

Independent Hygiene and Environmental Consultant Analysts



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DETERMINATION OF CATIONIC

FLOCCULANTS IN DRINKING WATER

Client

:The Secretary of State for the Environment

Department of the Environment

N3/03A

2 Marsham Street London SW1P 3EB

Contract Ref.

:PECD 7/7/351

Report Date

:31 December 1990

Report prepared by :Dr PJ Whittle, Head of Chemistry.

Signed

Paty Whith



1 BACKGROUND

Altwell were contracted by the Secretary of State for the Environment (contract reference No. PECD 7/7/351) to develop a reliable method which can be used to determine and monitor the concentrations of residual cationic flocculants in treated drinking water. Part A of the work was to review the published data on methods of analysis and recommend which publications, if any, might form the basis for developing and testing a method. The outcome has been reported (Altwell report No. R/0055-90, dated 30th April 1990). We recommended that the work of Parazak et al. (1) appeared potentially suitable to fulfil the requirements of the research programme. This report presents the results and conclusions of Part B of the contract, the development and testing of a method.

2 INTRODUCTION

- It is known that most of the colloidal and suspended 2.1 impurities in natural waters have negative surface charges Inorganic water treatment chemicals such as those containing iron or aluminium can act as primary coagulants as they neutralise the charge and the precipitate forms a settleable floc. Nonionic organic polymers act as coagulant aids by coating floc particles so that they will adhere to each other thus forming larger and heavier masses. Anionic polymers can also be used as coagulants but must be applied together with cationic chemicals to neutralise both polymer and the natural particulates. Cationic organic polymers, generally called cationic polyelectrolytes, can act as both primary coagulant and a flocculation aid as they will neutralise the natural particulates and then agglomerate together into larger masses for rapid separation by sedimentation or filtration. Cationic polyelectrolytes are therefore attractive as water treatment chemicals as two functions can be fulfilled with one chemical.
- As the reaction between cationic polyelectrolytes is a 2.2 process of charge neutralisation, there comes a point when cationic polyelectrolyte is added to water, at which the net charge is zero. For the purpose of this report we have "equivalence point", which called this point the conveniently measured in terms of the concentration of added polyelectrolyte. Below the equivalence point there will be insufficient cationic polyelectrolyte to precipitate all the natural charged particles, ie anions are in the excess, and clarification of the water may be inadequate. Above the equivalence point, cations will be in excess and there will residual amount of cationic polyelectrolyte be a solution.
- 2.3 The amount of anionically charged particulate matter suspended in a given water supply will vary dependent on the



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conditions prevailing at the time of abstraction. It is therefore desirable to be able to estimate the equivalence point and also to measure the amount of residual polyelectrolyte in a treated water. The method developed in this report is suitable for both tasks.

- 2.4 The method of Parazak et al. is based on the reaction of cationic polyelectrolytes with an anionic dye, Ponceau-S, to form an insoluble complex which is removed from solution and the remaining Ponceau-S measured spectrophotometrically. The cationic polyelectrolyte concentration is calculated from a calibration graph. The key feature of the method is the removal of the precipitated complex by shaking with (1,1,2-trichlorotrifluoroethane), whereby precipitate collected at the solvent/water interface and could be easily run off in a separating funnel. However we found this procedure unreliable and replaced it with a filtration stage using disposable syringe filters which was found to be simple and effective. The only other change to Parazak's method was to increase the sensitivity by increasing the pathlength of the cuvettes and adjusting the dye concentration accordingly.
- 2.5 The cationic flocculants approved by the DOE Committee on Chemicals and Materials of Construction for use with Potable Water Supplies and Swimming Pools (see Appendix 2) fall into groups. Those based quaternary on polyelectrolyte and those based on polyquaternary resin. Letters were written to all the manufacturers of approved products requesting a sample and details of any analytical methods. In the event only six samples were received out of 30 listed products. Some of the manufacturers explained that their products were very similar in nature and others that their products were bought from other firms and sold under a different label. It was considered that the six sample were probably representative of range of products available.
- 2.6 The six products tested were as follows:

Magnafloc LT31	Allied Colloids Ltd.
Superfloc C521	Cyanamid of Great Britain Ltd.
Superfloc C573	Cyanamid of Great Britain Ltd.
Superfloc C587	Cyanamid of Great Britain Ltd.
Busan 77	Buckman Laboratories SA.
Bubond 65	Buckman Laboratories SA.

3 <u>TEST PROTOCOLS</u>

3.1 The details of the method used are as described in the appended draft "Blue Book", "The Determination of Residual Cationic Polyelectrolyte in Potable Water" (Appendix 1).



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- 3.2 The limit of detection was determined by analysing 10 low standards in distilled water on one occasion. As the method involves determining the difference in absorption between a distilled water blank and the sample it was considered that the difference between 2 distilled water blanks was not an appropriate way to determine the limit of detection.
- 3.3 Within batch, between batch and total standard deviations were determined by analysing in duplicate on three occasions, distilled water samples spiked with a concentration 2-3 times the limit of detection; in duplicate on three occasions, distilled water spiked near the top of the linear range of the test; a filtered river water with a low residual cationic polyelectrolyte in duplicate on one occasion and a filtered river water with a low residual cationic polyelectrolyte, spiked with 2-3 times the limit of detection, in duplicate on 2 occasions.

