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Spectrophotometric determination of tin and zirconium in steels

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SPECTROPHOTOMETRIC DETERMINATION OF TIN AND ZIRCONIUM IN STEELS.

by

ANTHONY ASHTON, ARIC.

A Doctoral Thesis.

Submitted in partial fulfilment of the requirements for the award of:

Doctor of Philosophy of Loughborough University of Technology. November 1973.

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For the sake of clarity each part is independently indexed and referenced.

GENERAL INTRODUCTION.

GENERAL INTRODUCTION

The work presented in this thesis described the development of spectrophotometric methods of analysis for the determination of tin and zirconium in steels. This work was carried out under a second BISRA bursary awarded to the Chemistry Department of Loughborough University of Technology.

The work of the first bursary is described in the Ph.D. thesis of D. R. Marriott (1970) and was concerned with the spectrophotometric determination of tungsten and arsenic in steels. A recommended procedure for tungsten is given in which the tetraphenylarsonium tungsten(V)-thiocyanate ion association complex is extracted into chloroform and its absorbance measured spectrophotometrically. Investigations into methods of overcoming interference by molybdenum and vanadium are also described. The recommended procedure for arsenic involves solvent extraction of arsenic(III) iodide and colorimetric determination by a molybdenum blue procedure.

Tin is not found in any of the iron ores but the use of incompletely de-tinned scrap may cause a small residual amount of the element to be present in steel. Up to 0.15% m/m of tin may be tolerated in mild steels for most applications but as little as 0.02% m/m will have detrimental effects on deep drawing steels. Alloy steels must be virtually free from this element. In general therefore, tin can be considered to be a very undesirable constituent of steel.

Zirconium is added to steels in proportions of up to about 1% m/m. This element has a strong chemical affinity for oxygen, nitrogen, sulphur and carbon and is used to control the injurious effects of these elements.

In the routine quality control analysis of steels, the more convenient and rapid physical analytical methods are used. Wet chemical methods however, are required for the checking of these results, for the

calibration of standards, and for the analysis of those non-homogeneous samples that do not lend themselves to spectrographic methods of analysis. The present British Standard methods for the wet chemical determination of tin and zirconium in steel leave much to be desired. The method for tin is based upon a time consuming sulphide separation followed by iodiometric titration (BS 1121, Part 20, (1961)). Zirconium is determined by a tedious gravimetric procedure using a Cupferron separation followed by a mandelic acid separation (BS 1121, Part 46, (1966)). Furthermore, the method is not applicable to steels with a zirconium content of less than 0.03% m/m.

The aim of the present work was to replace these methods with spectrophotometric methods that are rapid, precise and applicable to the widest possible range of steels. Where these primary requisites were in conflict an acceptable compromise has been attempted. For both elements the basic approach has been the same. First, it has been ascertained, which of the numerous colorimetric reagents, available for the determination of each element is superior, with respect to sensitivity, selectivity and precision; then the scope of the procedure has been extended by the development of compatible dissolution, extraction and masking techniques.

SPECTROPHOTOMETRIC DETERMINATION OF TIN IN STEELS.

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INTRODUCTION TO THE SPECTROPHOTOMETRIC DETERMINATION OF TIN IN STEELS

A comparative study of the five most popular colorimetric reagents used for the determination of tin, chosen on the basis of a detailed literature survey, has revealed that Catechol Violet is superior in virtually every respect. If the cationic surface active agent, cetyltrimethylammonium bromide, is added to the tin(IV) - Catechol Violet system, overlap of the reagent and complex absorption bands is reduced to virtually zero and there is also a considerable increase in sensitivity. This possibility adds further weight to the argument in favour of Catechol Violet.

Phenylfluorone appears to be the most popular reagent for tin used in the British Steel industry at the present time; evidence is given that shows this reagent to be highly unsuitable, by virtue of the poor spectral characteristics of the tin-phenylfluorone system, poor reproducibility of results and non-uniformity of commercially available samples of the reagent.

Examination of the literature leaves little doubt that the best way of separating tin from the other constituent elements of steels, is by solvent extraction of tin(IV) iodide, followed by back-extraction into aqueous media. The proposed method is a combination of this selective extraction procedure and the Catechol Violet-cetyltrimethylammonium bromide colorimetric determination. Consequently, it is believed to be a combination of the best separation and colorimetric determination procedures available at the present time.

Lactic acid has been utilised as a masking agent for a number of the other metals found in steels; it is successful in overcoming the long standing problem of molybdenum interference. Application of the proposed method to a range of British Chemical Standards steels and an investigation of the effects of the fifteen other metals most commonly found in steels,

indicate that the method should be applicable to virtually every type of steel. In addition, a simplified procedure in which the iodide extraction is omitted, is given. This method should be applicable to those steels, such as mild steels, that do not contain large quantities of alloying elements.

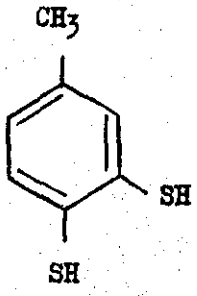
Finally, there has been an increased interest in recent years, in the action that certain surface active agents have on the visible absorption spectra of some metal-chelate systems. In view of this, an investigation of the tin(IV) - Catechol Violet-cetyltrimethylammonium bromide system, as used herein, has been carried out and a mechanism for the observed band shifts and increases in sensitivity has been proposed.

CHAPTER I

REVIEW OF COLORIMETRIC METHODS FOR THE DETERMINATION OF TIN

Since the development of the first spectrophotometric method for tin, in 1952, about fifty different colorimetric reagents have been used to varying extents, the most significant of these being Dithiol, Gallein, Phenylfluorone and Catechol Violet. There is no highly selective reagent for tin and even though masking agents have often been utilised to improve the situation, most colorimetric determinations have to be preceded by some type of separation procedure. Here again, a wide range of methods have been used. The coprecipitation of tin using manganese dioxide as a carrier is well established, solvent extraction and distillation have been used, as also have ion exchange and silica gel chromatography.

DITHIOL

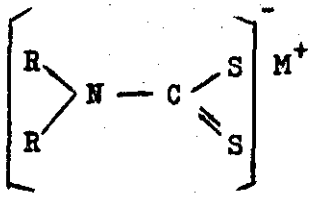


This reagent was the first compound to be used as a colorimetric reagent for the determination of tin. Clark (1), in 1936, made use of the red $Sn(II)L_2$ complex formed between tin and Dithiol, in a simple colour comparator method. Williams and Whitehead (2), in 1952, modified the earlier method and described the first spectrophotometric procedure. In 1967 and again in 1968 the Analytical Methods Committee (3,4) of the Society for Analytical Chemistry recommended the zinc complex of Dithiol as a reagent for the determination of tin, in the range 30-150 μg, in organic materials. The tin complex formed is insoluble in aqueous solution

and this fact has given rise to extensive studies to decide which is the best dispersing agent for the system (5-10); it was concluded that sodium lauryl sulphate was the best. This material has the advantage over the use of propriety products (e.g. Teepol) and natural products (e.g. agar-agar), since its inclusion in the British Pharmacopoeia ensures some degree of chemical consistency. Onishi and Sandell (7) made an attempt to carry out the absorbance measurement in organic solvents in which the complex is soluble and reported that in such media the complex is not red, but yellow.

Dithiol determination preceded by ion exchange separation has been used by Marley and Articolo (11) in a method for tin in zircaloy. Sanderson and Hanson (12) used separation of tin by distillation in a method for the analysis of industrial wastes. Separation of tin from copper was the subject of a paper by Dickinson and Holt (13) in which they suggest that copper should be removed by diethylammonium-diethyldithiocarbamate/chloroform extraction, before colorimetric determination with Dithiol, rather than with the more usual sodium or ammonium salts, since unlike the latter, the former does not extract tin.

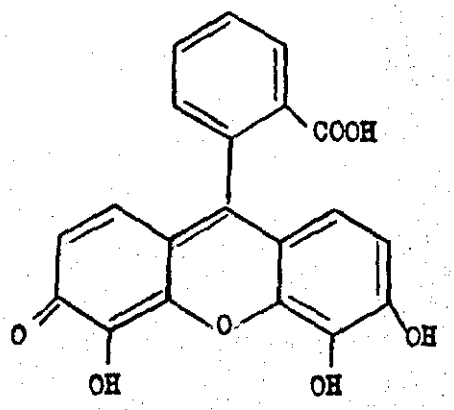
DITHIOCARBAMATES



Sodium diethyldithiocarbamate was used in a method by Davis and Easton (14) for the analysis of copper alloys. The brown complex of tin is first extracted into chloroform followed by back extraction of tin into alkali. Eberius (15) and Kovacs and Guyer (16,17) have developed methods employing sodium tetramethyldithiocarbamate, the latter papers being for the determination of tin in the 0.001 to 0.1% range in zinc and steel respectively. Carbamate/Chloroform extractions that precede a

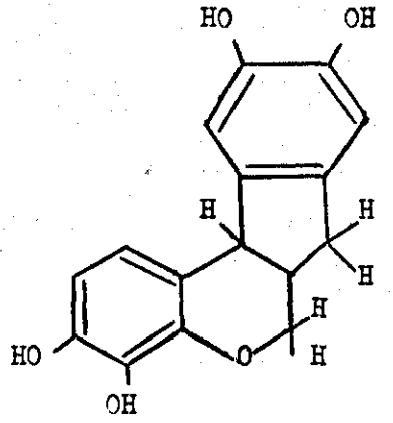
spectrophotometric determination using another reagent, particularly Phenylfluorone, have been widely applied (18-20).

GALLEIN



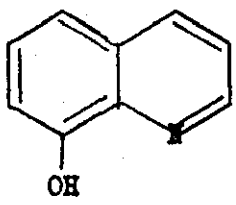
This reagent has been mainly used in the analysis of geological materials. McDonald and Stanton (21) described a method for tin in soils in 1962. This was further developed by Murano and Miyazaki (22) and Hutchin and Fiander (23), whilst Purushottam and Nayar (24) have used a modified Gallein method for the determination of tin in soils and rocks. Murano and Miyazuki (25) described a method for tin in metals and reported that antimony, tungsten and zirconium interference can be masked with tartrate, iron and vanadium by ascorbic acid and molybdenum and titanium by hydrogen peroxide. What is thought to be the first silica gel chromatographic separation of tin combined with a spectrophotometric method appears in a paper by Jones (26). Good separation of antimony and tin was achieved; Gallein was used for the colorimetric determination.

HEMATOXYLIN



In 1953 Teicher and Gordon (27) put forward a method based on the red, tin-Hematoxylin complex. They reported interference by iron(III), antimony(III), bismuth(III), and titanium(IV) but claimed that "in comparison with dithiol methods this method has a wider range, is more reproducible and suffers from fewer interferences." This work was followed by that of Norwitz (28) who produced a method for tin in propellents and by several Japanese workers, Kojima (29) with a method for tin in non-ferrous metals, Tanaka (30) with a method for tin in copper and aluminium alloys and Malkawa, Yoneyama and Fujimori (31) with a method for tin in iron and steel. A study of the nature of the complexes formed between tin(IV) and Hematoxylin was published in 1965 by Yosimura and Noguchi (32).

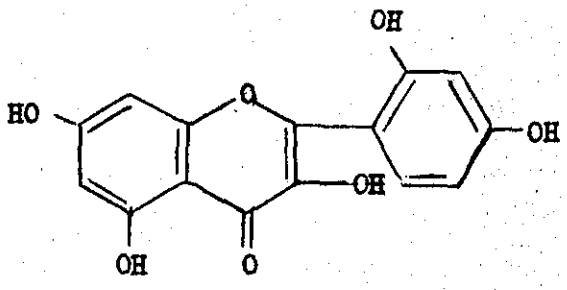
OXINE



Wakamatsu (33), in 1960, described the determination of tin in iron and steel; the method involves the extraction of the tin-8-hydroxyquinoline complex and was based on an earlier method by Gentry and

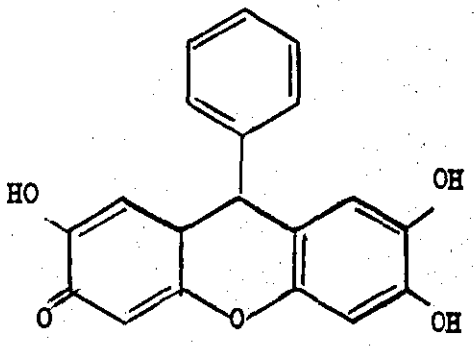
Sherrington (34). In the earlier method the non-selective nature of the reagent was overcome by a preliminary separation by distillation of tin(IV) iodide or tin(IV) bromide. Careful control of the distillation was necessary or antimony(III) interference occurred. Wakamatsu's later method utilised the co-precipitation of tin using manganese dioxide as a carrier. Any iron(III) present was masked by selective reduction with ascorbic acid.

MORIN



The blue complex formed between tin(IV) and Morin in weakly acid solution is the basis of methods by Feigl, Gentil and Goldstein (35) and Patrovsky (36). Patrovsky reported that molybdenum, tungsten, tantalum, niobium, zirconium, thorium, fluoride, oxalates, and tartrates interfere.

PHENYLFLUORONE



The original work by Luke (19), in 1956, on the red colloidal complex formed between tin and Phenylfluorone initiated extensive work with this reagent which has continued up to the present date. Luke described a method for tin in lead and antimony-lead alloys which has

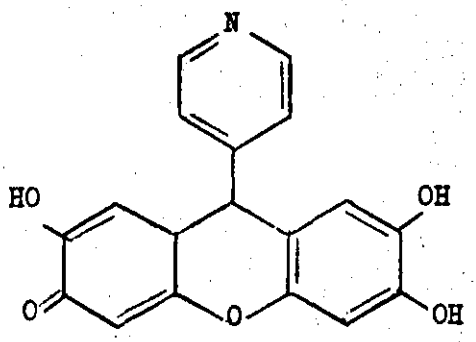
been extended by Bennet and Smith (37), who reported, amongst other things, that erratic results were caused by the gum arabic used as a dispersing agent in a later method by Luke (38). Oelschläger (39), when developing a method for traces of tin in biological and other materials, compared Dithiol and Phenylfluorone. Two papers on iron and steel analysis by Picasso and Pizzimenti (40) and Luke (41) followed this study.

The inherent problems of measurement of light absorption by colloidal suspensions are solved by working in methyl-isobutylketone and ethanol in both of which the complex is soluble, as was found by Luke (19,41) and Leblond and Boulin (42) respectively.

Solvent extraction methods that precede phenylfluorone colorimetric determinations have mainly been based on sodium diethyldithiocarbamate or cupferrate. Luke (19,20) made use of the "double carbamate" extraction technique of Wyatt (18). Cupferron in chloroform has been used by Raczka and Suchy (43) and Gur'ev and Saraeva (44). Ion-exchange methods include those of Speirs (45) and Hofer (46).

A related reagent to phenylfluorone and presumably with similar properties, is p-nitro-phenylfluorone, Nazarenko and Lebedava (47) have used this in the determination of tin in low grade ores.

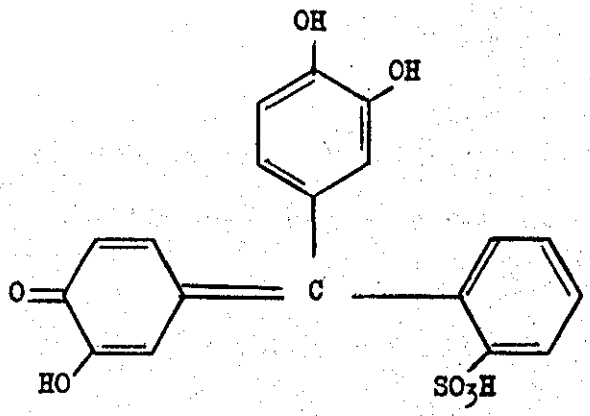
9-(3-PYRIDYL)FLUORONE



The replacement of the phenyl group in phenylfluorone by a pyridine group in this compound, confers water solubility upon the tin complex, thus overcoming the problems of colloidal systems met with in

the case of phenylfluorone. Asmus and Kraetsch (48) report an investigation of the use of 9-(2-pyridyl)fluorone, 9-(3-pyridyl)fluorone and 9-(4-pyridyl)-fluorone for the determination of tin. 9-(3-pyridyl)fluorone was preferred on selectivity grounds. Further work with this reagent includes that by Asmus and Kossmann (49) and Asmus and Weinert (50) on methods for tin in steels. With a reported molar absorptivity of a little over 100,000 l mol^{-1} cm^{-1}, this reagent has probably had less attention than it might deserve.

CATECHOL VIOLET

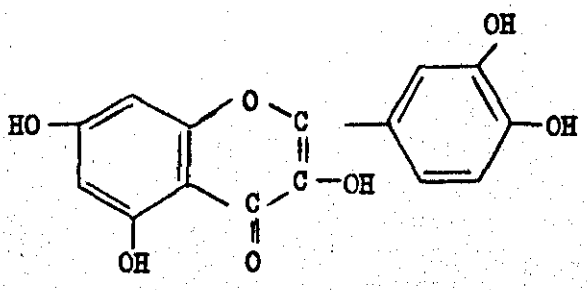


Suk and Malat (51) reported that a coloured complex was formed between Catechol Violet and tin and also gave information on other metallic species that would be expected to form colours with this compound. On the basis of this work, Ross and White (52) developed a procedure using Catechol Violet as a colorimetric reagent for tin. They reported a molar absorptivity of 65,000 l mol^{-1} cm^{-1} and gave information on the effects of pH, diverse ions, initial concentration of acid and a comparison with other reagents. Furthermore it was proved conclusively that the complex is formed only when tin was present as tin(IV). The same workers then combined their Catechol Violet determination with an extraction based on the cyclohexane soluble complex, $SnCl_4 : 2TEHPO$ (where TEHPO is tri-(2-ethylhexyl-phosphine oxide) to give methods for tin in lead, zinc, copper, iron and zinconium alloys (53). These extraction procedures generally showed excellent results and only antimony(III) was shown to interfere.

Other work combining extraction methods with Catechol Violet determinations include that of Gilbert and Sandell (54) and Tanaka (55,56), who used a benzene extraction of tin(IV) iodide. Tanaka's work on iron and steel was applied to tin in organic matter by Newman and Jones (57), except that they back extracted tin with sodium hydroxide solution, unlike Tanaka who used dilute hydrochloric acid. They stated that, "Catechol Violet is one of the most sensitive colorimetric reagents that have been used for tin, it forms a red complex in weakly acid solution which is water soluble, an advantage over dithiol and phenylfluorone which produce colloidal systems."

In the original colorimetric procedure for the determination of tin with Catechol Violet by Sagakova and Lyubivaga (58) in 1959, gelatin was added "to stabilise the colour" and absorbance measurements were made at 619 n.m. Malat (59) later carried out similar studies on the tin-Catechol Violet reaction in the presence of gelatin. He found a considerable bathochromic shift in absorbance maximum of the complex from 555n.m. in the absence of gelatin to 640 n.m. in the presence of gelatin. The absorption maximum due to excess reagent in solution remained at 445 n.m. in each case; in this way the analytically undesirable band overlap was greatly reduced. Prompted by this work, Dagnall et. al. (60) investigated the use of a number of surface active agents of which cetyltrimethylammonium bromide (CTAB) was found to be the best. CTAB produced a bathochromic shift of the complex's absorption maximum from 555 n.m. to 662 n.m. and greatly increased the sensitivity of the system to give an increase in molar absorbtivity from 65,000 to 95,000 $l\,mol^{-1}\,cm^{-1}$. They coined the term "sensitisation" for this phenonemon. In one of a series of papers in Talanta, on the applications of ternary complexes, the same school put forward a theory for this "sensitisation" on the basis of the formation of a true 1:2:4, tin-Catechol Violet-CTAB ternary complex (61).

QUERCETIN



When describing a method for the determination of tin in brasses and bronzes, Liska (62) reports that Quercetin is a "better reagent than Morin." Janoušek and Studlar (63) have put forward a method for tin in steel in the 0.001 to 0.1% range in which separation methods by distillation and by ion exchange were given. Kirk and Pocklington (64) have produced a method for tin in canned foods, in which they mask iron interference with thiourea. They state, "The method gives results similar to the Dithiol method but manipulation is easier and therefore it is better for routine analytical work, particularly at higher trace levels."

BASIC DYE METHODS

These methods are based on the formation of a ternary ion-association complex between a tin-bearing anion and a dyestuff cation. Ducret and Maurel (65) estimated tin, by extraction into 4-hectanone of the dye anion complex formed between tin(II) and Crystal Violet in hydrochloric acid solution. However, they reported that the dye chloride itself is extracted and that there are many interferences. Arnsen and Selmer-Olsen (66) have used Rhodamine B in a method for tin, in which they report that zinc(II), mercury(II), iron(III), antimony(III), antimony(V) and bismuth(III) interfere. The ternary complex formed by tin and Malachite Green in the presence of thiocyanate has been utilised by Chih-Shang and Li-Shu (67). Shumova and Blyum (68) have used Butyl Rhodamine S in a method in which a complex of the formula, $SnCl_4$-(Butyl Rhodamine S) is formed. Cupferron must be present for reasons that were not known.

OTHER METHODS

Lopez (69) reported a method in which Cacotheline was used for the determination of tin in lead; the separation procedure involved manganese dioxide and iron(III) hydroxide coprecipitation stages. Titanium(III), vanadium(IV), rhodium(III), niobium(III), arsenic(III), antimony(III), chromium(III) do not interfere. Nielsch and Böltz (70) have made use of the yellow colour given by tin(IV) bromide in concentrated hydrobromic acid. Beers Law was obeyed in the 8-1,200 µg/ml. range but the absorbance depends on hydrobromic acid concentration. After an ion exchange separation the absorbance of the iodostannate(IV) complex was used by Dawson and Magee (71) as the basis of a method for tin in white metal and tin alloys. Tanaka and Takagi (72) measured the ultra violet absorbance given by the tin(IV) iodide after its extraction from M sodium iodide/4M sulphuric acid media. The formation of the blue compound, of uncertain chemical composition ("Molybdenum blue"), when molybdic acid is reduced by tin(II), has been made the basis of indirect methods, Marczenko (73) and Namiki (74) amongst others. Finally, a more recent method uses salicylideneamino-2-thiophenol (SATP) due to Gregory and Jeffery (75); in their procedure ascorbic acid was used to mask iron(III), and thiosulphate can be used to mask silver and copper interference. Lactic acid is found not only to prevent hydrolysis of tin at the optimum pH of 2, but also to prevent molybdenum interference.

