4.7.12 from where it is evident that Sn(II) complexation does not take place, owing possibly to the size of the ion in solution and hence the steric hindrance involved while the form of the Sn(II) ion in solution (hydrolysis products) and its stability/reactivity must also be considered.



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Chapter V : Fluoride.

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5.1 Occurrence, Importance and Utilisation of Fluoride.

The most reactive form in which Fluorine is encountered in nature is as Hydrogen Fluoride HF, which can be present in amounts up to 0.03% in gases of volcanic origin. In combination, Fluorine represents about 0.065% of the earth's crust, being thirteenth of the elements in abundance and occurring there more widely than Chlorine.

The three most important Fluorine containing minerals are Fluorspar or Fluorite (CaF_2), Cryolite (Na_3AlF_6) and Fluorapatite which is apatite (calcium hydroxy phosphate) in which some hydroxide has been replaced by Fluoride.

By far, most of the Fluorine in the earth's crust is in combined form in Fluorapatite where it occurs to the extent of about 3.5% whereas it comprises about 50% of Fluorspar and of Cryolite.

Both the inorganic and organic chemistry of Fluorine received an enormous impetus during World War II. Separation of the isotopes of natural Uranium was carried out by a diffusion process involving Uranium hexafluoride vapour and various aspects of Fluorine chemistry were basic to the processing of Uranium and of Plutonium. Fluorinated oils, greases and polymers were needed in the associated technology. While the main effort in this field was concentrated in the war years, there has been continuing activity because of the peaceful application of fission processes. Also, because of the great oxidising strength of Fluorine and of many of its compounds, rocket technologists have been interested in the possibility of using Fluorine-containing fuels.

The large scale industrial application of inorganic Fluorides continues to be in the electrometallurgy of Aluminium, where the molten electrolyte is natural or synthetic Cryolite Na_3AlF_6 ; but there has been a growing use of anhydrous HF in alkylation processes in petroleum refining.

Although the quantity of Fluoride involved is relatively small, an aspect of inorganic Fluoride chemistry which has had a growing impact on most communities has been the artificial fluoridation of drinking water supplies:- a procedure adopted to minimise the incidence of dental caries. Toxicity of inorganic Fluorides to a human host is also of major importance. Hodge and Smith¹ distinguish between acute and chronic effects of same. They cite 5 - 10 g of Sodium Fluoride NaF as a reasonable estimate of a 'certainly lethal dose' for a 70 kg man, i.e. 70 - 140 mg/Kg⁻¹. Chronic toxic effects of Fluoride (fluorosis) are usually observed as skeletal abnormality or damage, ranging from stiffness and rheumatism to a permanent crippling skeletal rigidity. Early spectrophotometric methods were direct adaptations of the most common of the volumetric methods (based on non-stoichiometric reactions, the procedures being highly empirical). Alizarin Red S was added to a buffered solution of Zirconium or Thorium nitrate. The extent of bleaching of the resultant coloured solution was related to Fluoride concentration by standardizing with known Fluoride solutions. Procedures were reasonably rapid and reliable in the hands of a practised analyst, but as Horton² reviews for the Zirconium - Alizarin Red S reaction, many species caused marked interference.

In the Palin³ version of the method, a novel procedure is introduced in order to cancel out interference. This makes use of a proposed blank in which the Fluoride ion has been rendered inactive by complexing it with an excess of an aluminium salt. Elimination of any remaining interference caused by the possible presence of residual alum in waters which have undergone treatment with aluminium sulphate, or similar types of coagulant, requires a simple preliminary treatment with an ion-exchange resin. The only remaining interference is that due to phosphates. Normally, there is insufficient natural phosphate in waters to interfere significantly. Where waters are treated with hexametaphosphate amounts up to 2 p.p.m cause no interference. More recent methods (1985) include the Fluoride – Lanthanum(III) – Alizarin fluorine blue⁴ system where the formation of a ternary $F^- - Ia^{III}$ – Alizarin complexan complex at pH 4.8 and has been improved by the addition of sodium dodecyl sulphate. It has been applied to the determination of F^- in bottled mineral waters.

The ternary complex of Zirconium with Eriochrome cyanine R and hexadecylpyridinium ions (1986)⁵ makes use of a surfactant system and reports high sensitivity with $\varepsilon = 59,000 \ 1 \ mole^{-1} \ cm^{-1}$.