When analysing natural waters and spiked natural waters it was considered that sufficient polyelectrolyte had to be added to a level just above the equivalence point, and the precipitate filtered off, otherwise the added spikes would simply react with the natural anions and not give meaningful results.

- 3.4 Spike and recovery tests were also performed on a borehole water with a high iron and manganese content (Morton raw water, supplied by Severn Trent Water), and water from an upland reservoir (Alwen raw water, supplied by Welsh Water). The river water used for the tests in 3.3 was from the R. Dee.
- 3.5 Free chlorine, aluminium, anionic and cationic detergents were tested as possible interferents.

4 RESULTS

- 4.1 Calibration curves for the six polyelectrolytes in distilled water are shown in figures 1-6 of appendix 1.
- 4.2 Performance data are shown in tables 1-6 of appendix 1.
- 4.3 The iron and manganese contents of the ground water and upland waters were as follows:

	$egin{array}{c} { t Iron} \\ { t ug} \ { t l}^{-1} \end{array}$	Manganese ug l ⁻¹
Morton raw (borehole)	1320	77
Alwen raw (upland)	610	21



Interferences

- 4.4 During determinations of equivalence points it was observed that the calibration graphs produced after primary filtration sometimes differed in gradient from those produced in distilled water. It was particularly noticeable in water samples with a high organic content which resulted in enhanced sensitivity. An example showing the different curves produced is shown in figure 7 of appendix 1. Performance data presented in tables 1-6 of appendix 1 was produced from calibrations based on real water samples.
- 4.5 Residual chlorine interfered by slowly bleaching the Ponceau-S dye. The use of thiosulphate to destroy residual chlorine did not cause any problems in subsequent measurements.
- 4.6 Aluminium was tested as a potential interferent with the following results:

Type of water	Aluminium sulphate mg l ⁻¹	LT31 found mg 1 ⁻¹
Upland water Upland water	0 2	0.45 0.46
Spiked upland water (0.7 mg l ⁻¹ LT31)	2	1.15
Distilled water Distilled water	10 20	<0.28 <0.28

- 4.7 Sodium dodecylsulphate at 10 or 20 mg l⁻¹ did not show any interference.
- 4.8 Cetyltrimethylammonium bromide did interfere in the determination. A calibration graph for cetyltrimethylammonium bromide in distilled water is shown in figure 8 of appendix 1.
- 4.9 In waters treated with cationic polyelectrolytes, any floc which has not been removed by the filtration process will react partially or totally, dependent on the relative strength of the anion/cationic polyelectrolyte bond compared with the Ponceau-S/cationic polyelectrolyte bond.

5 <u>CONCLUSIONS</u>

5.1 The method developed is essentially simple, and will enable equivalence pints or residual cationic polyelectrolyte to be determined quickly. The performance data shows the method to be reliable, although early work gave a fair number of "rogue" results, particularly at low residual levels. This was considered possibly due to adsorption of



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the polyelectrolytes on to the surface of flasks or other containers. An investigation into the use of glass or plastic vessels with different types of cleaning did not reveal the reason for the problems and the number of "rogue" results decreased as the project continued. It is recommended that a set of glass ware is reserved solely for use with this method.

- 5.2 Calibration curves in distilled water were very reproducible for a specific polyelectrolyte. Why different calibration curves were produced in some waters, particularly those high in organic matter, is not clear, but the spike recovery data was good. How much day to day variation there is in real water calibrations will need to be determined locally.
- 5.3 The range of the test is limited by the linearity of the spectrophotometer used and because a reduction in colour is measured there is little scope for lowering the limits of detection. However since all the approved flocculants are limited to a maximum level of 10 mg l⁻¹ in use the range of application would seem satisfactory. It was observed that the cationic polyelectrolyte/Ponceau-S complex which is removed by filtration in the method can be redissolved in caustic solution to give a coloured solution and this could possibly form the basis of a low level method for cationic polyelectrolytes if required.
- 5.4 Three cationic polyelectrolytes (Magnafloc LT31, Bubond 65 and Superfloc C587) were chosen for additional testing on a borehole water high in manganese and iron and an upland water. The method performed well (there was insufficient sample available to test the C587 on the upland water). No interference was given by aluminium or sodium dodecylsulphate, an anionic detergent. Free chlorine does interfere but this problem is easily eliminated by addition of thiosulphate to the sample.
- 5.5 Cationic surfactants, as exemplified by cetyltrimethylammonium bromide, did interfere so effectively that the method could be used for the determination of cationic detergents in the absence of cationic polyelectrolytes. However cationic detergents should not be a problem in most situations. If cationic detergents are present, it would be expected that the naturally occurring anions would be neutralised in part or total and therefore the equivalence point would change and the residual flocculant increase substantially.



REFERENCES

- Determination of low levels of cationic polyelectrolytes in water.
 Parazak, DP; Burkhardt, CW; McCarthey, KJ; Anal. Chem., 1987, 59(10), 1444-5.
- 2 Kawamura, S; Hanna, GP; Proc. 21st Ind. Waste Conf. 1966, 141(1), 381.
- 3 Strumn, W; Morgan, JJ; 1962, J. Am. Water Works Assoc., 54(2), 971.



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APPENDIX 1

DRAFT METHOD

The Determination of Residual Cationic Flocculants (Polyelectrolytes) in Water

Introduction

Certain cationic polyelectrolytes are approved by the Committee on chemicals and Materials Construction for use with Potable Water Supplies or Swimming Pools, for use in the treatment of waters for potable use. This spectrophotometric method can be amount residual determine the used to polyelectrolyte remaining after treatment or how much polyelectrolyte is required for the treatment of a particular water, that is the point at which the added cations exactly balance the naturally occurring anions and called for the purpose of this method, the equivalence point.