CHAPTER II

COMPARATIVE EXPERIMENTAL STUDY OF THE PRINCIPAL SPECTROPHOTOMETRIC METHODS OF DETERMINING TIN

In spite of a good deal of previous work on reagents for tin, only one broadly based comparative study appears to have been published. This was by Babko and Karnaukhova (76); they studied eight reagent systems and the independence of absorbance on pH as their criteria for coming to the conclusion that the best reagents for tin(IV) are:- Catechol Violet, Hematoxylin and Quercetin. They did not consider sensitivity or overall precision. Consequently, their findings were only of limited assistance to the aims of the present work.

It would not have been possible here to examine every reagent that has been put forward for tin. Therefore, the four most popular, namely Dithiol, Phenylfluorone, Gallein and Catechol Violet, along with salicylidene-2-thiophenol (SATP), were selected.

EXPERIMENTAL

In carrying out the investigation, special regard was given to reproducibility of results and the inherent properties of a reagent; adherence to Beers' Law, molar absorbtivity and the spectral characteristics of the tin-reagent system. Selectivity was not considered since it was clear from the literature survey that there is no highly selective reagent for tin and there is little to choose, on selectivity grounds, between those reagents that have been put forward.

The tests for reproducibility were carried out by measuring the absorbance given, with each reagent, by each of fifteen equal aliquots of standard tin solution, taken in 3x5 aliquot batches. Batchwise and overall standard deviations are reported. The size of the aliquot was chosen to fall in the middle of the concentration range suggested by the authors of the respective papers, selected as the basis of the methods for the tests.

These generally gave absorbance readings that fell within the 0.3 to 0.6, the minimum error, absorbance range calculated by Ayres. (77).

Beers' Law plots were constructed over the suggested ranges and the mean molar absorptivities reported herein result from averaging of tin concentration/absorbance results in the Beers' Law plots.

Spectral characteristics were examined taking particular note of band separations between that for the excess reagent present and that for the metal complex itself.

All measurements were carried out on a Unicam SP600 spectrophotometer. Double distilled water, from silica apparatus, was used throughout. The reagents were used as supplied by the various commercial suppliers, no attempt at purification was made.

DITHIOL

This reagent suffers from the disadvantage that its complex with tin is insoluble in aqueous media. Consequently, the reaction must be carried out in the presence of a dispersing agent: Kenyon and Ovenston (10) used sodium lauryl sulphate for this purpose, and it was this method that was used for this investigation.

Reproducibility tests:

Table 2:1 Tests were carried out on solutions that contained 8 µg tin(IV)/ml. Using 10 mm. cells at 545 nm.

Batch 1 (absorbance)	Batch 2 (absorbance)	Batch 3 (absorbance)
0.407	0.383	0.440
0.405	0.409	0.449
0.409	0.383	0.436
0.409	0.393	0.423
0.395	0.376	0.426
mean	0.405	0.389	0.435
standard deviation	0.0058	0.0089	0.0106
coefficient of variation	1.4	2.3	2.5

Overall mean	0.408
Overall standard deviation	0.022
Overall coefficient of variation	5.4

Adherence to Beers' Law: (at 545 nm.)

Table 2:2

µg tin(IV) per ml.	4	8	12	16	20
absorbance	0.136	0.352	0.582	0.648	0.663

Adherence was very poor over the 4 to 20 µg tin(IV)/ml. range, the line gave strong curvature at concentrations greater than 12 µg tin(IV)/ml. and did not extrapolate through the origin.

Molar absorptivity:

Across the linear portion of the Beers' Law plot an average molar absorptivity of 5,900 l mol^{-1} cm^{-1} was obtained.

Spectral characteristics: (Fig. 2:1a)

The spectral characteristics of the tin(IV)-Dithiol system are in fact excellent, since the reagent itself is colourless there is no problem due to reagent/complex band overlap, which leads to high blank values with many other spectrophotometric reagents.

PHENYLFLUORONE

(A) IN AQUEOUS MEDIA

For the purpose of this investigation the method used was that of Picasso and Pizzimenti (40). This method is closely related to the two methods by Luke (20,38) as mentioned in the previous chapter.

Reproducibility tests:

Table 2:3 Tests were carried out on solutions that contained 0.4 µg tin(IV)/ml., using 20 mm. cells, at 510 nm.

Batch 1 (abs.-blank of 0.199)	Batch 2 (abs.-blank of 0.192)	Batch 3 (abs.-blank of 0.193)
0.396	0.281	0.355
0.419	0.305	0.339
0.392	0.286	0.365
0.406	0.331	0.369
0.360	0.336	0.357
mean 0.394	0.307	0.357
standard deviation 0.022	0.025	0.012
coefficient of variation 5.6	7.1	3.4

Overall mean 0.353

Overall standard deviation 0.041

Overall coefficient of variation 11.6

Adherence to Beers' Law: (at 510 nm.)

Table 2:4

µg tin(IV)/ml.	0.2	0.4	0.6	0.8
absorbance (sample+blank)	0.356	0.589	0.754	0.913
absorbance (sample)	0.162	0.395	0.560	0.719

As a result of the poor reproducibility of the method, adherence was only fair, the points being fairly widely scattered around a straight line that passed through the origin.

Molar absorptivity:

Over the range of 0 to 8 µg tin(IV)/ml., the average molar absorbtivity was 54,500 l mol^{-1} cm^{-1}.

Spectral characteristics: (Fig. 2:1b)

Spectral scan of the complete visible region of the system showed very noticeable reagent/complex band overlap.

(B) IN ORGANIC MEDIA (Methylisobutyl ketone)

The method used here was that due to Luke (41), in which the tin(IV) - Phenylfluorone complex after being formed in aqueous media is extracted in methylisobutyl ketone.

Reproducibility tests:

Table 2:5 Tests were carried out on solutions that contained 1 µg tin(IV)/ml. of methylisobutylketone using 10 mm. cells at 530 nm.

Batch 1 (abs.-blank of 0.086)	Batch 2 (abs.-blank of 0.116)	Batch 3 (abs.-blank of 0.095)
0.338	0.371	0.447
0.333	0.325	0.449
0.369	0.396	0.444
0.372	0.419	0.477
0.392	0.431	0.438
mean 0.361	0.388	0.356
standard deviation 0.025	0.042	0.015
coefficient of variation 6.9	10.8	4.2

Overall mean 0.368
Overall standard deviation 0.031
Overall coefficient of variation 8.4

Adherence to Beers' Law: (at 530 nm.)

Table 2:6

µg tin(IV)/ml.	0.5	1.0	1.5	2.0
absorbance (sample+blank)	0.300	0.489	0.669	0.848
absorbance (sample-~~blank~~)	0.202	0.391	0.571	0.750

Beers' Law was closely followed over the range 0.5 to 2.0 µg. tin(IV)/ml., the only deviation being at very low concentrations (less than 0.3 µg. tin (IV)/ml.), where there was slight curvature.

Molar absorptivity:

Average molar absorbtivity over the 0.5 to 2.0 μg tin(IV)/ml. range was found to be 45,000 l. mol^{-1} cm^{-1}.

Spectral characteristics: (Fig. 2:1c)

As with Phenylfluorone in aqueous media the reagent/complex band separation was non-existent, because of this absorbance measurements are taken at 530 nm., rather than at the wavelength of maximum absorption, presumably to reduce the absorbance due to excess reagent, although, of course, at the sacrifice of sensitivity.

Non-uniformity of commercially available samples of Phenylfluorone:

During the previous work, the question arose of non-uniformity of the various samples of Phenylfluorone that were commercially available. Four samples were examined, one from BDH, one from Fisons, and two from Hopkin and Williams. They gave quite different tin(IV)-Phenylfluorone spectra.

Thin layer chromatrography (Aluminium Oxide, Merck type E; eluent, 1% concentrated hydrochloric acid in methanol) showed that the samples consisted of two major components, a red species that was eluted upwards and a yellow species that remained on the starting line. The red species turned yellow on addition of acid and the yellow species turned red on addition of alkali.

Paper electrophoresis (Whatman No.1 filter paper, 0.05M potassium tetroxalate, i.e. pH 1.65 buffer, constant current of 5 milliamps for 18 hours) showed that the red species was electrically neutral and the yellow positively charged.

The foregoing evidence suggests that the two components are the non-protonated (R) and protonated (RH^+) equilibrium forms of the reagent respectively. The existence of these two forms in the original sample would not be detrimental, if at Picasso and Pizzimenti's working pH of

1.2 conditions were sufficiently acid to convert all the neutral form to the protonated form. However, this is not likely, since paper electrophoresis was carried out under buffered conditions of pH 1.65, that is at a pH close to Piccasso and Pizzimenti's working pH, and this work showed that the red, neutral form continues to exist, which means that the equilibrium is extremely slow.

In spite of this and the unfavourable spectral characteristics and poor reproducibility, given earlier, Phenylfluorone appears to be the most popular spectrophotometric reagent for tin used by the British Steel industry at the present time.

GALLEIN

McDonald and Stanton's (21) method for tin in soil, in which the tin(IV)-Gallein complex is extracted into n-pentanol, was used for this investigation.

Table 2:7 Tests were carried out on solutions that contained 1 μg tin(IV)/ml. of n-pentanol, using 10 mm. cells, at 500 nm.

Batch 1 (abs.-blank of 0.179)	Batch 2 (abs.-blank of 0.184)	Batch 3 (abs.-blank of 0.171)
0.333	0.328	0.322
0.333	0.309	0.448
0.321	0.309	0.315
0.333	0.309	0.351
0.333	0.331	0.364
mean 0.331	0.371	0.360
standard deviation 0.0054	0.0113	0.0532
coefficient of variation 1.6	3.6	14.7

Overall mean 0.336

Overall standard deviation 0.346

Overall coefficient of variation 10.3

Adherence to Beers' Law: (at 500 nm.)

Table 2:8

µg tin(IV)/ml.	0.5	1.0	1.5	2.0
absorbance (sample+blank)	0.348	0.493	0.641	0.778
absorbance (sample)	0.178	0.323	0.471	0.608

Adherence to Beers' Law was good over the 0.5 to 2.0 µg tin(IV)/ml. range used, but there was some slight curvature at concentrations less than 0.5 µg/ml.

Molar absorptivity:

Across the 0.5 to 2.0 µg/ml. range the average molar absorbtivity found was 37,500 l mol^{-1} cm^{-1}.

Spectral characteristics: (Fig. 2:1d)

The spectral characteristics of the system were far from satisfactory, there being almost complete overlap of reagent and complex bands.

CATECHOL VIOLET

This reagent has the advantage that its complex with tin(IV) is water soluble, which allows the use of simpler manipulative techniques than can be used with most of the other colorimetric reagents for tin.

(A) WITHOUT CETRYLTRIMETHYLAMMONIUM BROMIDE (CTAB)

The method used was that due to Newman and Jones (57).

Reproducibility tests:

Table 2:9 Tests were carried out on solutions that contained 0.7 µg tin(IV)/ml. using 10 mm. cells at 552 mm.

Batch 1 (absorbance)	Batch 2 (absorbance)	Batch 3 (absorbance)
0.368	0.373	0.374
0.370	0.373	0.374
0.377	0.367	0.355
0.377	0.365	0.374
mean	0.373	0.370	0.369
standard deviation	0.0015	0.0013	0.0030
coefficient of variation	0.40	0.35	0.81

Overall mean	0.371
Overall standard deviation	0.00621
Overall coefficient of variation	1.7

Adherence to Beers' Law: (at 552 nm.)

Table 2:10

µg tin(IV)/ml.	0.2	0.4	0.6	0.8	1.0	1.2
absorbance	0.108	0.222	0.348	0.455	0.552	0.677

Beers' Law was closely followed, there being only slight scattering of points around a basic straight line.

Molar absorbtivity:

Over the 0.2 to 1.2 µg tin(IV)/ml. range considered, the average molar absorbtivity was 67,000 l mol^{-1} cm^{-1}.

Spectral characteristics: (Fig. 2:1e)

The spectral characteristics are a great improvement on those of Phenylfluorone and Gallein already reported. In this tin(IV)-reagent system there is good, though not perfect, separation of absorbance bands.

(B) WITH CETYLTRIMETHYLAMMONIUM BROMIDE (CTAB)

The methol used was essentially that due to Dagnall et. al. (60). The method, as laid down by these workers, infers that after adjustment of the pH to the optimum value of 2.2, the solution should be made up to volume (100 ml.) by addition of water; this would result in a change of the pH from the optimum value of 2.2. To avoid this, the volume was made up using a sulphuric acid solution at pH 2.2. Furthermore, in this work the 10^{-4}M standard tin solution was made up 10% V/V in sulphuric acid when prepared by dilution of 10^{-3}M standard tin solution - (see Chapter 4, stability of standard tin (IV) solutions).

Reproducibility tests:

Table 2:11 Tests were carried out on solutions that contained 0.593 µg tin(IV)/ml. using 10 mm. cells at 662 mm.

Batch 1 (absorbance)	Batch 2 (absorbance)	Batch 3 (absorbance)
0.445	0.446	0.466
0.465	0.456	0.471
0.447	0.447	0.456
0.464	0.466	0.468
0.465	0.473	0.473
mean	0.457	0.458	0.467
standard deviation	0.0103	0.0118	0.0066
coefficient of variation	2.3	2.6	1.5

Overall mean	0.461
Overall standard deviation	0.0101
Overall coefficient of variation	2.2

Adherence to Beers' Law: (at 662 nm.)

Table 2:12

ug tin(IV) /ml.	0.2	0.4	0.6	0.8	1.0	1.2
absorbance	0.130	0.292	0.468	0.629	0.822	0.985

Beers' Law was very closely adhered to over the whole of the 0.2 to 1.2 μg/ml. range considered, there being very slight curvature at concentrations of less than 0.2 ug/ml.

Molar absorptivity:

Over the range of the Beers' Law plot the average molar absorbtivity was found to be 92,000 $l mol^{-1} cm^{-1}$.

Spectral characteristics: (Fig. 2:1f)

The recommendation of this method emerges from a study of the spectral characteristics of the system. "Sensitisation" with CTAB results in a bathochromic shift of the absorption maximum of the metal complex from 550 nm. to 662 nm., whilst the adsorption maximum of the excess reagent remains at 445 nm. This shift has the effect of removing all reagent/complex band overlap and to quote Dagnall, et. al. (60), "promotes conditions that are almost ideal for analytical measurement."

SALICYLIDENEAMINO-2-THIOPHENOL

The method that involves extraction of the complex into xylene is due to Gregory and Jeffery (75).

Reproducibility tests:

Table 2:13 Tests were carried out on solution that contained 3 µg tin(IV)/ml. of xylene using 10 mm. cells at 415 nm.

Batch 1 (absorbance)	Batch 2 (absorbance)	Batch 3 (absorbance)
0.267	0.315	0.358
0.270	0.322	0.346
0.294	0.325	0.352
0.287	0.375	0.366
0.297	0.343	0.322
mean	0.283	0.338	0.349
standard deviation	0.0137	0.0231	0.0167
coefficient of variation	4.8	6.8	4.8

Overall mean 0.323
Overall standard deviation 0.0342
Overall coefficient of variation 10.6

Adherence to Beers' Law: (at 415 nm.)

Table 2:14

µg tin(IV)/ml.	1.0	2.0	3.0	4.0	5.0
absorbance	0.107	0.216	0.306	0.400	0.492

Adherence was good over the recommended range.

Molar absorptivity:

Over the 1.0 to 5.0 µg tin(IV)/ml. range used, the average molar absorptivity was found to be 13,400 $l mol^{-1} cm^{-1}$.

Spectral characteristics: (Fig. 2:1g)

At the wavelength of maximum absorbance for the complex there is only slight overlap of the reagent and complex bands.

SUMMARY OF RESULTS

Table 2:15

Reagent	Adherence to Beers' Law	molar absorptivity $l mol^{-1} cm^{-1}$	spectral characteristics	reproducibility	
				Batchwise coeff.of var.	Overall coeff.of var.
DITHIOL (aqueous)	very poor	5,900	excellent	1.4 2.3 2.5	5.4
PHENYLFLUORONE (aqueous)	fair	54,500	very poor	5.6 8.1 3.4	11.6
PHENYLFLUORONE (methylisobutyl ketone)	good	45,500	poor	6.9 10.8 4.2	8.4
GALLEIN (n-pentanol)	good	37,500	poor	1.6 3.6 14.7	10.3
CATECHOL VIOLET (aqueous without CTAB)	good	67,000	good	0.40 0.35 0.81	1.7
CATECHOL VIOLET (aqueous) with CTAB	good	92,000	excellent	2.3 2.6 1.5	2.2
STAP (in xylene)	good	13,400	good	4.8 6.8 4.8	10.6

CONCLUSIONS

The foregoing experimental evidence clearly illustrates that Catechol Violet is superior, in virtually every respect, to all the other reagents investigated. As such, it is probably the best reagent available at the present time. The greater reproducibility of the Catechol Violet method is undoubtedly largely due to the water solubility of the tin(IV)-Catechol Violet complex. The system is non-colloidal; this avoids the problems of light scattering and the use of dispersing agents which are not generally of uniform chemical consistency.

Furthermore, the possible sensitisation of the Catechol Violet method with CTAB, which results in greater sensitivity and complete

separation of reagent and complex absorption bands added still further weight to arguments in favour of using Catechol Violet as the reagent of choice in the present task, that is to develop a rapid and precise method that it applicable to the widest range of steels possible.

PRINCIPAL SPECTROPHOTOMETRIC REAGENTS FOR TIN.

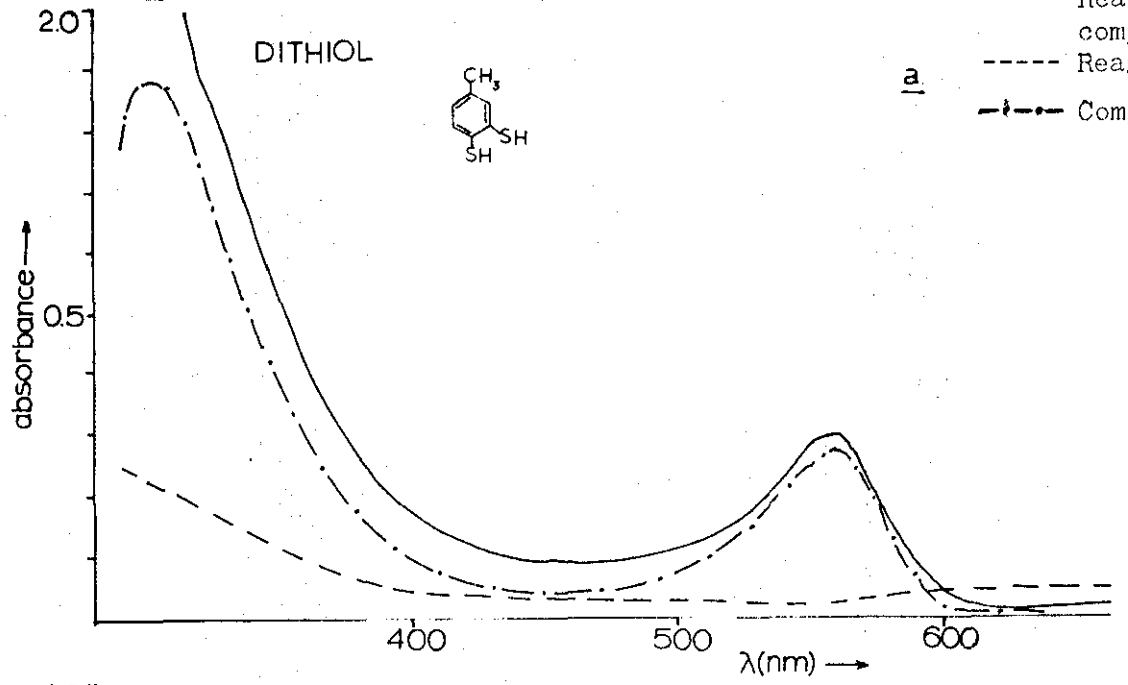
VISIBLE ABSORPTION SPECTRA OF THE TIN-REAGENT SYSTEMS.

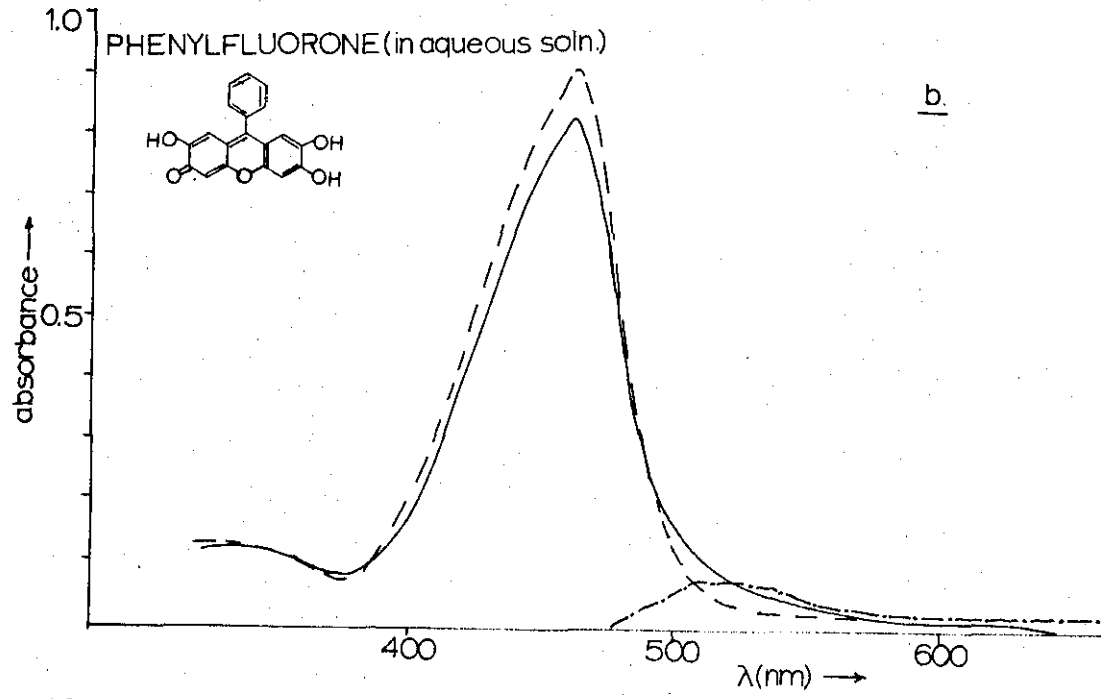
Fig. 2:1.