Many metal cations⁶ and complexing chromophores have been investigated and reported as alternatives to the Zirconium – Alizarin system. One chromophore reported as giving good results when used with Zirconium solutions is Xylenol Orange⁷ however, Leonard and West⁸ in 1960 introduced a new rigour into the field by designing an alizarin derivative which chelates specifically to Cerium(III) forming a red compound which in turn is complexed by Fluoride to give a blue compound containing Fluoride and the Cerium – Alizarin complex in the mole rate 1:1. A more recent⁹ modification (1983) on the above reports detectable Fluoride levels of 76 – 1134 p.p.b.

By 1968, a valuable survey of several spectrophotometric methods for determination of Fluoride in potable waters and other aqueous solutions was made by Crosby, Dennis and Stevens¹⁰.

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For each method, including the Cerium - complexone procedure described above, linearity of the calibration graph, stability of the solution of the complex, sensitivity of the method, reproducibility results in the hands of different analysts and the effect of interfering species were all examined. They found the Cerium(III) - complexone method to be far superior to the Zirconium - Alizarin and other spectrophotometric methods studied.

During investigations of Germanium determination with Bromopyrogallol red¹¹, Fluoride ion was found to interfere significantly (13% interference at a 1:10 ratio of Ge^{IV} : F⁻); the possibility of its determination with BPR was thus realised. Having pKa's of 0.16, 4.4, 9.1 and 11.3, BPR is singly ionised at pH 4 (operating pH) and with nothing present in solution to replace H^+ at the $-SO_3^-$ position (see Fig. 2.6.1), no logical mechanism for complexation with Fluoride ion, being a negative species, was initially envisaged. However, due to a variety of indirect spectrophotometric methods available in the literature¹⁰ where e.g. the Fluoride ion can abstract cations $(Zr^{3+}, Al^{3+} etc.)$ from strongly absorbing complexes, liberating the free dyestuff (bleaching effects), then various theories could be put forward. The aim of the present study was thus to investigate the reaction of Fluoride ion and BPR in an aqueous medium and to monitor the effect (if any) of dispersants on such a reaction.

5.3 Experimental:

Reagents:

All solutions were prepared with de-ionised water and analytical reagent grade materials unless otherwise stated.

<u>Standard F – Stock Solution, 100 p.p.m</u>: Prepared by dissolving 55.2523 mgs of Sodium Fluoride, NaF, (Analar (Riedel de Haen) and GPR grade) in 250 mls H_2O .

<u>F</u> Solution, 10 p.p.m.: Prepared by diluting 10 mls of the stock 100 p.p.m. solution to 100 mls.

Standard Cl⁻, Br⁻ and I⁻ Stock Solutions. 500 p.p.m: Prepared by dissolving 824.23 mgs Sodium Chloride, NaCl, 643.86 mgs of Sodium Bromide, NaBr, and 590.58 mgs Sodium Iodide, NaI in 1 litre with H_2O . 100 p.p..m solutions in each case were prepared by suitable dilution of the stock 500 p.p.m.

<u>Bromopyrogallol Red Solution (BPR) 0.03</u>^{*}: Prepared by dissolving 150 mgs BPR in 500 mls of 50^{*} (v/v) aqueous ethanol. (Pre-mixing of EtOH and H₂O is necessary here).

Sodium Dodecyl Sulphate (SDS) Solution 1.0%: Prepared by dissolving 1 g SDS (special grade) in ~ 50 mls H_2O , heating to effect dissolution and upon cooling transferring quantitatively to a 100 ml calibrated flask and diluted to the mark.
<u>Oetyltrimethylammonium Bromide (CTAB) Solution 0.5%</u>: Prepared as for SDS using 0.5 g CTAB in 100 mls H_2O .

<u>Gelatine 0.5%</u>: Prepared as for SDS, constant agitation being necessary to effect dissolution.

<u>Britton-Robinson Buffer (0.04 M):</u> Prepared by dissolving 2.4732 g Boric Acid, 3.9200 g Orthophosphoric Acid (BDH Chemicals laborotory grade) and 2.29 mls of Glacial Acetic Acid in 1 litre H_2O , adjusted to the required pH using 1M and 0.2M NaOH.

<u>Sulphuric Acid (0.1M), Hydrochloric Acid (0.1M)</u>: AnalaR grade. <u>Sodium Hydroxide (0.1M)</u>: AnalaR Grade.

Apparatus:

Absorption spectra and single wavelength spectrophotometric measurements were made using a Shimadzu UV 240 recording spectrophotometer, using 1 cm silica cells at ambient temperature (about 22° C).

A Philips PW 9410 digital pH meter was used to record pH measurements.