Performance Characteristics of the Method

2.1 Substance Candetermined Wil

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- Cationic polyelectrolytes or other cationic species which form an insoluble complex with the anionic dye.
- 2.2 Type of Sample Raw and treated waters.
- 2.3 Basis of method The

The cationic species are reacted under acidic conditions with an anionic dye, Ponceau-S, and, after filtration, the reduction in dye concentration determined spectrophotometrically.

- 2.4 Range of application
- Variable, dependent on the polyelectrolyte, but typically 0 to 10 mg $1^{-1}\,.$
- 2.5 Calibration curves
- Linear, see figures 1-6.
- 2.6 Standard deviations
- See tables 1-6.
- 2.7 Limits of detection
- See tables 1-6

2.8 Bias

- See tables 1-6
- 2.9 Interferences

Residual chlorine, cationic detergents and any substance which reacts with Ponceau-S to produce an insoluble complex or alter its absorbance in any way.



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Principle

The method is based on the reaction in acidic solution of cationic polyelectrolytes with the anionic dye, Ponceau-S, to form an insoluble complex which is removed by filtration. The absorbance of the filtrate is measured spectrophotometrically at 520 nm and compared with the absorbance of a distilled water blank.

Interferences

Residual chlorine must be removed with thiosulphate before testing otherwise the dye is slowly bleached. Cationic detergents interfere. Aluminium sulphate and sodium dodecylsulphate do not show any interference at 10 or 20 mg 1^{-1} each. Any substance which reacts with Ponceau-S to form an insoluble complex or alter its absorbance characteristics will interfere.

With treated waters, any floc which has not been removed by the filtration process will also react partially or in total and therefore will contribute to the result.

Hazards

- 5.1 Sulphuric acid is corrosive and causes burns. Eye protection and gloves should be worn when handling and any spillages washed away with copious quantities of water.
- 5.2 Considerable pressure can be developed using syringe filters and eye protection should be worn.

Reagents

6.1 Water

Distilled or deionised water is required.

6.2 0.5M Sulphuric acid solution

Cautiously add with stirring 27.0 ± 0.5 ml of sulphuric acid(d₂₀ 1.84) to about 800 ml of water (6.1). Cool and make up to 1 litre in a calibrated flask. This solution is stable for at least 3 months.

6.3 Ponceau-S Reagent

Dissolve 0.250 ± 0.001 g of Ponceau-S dye (75%, Aldrich Chemical Co.) in 1 litre of water (6.1) in a calibrated flask. This solution is stable for at least a month if stored in the dark.

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6.4 Cationic Polyelectrolyte Stock Standard

Dissolve 5.00 ± 0.01 g of cationic polyelectrolyte in distilled water and make up to 1 litre with distilled water in a volumetric flask.

1 ml = 5.0 mg polyelectrolyte

Note: The concentration ranges chosen will vary with different polyelectrolytes. The concentrations used in this method provide a convenient starting point and are suitable for a number of polyelectrolytes.

6.5 Cationic Polyelectrolyte Working Standard

Dilute 2.00 ± 0.01 ml of cationic polyelectrolyte stock standard (6.4) to 1 litre with distilled water in a calibrated flask.

1 ml = 0.01 mg polyelectrolyte

Apparatus

- 7.1 A spectrophotometer capable of holding 40 mm cuvettes and operating at 520 nm.
- 7.2 Disposable 0.2 um syringe filters with Luer fitting (Acrodisc, Gelman Sciences UK).
- 7.3 Glass syringe, 20 or 25 ml capacity, with glass or metal Luer fitting.

Sample Collection and Preservation

Samples should be collected in glass containers which have been cleaned with a proprietary cleaning agent that does not interfere with the analysis, thoroughly rinsed with water, rinsed with distilled water and air dried in a warm air oven $(60-80^{\circ}\text{C})$. It is recommended that a set of glassware is kept for use only with this method.

No special preservation techniques are employed. However, samples should be analysed as soon as possible or within 24 hours if stored in a refrigerator between 1 and 5°C .

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Analytical Procedure

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Step Procedure

3

Notes

9.1 S w i t c h o n t h e spectrophotometer, set the wavelength to 520 nm and allow to warm up according to the manufacturers instructions.

Calibration

- 9.2 Add 5.0, 10.0, 20.0, 30.0 and 40.0 ml aliquots of the cationic polyelectrolyte working standard (6.5) to each of five 50 ml volumetric flasks. A sixth flask is used as a blank.
- 9.3 To each flask add 2.0 ml of 0.5M sulphuric acid solution (6.2) and 1.0 ml of Ponceau-S dye solution (6.1). Make up to the mark with water (6.1), mix well and stand for 5 minutes (note a)
- 9.4 Fill a 25 ml glass syringe (7.3) with each solution in turn and filter through a syringe filter (7.2) into a 40 mm cuvette using some of the filtrate to rinse the cell.
- 9.5 Measure the absorbance of each solution at 520 nm.
- 9.6 Subtract each reading from the blank value and plot a calibration graph of absorbance difference versus concentration.