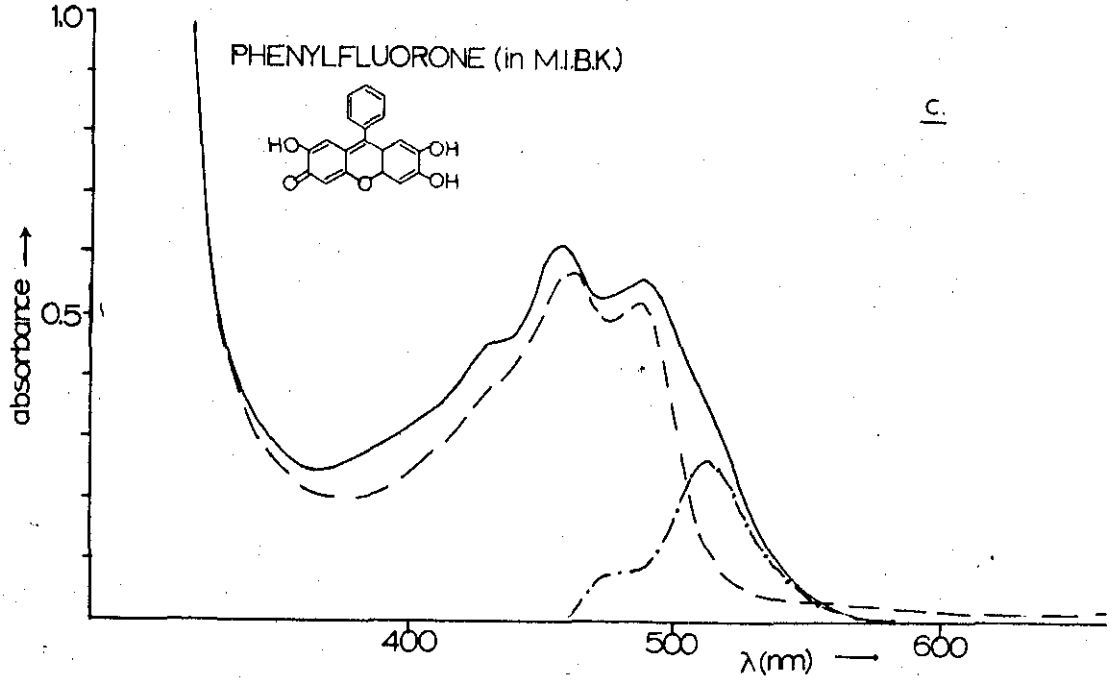
——— Reagent and complex.

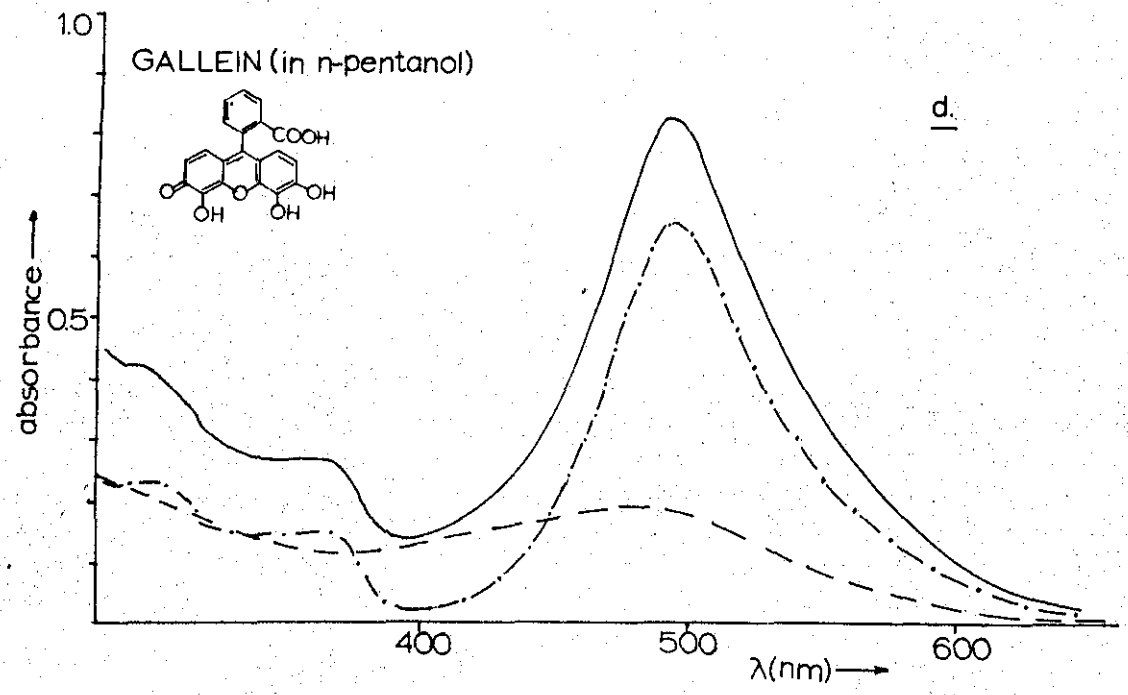
----- Reagent.

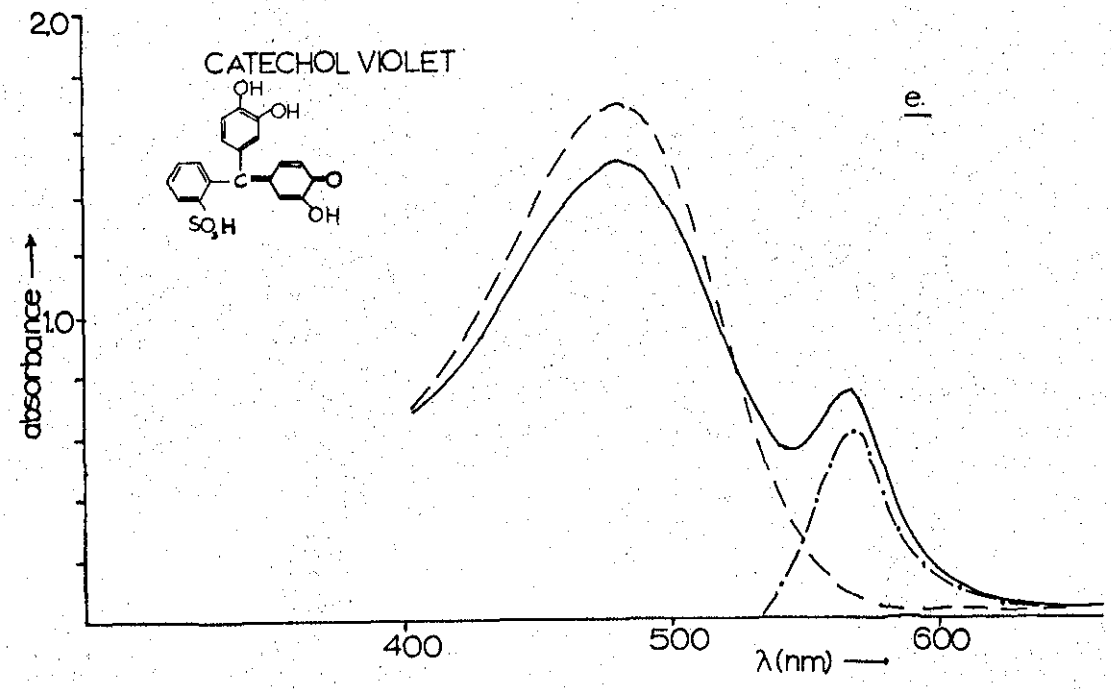
—•—•— Complex.

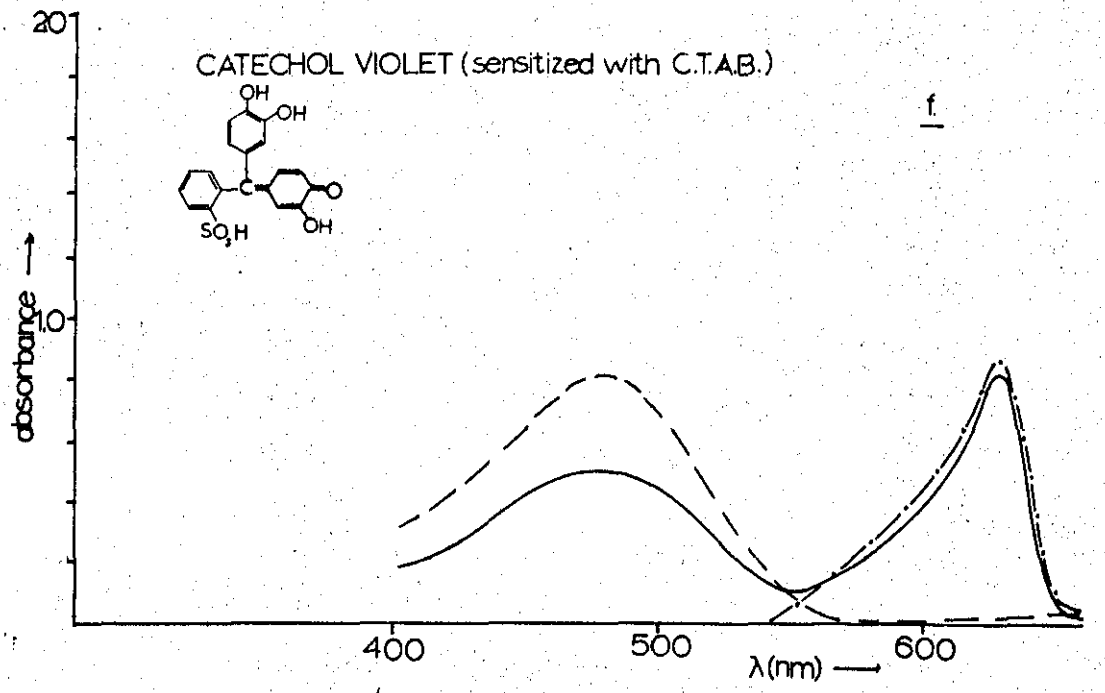


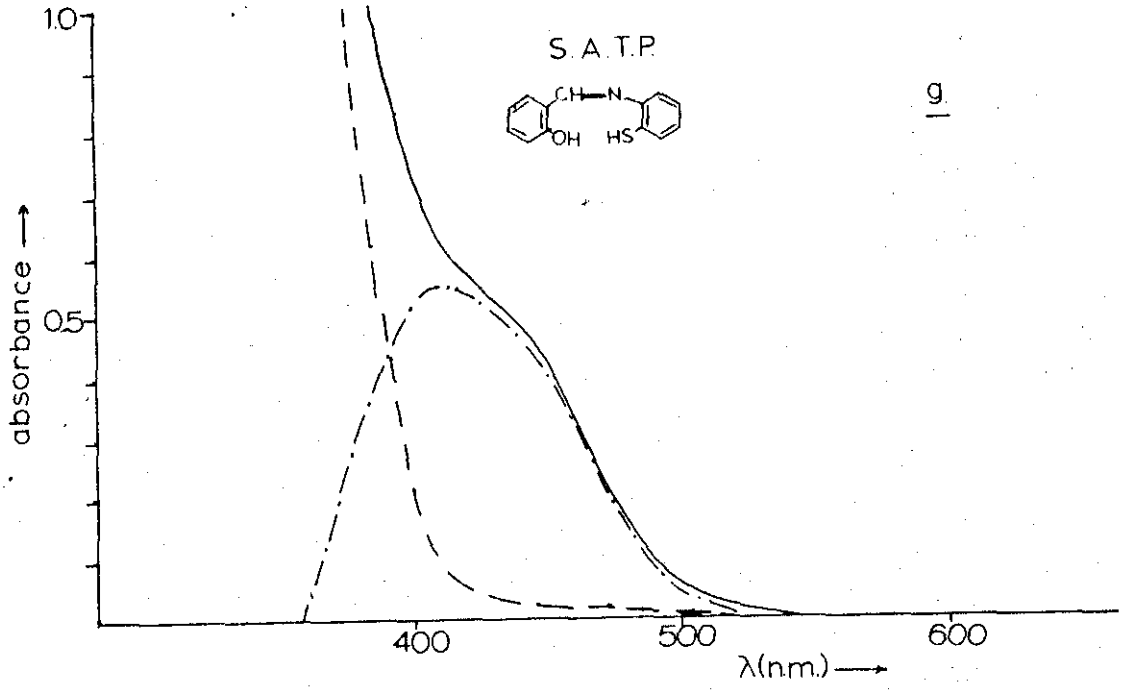





GALLEIN (in n-pentanol)
d.
1.0
0.5
absorbance
400
500
600
λ(nm)


CATECHOL VIOLET
e.
2.0
1.0
absorbance
400
500
600
λ(nm)


CATECHOL VIOLET (sensitized with C.T.A.B.)
f.
2.0
1.0
absorbance
400
500
600
λ(nm)


S. A. T. P.
CH—N
OH HS
g
1.0
0.5
absorbance
400
500
600
λ(n.m.)

CHAPTER III

EXTRACTIVE SEPARATION OF TIN

There is no highly selective reagent for the colorimetric determination of tin. Consequently, if a method is to be applicable to anything other than a narrow range of steels, the colorimetric determination must be preceded by a selective separation procedure. The Catechol Violet–CTAB colorimetric determination had been chosen on the strength of the experimental evidence reported in the previous chapter. This determination takes place in aqueous solution and, therefore, if a solvent extraction procedure is to be compatible with this colorimetric determination, it must include a back-extraction into aqueous media. Undoubtedly, the simplest and most satisfactory way of achieving the required separation is by solvent extraction of tin(IV) iodide and back-extraction of tin into aqueous media.

Gilbert and Sandell (54), in 1960, were the first to realise the potential of the tin(IV) iodide extraction as a selective method - their work was further developed by Tanaka (55,56). Benzene was used as the extractant and dilute sulphuric and hydrochloric acids were used respectively for back-extraction. The success of the iodide extraction is due to the very slight tendency of tin to form anionic iodo species, even at high iodide concentrations. This behaviour may be explained by the difficulty in reaching the maximum coordination number of six because of the spatial problems involved in arranging six large iodide ions around a small tin(IV) ion to give SnI_6^{2-}.

In 1966, Newman and Jones (57) developed a procedure, for the SAC Analytical Methods Committee, for the determination of tin in organic matter. They substituted toluene for benzene because of its lower toxicity, but were unable to obtain quantitative recoveries by back-extraction into an aqueous phase of dilute hydrochloric, sulphuric or perchloric acids. Instead, they back-extracted the tin with sodium hydroxide solution and in this way obtained 100% reversion. Modifications that improve this

method have been made herein and the procedure adapted to give an extraction procedure that is compatible with the previously selected Catechol Violet-CTAB colorimetric determination.

EXPERIMENTAL

(A) TOLUENE EXTRACTION OF TIN

The optimum conditions of acid and iodide strength, for the extraction of tin(IV) iodide have been previously determined by Gilbert and Sandell (54) and Tanaka (55,56).

Number of extractions required:

Table 3:1 The extraction procedure was applied to 20 µg of tin in the form of a standard solution.

Absorbance when 20 µg of tin were determined using the Catechol Violet-CTAB system = 0.293 at 662 nm., (i.e. by definition 100% recovery).

No. of extractions	absorbance (mean of 6 results) at 662 nm.	µg tin found	% recovery
1	0.272	18.6	93.0
2	0.291	19.9	99.5

In contrast to the findings of Newman and Jones (57), it was found that two toluene extractions were necessary if recoveries approaching 100% are to be achieved. These findings are in accordance with those of Gilbert and Sandell (54), who state that a second extraction may be necessary if the sulphate concentration in the solution exceeds 0.5M.

Extraction time required:

Table 3:2 The extraction procedure was applied to 20 μg of tin in the form of aliquots of standard solution.

time in secs.	15	30	60	120	180	240
absorbance	0.279	0.279	0.276	0.285	0.285	0.285
(in triplicate)	0.287	0.290	0.286	0.292	0.292	0.285
at 662 nm.	0.260	0.284	0.276	0.289	0.292	0.290
average abs.	0.275	0.284	0.279	0.289	0.290	0.287

Poor reproducibility and less than 100% extraction given by extraction times of less than 120 seconds.

Stability of toluene extract:

In view of the volatile nature of tin(IV) iodide a stability test on the extract in toluene was carried out.

Table 3:3 Three extracted solutions were allowed to stand in open separating funnels for 5 hours.

tin added (μg)	tin found (μg)		
	Sample 1	Sample 2	Sample 3
20	19.7	20.0	20.0

Loss was only slight and was negligible within experimental error.

(B) SODIUM HYDROXIDE BACK-EXTRACTION OF TIN

Newman and Jones (57) added 5M sodium hydroxide solution dropwise until the toluene layer became colourless. In this work however, it was thought that it would make manipulation simpler by using a pre-determined volume of a solution of sodium hydroxide of optimum strength.

Molarity of sodium hydroxide

The sodium hydroxide back extract has to be subsequently acidified and adjusted to pH 2.2, the optimum pH for the Catechol Violet-CTAB colorimetric determination of tin. Therefore, in order to reduce the volume of acid and the heat of reaction involved in this step, it was advantageous to determine the minimum permissible strength of the sodium hydroxide solution to be used for the back-extraction.

Table 3:4 Aliquots of standard tin solution containing 20 µg tin were back extracted from toluene using a 5 ml. followed by a 2 ml. aliquot of sodium hydroxide solution.

M of sodium hydroxide soln.	0.1	0.5	1.0	2.0	3.0	5.0
absorbance	0.288	0.280	0.294	0.302	0.294	0.295
(in triplicate)	0.278	0.290	0.291	0.300	0.295	0.295
at 662 nm.	0.272	0.280	0.293	0.300	0.293	0.300
average abs.	0.279	0.283	0.292	0.300	0.294	0.296

For 100% extraction and good reproducibility the sodium hydroxide solution must be at least 1M.

(C) PROBLEMS OF HYDROLYSIS DURING EXTRACTION OF TIN

In solutions of insufficient acid or alkali strength, tin is readily hydrolysed via a complex series of reactions of which the following are examples (78):-

(i) $Sn^{4+} + 2H_2O \rightleftharpoons SnO_2 + 4H^+$

(ii) $Sn^{4+} + 2H_2O \rightleftharpoons Sn(OH)_2^{2+} + 2H^+$

(iii) $Sn(OH)_2^{2+} + 2H_2O \rightleftharpoons Sn(OH)_4 + 2H^+$

The back-extract, at a pH of about 11, must be adjusted to the low pH of 2.2, the optimum for the Catechol Violet-CTAB colorimetric determination. The problem arises of hydrolysis occurring during passage through the middle pH ranges; Fig. 3:1 shows the pH range in which considerable hydrolysis occurs. Tanaka (55,56) used dilute hydrochloric acid as the back-extraction agent, so there was no hydrolysis problem in this case, but it was found that hydrochloric acid did not give 100% reversion, at least not with volumes that would have been practical for the present requirements.

In the case of an alkaline back-extract the hydrolysis problem can be overcome by running it into a stirring excess of dilute hydrochloric acid in order to almost instantaneously bring the pH down to about 1, a pH at which the solution was found to be stable for at least several days.

The subsequent additions of reagents can then be made and the pH adjusted to 2.2 by addition of dilute sodium hydroxide solution.

If a direct adjustment of the alkaline back-extract is made, by simply adding acid dropwise, transition through to 10 to 2 pH range is not sufficiently rapid and substantial hydrolysis occurs:-

Table 3:5 Back-extracts were adjusted directly to pH 2.2 by dropwise addition of dilute hydrochloric acid.

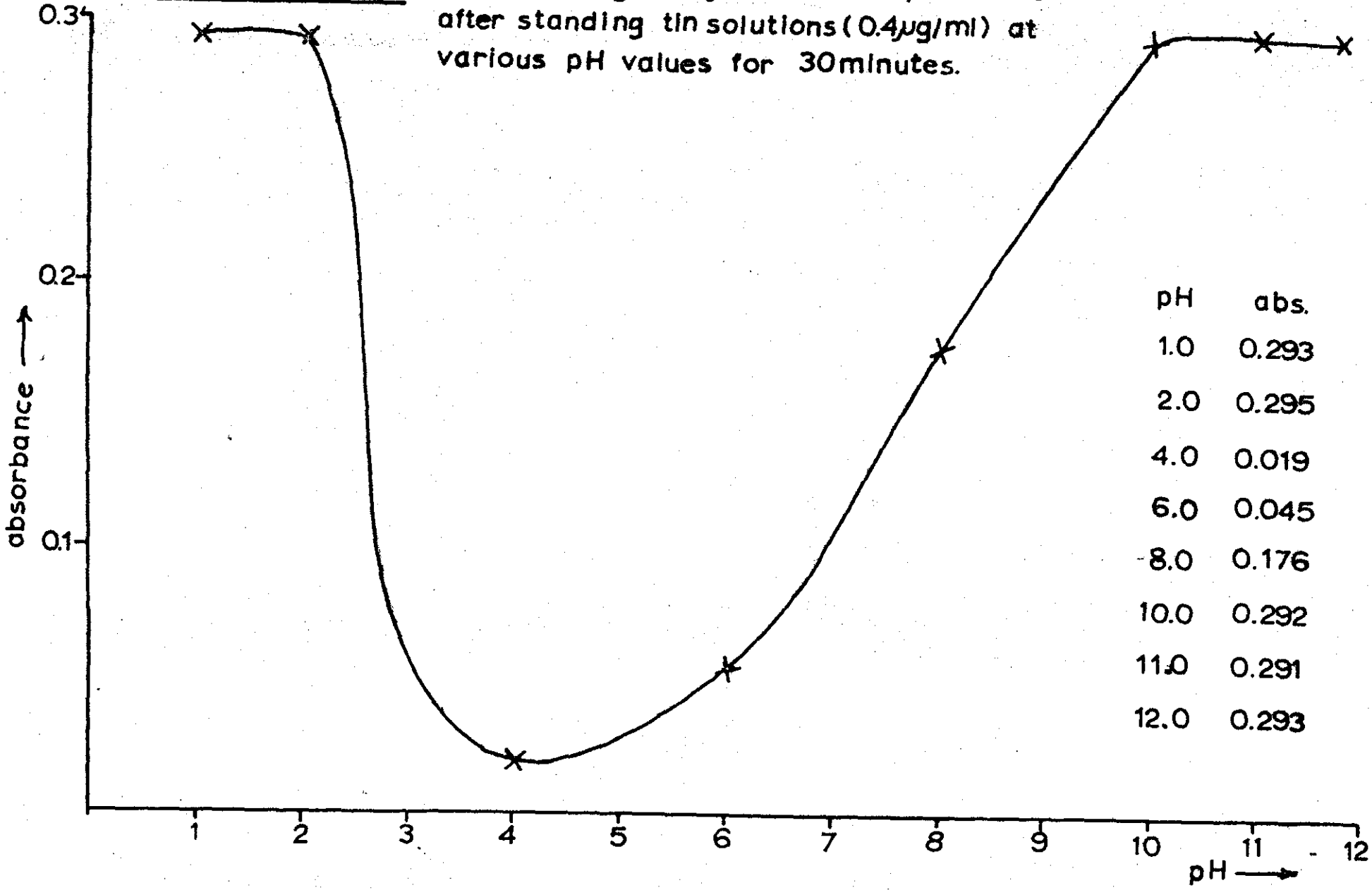
tin added (μg)	tin found (μg)
20.0	10.1, 18.0, 10.8 16.5, 10.8, 17.7

(D) PROBLEM OF CARRIED-OVER IODINE

The liberation of small amounts of iodine during the extraction procedure, owing to atmospheric oxidation of potassium iodide, is inevitable. It is extracted into toluene and then in turn, back-extracted

Fig. 3:1.