5.4 Results and Discussion:

Initial investigations concentrated on a pH study of the reaction, both with and without the addition of the dispersant CTAB (since when F⁻ was determined in the presence of Ge-BPR complex, CTAB suited best). That pH of 4.0, for a concentration of 2 p.p.m F⁻, without acid or base addition yielded maximum absorbance at $\lambda = 550$ nm. (Compare the wavelength of maximum absorbance for the reagent alone, where considerable overlapping occurs - i.e. 540 nm against a blank of H₂O).

The addition of CTAB resulted in the gradual appearance of a second peak at $\lambda = 590$ nm, but proving very unstable and insensitive. SDS was found to stabilize the reaction with little enhancement in sensitivity, again, an optimum pH of 4.0 found. The possibility that our maxima were due to pH effects was ruled out here, due to buffering experiments with Britton-Robinson buffer (0.04 M). A series of concentrations from 0 - 100 p.p.m F, all presumably buffered to pH 4.0 was prepared and a linearity profile drawn up. The anomaly here was such that with different aliquots of the stock F solution (although differing in volume by only 0.1 ml at a time) were sufficient to alter the pH of the resulting solution by very small amounts and were, in fact, resisting the buffer action. Hence, a gradual pH difference between reagent blank and sample solution for increasing concentrations resulted. So insignificant appeared the difference (0.05 units in some cases), that again pH effects were ruled out.

Linearity (assumed) was 4 p.p.m. For a 10 p.p.m F^- solution, three dispersants were applied at pH 4.0 namely SDS (anionic), CTAB (cationic) and Gelatine (non-ionic). Fig. 5.3.1 illustrates the profiles of each, none of which contribute significantly to sensitivity enhancement. What could however be noted here is the second absorbance at 590 nm for CTAB, which could be due to reagent-dispersant reaction differing in each case by the presence (sample) or absence (blank) of Fluoride (apparently giving rise to the pH difference) and hence a residual absorbance (at longer wavelength) observed.



Fig. 5.4.1 Absorbance profiles of assumed F^-BPR complexation with the effect of surfactants.

Other halogen anions Cl⁻, Br⁻ and I⁻ were each in turn treated in a similar manner to F⁻, with no visible reaction until 100 p.p.m in each case was reached. Profiles were similar to those of F⁻ i.e λ_{max} at 550 nm with comparable pH trends. Ionic size, electronegativity and hence reactivity differ in each case, however, similar behaviour is observed in an aqueous medium of pH 4.0.

The possibility that we were measuring cationic impurities of Sodium Fluoride had next to be eliminated where two sources of F^- were used (Lab. Grade (Riedel de Haen) and GPR Grade). No difference in absorbance resulted and similar profiles on applying SDS were achieved.

In a final attempt to combat possible pH effects, Britton-Robinson buffer was dispensed with and both reagent blank and sample solution treated separately with acid/base to achieve the desired pH. Absorbances for a 10 p.p.m solution (previously giving an absorbance of 0.3 units) were negligible at this stage. There was however, a residual absorbance noted, perhaps due to the addition of different amounts of acid or base to each solution, reagent in each case being treated differently and may or may not have a higher/lower concentration of ionised reagent in one flask and hence a complete cancellation of absorbances is not achieved.

Therefore, conclusions are such that critical pH control is imperative (variations of 0.05 - 0.10 pH units between sample and reagent blank are intolerable in such circumstances). Bibliography.

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APPENDIX.

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Systematic Name. 1,2, dihydroxyanthraquinone. $5-[\alpha - (3-\text{Carboxy}-5-\text{methy})-4-\text{ox}-2, 5$ cyclohexadien-1-ylidene)-2,6,dichloro-3-sulphobenzyl]-3methylsalicyclic acid, trisodium salt. Dithizone (phenylazo) thioformic acid 2-phenylhydrazide.

 $5-[\alpha (3-Carboxy-5-methyl-4-oxo-2,5-$ Eriochrome Cyanine R cyclohexadien-1-ylidene)-2sulphobenzyl]-3-methyl salicyclic acid, trisodium salt.

3,'3''-bis {[bis(carboxymethyl)amino] methyl)-5',5''-di-isopropyl-2'-2''dimethylphenolsulphophthalein, sodium salt.

Rhodamine B [9-(o-carboxyphenyl)-6-(diethylamino)-3H-Xanthen-3-ylidene]diethylammonium chloride.

Stilbazo 4,4'-bis[(3,4-dihydroxyphenyl)azo]-2,2' -Stilbene disulphonic acid, diammonium salt.

Abbreviation

Alızarın

Chromazurol S

Methylthymol Blue

Xylenol Orange

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3,3'-bis[N,N-di(carboxymethyl)amino methyl]-o-cresolsulphophthalein, sodium salt.

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