Determination of Equivalence Point

9.7 Add 100, 200, 500, 750 and 1000 ul aliquots of cationic polyelectrolyte stock standard (6.4) to each of 5 250 ml measuring cylinders (stoppered type) containing 250 ml of the water to be tested.

(a) 5 minutes was found to be satisfactory for the polyelectrolytes tested.



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- Stopper, mix well and allow to stand for at least 5 minutes. (notes b & c)
- 9.8 Filter each solution under vacuum through a glass fibre filter (Whatman GF/C) into clean Buchner flasks.
- 9.9 Pipette 40 ml of each filtrate into each of 5 50 ml volumetric flasks. A sixth flask is used as a blank.
- 9.10 Repeat steps 9.3 to 9.6. (note d)

Analysis of Samples

- 9.11 Add 40.0 ml of sample to a 50 ml volumetric flask and use a second flask as a blank.
- 9.12 Repeat steps 9.3 to 9.5.
- 9.13 Subtract the sample absorbance from the blank value and read the concentration from the calibration graph. (notes d & e)

- (b) Volume differences are
 insignificant.
- (c) Appropriate flocculation times should be determined experimentally for each polyelectrolyte and water source tested.

- (d) If the gradient of the graph is significantly different from the distilled water calibration this graph should be used for the analysis of samples.
- (e) If the equivalence point graph is used, read the concentration from the graph and subtract the equivalence concentration ie the value at which the graph intercepts the concentration axis.



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TABLE 1

Magnafloc LT31

Standard deviations

	LT31 Concentration mg l ⁻¹	Standard Within Batch mg l ⁻¹	Deviations* Between Batch mg 1 ⁻¹	Total mg l ⁻¹
Standards	1.0	0.099(3) 0.14(3)	NS(2) NS(2)	0.01(5) 0.015(4)
Samples		()	• ,	` ,
River water	3.76			
Spiked river water	4.51	0.15(2)	0.0(1)	0.15(3)
Ground water	4.65			0.10/05
Spiked ground water		0.17(2)	NS(1)	0.18(3)
Upland water	1.35	0.03(2)	NC/1\	0.03(2)
Spiked upland water	2.03	0.03(2)	NS(1)	0.03(2)

^{*}Figures in parentheses are the degrees of freedom. NS indicates that the result is not statistically significant.

Limit of Detection $0.28 \text{ mg } 1^{-1} (9)$

Bias

Less than 10% as indicated by a mean recovery of 107% from river water (mean LT31 concentration 3.76 mg 1^{-1}) spiked with 0.7 mg 1^{-1} of LT31. Less than 10% as indicated by a mean recovery of 103% from ground water (mean LT31 concentration 4.65 mg 1^{-1}) spiked with 0.7 mg 1^{-1} of LT31. Less than 10% as indicated by a mean recovery of 106% from upland water (mean LT31 concentration 1.35 mg 1^{-1}) spiked with 0.7 mg 1^{-1} of LT31.



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TABLE 2

Superfloc C573

Standard deviations

	C573 Concentration mg l ⁻¹	Standard Within Batch mg l ⁻¹	Deviations* Between Batch mg 1 ⁻¹	Total
Standards	0.5 7.0	0.19(3) 0.19(3)	NS(2) NS(2)	0.21(4) 0.20(5)
Samples River water	1.56		(- ,	
Spiked river water	1.95	0.062(2)	NS(1)	0.074(2)

^{*}Figures in parentheses are the degrees of freedom. NS indicates that the result is not statistically significant.

Limit of Detection 0.16 mg l⁻¹ (9)

3ias

Less than 10% as indicated by a mean recovery of 97.5% from river water (mean C573 concentration 1.56 mg 1^{-1}) spiked with 0.4 mg 1^{-1} of C573.

TABLE 3

3usan 77

Standard deviations

	Busan 77 Concentration mg l ⁻¹	Standard Within Batch mg l ⁻¹	Deviations* Between Batch mg 1 ⁻¹	Total mg l ⁻¹
Standards	0.5 6.0	0.11(3) 0.30(2)	NS(2) NS(1)	0.12(4) 0.31(3)
Samples		()	· /	. (-)
River water	1.76			
Spiked river water	2.25	0.24(2)	NS(1)	0.26(2)

^{*}Figures in parentheses are the degrees of freedom. NS indicates that the result is not statistically significant.

Limit of Detection $0.18 \text{ mg } 1^{-1} (9)$

3ias

Less than 10% as indicated by a mean recovery of 109% from river water (mean Busan 77 concentration 1.76 mg 1^{-1}) spiked with 0.45 mg 1^{-1} of Busan 77.



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TABLE 4

Bubond 65
Standard deviations

	Bubond 65 Concentration mg l ⁻¹	Standard Within Batch mg l ⁻¹	Deviations* Between Batch mg 1 ⁻¹	Total mg l ⁻¹
Standards	2.0	0.21(3) 0.14(2)	0.0(2) 0.0(1)	0.21(5) 0.14(2)
Samples				
River water	4.47			
Spiked river water	6.46	0.28(2)	NS(1)	0.33(2)
Ground water	4.52		• •	
Spiked ground water Upland water	6.70 2.39	0.06(2)	0.0(1)	0.06(3)
Spiked upland water		0.27(2)	NS(1)	0.32(2)

^{*}Figures in parentheses are the degrees of freedom. NS indicates that the result is not statistically significant.