HYDROLYSIS OF TIN. absorbance given by recommened procedure after standing tin solutions (0.4µg/ml) at various pH values for 30 minutes.



pH	abs.
1.0	0.293
2.0	0.295
4.0	0.019
6.0	0.045
8.0	0.176
10.0	0.292
11.0	0.291
12.0	0.293

as hypoiodite into the sodium hydroxide; on acidification iodine is released again. This must be removed for two reasons: Catechol Violet is oxidised and CTAB is precipitated, presumably as the triodide, if iodine is present. Ascorbic acid solution is therefore added in order to discharge the iodine colour before any further additions of reagents are made.

(E) CONCENTRATION RANGE OF THE PROPOSED EXTRACTION PROCEDURE

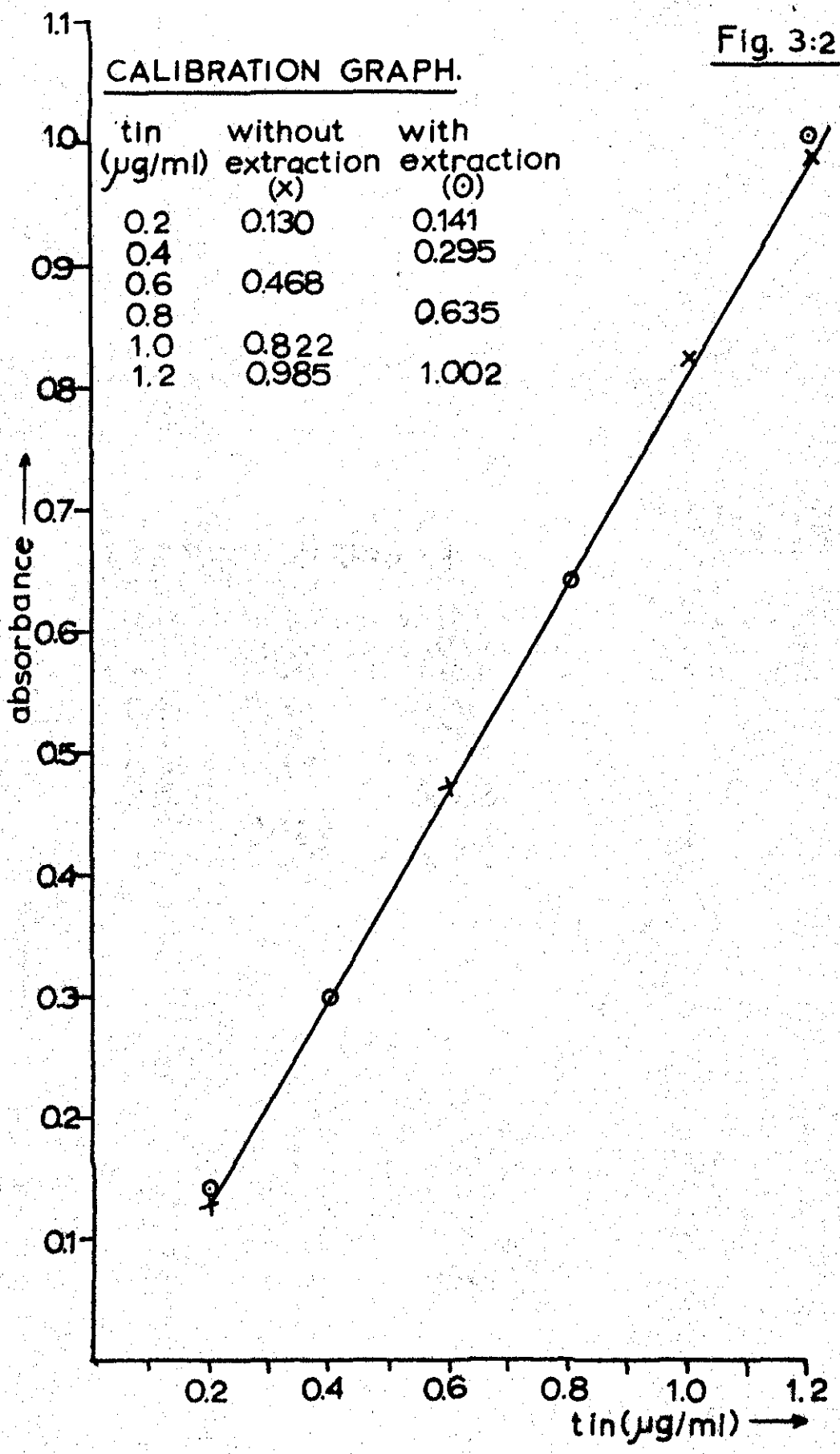
Over the range 10-60 μg of tin the calibration plot obtained after extraction was identical, within expected error, to that obtained without the extraction procedure being used first. (Fig. 3:2).

This means that in the developed method, given in the next chapter, the calibration plot can be constructed without including the extraction stage in the procedure.

Fig. 3:2

CALIBRATION GRAPH.

tin (µg/ml)	without extraction (x)	with extraction (⊙)
0.2	0.130	0.141
0.4		0.295
0.6	0.468	
0.8		0.635
1.0	0.822	
1.2	0.985	1.002



CHAPTER IV

DEVELOPMENT OF A PROCEDURE FOR THE DETERMINATION OF TIN BASED ON THE EXTRACTION OF TIN(IV) IODIDE FOLLOWED BY COLORIMETRIC DETERMINATION WITH CATECHOL VIOLET AND CETYLTRIMETHYLAMMONIUM BROMIDE

The tin(IV) iodide solvent extraction procedure, adapted in the previous chapter, has been combined with the Catechol Violet-CTAB determination chosen on the experimental evidence of Chapter II. Conditions are also given for obtaining a standard tin(IV) solution that is stable and free from hydrolysis and for the utilisation of lactic acid as a masking agent for other metals found in steels, including its successful application to the long standing problem of molybdenum interference.

EXPERIMENTAL

When the combined solvent extraction-spectrophotometric procedure was applied to a range of British Chemical Standard Steels of various types, it was often the case that excessive quantities of iodine were liberated on adding potassium iodide to the steel solutions, owing to metal ions with oxidising properties being present. This aggravated the problem of carried-over iodine already discussed in Chapter III. For this reason, addition of ascorbic acid to the steel solution, before addition of iodide, is recommended. In this way many of the oxidising metal ions are reduced to oxidation states that will not liberate iodine from iodide.

(A) RECOMMENDED PROCEDURE AND ITS APPLICATION TO BCS STEELS

Reagents:

CONCENTRATED HYDROCHLORIC ACID, sp.gr. 1.16 to 1.18 - Analytical-reagent grade.

CONCENTRATED SULPHURIC ACID - Analytical-reagent grade.

HYDROGEN PEROXIDE, 100 volumes - Analytical-reagent grade.

ASCORBIC ACID SOLUTION, 5 per cent M/V.

POTASSIUM IODIDE SOLUTION, 80 per cent m/V - Dissolve 80 *g.* of potassium iodide in water and dilute to 100 ml. Prepare fresh daily.

DILUTE SULPHURIC ACID SOLUTION, 25 per cent V/V - Dilute 250 ml. of concentrated sulphuric acid to 1 litre.

ACIDIC POTASSIUM IODIDE WASH SOLUTION - Mix 25 ml. of the dilute sulphuric acid and 2.5 ml. of the potassium iodide solution.

TOLUENE - Analytical-reagent grade.

SODIUM HYDROXIDE SOLUTION, 8 per cent m/V - Dissolve 40 *g.* of analytical-reagent grade sodium hydroxide in water and dilute to 500 ml.

CATECHOL VIOLET SOLUTION, 0.04 per cent m/V - Dissolve 0.1 g. of Catechol Violet in water and dilute to 250 ml.

CETYLTRIMETHYLAMMONIUM BROMIDE SOLUTION, 0.1 per cent m/V - Dissolve 0.1 *g.* of cetyltrimethylammonium bromide in water with gentle warming and dilute to 100 ml.

CONCENTRATED STANDARD TIN(IV) SOLUTION, 100 $\mu g\ ml^{-1}$ - Dissolve 0.1000 g. of analytical-reagent grade granulated tin in 20 ml. of hot concentrated sulphuric acid. Cool the solution and add it cautiously to about 200 ml. of water contained in a 1 litre calibrated flask. Cool the solution, add cautiously a further 60 ml. of concentrated sulphuric acid and, after cooling, dilute the mixture to 1 litre with water; ignore any globules of sulphur that are formed.

DILUTE STANDARD TIN(IV) SOLUTION, 10 $\mu g\ ml.^{-1}$ - Add 10 ml. of concentrated sulphuric acid to about 50 ml. of water in a 100 ml. calibrated flask. Cool the solution, add 10.0 ml. of concentrated standard tin(IV) solution and dilute to 100 ml. with water. (See later work on stability of standard tin solutions, Chapter IV: Section B). It is advisable to prepare this solution fresh daily, although good results have been obtained with solutions prepared several days previously.

ACIDIFIED WATER, pH 2.2 - Adjust the pH of de-ionised water to 2.2 with dilute hydrochloric acid. If this solution is stored, it is advisable to check its pH before use.

LACTIC ACID SOLUTION, 20 per cent V/V - Dilute 20 ml. of analytical-reagent grade lactic acid to 100 ml. with water.

Preparation of calibration graph:

By pipette, introduce an aliquot of the dilute standard tin solution (1 to 5 ml.) into a 50 ml. beaker and dilute it with water to 25 ml. Add 2.5 ml. of Catechol Violet solution and 1 ml. of cetyltrimethyl-ammonium bromide solution. Insert a combined calomel-glass electrode into the solution and adjust the pH carefully to 2.2 with 2M sodium hydroxide solution while stirring with a magnetic stirrer (Note 1).

Remove the electrode, wash it with acidified water and transfer the solution and washings quantitatively with acidified water to a 50 ml. calibrated flask that has been previously washed with acidified water. Finally, dilute the solution to 50 ml. with acidified water and mix well. Allow the colour to develop fully for 40 minutes at room temperature and then measure the absorbance at 662 nm. against water in a 1 cm. cell (Note 2).

Procedure:

Dissolve an appropriate amount of steel (see Table 4:1), contained in a 100 ml. conical flask covered with a watch-glass, in 5 to 10 ml. of concentrated hydrochloric acid by using very gentle heating (Note 3). Wash the watch-glass with the minimum amount of water (about 0.5 ml.) and cool the solution slightly. Add concentrated sulphuric acid (see Table 4:1) gently down the side of the flask, avoiding loss of sample by excessive effervescence. Without replacing the watch-glass, boil the solution gently (until fumes of sulphur dioxide appear) to drive off the hydrochloric acid (Note 4). (For steels that give a black carbide residue see Note 5).

Cool the solution and add about an equal volume of water. Heat the mixture gently so as to dissolve any crystalline solids, then cool it again.

SUGGESTED SAMPLE SIZES AND ALIQUOTS FOR VARIOUS STEELS

Table 4:1 Although in many instances the tin content of the steel will not be known even approximately, the sample sizes and aliquots given here will give an indication of a suitable amount of sample to take as a trial. The sample size and aliquots recommended for each range of tin content give absorbance values between 0.31 and 0.62.

Expected tin content	Amount of steel to be taken	Volume of concentrated sulphuric acid to be added after dissolution	Volume of sample solution	Aliquot taken
%	g.	ml.	ml.	ml.
0.005 - 0.01	0.4	7	)	
0.01 - 0.02	0.2	7	)All sample taken	
0.02 - 0.04	0.1	7	)	
0.04 - 0.08	0.1	14	50	25
0.08 - 0.16	0.1	28	100	25
0.16 - 0.32	0.125	28	100	10*

* In this case, add 15 ml. of 25 per cent. V/V sulphuric acid before extraction.

For steels that contain less than 0.04 per cent of tin, all the solution is transferred into an 100 ml. separating funnel, fitted with a PTFE tap and diluted to approximately 25 ml. with water (for steels that contain more than 0.04 per cent of tin, see Table 4:1 for dilution volumes and aliquot taken). Add 5 ml. of ascorbic acid solution and 2.5 ml. of potassium iodide solution, in that order, mixing thoroughly after each addition. Add 10 ml. of toluene, stopper the funnel and shake it for at least 2 minutes. Wash the stopper and neck of the flask with about

0.5 ml. of water. Run the aqueous layer into a second separating funnel and extract it again with a second 10 ml. portion of toluene. Run the aqueous layer to waste and combine the toluene extracts in the first separating funnel. Wash the combined extracts with 5 ml. of acidic potassium iodide wash solution, which is then discarded, avoiding loss of toluene.

Add from a calibrated pipette, 5 ml. of 2M sodium hydroxide solution and back-extract the tin into this layer by shaking the separating funnel for at least 30 seconds. Run the sodium hydroxide solution into 5.0 ml. of 5M hydrochloric acid, contained in a 50 ml. beaker, while stirring efficiently with a magnetic stirrer (Note 6). Extract the toluene with two further 2.0 ml. volumes of 2M sodium hydroxide solution and add the extracts to the beaker as before.

Add ascorbic acid dropwise until the iodine colour is discharged and then add one drop in excess. (For steels that contain ~~applicable~~ appreciable amounts of molybdenum, cobalt, chromium, nickel or vanadium, see Note 7). Add 2.5 ml. of Catechol Violet solution and 1 ml. of cetyltrimethylammonium bromide solution. Insert a combined calomel-glass electrode into the solution and adjust the pH to 2.2, carefully, with 2M sodium hydroxide solution (Note 1).

Remove the electrode, wash it with acidified water and transfer the solutions and washings quantitatively with acidified water into a 50 ml. calibrated flask that has been previously washed out with acidified water. Finally, dilute the solution to 50 ml. with acidified water and mix well. Allow the colour to develop fully for 40 minutes, (see later work on colour development time, Chapter IV: Section C), at room temperature and then measure the absorbance at 662 nm. against water in a 1 cm. cell (Note 2).

Notes:

1. Efficient stirring, preferably with a magnetic stirrer, is important at this stage. Local concentrations of sodium hydroxide must be avoided, and the pH must not be allowed to increase above 2.2, otherwise hydrolysis of tin may result.

2. Small amounts of the complex are absorbed on to glassware, which becomes noticeable after sometime if the glassware is not cleaned effectively. The absorption cells and calibrated flasks should be cleaned with dilute sulphuric acid after use.

3. Careful heating is recommended so as to prevent loss of tin by volatilisation from chloride media.

4. Chloride interferes in the extraction of tin(IV) iodide (54).

5. At this stage, the black carbide residue should be removed by slow addition of 2 ml. of 100 volume hydrogen peroxide, and then boiling so as to destroy the excess. For steels that contain appreciable amounts of tungsten, this treatment causes precipitation of tungstic acid with co-precipitation of tin. Instead of hydrogen peroxide treatment, dilute the sulphuric acid with an equal volume of water and filter off the black residue with a Whatman No.541 filter-paper. Wash the flask and filter paper with three, 3 ml. portions of 5 per cent V/V sulphuric acid.

6. Efficient mixing is important in order to prevent hydrolysis of tin(IV).

7. If molybdenum, chromium, vanadium, cobalt or nickel is present in the steel, add 10 ml. of lactic acid solution, (see later work on interferences and masking techniques, Chapter 4: Section D).

Application to BCS steels

Table 4:2

Steel	Tin present*	Tin found (mean of 6 results)	Coefficient of variance (6 results)
	% m/m	% m/m	
Mild steel 273	0.065	0.065	1.2
Mild steel 324	0.13	0.130	3.6
0.15% carbon steel 218/3	0.042	0.039	3.5
0.3% carbon steel 239/3	0.030	0.027	3.8
Low-alloy steel 254	0.005+	0.0063	4.1
High speed steel 220/2	0.019	0.019++	5.6
High speed steel 241/2	0.025	0.025++	8.5

* standardised values

\+ approximate value only

++ lactic acid masking used

High speed steels contain a high proportion of tungsten; consequently, the procedure described for these types of steel in Note 5 was used in the case of BCS steels 220/2 and 241/2. This probably accounts for the higher cooefficients of variance shown in Table 4:2 with these steels.

(B) STABILITY OF STANDARD TIN(IV) SOLUTIONS

The problem of hydrolysis of tin(IV) solutions of insufficient acid strength has already been discussed in Chapters II and III. Dagnall, et. al. (60) gave no details with regard to the dilution of their concentrated standard tin(IV) solution (10^{-3}M) to yield a dilute standard tin(IV) solution (10^{-4}M) for preparation of the calibration graph, and this infers that dilution should be made with water.

Investigation of stability of standard tin(IV) solutions (10^{-4}M) prepared by dilution of the concentrated standard tin(IV) solution (10^{-3}M) of Dagnall et. al. (60):

Table 4:3 Tests were carried out on solutions that were 0.6×10^{-5}M in tin, using 1 cm. cells, at 662 nm.

Tin solution	Time in hours				
	0	2	4	9	12
Dilution with water	0.448	0.403	0.363	0.306	0.256
Dilution with 10% V/V sulphuric acid	0.532	0.515	0.523	0.527	0.520

It is essential that more sulphuric acid is added when diluting the concentrated standard tin solution. Table 4:3 clearly illustrates the hydrolysis that occurs when dilution is made with water alone. This acidic solution incidentally, has the composition of a dilute standard tin(IV) solution recommended previously by the Analytical Methods Committee of the SAC (4).

(C) COLOUR DEVELOPMENT TIME

Dagnall et. al. (60) recommended a colour development period of only 10 minutes for their work with standard tin solutions. However, this time was checked using the back-extract from the iodide extraction procedure applied to a steel solution.

Investigation of colour development time using the back-extract of BCS mild steel 273:

Table 4:4 Absorbance measurements were taken in 1 cm. cells, at 662 nm.

Weight of steel taken		Time (minutes)						
		15	20	25	30	40	50	60
0.508	absorbance	0.508	0.510	0.511	0.521	0.518	0.520	0.522
0.0556	absorbance	0.582	0.585	0.589	0.601	0.600	0.601	0.601
0.0590	absorbance	0.616	0.619	0.623	0.632	0.636	0.642	0.639

A period of at least 30 minutes must be allowed for full colour development.

(D) INTEFERENCES AND MASKING TECHNIQUES

Investigation of the effects of other metals commonly found in steels:

The metal to tin ratios shown in Table 4:5 were chosen with reference to the publication of the London and Scandinavian Metallurgical Co., "Constituent Elements in Steel and Cast Iron", (79), as a guide to the highest possible ratios that could be expected in the everyday analysis of steels. The metals, cerium, magnesium, niobium and tantalum, were not considered, since they are either rarely found in steels or are only present in very small amounts. The recommended procedure, including the dissolution procedure, was carried out on an aliquot of standard tin(IV) solution and a known quantity of the other metal, either as the element or in the form of an appropriate salt.

Table 4:5 Amount of tin(IV) added = 30.0 µg.

Metal	Form of metal used	metal: tin ratio	tin found/µg (in triplicate)		
Antimony	element	5	29.7,	29.7,	30.0
		10	31.7,	31.4,	30.9
Arsenic	As_2O_3	100	30.4,	30.0,	29.7
		1,000	29.4,	29.7,	29.2
Manganese	$MnSO_4:4H_2O$	10,000	28.5,	28.5,	29.5
Copper	$CuSO_4:5H_2O$	20	29.2,	29.4,	29.7
Titanium	element	300	29.2,	29.2,	30.4
Aluminium	element	1,000	29.0,	29.2,	29.2
Zirconium	$ZrOCl_2:8H_2O$	1,000	30.2,	29.2,	30.4
Lead	$Pb(NO_3)_2$	100	29.0,	29.2,	29.7
Beryllium	$BeSO_4:4H_2O$	1,000	29.0,	30.0,	29.2
Molybdenum	$(NH_4)_6Mo_7O_{24}:4H_2O$	1,000	45.0,	45.6,	47.2
		1,000	29.7,*	30.0,*	30.2*
Chromium	$CrK(SO_4)_2:12H_2O$	10,000	33.2,	33.7,	33.6
		10,000	29.5,*	31.2,*	30.2*
Vanadium	$VOSO_4$	1,000	27.4,	21.0,	24.7
		1,000	31.9*,	28.2,*	30.9*
Cobalt	$CoSO_4:7H_2O$	10,000	26.2,	25.7,	27.2
		10,000	30.4,*	29.5,*	28.2*
Nickel	$NiSO_4+H_2O$	3,000	25.4,	23.8,	26.2
		3,000	30.7,*	30.0,*	29.5*

* lactic acid masking used.

Amounts of copper present in some steels will interfere because copper(I) iodide, which is formed on addition of potassium iodide, causes emulsification of the aqueous and organic phases. Nevertheless, copper can be tolerated up to a copper:tin ratio of 20:1, (see later work on a direct method, Chapter V). Lead also forms an insoluble iodide, but at levels found in steels it does not interfere.

Utilisation of lactic acid as a masking agent:

Gregory and Jeffery (75) used lactic acid to mask molybdenum in the determination of tin with salicylideneamino-2-thiophenol (SATP). Table 4:5 shows that it can be applied in the same way to the Catechol Violet-CTAB determination, and is also effective in the masking of chromium, vanadium, cobalt and nickel.

CHAPTER V.

DEVELOPMENT OF A DIRECT METHOD FOR THE RAPID ANALYSIS OF MILD STEELS USING CATECHOL VIOLET AND CETYLTRIMETHYLAMMONIUM BROMIDE

Picasso and Pizzimenti (40) have already described a spectrophotometric method for the determination of tin in steel, which does not require a prior separation of tin. However, Phenylfluorone was used as the colorimetric reagent. The various disadvantages of this reagent have been discussed earlier, (see Chapter II). Furthermore, the only masking technique used is that of iron(III) with ascorbic acid, Phenylfluorone has little inherent selectivity. Consequently, the method could not be applicable to as wide a range of steels as a procedure that includes a selective extraction of tin.

The following work shows that for steels, which do not contain large quantities of alloying elements, such as mild steels, the extraction procedure, described in Chapters III and IV, can be omitted. The colorimetric determination with Catechol Violet and cetyl-trimethylammonium bromide is then simply carried out directly on the steel in acid solution. Ascorbic and lactic acids are used as masking agents, and because no iodide is used, this procedure should be applicable to steels with high copper contents. It should also be more adaptable to an automated technique.

EXPERIMENTAL

RECOMMENDED, DIRECT PROCEDURE AND ITS APPLICATION TO BCS STEELS

Reagents:

DILUTE SULPHURIC ACID SOLUTION, 25 per cent V/V.

HYDROGEN PEROXIDE, 100 volumes - Analytical-reagent grade.

ASCORBIC ACID SOLUTION, 5 per cent m/V.

LACTIC ACID SOLUTION, 20 per cent V/V.

CATECHOL VIOLET SOLUTION, 0.1 per cent m/V.

ACIDIFIED WATER, pH 2.2.

CONCENTRATED STANDARD TIN(IV) SOLUTION, 100 $\mu g\ ml^{-1}$.

All solutions are prepared as described in Chapter IV.

Preparation of calibration graph:

Prepare as described in Chapter IV.

Procedure:

Dissolve 1.000 g. of steel (0.500 g. if the tin content is expected to be greater than 0.08 per cent m/m) contained in an 100 ml. flask, covered with a watch-glass, in 50 ml. of dilute sulphuric acid solution, with the aid of gentle heating. When evolution of hydrogen has ceased, add hydrogen peroxide, dropwise, to destroy any carbon or carbide residue. Boil to destroy the excess hydrogen peroxide. Cool and make up to the mark, with water, or in a 100 ml. calibrated flask.

Take a 5 ml. aliquot of this solution and add, in the following order, mixing between additions:- 10 ml. of ascorbic acid solution, 10 ml. of lactic acid solution, 2.5 ml. of Catechol Violet solution and 1 ml. of cetyltrimethylammonium bromide solution. Insert a combined calomel-glass electrode into the solution and, with the aid of a magnetic stirrer, carefully adjust the pH to 2.2 by dropwise addition of dilute sodium hydroxide ~~sulphuric acid~~ solution.

Remove the electrode and wash it down with acidified water. Quantitatively transfer the solution and washings to a 50 ml. calibrated flask that has previously been washed out with acidified water. Finally, dilute the solution to 50 ml. with acidified water and mix well. Allow the colour to develop for 40 minutes at room temperature and then measure the absorbance at 662 nm. against water in a 1 cm. cell.

Application to BCS steels:

Table 5:1

Steel	Tin present	Tin found (mean of 6 results)	Coefficient of variance (6 results)
	% m/m	% m/m	
Mild steel 273	0.065	0.063	1.56
Mild steel 324	0.13	0.136	1.59
Carbon steel 218/3	0.042	0.025	5.50
Carbon steel 221/1	0.02	0.012*	-
Low alloy steel 251	0.007	0.101	3.95
High speed steel 220/2	0.019	0.010*	-

* mean of 2 results.

Good results with a reasonable degree of precision were obtained with mild steels.

In the case of carbon steels, low recoveries of tin were obtained with this direct procedure. The reason for this was not clear, since the elements present, in the steels, did not interfere when added individually to a standard tin solution. Neither was the dissolution procedure at fault, since good results were obtained with 218/3 when an iodide extraction was used, (see Table 4:2).

As may be expected, in view of the non-selective nature of Catechol Violet, serious interference was observed when the procedure was applied to alloy steels.

CHAPTER VI

THE RELATIONSHIP BETWEEN OPTIMUM CONDITIONS FOR FULL COLOUR DEVELOPMENT AND THE CRITICAL MICELLE CONCENTRATION OF CETYLTRIMETHYLAMMONIUM BROMIDE

It is often the case in the spectrophotometric determination of metal ions that the chromogenic reaction of a dyestuff with a metal ion results in a waterinsoluble complex. In these cases the analyst can adopt one of two procedures. On one hand, measurement can be carried out in an organic solvent in which the complex is soluble or aqueous media can be retained, but a substance must be added that can act as a dispersing agent and prevent the precipitation of the complex. For this purpose early workers used natural gums, such as gum arabic or gelatin. Others used soaps such as sodium lauryl sulphate because with soaps a greater degree of chemical uniformity could be expected. Generally speaking though, the surface active agent was treated as if it always played an inert role, and as such, the choice of substance appeared to have been casual.

More recent work however, has shown that careful choice of dispersing agent can often lead to considerable improvements in the analytical characteristics of a chromogenic system. In addition to the effect of CTAB upon the visible absorption spectra of the tin(IV)-Catechol Violet system, (60,61), papers have also been published that describe the effects of this surface active agent on the systems of Catechol Violet with molybdenum (61), antimony (61), aluminium (80), and germanium (81), and Gallein with molybdenum (82). In all cases, in the absence of CTAB the dye and complex bands are overlapped. When CTAB is added the complex bands are moved to much longer wavelengths and in this way band overlap is reduced to virtually zero at the wavelength of maximum absorbance of the complex. Thus blank readings are reduced as are the inherent errors that result from high blank readings and in addition the bands shifts are often accompanied by increases in sensitivity. This phenomenon is

illustrated by the visible absorption spectra of the tin(IV)-Catechol Violet system, with and without the presence of CTAB (Fig. 6:1). It can be considered a typical example.

The considerable influence that a change of dispersing agent can have on the spectra of a chromogenic system is illustrated by the following data from the present work:-

Table 6:1 Effect of various dispersing agents upon the tin(IV)-Catechol Violet system.

Dispersing agent used	Type of dispersing agent	Wavelength of maximum absorbance for the complex/nm.	Maximum molar absorb-tivity for the complex
None	-	552	65,000
Sodium lauryl sulphate	anionic	552	65,000
Poly vinyl alcohol	-	565	60,000
"Brij" 35	non-ionic	575	70,000
Gelatin	cationic(?)	619	40,000
CTAB	cationic	662	92,000

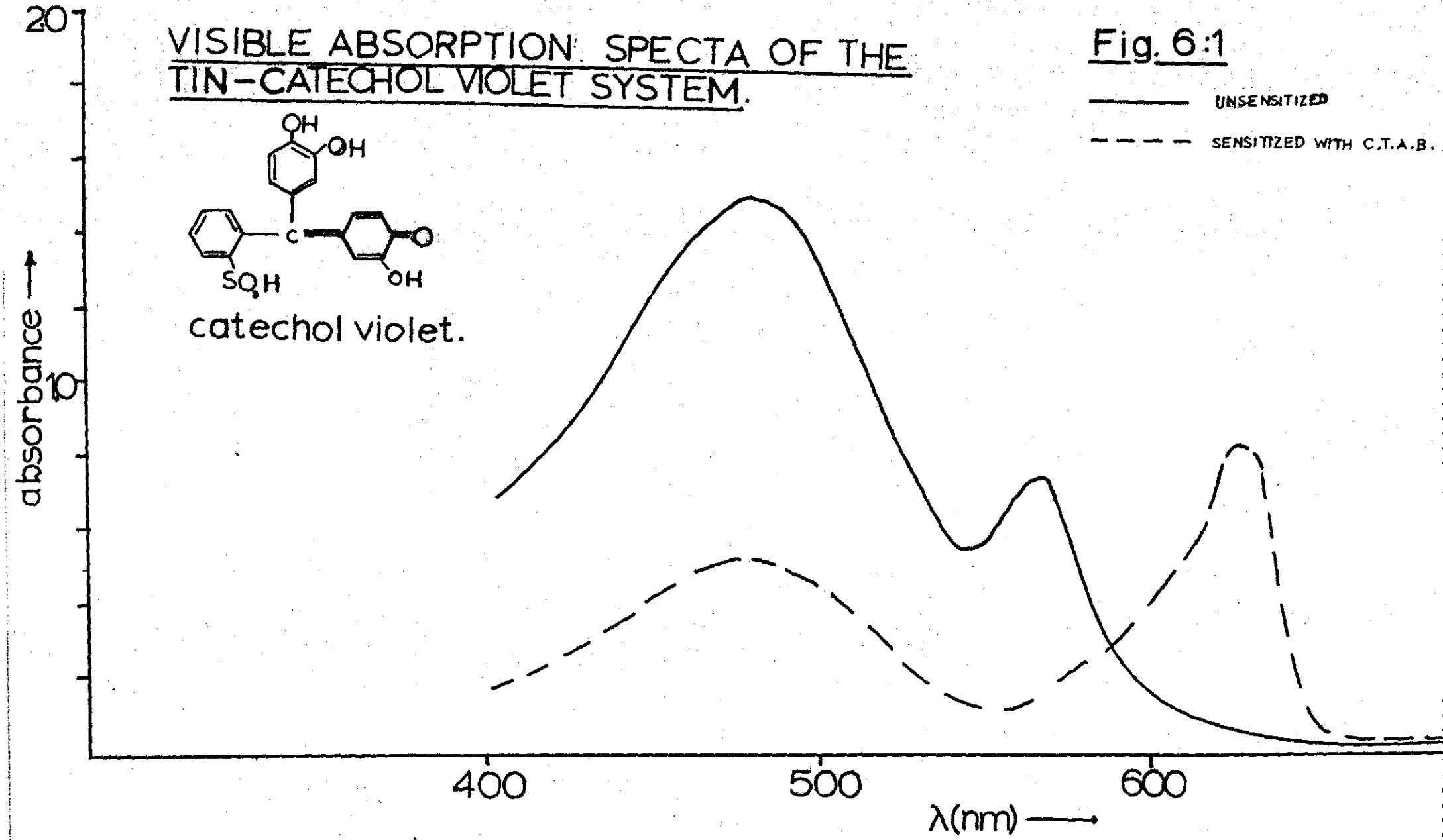
In all these cases the absorbance band of the excess free reagent, present in solution, is unaltered by the dispersing agent, whereas the complex band is moved to longer wavelengths in all cases except with the anionic, sodium lauryl sulphate. In view of the increased interest in the effects that various surface active agents have upon a chromogenic system, it was decided to carry out an investigation in order to establish the mechanism of the sensitisation.

Bailey et. al. (61) have studied the mode of formation of metal chelate systems sensitised by surface active agents. By means of photometric titrations and the method of continuous variations, they have shown that in the tin(IV)-Catechol Violet-CTAB system a true 1:2:4 ternary complex is formed. In addition they claim that appreciable complex

VISIBLE ABSORPTION SPECTA OF THE TIN-CATECHOL VIOLET SYSTEM.

Fig. 6:1

catechol violet.



formation only takes place if the CTAB is present in solution in micellular form.

The present work does not support the argument that micelles of CTAB are necessary for formation of the ternary complex, but that they are a fundamental requirement for maximum colour development. This is explained by a proposed mechanism for the system in which the surface active agent plays a dual role, that of an associating cation and that of a dispersing agent. The proposed mechanism is confirmed by results of studies of the effects of basic dye cations upon the tin(IV)-Catechol Violet system in the presence of an inert dispersing agent.

EXPERIMENTAL

For solutions of surface active agents there is a critical concentration above which the ions, instead of existing individually in true solution, agglomerate and form micelles, that is the solution becomes colloidal in character. This concentration is given the name "critical micelle concentration" (CMC). The CMC is marked by a sudden change in many of the properties of the solution, such as electrical conductivity, surface tension, light scattering and its ability to solubilise certain substances. Measurement of a change in one or other of these properties can be used to determine the CMC for a particular surface active agent.

(A) ESTIMATION OF THE CMC OF CTAB UNDER ACTUAL ANALYSIS CONDITIONS

In this work a Du Nouy tensiometer, in a constant temperature bath at 25°C., was used to detect the sudden change in rate of change of surface tension with concentration of CTAB which takes place when the CMC of CTAB is reached.

A physical method was chosen in preference to a chemical method, such as solubilisation of a dyestuff, since chemical methods may be self-defeating in that the environment of the surface active agent is modified in the course of making the measurement.

It is well known that CMC is highly dependent on such solution parameters as pH and total ionic strength. Therefore, for the requirements of this investigation, any meaningful result had to be obtained from measurements made on the solutions prepared as for analytical work.

The procedure was first checked to determine whether it gave a result that agreed with the well established literature CMC value for CTAB, in pure water at 25°C., of 0.9×10^{-3}M.

As well as determining the CMC of CTAB in the actual analysis solutions, a determination was also carried out on a solution of CTAB in water at the optimum pH of 2.2, for the spectrophotometric determination of tin, in this way the effect of Catechol Violet in solution upon the CMC value could be assessed. (Table 6:2 and Fig. 6:2).

Table 6:2 Tests carried out on solutions of CTAB in pure water at 25°C.

Concentration of CTAB x 10^{-3}M	Gauge reading (average of 3 results)
2.0	34.8
1.5	35.0
1.0	35.2
0.7	37.2
0.5	40.3
0.2	49.0

Test carried out on solution of CTAB in water at pH 2.2 at 25°C.

Concentration of CTAB x 10^{-3}M	Gauge reading (average of 3 results)
2.0	35.4
1.5	35.5
1.0	35.6
0.7	35.9
0.5	36.0
0.2	42.7
0.1	46.4
0.04	53.0

Tests carried out on actual analysis solutions at 25°C.

Concentration of CTAB x 10^{-3}M	Gauge reading (average of 3 results)
1.0	36.2
0.7	36.3
0.5	36.2
0.2	35.3
0.1	35.1
0.04	37.0
0.02	53.1
0.01	67.0

By this method the CMC of CTAB under actual analysis conditions was shown to be approximately 0.04 x 10^{-3}M.

(B) INVESTIGATION OF THE VISIBLE ABSORPTION SPECTRA OF THE TIN(IV)-CATECHOL VIOLET-CTAB SYSTEM UNDER CONDITIONS OF VARIOUS CTAB CONCENTRATIONS.

Fig. 6:3 shows the results of this investigation. The CTAB concentration of 0.055 x 10^{-3}M is that used in the solutions for the spectrophotometric determination of tin, and is the optimum for maximum colour development according to Dagnall et. al. (60). However, appreciable formation of the ternary complex takes place at concentrations well below this optimum concentration. This is indicated by considerable development of the band with its absorbance maximum at 662 nm and corresponding decrease of the band due to the binary, tin(IV)-Catechol Violet complex, with its absorbance maximum at 555 nm.

(C) PROPOSED MECHANISM OF THE SENSITISATION PHENOMENON

The fact that the formation of the ternary complex takes place at CTAB concentrations well below the CMC of CTAB, under the actual analysis conditions, contradicts the argument of Bailey et. al. (61), that micelles

Fig. 6:3

TIN(IV)-CATECHOL-VIOLET SYSTEM:-
THE VISIBLE ABSORPTION SPECTRA AT VARIOUS CTAB CONCENTRATIONS.

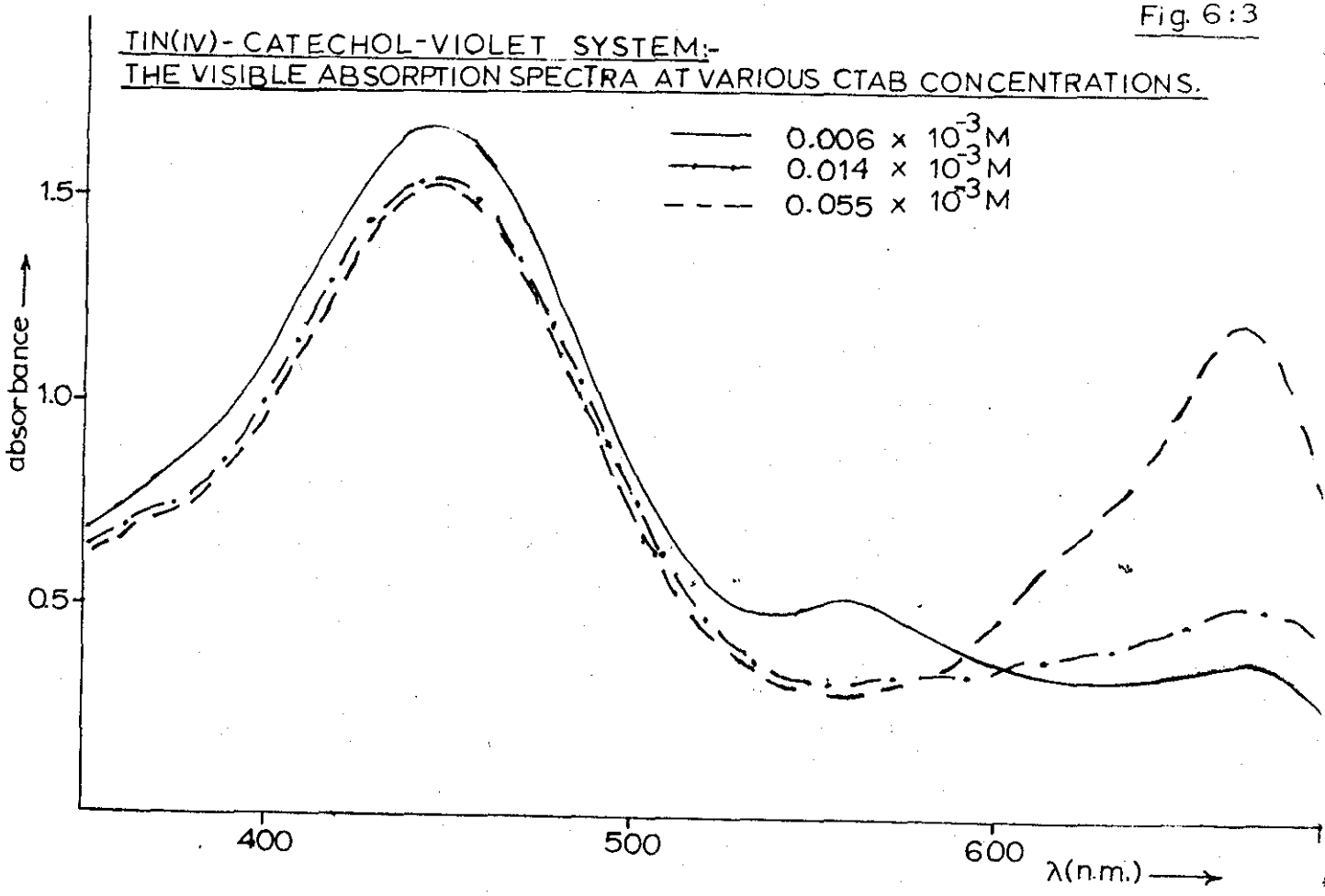
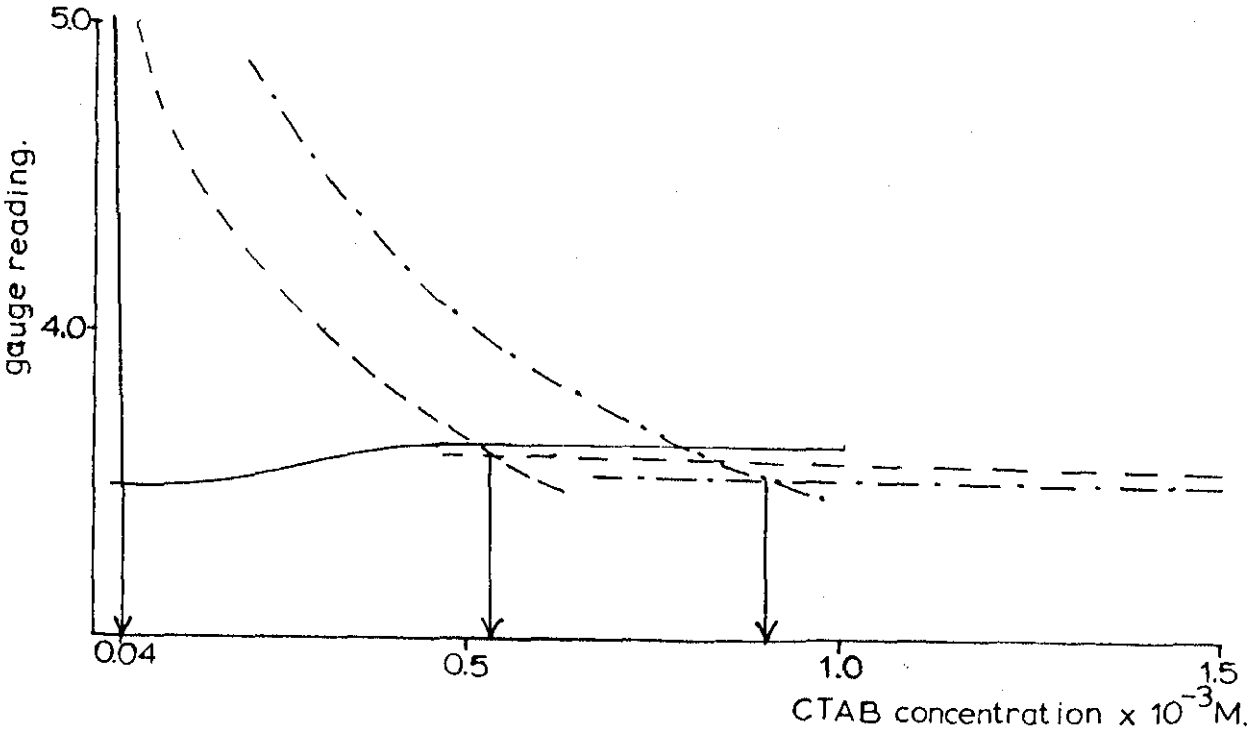


Fig. 6:2

ESTIMATION OF THE CMC OF CTAB.

—in analysis solutions, -·-·-in pure water, – – in water at pH 2.2.



of the surface active agent must be present before there is any appreciable degree of complex formation. Nevertheless, there would appear to be a close relationship between the optimum CTAB concentration for full colour development of 0.055×10^{-3}M and the CMC value of CTAB under analysis conditions of 0.04×10^{-3}M.