Limit of Detection $0.86 \text{ mg } 1^{-1}$ (9)

Bias

Less than 10% as indicated by a mean recovery of 93% from river water (mean Bubond 65 concentration 4.47 mg 1^{-1}) spiked with 2.15 mg 1^{-1} of Bubond 65. Less than 10% as indicated by a mean recovery of 101% from ground water (mean Bubond 65 concentration 4.52 mg 1^{-1}) spiked with 2.15 mg 1^{-1} of Bubond 65. 10% as indicated by a mean recovery of 110% from upland water (mean Bubond 65 concentration 2.39 mg 1^{-1}) spiked with 2.15 mg 1^{-1} of Bubond 65.



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TABLE 5

Superfloc C521

Standard deviations

	C521 Concentration mg l ⁻¹	Standard Within Batch mg l ⁻¹	Deviations* Between Batch mg 1 ⁻¹	Total
Standards	1.0	0.16(3) 0.30(3)	0.0(2) NS(2)	0.16(5) 0.34(4)
Samples River water	3.25		115(2)	0.01(1)
Spiked river water	4.06	0.13(2)	NS(1)	0.15(2)

 $^{^{}st}$ Figures in parentheses are the degrees of freedom. NS indicates that the result is not statistically significant.

Limit of Detection $0.86 \text{ mg } 1^{-1} (9)$

Bias

10% as indicated by a mean recovery of 90% from river water (mean C521 concentration 3.25 mg 1-1) spiked with $0.9 \text{ mg}^{1-1} \text{ of } C521.$

TABLE 6

Superfloc C587

Standard deviations

	C587 Concentration	Standard Within Batch	Deviations [*] Between Batch	Total
	mg 1 ⁻¹	mg 1 ⁻¹	mg 1 ⁻¹	$mg 1^{-1}$
Standards	2.08.0	0.26(3) 0.19(3)	0.0(2) NS(2)	0.26(5) 0.19(5)
Samples River water	2.55			
Spiked river water Fround water	4.70 3.5	0.10(2)	NS(1)	0.10(2)
3piked ground water		0.06(2)	0.0(1)	0.06(3)

^{*}Figures in parentheses are the degrees of freedom. NS indicates that the result is not statistically significant.

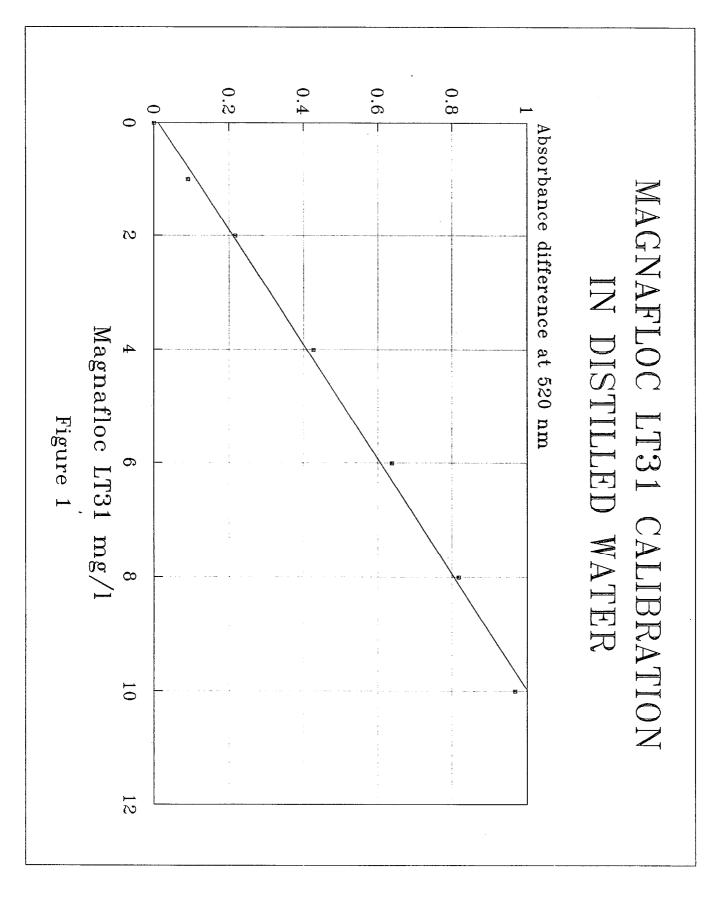
Limit of Detection $0.80 \text{ mg } 1^{-1} (9)$