Close observation of the system showed that there is a finely dispersed, insoluble, blue species present at CTAB concentrations below the CMC value, this is probably the ternary complex in question.

All the facts mentioned so far could be explained by a mechanism for the sensitisation, in which CTAB plays a dual role, that of an associating cation and that of a dispersing agent:-

$$\underset{\text{(soluble)}}{\left[Sn\text{-}(CV)_2\right]} \xrightarrow{CTAB} \underset{\text{(insoluble)}}{\left[Sn\text{-}(CV)_2\text{-}(CTA)_4\right]} \xrightarrow[> CMC]{\text{excess CTAB}} \underset{\text{(dispersed)}}{\left[Sn\text{-}(CV)_2\text{-}(CTA)_4\right]}$$

where, CV = Catechol Violet

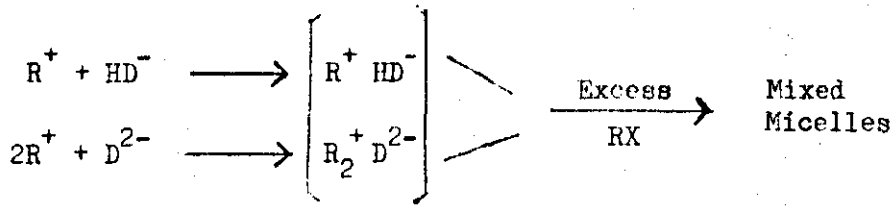
CTA = the cetyltrimethylammonium cation of CTAB.

It is well known that the CMC of a detergent must be reached before it begins to show dispersing ability. Thus, the above scheme could be written down in a more general form:-

$$\underset{\text{(soluble)}}{\left[\text{Binary complex}\right]} \xrightarrow[\text{ion}]{\text{associating}} \underset{\text{(insoluble)}}{\left[\text{Ternary complex}\right]} \xrightarrow[> CMC]{\text{surface active agent}} \underset{\text{(dispersed)}}{\left[\text{Ternary complex}\right]}$$

Further weight was added to the argument in favour of this mechanism by a survey of the literature on surface active agents and their CMC values. This revealed that although the applications of interaction of these compounds with dyestuffs is comparatively new to analytical work, it is well established in surface active agent fields. For instance, as long ago as 1951 Colichman (83) published a paper on the determination of CMC of long chain quaternary ammonium salts, such

as CTAB, using dyestuffs of opposite charge. This paper contained an analogous scheme to the two outlined above:-



where HD^- and D^{2-} = different ions of the same dyestuff.

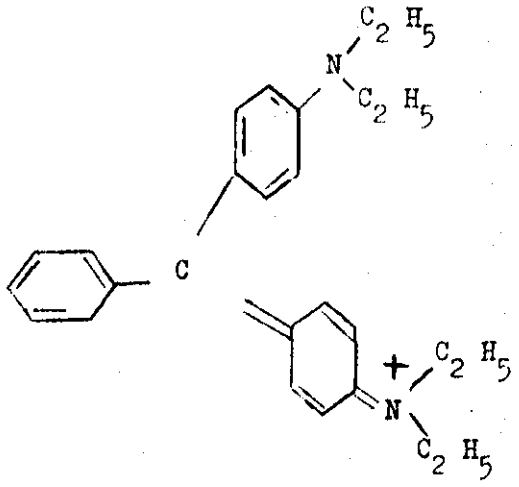
R^+ = the cation of a long chain quaternary ammonium salt.

The sensitising effect of CTAB is more marked than with most other surface active agents. In addition to the fact that it forms a definite ternary complex with the tin(IV)-Catechol Violet binary complex, another contributory factor to this could be the "exceptionally high solubilising power,(84,85), that cationic surfactants, such as CTAB have on dyestuffs. This is attributed to the "large degree of disorder" in the micelles and "larger intramicellar spacing" allowing more dyestuff to be absorbed into the interior of the micelles. In addition, it has been suggested that this "larger intramicellar spacing" is associated with a spherical, rather than any other shape of micelle.

(D) SENSITISATION WITH OTHER CATIONS - BASIC DYES AS THE ASSOCIATING CATION

Following the idea of a dual role played by the cationic surface active agent, that of associating ion and that of a dispersing agent, an attempt was made to develop methods using a different compound for each role. Firstly an "inert dispersing agent" was required, that is one which did not produce a significant effect on the spectrum of the tin(IV)-Catechol Violet system and at the same time did not react with the compound being used as the associating ion. Poly vinyl alchol was found suitable for this purpose.

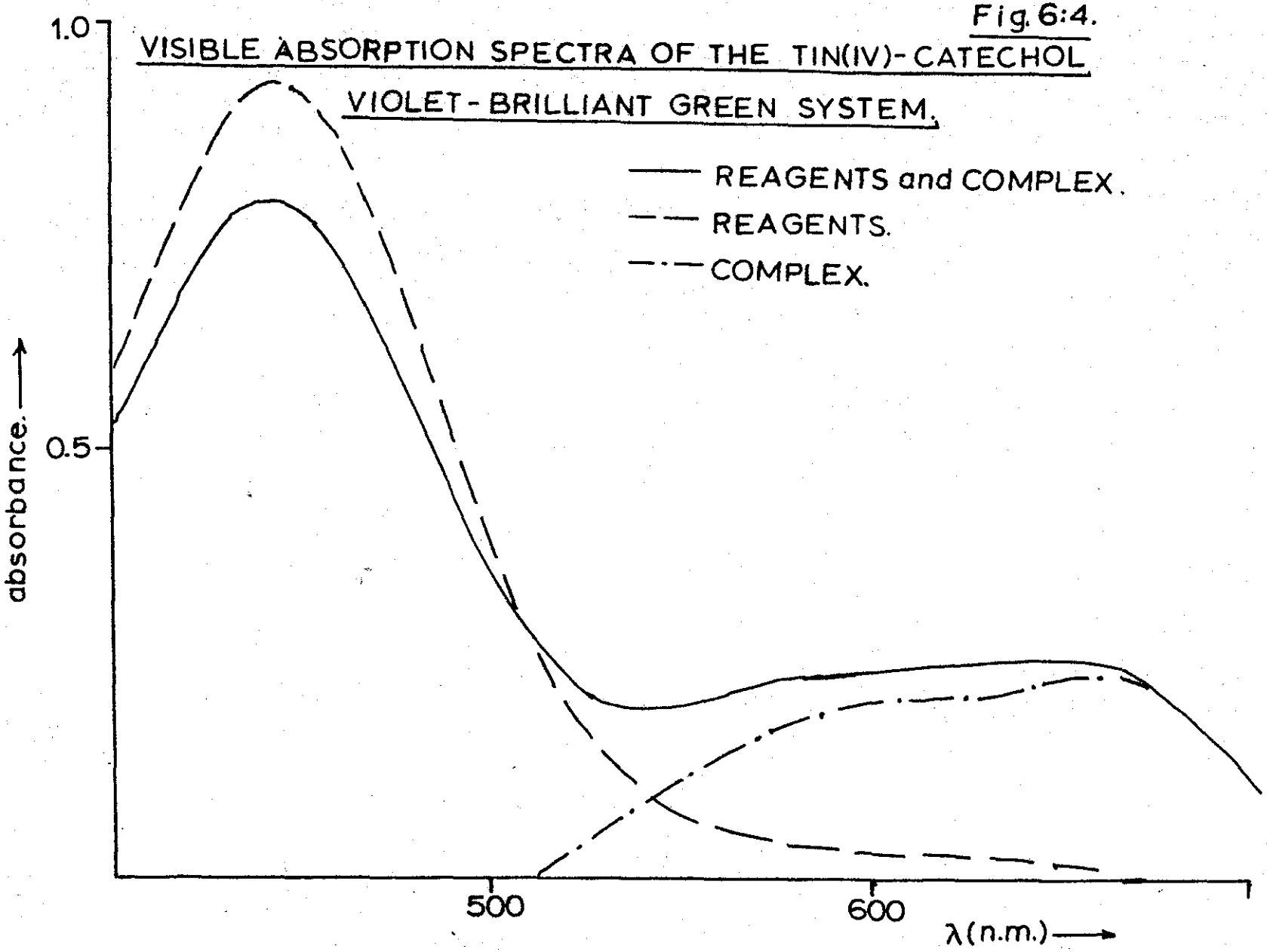
As the associating cation the highly coloured basic dyes were chosen. It was hoped that the additive effect of the absorbance of the binary tin(IV)-Catechol Violet complex and that of the associating basic dye ion would lead to increased sensitivity. A typical example of results obtained in this fashion is shown in Fig. 6:4 where the associating cation was Brilliant Green (C.I.42040):-



The R^+ form of Brilliant Green is intensely green in colour, but at the pH and concentration used in this work, the excess free R^+ form is converted to the pale yellow RH^{2+} protonated form. The R^+ form that is combined with the tin(IV)-Catechol Violet complex however, does not protonate. This phenomen was very useful in reducing the blank absorbance to virtually zero.

Unfortunately, the desired increase in sensitivity did not materialise, owing to band spreading, and the methods proved to be no improvement on the original CTAB method. Nevertheless, the fact that here again large bathochromic shifts of the metal complex absorption bands were observed, in all cases, meant that the work at least added further evidence in support of the dual role proposed in the previous section, played by CTAB when this compound is used for sensitisation.

Fig. 6:4.


VISIBLE ABSORPTION SPECTRA OF THE TIN(IV)-CATECHOL VIOLET-BRILLIANT GREEN SYSTEM.
REAGENTS and COMPLEX.
REAGENTS.
COMPLEX.
1.0
0.5
absorbance.
500
600
λ(n.m.)

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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN STEELS.

CONTENTS

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17	Development of a procedure for the complete dissolution of steels in acid media, before determination of zirconium with Arsenazo III.
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INTRODUCTION TO THE DEVELOPMENT OF A METHOD FOR THE DIRECT DETERMINATION OF ZIRCONIUM IN STEELS

The determination of zirconium in steels can be greatly simplified and the metal determined directly if the steel is dissolved in acid media using a PTFE-lined pressure digestion vessel. In this way the chemically inert silicaceous forms of zirconium, that are the result of the conventional acid dissolution techniques at atmospheric pressure, are completely decomposed. As a result, the tedious and time consuming necessity of filtration and alkali metal salt fusion techniques can be avoided.

The colorimetric determination is carried out using the reagent Arsenazo III. As would be expected, in view of the highly selective and sensitive nature of this reagent, an interference investigation using the fifteen other metals most commonly found in steels indicates applicability to a wide range of steels. In addition, results obtained with a range of British Chemical Standard steels show a high degree of precision for the recommended procedure. In its present form however, the method would not be applicable to high tungsten steels, owing to precipitation of tungstic acid at an intermediate stage.

CHAPTER I.

REVIEW OF COLORIMETRIC METHODS FOR THE DETERMINATION OF ZIRCONIUM

The first colorimetric procedure for the determination of zirconium was put forward in 1941 (1). It was an indirect method and used Pararsonic acid as the reagent. Since then a large number of dyestuffs have been utilised as reagents for zirconium. The most popular of these appear to be: Alizarin Red S, Catechol Violet, Arsenazo III and Xylenol Orange.

None of these, with the exception of Arsenazo III, are particularly selective. Consequently, a considerable number of methods have been put forward which include some type of separation procedure before the colorimetric determination. The usual techniques, such as coprecipitation, solvent extraction, ion exchange and silica gel chromatography have been employed.

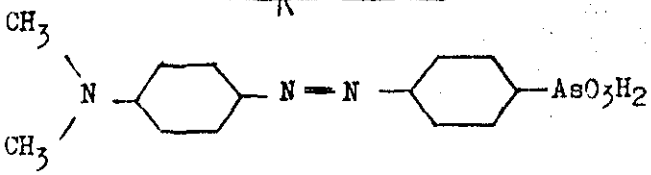
Zirconium is very readily hydrolysed in aqueous solutions to give polymeric species containing chains of zirconium-oxygen bonds. Unless these species are completely depolymerised before colorimetric analysis, considerable errors are likely. This phenomenon has prompted work on the depolymerisation of zirconium solutions (38).

In addition to errors that may arise owing to the presence of polymerised species, a further problem, peculiar to steel analysis, is that inert forms of zirconium persist after the conventional acid digestion techniques commonly used in the dissolution of steels. One report in particular clearly illustrates the errors that are to be expected if these compounds are not decomposed before a colorimetric determination is applied to the solutions (39).

Throughout the last twenty years a number of reviews and comparative studies of the colorimetric reagents for zirconium have

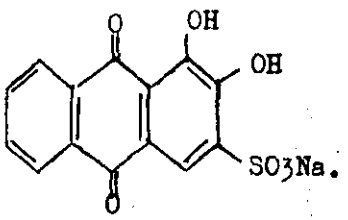
appeared (42, 46). The concensus opinion is that on the grounds of selectivity and sensitivity, at least, Arsenazo III is the best reagent available at the present time.

PARASONIC ACID



In hydrochloric acid solution, zirconium is precipitated by Pararsonic acid. On treating the precipitate with either an alkaline or acidic fluoride solution, the pararsonic acid anion is released to give a yellow colour in alkaline solution and a more intense red colour in acidic solution. In 1941, a procedure for the determination of zirconium in steel, based upon these reactions, was described by Hayes and Jones (1). This work was followed by methods for the determination of zirconium in uranium (2) and in thorium-zirconium alloys (3). In the latter method thorium is coprecipitated to a small extent. The authors however, claim that when the specified precipitation conditions are used, coprecipitation is constant and reproducible over a wide range of thorium concentrations. Several metals, fluoride, phosphate, large amounts of sulphate and strong oxidising agents are potential interferences.

ALIZARIN RED S



This dyestuff is one of the more popular reagents for the determination of zirconium. In 1955, Mills and Herman (4) described a method for the determination of zirconium in hiduminium and similar

aluminium alloys and Narita (5) a method for zirconium in iron and steel in which iron was removed as iron(III) chloride, by ether extraction and titanium was masked with hydrogen peroxide. Two methods for the analysis of geological samples are those of Degenhardt (6) and Stanton (7). Williams - Wynn (8) put forward a method for zirconium in leather. Alizarin Red S was used in the presence of sodium tartrate; titanium, aluminium, iron and chromium(III) are reported not to interfere but Cr(VI) must first be reduced.

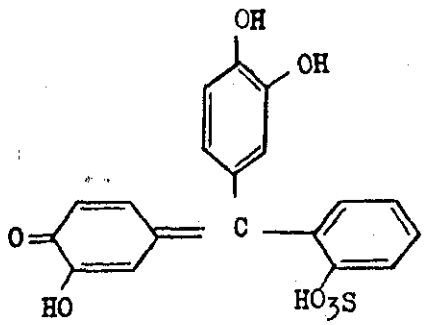
The analytical problems that can arise from the fact that zirconium readily hydrolyses to form polymeric species in solution is highlighted by Gübeli and Jacob (9). They report that from pH 1-3 zirconium is present, on average, as a triatomic species and that the polymers can be broken down by increasing the acidity or by the action of heat.

The solvent extraction of the Alizarin Red S complex of zirconium into n-butanol and trioctylammonium chloro-acetate/toluene has been made the basis of methods by Dragulescu et al (10) and Ishibashi et al. (11) respectively. Two examples of colorimetric determinations with Alizarin Red S after solvent extraction using another reagent are those of Morimato and Ashizawa (12), with a Cupferron/chloroform extraction, and Khopkar and Dhara (13) who extracted zirconium(IV) from 4M nitric acid/4M sodium nitrate solution with mesityl oxide.

Ion exchange separations combined with an Alizarin Red S determination have been used by Kato et al. (14) and Sastry et al.(15).

A physio-chemical study of the zirconium-Alizarin Red S complex has been made by Parissakis and Konotoyaunakos (16). They claim that in the complex the ionised α-phenoxyquinonoid form of the reagent is present; between pH 1.0-1.8 the molar ratio of metal to reagent is 1:1, and that at pH greater than 3, voluminous suspensions are formed.

CATECHOL VIOLET



Catechol Violet has been widely used for the spectrophotometric determination of zirconium. The original method was due to Flaschka and Farah (17) and was based on the intense colour given in the presence of EDTA as a masking agent. Serious interference was reported from oxidising agents, complex forming anions, antimony(III), tin(IV) and mercury(I). Young et al. (18) followed up this work and developed a method which they claimed was twice as sensitive as that of Flaschka and Farah. Thioglycollic acid was used to mask small amounts of iron, and a mercury cathode was used to remove larger amounts. Aluminium, titanium and vanadium were reported to interfere.

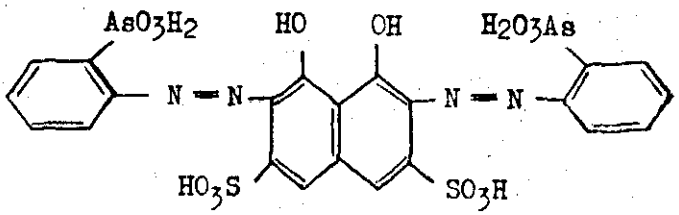
The reagent has since been applied to zirconium determinations in phosphates (19) and iron and steel (20,21,22).

Catechol Violet is used for the direct determination of zirconium in the organic phase after extraction with tri-n-octylphosphine oxide (TOPO)/cyclohexane in a method by Young and White (23). The results of interference studies were reported when extractions were made from both chloride and from nitrate media. Several later extensions to this work have been made. Hibbits et al. (24) preceded the basic method with a Cupferron precipitation of zirconium using iron(III) as a carrier and claimed that interference by 81 different ions is overcome in this way. Wood and Jones (25) have applied the method to the determination of zirconium in niobium and other metals. Hafnium interference is reported in both these procedures (24,25). Iron and steel has been analysed in this way by Kajiyama and Senuma (26). Chromate is reduced

by addition of sodium nitrite; a molar absorptivity of 50,000 l mol^{-1} cm^{-1} is reported. Interference was observed for steels with tungsten contents greater than 10% m/m.

Solvent extraction techniques that have been combined with Catechol Violet colorimetric determinations are those of Dragulescu et al. (27) who used butanol extraction from trichloroacetic acid media and Uzumasa et al. (28) who first separated iron, chromium, molybdenum and tin from hydrochloric acid media by ethyl acetate extraction. Zirconium was then extracted with 2-thenoyltrifluoro-acetone/xylene and back-extracted with 5M sulphuric acid. Hydrogen peroxide was used to keep titanium in the aqueous phase and masking of the zirconium by fluoride was prevented by adding aluminium(III).

ARSENAZO III.



This reagent belongs to the same group as those proposed by Kuznetsov (29), Thoron, Arsenazo I and Arsenazo II. Its synthesis and development as a colorimetric reagent however is mainly due to Savvin who has produced numerous papers covering the mechanism of complex formation and its analytical applications, including comparisons with other reagents.

In his first paper (30), which describes the synthesis of Arsenazo III, the determination of thorium and uranium was reported. A later paper (31) described the determination of zirconium and includes suggestions for masking and solvent extraction techniques. Arsenazo III has since been the subject of publications right up to the present date,

during which period it has been applied to the determination of zirconium in hafnium (32), alloys (33,34), bronzes (35), and steel (36,37,38). In the last of these papers on steel analysis Pakalns discusses the considerable errors that are likely to occur as a result of the chemically inert forms of zirconium that arise from the usual acid digestion techniques employed in steel analysis.

An earlier paper by Pakalns (39) deals with the depolymerisation of zirconium solutions for use in spectrophotometry with Arsenazo III. Results from a very detailed study were given, along with recommendations for the preparation of standard solutions, that are completely free from polymeric zirconium species.

Silica gel chromatography before Arsenazo III determination of zirconium has been used by Sulek et al. (40).

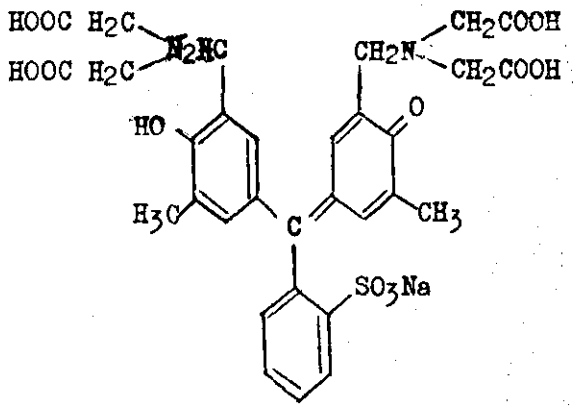
Solvent extraction with thenoyltrifluoroacetone/xylene combined with an Arsenazo III colorimetric determination has been applied to nickel base alloys (41) and an interesting approach to achieving selectivity in solvent extraction-spectrophotometry is included in a paper by Dedkov, Ryabchikov and Savvin (42). They make the point that Arsenazo III, though highly selective, is not completely specific for zirconium(IV), Thorium(IV), titanium(IV), lanthanum(III) and uranium(IV) interfere to some extent. Under the appropriate conditions, the dyestuff Picramine R(often mistranslated as Picramine P from Russian Journals) forms a complex with zirconium(IV) and several other ions but not with those ions that interfere with the Arsenazo III determination. Thus, the two reagents supplement each other on selectivity grounds. In this method the zirconium(IV) complex of Picramine R is first extracted into n-butanol and then back-extracted into strong hydrochloric acid which decomposes the Picramine R complex before application of an Arsenazo III determination. The outcome is a method that is completely specific for zirconium. In a later paper (43) this procedure was applied to high

alloy steels. Unfortunately, Picramine R does not appear to be commercially available in the United Kingdom. Brief instructions however for its synthesis have been given (42).

Two physico-chemical studies of the zirconium-Arsenazo III system are those of Savvin (44) and Muk and Savvin (45). The first concludes that the complex formation takes place through only one of the functional groups of the molecule, that elements with ionic radii less than 0.07 to 0.08 nm give no colour reactions with Arsenazo III and that the metal to reagent ratio of the complex is 1:1 or 1:2 depending upon the acidity and concentration of the components. The second paper is concerned solely with the sharp increase in the absorbtivity of the complex which takes place when the acidity of the system is increased. It was concluded that the increase was due to a change in the nature of the metal-ligand bonds rather than composition change. This contradicts the earlier findings which suggested that composition of the complex depends on acidity.

In a comparative study involving the three reagents, Catechol Violet, Xylenol Orange and Arsenazo III (46), the authors considered Arsenazo III to be superior on selectivity grounds. A much more detailed study is that of Dedkov, Ryabchikov and Savvin (42), published in 1965. Sensitivity, selectivity and, because of the easily hydrolysable nature of zirconium, the maximum permissible acidity of the medium were chosen as criteria for comparison. Again the conclusion was, that Arsenazo III is the best reagent for zirconium.

XYLENOL ORANGE



This dyestuff was first introduced to analytical chemistry by Körbl and Přibil (4) and was later used as a spectrophotometric reagent for zirconium by Cheng (48). It was reported that iron can be masked with ascorbic acid and bismuth with chloride. Hafnium, and the common chelating anions however interfere. Later the same author (49) compares the analytical characteristics of Xylenol Orange and Methylthymol Blue, a dyestuff of similar structure to Xylenol Orange. The possibility to determine zirconium and hafnium in the presence of each other, using a peroxide and sulphate masking and demasking technique was suggested.

The reagent has been employed in the analysis of steels by several workers. They include Rericha and Mayer (50), who first separate iron and chromium at a mercury cathode, and Chechova (51) who used mercaptoacetic acid and EDTA as masking agents for iron(III) and most other metals respectively. This latter paper also gives detailed information on interference tolerances. Keller and Hennesen (52) used a precipitation with Cupferron to separate zirconium before determination with Xylenol Orange.

Procedures for the determination of zirconium in uranium is given by Budesinsky (53) and for nickel based alloys by Challis (54).

Differential spectrophotometry using Xylenol Orange is the subject of a paper by Ishiwatari (55), fluoride interference is overcome by

adding aluminium (III).

Solvent extraction of the complex into butanol in the presence of a large excess of diphenylguanidine, has been used by Tolmachev et al. (56), and the long chain amine salt, methyltrioctylammonium chloride, has been used by Přibil and Vesely (57). Extraction of zirconium from hydrochloric acid solution using esters of phosphoramidic acid has been investigated by Alimarin et al. (58). Xylenol Orange was used for the colorimetric determination in the above cases.

Ion exchange for the separation of zirconium from hafnium and other elements combined with a Xylenol Orange determination has been used by Nabivanets (59).

Champion et al. (60) have carried out a study of the complex formation between zirconium and Xylenol Orange. A 1:1 complex is reported to exist under analysis conditions, molar absorptivities are also given.

In a comparative study, in 1961, of sixteen reagents that were available for the determination of zirconium, Babko and Vasilenko (61) concluded that on the grounds of independence of absorptivity of the complex, upon pH, Xylenol Orange, along with Methylthymol Blue, was superior to the rest.

OTHER METHODS

A number of workers have used various polyhydroxy derivatives of flavanone for the determination of zirconium (62,63,64,65) but many ions are reported to interfere even at trace levels. Methylthymol Blue has been studied by Luk'yanov and Kuyazeva (66) and Tikhonov (67), at the absorbance maximum of the 1:2 complex. There is little band overlap with that of the reagent. Interference by tin(IV), titanium(III), bismuth(III) and iron(III) is reported. Morin has been used for the

determination of zirconium in magnesium alloys and in platinum, by Tůma and Kabický (68) and Geissler et al. (69) respectively. Phenylfluorone forms a red precipitate with zirconium and this phenomenon has been made the basis of spectrophotometric methods after stabilisation of the colloidal precipitate with cyclohexanol (70) or gelatin (71,72).

REVIEWS

Several review articles on the determination of zirconium have appeared at various times throughout the last twenty years, the more recent of these being "Sets of reagents for the photometric determination of zirconium" - Dedkov et al. (42); "New reagents for zirconium" - Chevkesov and Pushinov (73) and "Analytical Chemistry of hafnium and zirconium" - Brookes and Townsend (74).

CHAPTER II.

CHOICE OF REACTION MEDIA FOR THE SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH ARSENAZO III

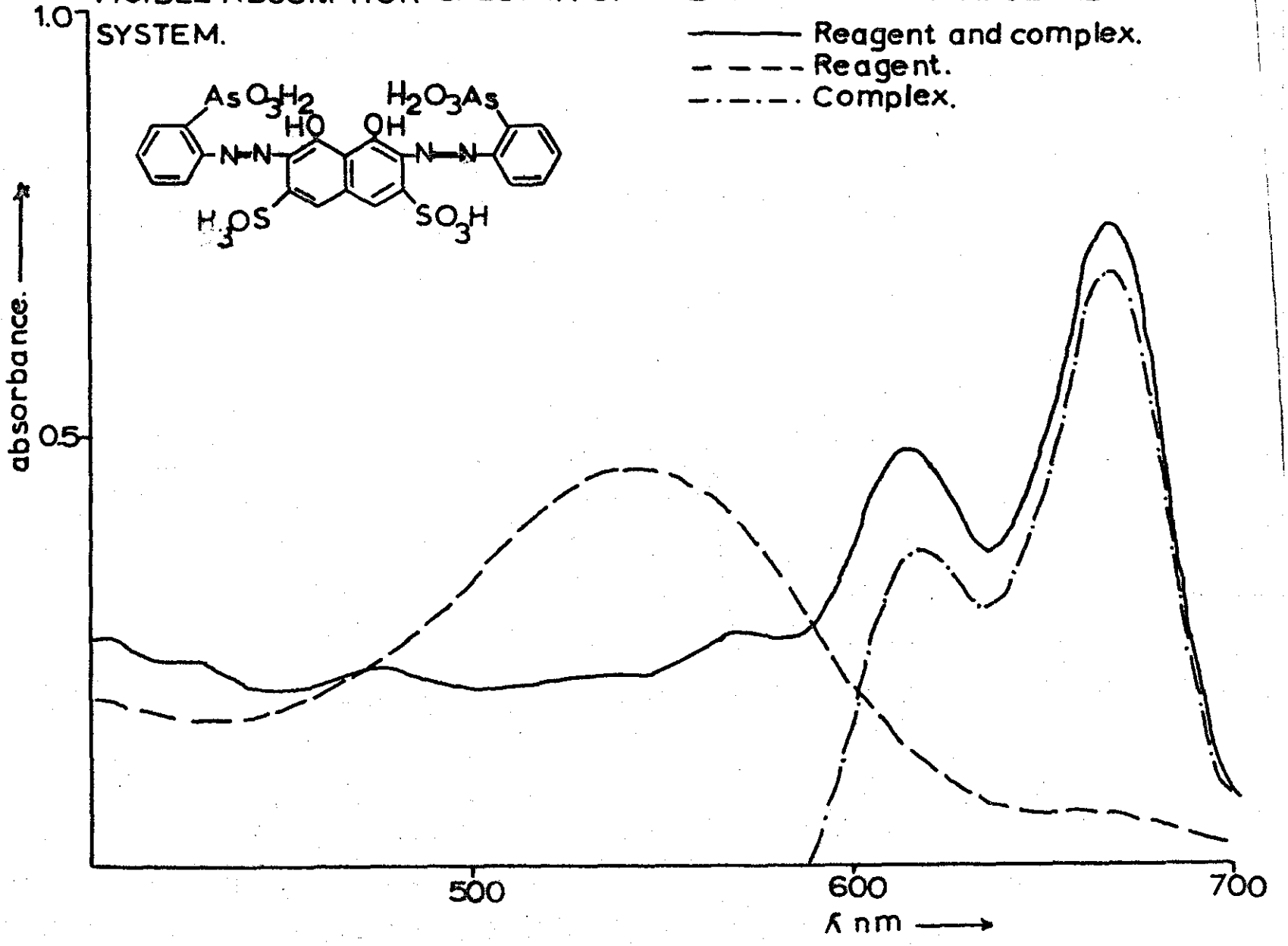
Arsenazo III is an excellent colorimetric reagent for zirconium (42). The sensitivity is high, the zirconium complex having a molar absorptivity of 120,000 l mol^{-1} cm^{-1} under the conditions used by Dedkov et al. (42). The spectral characteristics of the zirconium-Arsenazo III system are almost ideal for spectrophotometric measurement, there being virtually no overlap of reagent and complex bands at the wavelength of maximum absorbance of the complex (Fig. 2:1). Furthermore, the reagent is highly selective; hafnium(IV), thorium(IV), titanium(IV), lanthanum(III) and uranium(VI) are the only metals reported to interfere (42,75).

Normally there is a relationship between the ease with which a metal hydrolyses and the stability of its complexes (42,43). Zirconium is one of the most readily hydrolysable metals and in keeping with this property its complexes are generally stable, even at high acidities. Arsenazo III can be used in strongly acidic solutions, its zirconium complex can be formed at acidities as high as 10M hydrochloric acid. If full advantage of the selective nature of zirconium Arsenazo III reaction is to be taken, then the chromogenic reaction must be carried out in concentrated solutions of a strong acid. Methods have been put forward which use 6M hydrochloric acid (75,76). In this way, in conditions of high acidity, where most other metal complexes of Arsenazo III are dissociated, the reagent is rendered selective for the few most readily hydrolysable metals.

High concentrations of sulphate (39), phosphate (39) and nitrate (44,76) interfere with the determination. Although it has been claimed by some workers (37) that nitrate interference can be overcome

Fig.2:1.

VISIBLE ABSORPTION SPECTRA OF THE ZIRCONIUM(IV)-ARSENAZO III SYSTEM.



by carrying out the reaction in the presence of urea, the experimental work herein does not confirm these findings. The choice of strong acid was therefore effectively limited to hydrochloric or perchloric acid, of which perchloric acid proved to be the most suitable.

EXPERIMENTAL

(A) NITRIC ACID/UREA MEDIA

Kammori et al. (37) claim that if urea is present in the chromogenic system, interference by nitric acid is prevented. They further state that nitric acid is the best media for the determination of zirconium with Arsenazo III because the absorbance of the complex was not as dependent on acid strength as it is in hydrochloric acid media. The following work was carried out in an attempt to confirm these claims.

Colour Stability:

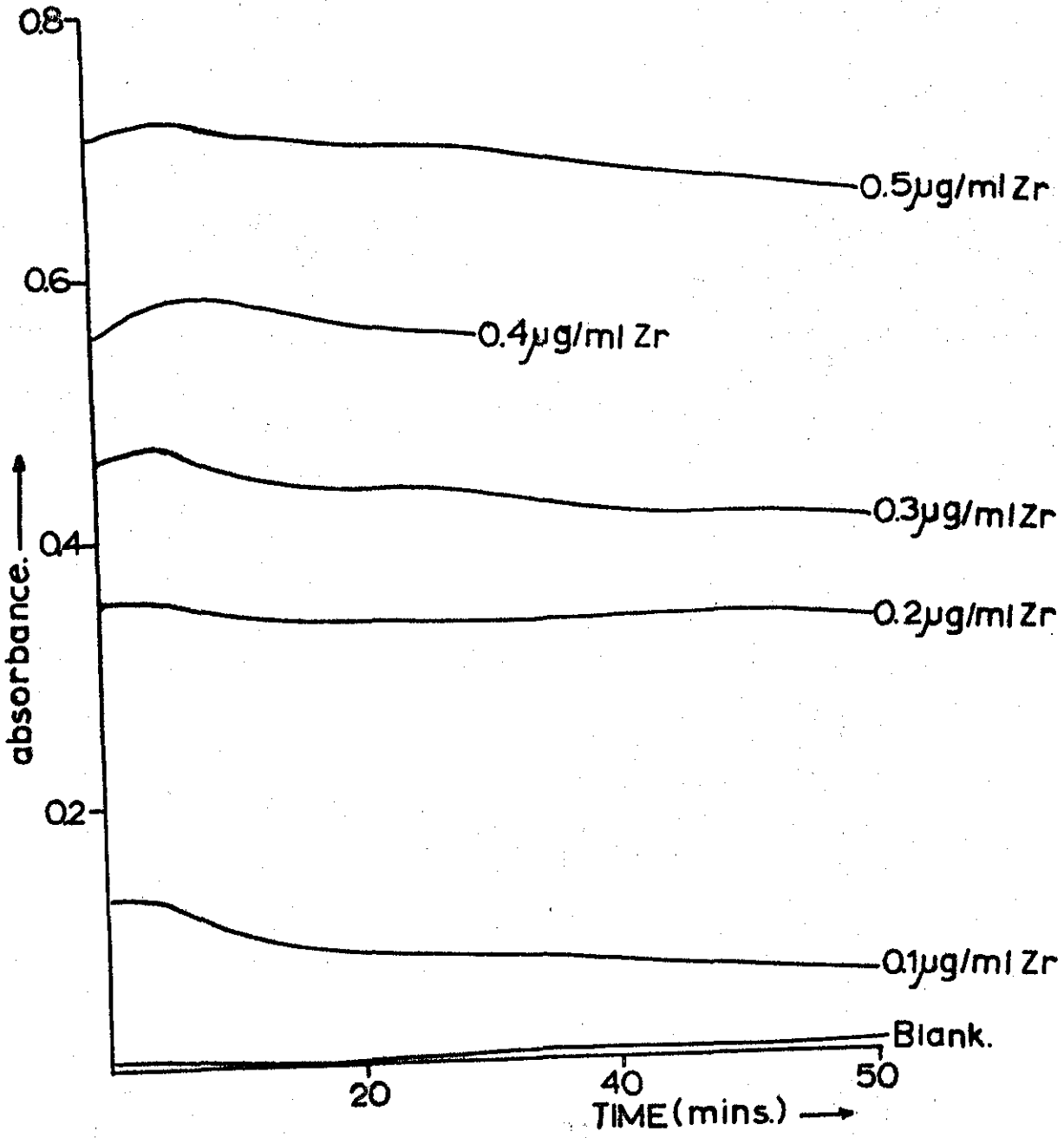
Table 2:1 (Fig. 2:2)

	Zirconium per ml. (µg)					
	0	0.1	0.2	0.3	0.4	0.5
Time (Minutes)			ABSORBANCE			
0	0.006	0.125	0.351	0.457	0.553	0.707
5	0.006	0.123	0.350	0.468	0.581	0.718
10	0.005	0.099	0.342	0.450	0.581	0.710
15	0.000	0.090	0.340	0.439	0.572	0.700
20			0.334			
25			0.334			
30	0.004	0.079	0.334	0.429	0.550	0.691
60	0.003	0.062	0.325	0.401		0.656

The colour was never stable for any appreciable length of time nor was the rate of development or disappearance constant, at the various concentrations of zirconium investigated.

Fig. 2:2.

COLOUR STABILITY in nitric acid / urea media.



Reproducibility:

Table 2:2 Tests were carried out on solutions that contained 0.4 µg/ml. zirconium

Absorbance at 665 nm.		
0.510; 0.422;	0.491; 0.433;	0.363; 0.457.

mean = 0.449
Standard deviation = 0.039
coefficient of variance = 8.7

As would be expected from the results of the work on colour stability, reproducibility was poor.

Adherence to Beers' Law:

Table 2:3

Zirconium (µg/ml.)	0	0.1	0.2	0.3	0.4	0.5
Absorbance	0.006	0.125	0.351	0.457	0.553	0.707

The results are widely scattered around a straight line.

The foregoing results are contrary to the claims of Kammori et al. (37) and as a result no further consideration was given to nitric acid as reaction media for the determination of zirconium with Arsenazo III.

(B) COMPARISON OF HYDROCHLORIC AND PERCHLORIC ACID

Dependence of absorptivity of the complex on acid strength:

Table 2:4 (Fig. 2:3)

Tests were carried out on solutions that contained 0.6 µg/ml. zirconium. Absorbance was measured at 670 nm., in 1 cm. cells, after 30 minutes.

In hydrochloric acid media:-

Acid Molarity	2.0	4.0	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	11.0
Absorbance + Blank	0.150	0.206	0.428	0.588	0.628	0.663	0.702	0.729	0.761	0.729	0.725	0.687
Blank	0.004	0.000	0.004	0.006	0.004	0.004	0.004	0.007	0.011	0.012	0.022	0.073
Absorbance	0.146	0.206	0.424	0.582	0.624	0.659	0.698	0.722	0.750	0.717	0.703	0.614

In perchloric acid media:-

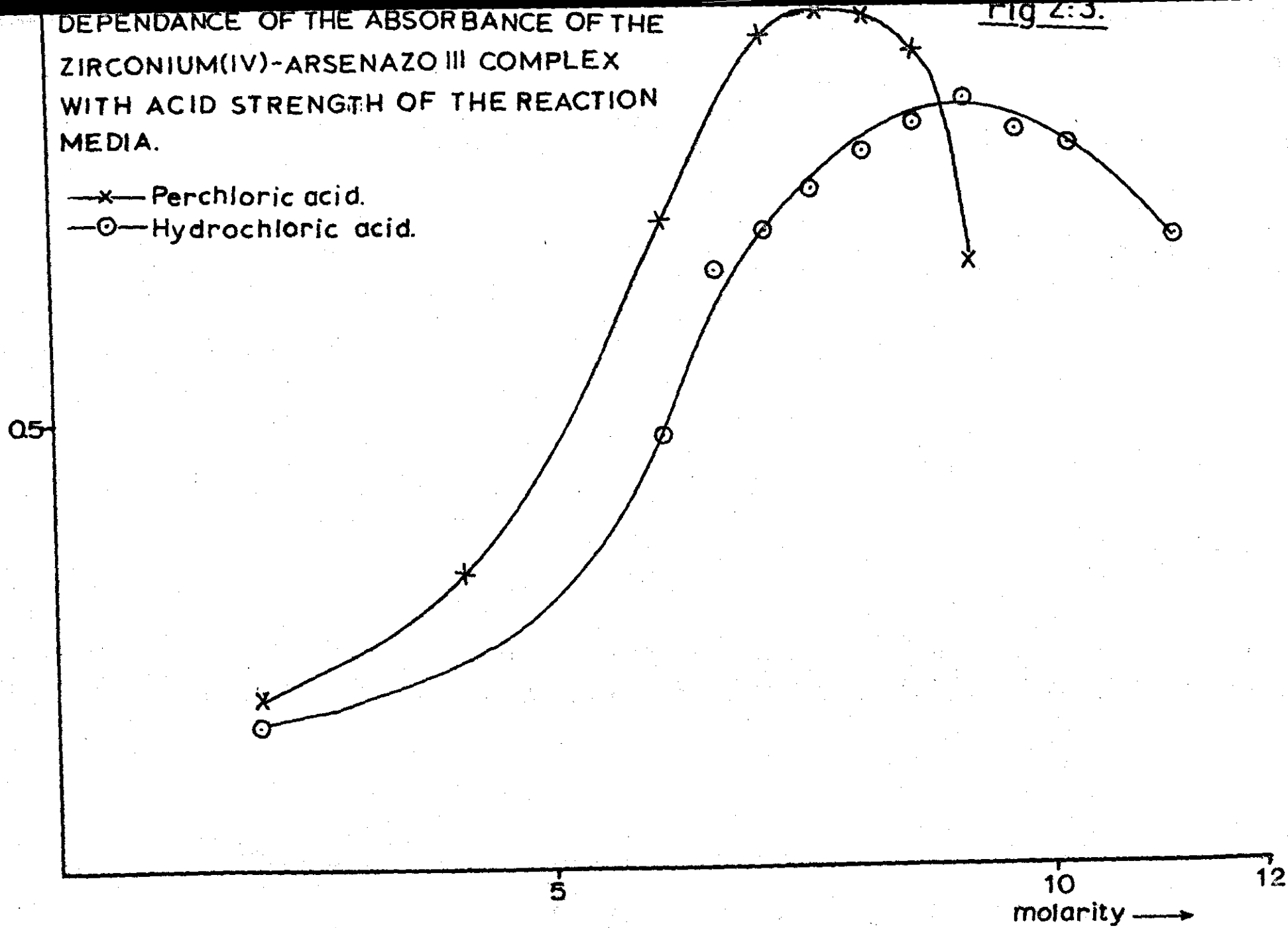
	2.0	4.0	6.0	7.0	7.5	8.0	8.5	9.0
Absorbance + Blank	0.175	0.298	0.650	0.845	0.890	0.930	0.965	0.965
Blank	0.005	0.009	0.018	0.032	0.052	0.103	0.107	0.378
Absorbance	0.170	0.289	0.632	0.813	0.838	0.827	0.858	0.587

Similar plots were obtained with both media. As the acidity is increased the absorbance gradually increases and reaches a maximum at 9M for hydrochloric acid, and 7.5M for perchloric acid. After this point the absorbance becomes less as the acidity is increased.

The gradual increase in absorbance with acidity has been studied at length by Muk and Savvin (45) and is believed to be due to a gradual change in the nature of the metal-ligand bonds rather than a change in the composition of the complex. When the acidity is low, the nature of the bonds approximates to that between the hydrolysed ion ($Zr(OH)_n^{(4-n)+}$)

Fig 2:3.

DEPENDANCE OF THE ABSORBANCE OF THE ZIRCONIUM(IV)-ARSENAZO III COMPLEX WITH ACID STRENGTH OF THE REACTION MEDIA.



and the ligands, whereas in strongly acid media it is more like the nature of the bond between the unhydrolysed ion (Zr^{4+}) and the ligands.

In the region of maximum absorbance for the complex, the effects of variation in acid concentration were found to be slightly less critical in the case of perchloric acid (Fig. 2:3). On this basis alone, perchloric acid media should give better precision. Furthermore, at their molarities of maximum absorbance, hydrochloric acid is above and perchloric acid is below its respective azeotropic concentration. Therefore, at the conditions for maximum colour development, hydrochloric acid presents the problems of acidity control, manipulation, and injurious effects to instruments that accompany the use of a fuming corrosive acid. For these reasons perchloric acid was used as the reaction media of choice.

CHAPTER III.

DEVELOPMENT OF A PROCEDURE FOR THE COMPLETE DISSOLUTION OF STEELS IN ACID MEDIA, BEFORE DETERMINATION OF ZIRCONIUM WITH ARSENAZO III

Zirconium(IV), hafnium(IV), thorium(IV), titanium(IV), lanthanum(III) and uranium(VI) are the only metal ions reported to form complexes with Arsenazo III. (42,75), in strong acid media. Of these only zirconium and titanium are commonly found, in any appreciable quantity, in steels. Arsenazo III is therefore an ideal reagent for the determination of zirconium in steels.

In spite of the fact that there is a highly selective reagent available for this determination, no generally applicable method, which does not include a prior separation of zirconium, has been described. This is because solutions of steels obtained by the conventional acid-digestion techniques leave some of the zirconium in a chemically inert form and this remains, even if hydrofluoric acid is used. Consequently, a time consuming filtration and alkali metal salt fusion procedure is necessary to decompose these compounds.