3ias

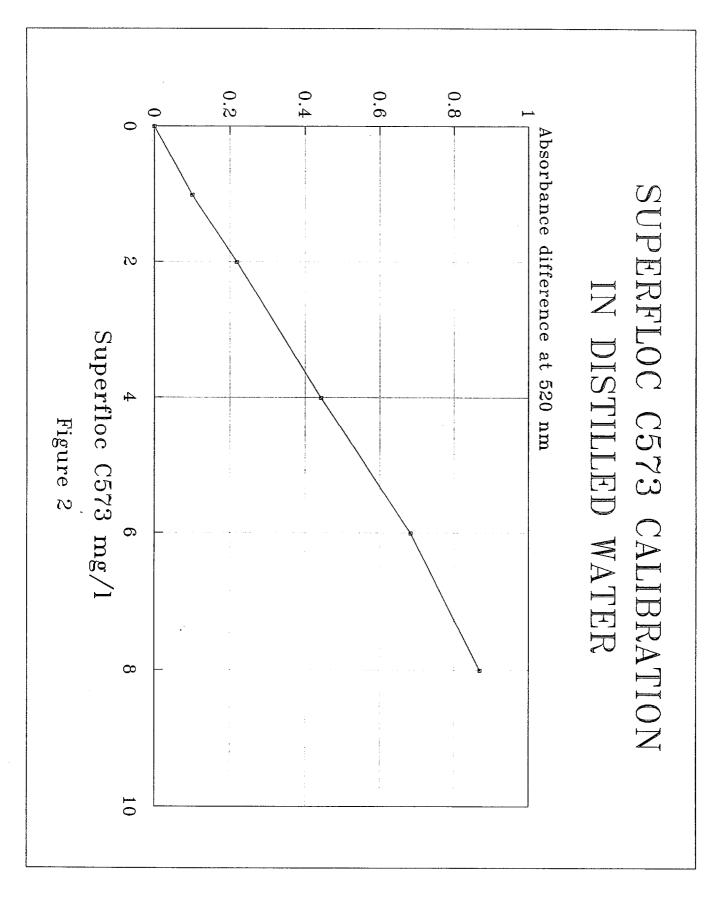
Less than 10% as indicated by a mean recovery of 107.5% from river water (mean C587 concentration 2.55 mg 1⁻¹) spiked with 2.0 mg 1⁻¹ of C587.

12% as indicated by a mean recovery of 112% from ground water (mean C587 concentration 3.5 mg l^{-1}) spiked with 2.0 mg l^{-1} of C587.