The problem was highlighted by Pakalns (39), who confirmed earlier work by Chechova (77) and stated that direct methods are only accurate when no hydrolytic precipitates or silica are formed during the dissolution procedure. This was used as the basis of an argument for always carrying out a separation procedure before colorimetric determination of zirconium in steels. In the same paper a recommended method was put forward; the zirconium is precipitated with Cupferron using iron as carrier. In this way, when the cupferrates are filtered off, the inert forms of zirconium are filtered off along with the cupferrates, thus avoiding loss of zirconium. The method is of course tedious since it requires a number of filtration ignition and fusion stages that are designed to collect and decompose these inert materials.

In 1968, Bernas published a paper entitled, "A New Method for the Determination and Comprehensive Analysis of Silicates by Atomic Absorption Spectrometry"(78). By using a mixture of concentrated hydrochloric, nitric and hydrofluoric acids in a sealed PTFE lined pressure digestion vessel at 170°C., complete decomposition of the silicates was brought about. Since then this new dissolution technique has been used extensively for the decomposition of ~~siliceous~~ siliceous materials before carrying out atomic absorption spectrometry, including rocks and minerals (79), ceramic materials (80) and Apollo 14 soils (81). The vessel has also been used for decomposing organic matter before atomic absorption spectrometry, for trace metals in foodstuffs (82) and mercury in tuna fish (83). The advantage in these cases is that as digestion is carried out in a sealed vessel there can be no losses of volatile materials. In steel analysis the pressure digestion vessel has already been used for the determination of nitrogen (84) and total aluminium (85).

In the work described in this chapter it is shown that the pressure digestion vessel technique of dissolution, due to Bernas (78), can be used to completely decompose the inert zirconium compounds that are the result of the conventional acid-dissolution techniques used in steel analysis. In this way, owing to the availability of the highly selective reagent Arsenazo III, possibilities are opened for the development of *the first generally applicable, direct colorimetric method for the determination of zirconium in steels.*

EXPERIMENTAL

(A) DISSOLUTION PROCEDURE

Table 3:1 Tests were carried out on BCS steel 271

Dissolution Procedure	Zirconium found (% m/m)	Coeff. of var*	Recovery (%) X
Boiling 7.5M $HClO_4$ for 30 minutes	0.0033	7	7.5
Preliminary dissolution in HCl and HF followed by fuming with 7.5 $HClO_4$ to drive off excess HF	0.0395	6	88
Recommended procedure using pressure digestion vessel as described in Chapter IV.	0.044	2	100

* Six determinations
X Based on results in Table 4:5.

The results shown in Table 3:1 indicate the necessity for using a pressure vessel. The inclusion of hydrofluoric acid in the dissolution mixture was found necessary even when the pressure vessel was used. Because of this necessity for a pressure treatment with a media that contains hydrofluoric acid, it seems more probable that the low recoveries of zirconium otherwise experienced are not the result of coprecipitation of the zirconium during the dissolution procedure (39) but are due to the presence of refractory zirconium compounds already present in the steel.

(B) ELIMINATION OF INTERFERENCE BY THE DISSOLUTION MEDIA

After dissolution of the steel in the pressure digestion vessel all traces of fluoride and oxides of nitrogen must be removed from the solution, as even low concentrations of fluoride ion in particular will interfere with the reaction of zirconium with Arsenazo III.

Attempts to simply mask the fluoride with Aluminium (III) or boric acid were unsuccessful and unfortunately a more time consuming evaporation technique has to be adopted. Perchloric acid was used since this was the media of choice for the colorimetric determination with Arsenazo III (Chapter II).

Table 3:2 Tests were carried out on BCS steel 271 (Zirconium content 0.044% m/m).

Evaporation technique	Zirconium found (% m/m)		
Evaporation to less than 10 ml. with concentrated $HClO_4$	0.023	0.032	0.032
Evaporation to less than 10 ml. with 7.5M $HClO_4$	0.044	0.045	0.043

Evaporation to a low volume must be carried out with dilute perchloric acid. Low results were obtained when the concentrated acid was used.

Hydrogen fluoride forms a constant boiling mixture with water. In the process of evaporation the hydrogen fluoride is removed in the form of its water azeotrope. This could possibly explain the necessity of dilute, rather than concentrated, perchloric acid for the efficient removal of hydrogen fluoride from the steel solutions.

CHAPTER IV.

DEVELOPMENT OF A DIRECT METHOD FOR ZIRCONIUM IN STEEL, BASED ON A PRESSURE DIGESTION TECHNIQUE FOLLOWED BY COLORIMETRIC DETERMINATION WITH ARSENAZO III.

A survey of the literature of previous work in the field leaves little doubt that Arsenazo III is the best reagent available for the determination of zirconium. The following work described the development of a method which is a combination of a spectrophotometric determination using this reagent and the pressure digestion technique described in Chapter III. Owing to the success of this digestion technique in completely decomposing the otherwise inert forms of zirconium found in steels, it is the first widely applicable procedure to be described that does not require a prior separation procedure.

Results obtained with British Chemical Standard steels show a high degree of precision for the recommended procedure. As would have been expected from the highly selective and sensitive nature of Arsenazo III in strong acid media, an investigation into possible interferences by the fifteen other metals most commonly found in steels, indicate applicability to a wide range of steels. The recommended procedure however, would not be applicable, in its present form, to high tungsten steels owing to the precipitation of tungstic acid at an intermediate stage.

EXPERIMENTAL

(A) OPTIMISATION OF REACTION CONDITIONS

Although a number of procedures which use Arsenazo III have been described, a detailed set of optimum conditions for its use in perchloric acid media were not available.

Colour development and stability time:

Table 4:1 Tests were carried out on solutions that contained 0.4 µg/ml. zirconium, in 1 cm. cells at 670 nm.

Time in Minutes	Absorbance against blank		
	Sample 1	Sample 2	Sample 3
0	0.558	0.552	0.552
5	0.558	0.552	0.554
10	0.558	0.550	0.552
15	0.557	0.550	0.552
30	0.552	0.545	0.551
40	0.553	0.543	0.550
50	0.551	0.541	0.550
60	0.550	0.538	0.548

Over this period the absorbance of the blank remained constant.

Full colour development is immediate and the complex is stable for 15 minutes.

Measurements should be made within fifteen minutes of adding the reagent.

Wavelength of maximum absorbance of the complex:

Measurements were made on Unicam SP600 spectrophotometer, calibrated immediately before use with a holmium filter at 637.5 nm. and a ~~dydymium~~ didymium filter at 685 nm.

Table 4:2 Tests were carried out on solutions that contained 0.4 µg/ml. zirconium, using 1 cm. cells, against a blank.

Wavelength (nm)	590	600	605	610	615	620	630	640	650
absorbance	0.032	0.166	0.246	0.291	0.300	0.284	0.240	0.281	0.396
Wavelength (nm)	660	662	664	666	668	670	675	680	700
absorbance	0.565	0.588	0.594	0.592	0.581	0.550	0.437	0.284	0.025

For maximum sensitivity, absorbance measurements should be made at 664 nm.

Concentration of Arsenazo III:

Table 4:3 Tests were carried out on solutions that contained 0.6 µg/ml. zirconium, since this is the maximum in the proposed method. Measurement was in 1 cm. cells at 664 nm.

Arsenazo III % m/V.	0.0004	0.0008	0.0012	0.0016	0.0020	0.0040
absorbance + blank	0.267	0.565	0.845	0.945	0.950	1.055
blank	0.017	0.044	0.054	0.070	0.070	0.148
absorbance	0.250	0.521	0.791	0.875	0.880	0.907

The minimum permissible concentration of Arsenazo III is 0.0016% m/V.

For minimum blank absorbances, without the risk of impairing sensitivity, an Arsenazo III concentration of 0.002% m/V should be used.

(c) RECOMMENDED PROCEDURE AND ITS APPLICATION TO BCS STEELS

The instructions, given below, for the preparation of the standard zirconium solutions were compiled with reference to a detailed study of the subject by Pakalns (38). The claim that they should be completely depolymerised and therefore immediately available for use has been confirmed by the findings of the present work. It would have been preferable to have prepared these solutions from pure zirconium metal since zirconium salts of guaranteed analytical-reagent grade are difficult to obtain. Unfortunately, zirconium metal is not readily soluble in perchloric acid. For the purposes of trace analysis however, the use of non analytical-reagent grade zirconyl chloride octahydrate should not be detrimental, provided that the salt is of a reasonable purity.

Ascorbic acid has been used as a masking agent for iron(III) and since identical calibration plots were obtained, with and without its inclusion, it was not considered necessary to add it to the solutions during preparation of the calibration plot.

On the strength of the evidence of the investigation described in Chapter II, 7.5M perchloric acid has been used as the reaction media. The slight changes from this optimum strength, that are a result of the evaporation stage, have been calculated not to be significant within the expected error of the procedure.

The pressure digestion vessel used in this work was obtained from S. and J. Juniper and Co., Harlow, Essex.

Reagents:

AQUA REGIA - Mix equal volumes of concentrated hydrochloric acid (analytical-reagent grade, sp.gr. 1.16 to 1.18) and concentrated nitric acid (analytical-reagent grade, sp.gr. 1.42).

HYDROFLUORIC ACID, 40 PER CENT m/V - Analytical-reagent grade.

PERCHLORIC ACID, 7.5M - Dilute 1,300 ml. of concentrated perchloric acid (70 per cent m/V, analytical-reagent grade) to 2 litres in a volumetric flask.

ASCORBIC ACID - Analytical-reagent grade.

ARSENAZO III SOLUTION, 0.1 PER CENT m/V - Dissolve 0.1 g. of Arsenazo III and about 0.5 g. of sodium hydroxide in about 50 ml. of water. Add concentrated hydrochloric acid dropwise with stirring, until the colour of the solution first changes to red-violet. Dilute to 100 ml. with water in a calibrated flask.

CONCENTRATED STANDARD ZIRCONIUM SOLUTION, 100 μg Zr $ml.^{-1}$ IN M PERCHLORIC ACID - Dissolve 0.177 g. of zirconyl chloride octahydrate in about 200 ml. of M perchloric acid by boiling under reflux for 1 hour. Cool and dilute the solution to 500 ml. with M perchloric acid in a calibrated flask.

DILUTE STANDARD ZIRCONIUM SOLUTION, 10 μg Zr $ml.^{-1}$ IN 7.5M PERCHLORIC ACID - By pipette transfer 10 ml. of concentrated standard zirconium solution to a 100 ml. calibrated flask, add 62 ml, of 70 per cent m/V perchloric acid solution and dilute to 100 ml. with water.

Preparation of calibration graph:

By pipette introduce an aliquot of the dilute standard zirconium solution (0 to 3.0 ml.) into a dry 50 ml. calibrated flask. Add by pipette 1 ml. of Arsenazo III solution and dilute to 50 ml, with 7.5M perchloric acid solution. Measure the absorbance, at 664 nm., of the solution within 15 minutes of preparation against water using 1 cm. cells. Substract the absorbance of the solution containing no zirconium.

Procedure:

Remove the PTFE liner from the pressure vessel and weigh into it an appropriate amount of steel (Note 1 and Table 4:4). Add 20 ml. of aqua regia and allow the steel sample to dissolve without heating. When evolution of hydrogen has ceased, add 5 ml. of 40 per cent m/V hydrofluoric acid solution, place and seal the liner in the pressure vessel (Note 2 and instruction manual where appropriate) and leave the pressure vessel in an oven at 200°C. overnight (Note 3).

Cool the pressure vessel to room temperature and open it carefully. Transfer the contents quantitatively to a suitable PTFE vessel with 25 ml. of 7.5M perchloric acid solution. Reduce the volume to less than 10 ml. by heating the vessel on a hot plate (Note 4), add 25 ml. of 7.5M perchloric acid solution and warm the mixture, if necessary, to dissolve any crystalline material (Note 5). Transfer the solution to a 50 ml. calibrated flask and dilute it to 50 ml. with 7.5M perchloric acid solution.

Pipette an appropriate aliquot of the solution (see Table 4:4) into a second 50 ml. calibrated flask, add 1 g. of ascorbic acid, dilute to about 30 ml. with 7.5M perchloric acid solution and swirl the flask to dissolve the ascorbic acid without heating. Continue the determination as described in "Preparation of Calibration Graph" beginning at "Add by pipette 1 ml. of Arsenazo III solution". For

steels containing large quantities of metals giving coloured ions, determine the absorbance at 664 nm. of an aliquot of steel solution in the absence of Arsenazo III and deduct this absorbance together with the Arsenazo III reagent blank from the absorbance value obtained with the sample.

Notes:

1. Safety note. Perchloric acid must NOT be included in the digestion mixture in the sealed pressure vessel. The liner should be perfectly clean and dry, and care should be taken that no traces of perchloric acid from the previous determination remain in the liner.

2. Corrosion products tend to form at the surfaces between the metal and the liner. These surfaces should be cleaned regularly in order to avoid difficulties in removing the liner after digestion.

3. For some steels this digestion period can be reduced. Complete recovery of zirconium was made from British Chemical Standards Steels Nos. 271, 272, 274 and 275after only 2 hours digestion.

4. This evaporation stage to remove hydrogen fluoride and oxides of nitrogen, although time consuming, is very important. Traces of fluoride, in particular, interfere with the reaction of zirconium with Arsenazo III.

5. With steels that have a high chromium content, a red chromium(VI) compound may crystallise out on evaporating to 10 ml. This precipitate dissolves more readily if about 1 g. of ascorbic acid is added after the 7.5M perchloric acid solution. This treatment should be carried out without warming as ascorbic acid is rapidly decomposed by warm perchloric acid solutions.

Results obtained with the procedure described for the preparation of the calibration graph using the dilute standard zirconium solution had a coefficient of variation of 1.5 at the 0.4 μg Zr ml^{-1} level for 10 determinations.

The calibration graph was linear in the range 0.1 to 0.6 μg Zr $ml.^{-1}$, and its slope corresponded to a molar absorptivity at 664 nm. for the complex of 1.32×10^5 l. mol^{-1} cm^{-1}.

Results obtained with six British Chemical Standards steel samples using the recommended procedure are given in Table 4:5. These show good reproducibility and compare well with results obtained by other methods.

SUGGESTED SAMPLE SIZES AND ALIQUOTS FOR VARIOUS STEELS

Table 4:4

Although in many instances the zirconium content of the steel will not be known even approximately, the sample sizes and aliquots recommended here will give an indication of a suitable amount of sample to take as a trial. The sample size and aliquots recommended for each range of tin content give absorbance values between 0.3 and 0.6, except for steel samples containing less than 0.004 per cent m/m of zirconium.

Expected zirconium content per cent, m/m.	Amount of steel to be taken g.	Aliquot taken ml.
0.001 - 0.006	0.5	25
0.006 - 0.01	0.5	15
0.01 - 0.02	0.5	10
0.02 - 0.04	0.5	5
0.04 - 0.05	0.1	15
0.05 - 0.10	0.1	10
0.10 - 0.20	0.1	5

Determination of zirconium in BCS steels:

Table 4:5

Zirconium content, per cent m/m

Steel	BCS values* Chemical	BCS values* Spectrographic	Xylenol** orange procedure	X-ray + fluorescence	Recommended procedure++
271	$.04_5$	$.04_5$	.044	.043	.044, .045, .043
272	$.03_0$	$.03_0$	.031	.029	.031, .033, .033
274	$.00_5$	$.01_0$	.012	.010	.010, .011, .011
275	$.01_5$	$.02_0$	.021	.019	.020. .020, .021
276	$.00_5$	$.00_5$	.008	.006	.006, .006, .005
277	$.04_0$	$.05_0$	.051	.050	.050, .048, .047

* Zirconium is a non-standardised element in these steels

** Results of Keller and Hennesen (52).

\+ Results of Klima and Scholes (86).

++ Results obtained from three different dissolutions of the steel sample.

(D) INVESTIGATION INTO POSSIBLE INTERFERENCES

The effects of fifteen other metals on the determination of zirconium are shown in Table 4:6. The metal:zirconium ratios chosen for study are well above those normally found in steels (87).

Table 4:6

Amount of zirconium added = 20.0 µg.

Metal	Metal to zirconium ratio	Zirconium found/µg.
Antimony	10	19.3, 19.2
Arsenic	100	19.6, 19.5
Manganese	10,000	20.0, 20.2
Copper	10,000	20.7, 20.9*
Titanium	30	19.3, 19.3
	50	18.8, 19.0
	100	17.5, 17.9
	300	11.3, 9.3
Aluminium	1,000	19.8, 19.2
Tin	100	19.8, 19.0
Lead	100	20.3, 19.5
Beryllium	1,000	20.5, 19.5
Molybdenum	1,000	19.3, 19.3
Chromium	10,000	18.8, 19.3*
Vanadium	1,000	19.5, 19.3*
Cobalt	10,000	19.3, 19.0
Nickel	3,000	19.3, 19.0*

* These metals produced ions in the dissolution process which absorbed at 664 nm. A correction was made for this (see procedure).

Titanium interferes to some extent. Increasing the quantity of Arsenazo III used did not improve the situation. Attempts to mask the titanium with hydrogen peroxide, which forms an orange peroxo-complex with it, were unsuccessful. The presence of peroxide in the system resulted in the oxidation of the Arsenazo III. Nevertheless, titanium could be tolerated up to a level of 100-fold that of zirconium, where the error is only about 10 per cent. This would suffice for the vast majority of steels.

Tungsten, which has not been included in Table 4:6 is the only metal that interferes seriously. A colloidal precipitate of yellow tungstic acid forms when the digestion mixture is evaporated to 10 ml. This precipitate cannot readily be filtered or centrifuged, and it is probable that zirconium is coprecipitated. Consequently, the procedure in its present form cannot be applied to high tungsten steels. Of the steels studied here, BCS 276 and 277 contained the largest amount of tungsten (0.20 and 0.12 per cent m/m respectively) and this amount of tungsten did not interfere in the determination.

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GENERAL DISCUSSION.

GENERAL DISCUSSION

The development of the method for the determination of tin in steel, described earlier, required essentially a rationalisation of the findings of previous work and the development of separation and masking techniques to compensate for the absence of a highly selective reagent.

It was not apparent from a survey of the literature which of the reagents for the colorimetric determination of tin was superior. Consequently, a comparative study was necessary. As none of the reagents could be described as highly selective, selectivity was not used as one of the criteria of this study. Catechol Violet, in the presence of CTAB, emerged as the best reagent on the grounds of the remaining criteria, namely adherence to Beers' Law, spectral characteristics, sensitivity and reproducibility of results.

The absence of a highly selective reagent for the determination of tin means that, if a method is to be applicable to a wide range of steels, the spectrophotometric determination must be preceded by a selective extraction procedure. The literature survey on this subject proved more fruitful than in the case of the choice of a reagent. There is no doubt that the simplest and most convenient method of separating tin is by solvent extraction of tin(IV) iodide followed by back-extraction with sodium hydroxide solution.

In view of the absence of a highly selective reagent for tin therefore, the recommended method is the best possible compromise; it is a combination of the best separation and spectrophotometric procedures available, and the success of lactic acid in overcoming interference by several alloying elements, including the longstanding problem of molybdenum interference, renders the method applicable to a wider range of steels than any other method previously described.

At the present time, the most popular reagent for tin, used in the British Steel Industry, appears to be Phenylfluorone. On the

evidence of this work its use should be discontinued. Direct methods have been published using this reagent and its popularity would appear to have sprung from the obvious attraction of these. Phenylfluorone however, is not highly selective for tin and therefore there is no more justification for using this reagent in a direct procedure than there is for using the many other reagents that are, in fact, superior in most other respects.

Because of the high degree of selectivity achieved by combining the Catechol Violet/CTAB colorimetric procedure with lactic acid masking and with the iodide extraction procedure where necessary, the full procedure should be applicable to the determination of tin in other metals and alloys. As interferences in many of these matrices would be considerably less than in steels, the direct procedure without iodide extraction would often suffice.

Recent work has shown that dispersing agents, used in chromogenic systems, do not always simply act as dispersants but react chemically with the coloured species. Careful choice of dispersing agent can often lead to considerable improvements in the analytical characteristics of the system. The tin(IV)-Catechol Violet-CTAB system can be considered as a typical example and CTAB has been shown to play a dual role in this system; that of forming a salt with the coloured species and that of a dispersing agent. Cationic surfactants, such as CTAB, have an exceptionally high solubilising effect on dyestuffs and on this point alone, they could therefore be used to advantage in many other systems which required a dispersing agent. The dual role mechanism of the CTAB action however, suggests that marked improvements, of the type observed with the tin(IV)-Catechol Violet system, could only be expected in cases where the binary complex is capable of forming an anion.

There is a highly selective reagent available for the determination of zirconium, namely Arsenazo III. For this reason, in the development of a method for the determination of zirconium in steel, the choice of reagent was simpler and less rationalisation of previous work was necessary than in the case of a method for tin. In addition Arsenazo III is highly sensitive, its complex with zirconium(IV) is soluble in aqueous solution, and the spectral characteristics of the zirconium(IV)-Arsenazo III system are virtually ideal for spectrophotometric measurement.

One major problem however remained in applying a colorimetric procedure to the determination of zirconium in steels. Zirconium exists in steels in chemically inert ~~siliceous~~ siliceous forms which are not decomposed by the conventional acid dissolution techniques. Previously, it was necessary to collect and decompose these compounds by lengthy and tedious precipitation, filtration and alkali metal salt fusion procedures. Consequently, in spite of the availability of a highly selective reagent for zirconium, no direct method, which was generally applicable, had been described.

By using a PTFE lined pressure digestion vessel, the steels can be treated with strong acids at higher temperatures than are possible at atmospheric pressure. In this way the chemically inert forms of zirconium are completely decomposed and it is possible to apply the Arsenazo III spectrophotometric determination directly to the steel solution.

The pressure digestion vessel used in this work was originally designed for the preparation of solutions of silicates for trace metal determinations by atomic absorption spectrometry. Zirconium is one of the least sensitive elements in atomic absorption spectrometry and for this reason spectrophotometric methods would be preferable. If however, atomic absorption spectrometry is to be used, there appears to be no reason why the dissolution procedure, outlined here, should not be used for this purpose also.

The work described in this thesis, along with that contained in the Ph.D. thesis of D. R. Marlott (1970), involving the determination of tungsten and arsenic, largely completes the required investigation into the spectrophotometric analysis of steels, the possible remaining exception being the determination of boron for which, at present, there is still no reliable method.