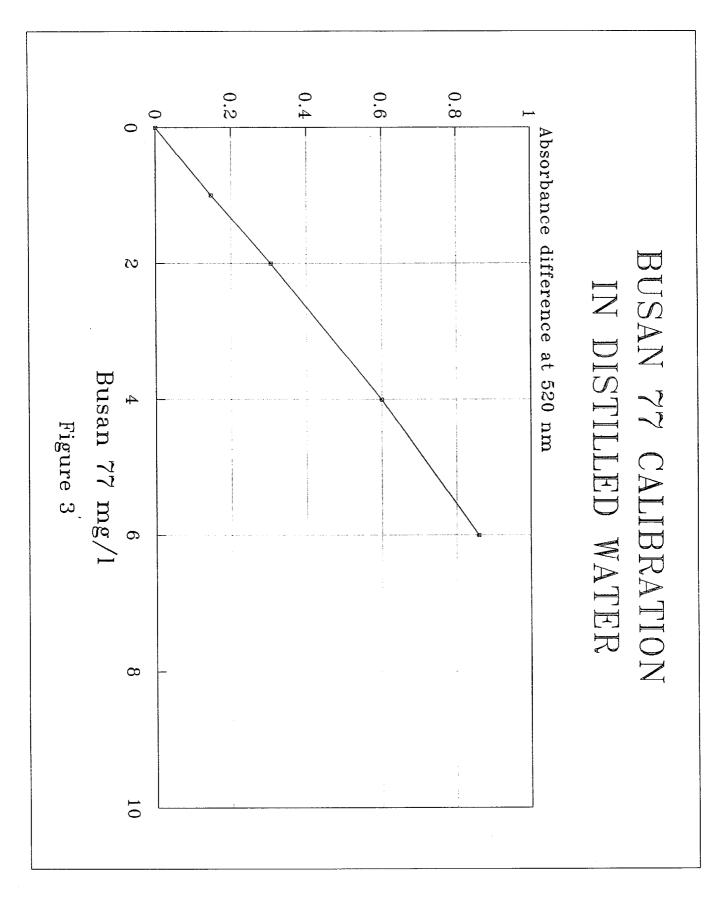




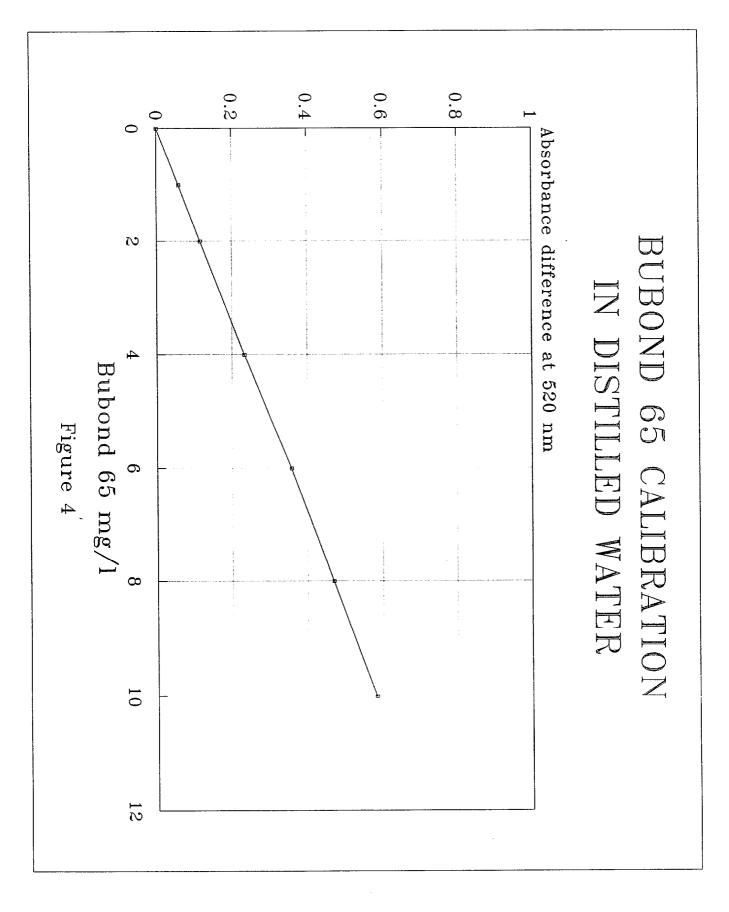




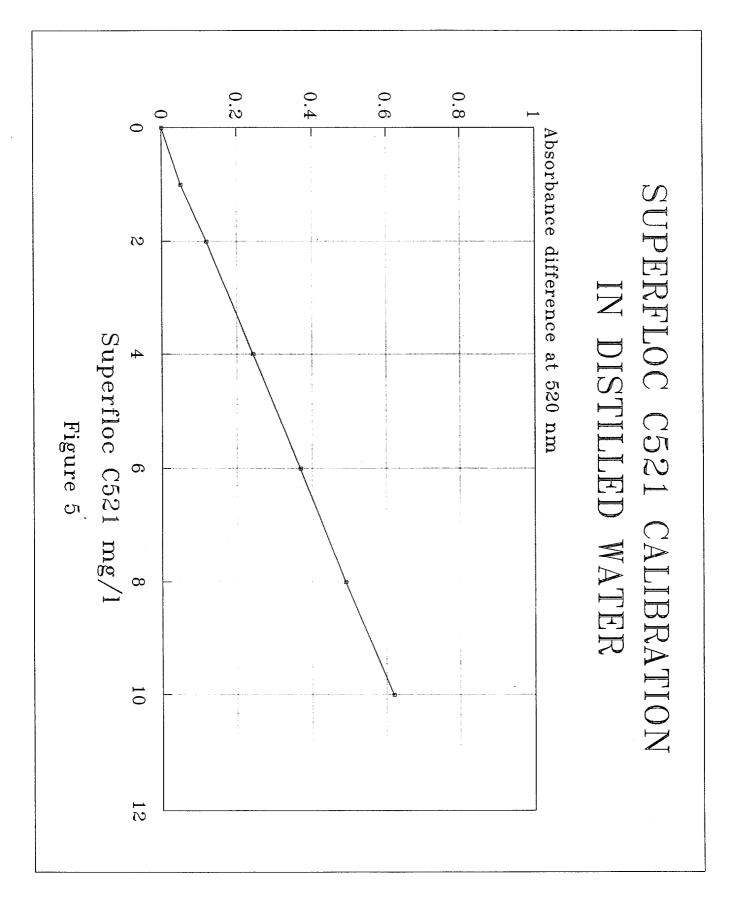




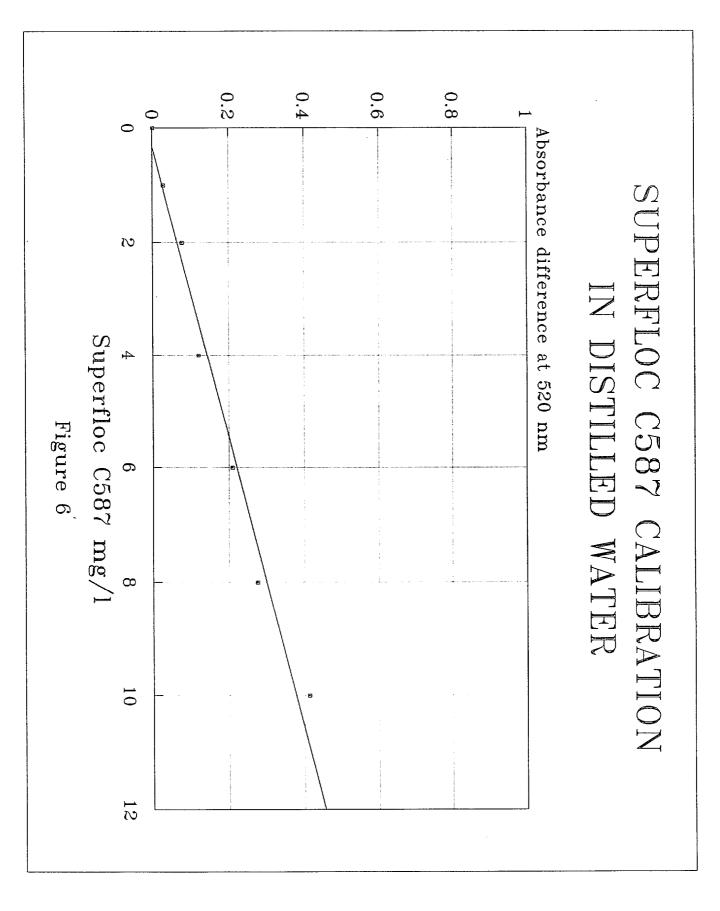




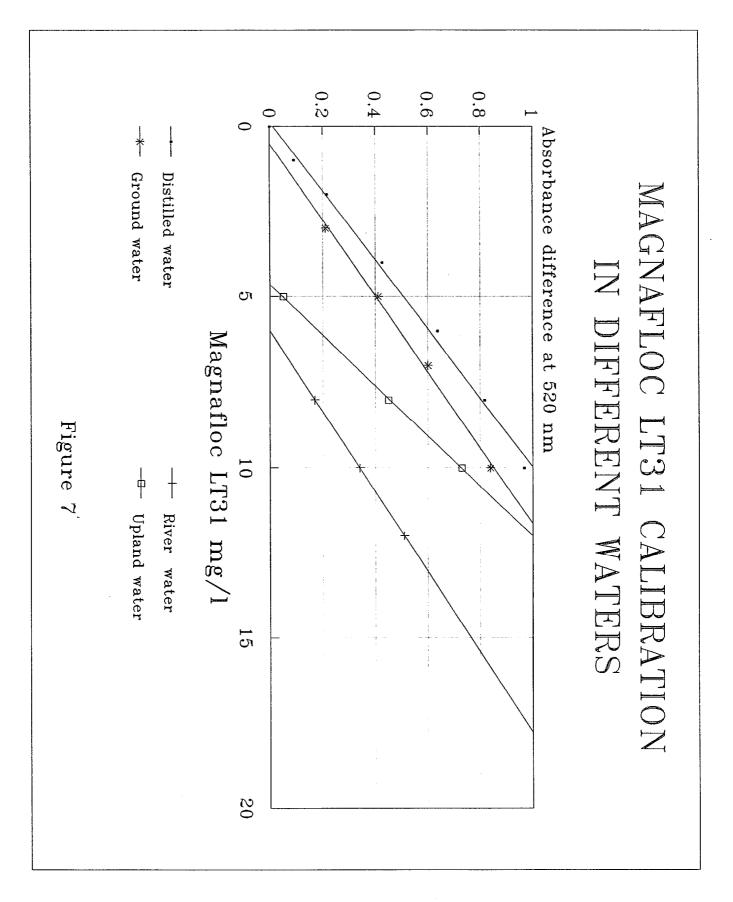




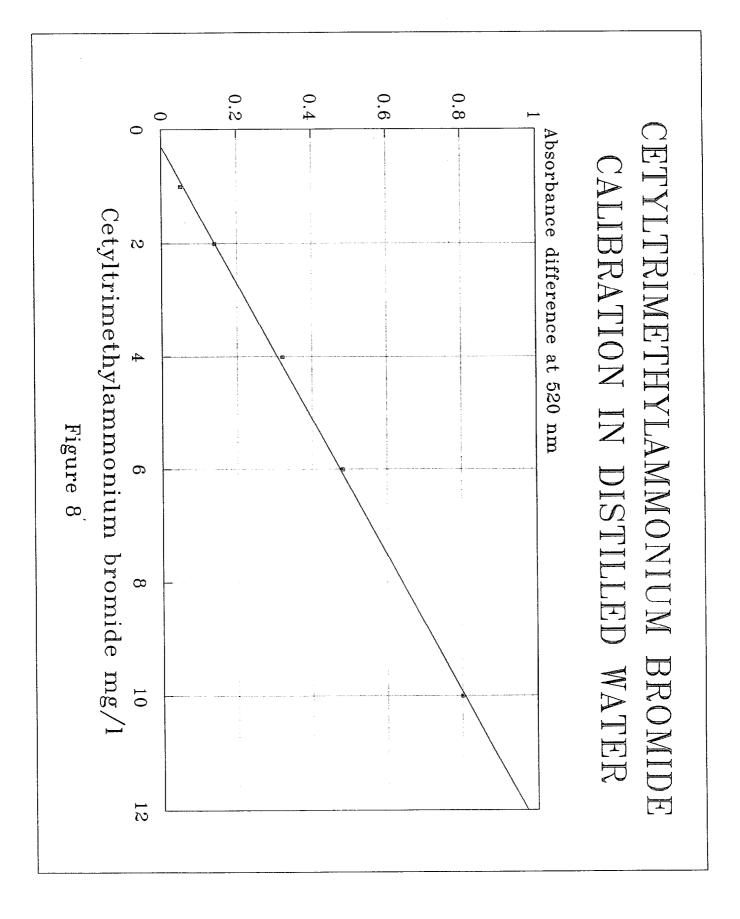












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APPENDIX 2

I(1)I PRODUCTS BASED ON POLYQUATERNARY RESIN

For these products the following conditions apply:

i. The dose used must not exceed 10 mg/l.

BETZ POLYMERS 1190, 1290

Betz Ltd

BUBOND 65, HICAT-1

Buckman Laboratories SA

CLEARFLOC C77C

Clearway Water Treatment

DECAPOLS C101P, C102P

Fospur Ltd

HATAFLOC 626

Houseman (Burnham) Ltd

GOLKEM CL 118

Goldcrest Chemicals Ltd

KEMAZUR 4553

Degremont Laing Ltd

MAGNAFLOCS LT31, LT33

Allied Colloids Ltd

SUPERFLOCS C573, C577

Cyanamid of Great

Britain Ltd

ii. The dose used must not exceed 33 mg/1.

HATASPERSE 307

Houseman (Burnham) Ltd

iii. The dose used must not exceed 150 mg/l.

ULTRION 8109

Nalfloc Ltd

I(1)F PRODUCTS BASED ON QUATERNARY AMMONIUM POLYELECTROLYTE

For these products the following condition applies:

The dose used must not exceed 10 mg/l of the active polymer.

CATFLOC

Chemviron Speciality Chemicals SA/NV

CATFLOCS A, C, R, S, T, T-1, 21, 121

M-502, M-503, M-506

SUPERFLOCS C585, C587, C589

Cyanamid of Great Britain Ltd