THE DETERMINATION OF NITRILOTRIACETIC ACID IN WATERS AND WASTE WATERS

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INTRODUCTION

The synthetic polyamino carboxylic acid nitrilotriacetic acid (NTA) has been suggested as a replacement for condensed polyphosphate builders in detergent formulations, and if introduced would be widely distributed, both in waste and natural waters.

Incorporation of NTA in detergents was discontinued in the United States as a result of the concern expressed by the U.S. Surgeon General regarding possible health effects /1/. However, its use in Canada and Sweden was continued after an evaluation of the available toxicological data /2/.

The heavy metal chelating properties of NTA have led to concern over its use /3/ and Infante in Means *et al.* /4/ states that it is listed as a No. 1 carcinogen

To investigate the fate of NTA in waste and natural waters a pre-requisite is the ability to determine trace quantities in lakes, rivers, streams, ground and saline waters as well as in sewage and effluents. Estimated NTA concentrations in raw municipal waste waters have ranged from 0.8 mg l^{-1} /4/ to 25 mg l^{-1} /5/; whilst activated sludge effluents have been found to contain between $10 \text{ } \mu\text{g l}^{-1}$ and 11.7 mg l^{-1} /2, 3, 6, 7/.

Two major studies have been undertaken to monitor NTA in drinking water, both utilising gas-liquid chromatographic techniques (GLC). The first, summarised by Thayer and Kensler /3/ was carried out in New York over the winters of 1970 and 1971 before the voluntary suspension of the use of NTA. Concentrations between 25 and $125 \text{ } \mu\text{g l}^{-1}$ were reported in 6 of 279 samples, the remainder being below the detection limit of $25 \text{ } \mu\text{g l}^{-1}$. The second study by the Proctor and Gamble company /8/ was undertaken in Canada from October 1971 to 1975, and reported NTA concentrations as being less than $60 \text{ } \mu\text{g l}^{-1}$ in all samples and less than $25 \text{ } \mu\text{g l}^{-1}$ in 95% of all samples. To determine NTA in environmental samples, the analyst is faced with the problem of detecting low concentrations, often with high matrix interference. Analytical techniques applied to the determination of NTA have included gas liquid chromatography /4, 9-21/; polarography /13, 22-33/; colorimetric /34-39/; potentiometric /40-42/; specific ion activity /13, 43, 44/; kinetic /45-48/; and complexometric procedures /49/.

In natural waters NTA exists mainly chelated with metals such as calcium and magnesium although many heavy metals form com-

plexes with higher stability constants /50/. The majority of the analytical techniques applied determine NTA as the free acid or as a chelate of low stability. Thus a significant proportion of the analytical effort has been involved with the isolation and preconcentration of the NTA.

Since protons compete with metals for NTA, a decrease in pH below neutrality rapidly diminishes metal chelant concentrations, while an increase in pH may also decrease metal chelation with NTA due to hydroxyl ion competition. Sulphide, phosphate, carbonate and silicate will also compete with NTA to a degree depending upon the solubility product of the corresponding metal salts /50/. However, even at pH 1.2 certain metal ions including Fe(III), Cu (II), Cr (III) and Hg (II) are still able to chelate NTA /28/.

Alternative isolation techniques besides pH control include the use of cation exchange resins to remove interfering metals /37/ or anion exchange to concentrate NTA /57/ while interfering ions may be eluted. Extraction procedures have been proposed either to extract interfering ions /12/ or esterified NTA /14/ prior to gas-liquid chromatographic analysis.

Gas liquid chromatography and polarography have been most widely applied to trace analysis of NTA, while colorimetric techniques provide a convenient method for the mg l^{-1} range.

GAS LIQUID CHROMATOGRAPHIC ANALYSIS OF NTA

Gas-liquid chromatographic analysis has been applied to NTA determination in raw water, potable supplies and sewage effluent. Although extended preparative procedures are frequently required GLC has the advantages of high specificity and sensitivity. The method is based upon the isolation and subsequent esterification of the poly-aminocarboxylic acid (NTA) to form a suitably volatile derivative which is well isolated from the interferant ester derivatives of the many natural fatty and amino acids; the identity of the derivatives are generally confirmed by a GLC-Mass Spectrometer combination.

The derivatization of NTA or its ammonium salt is not quantitative in the presence of Group Ia and IIa elements together with certain transition metals and "heavy metals" /15, 17/. Acidification may be adequate with regard to the lower stability metal complexes, but the presence of cations such as Fe(III) and Cu(II) leads to incom-

plete and unreliable esterification. Therefore, the determination of total NTA requires its separation from metal complexes.

Following the work of Davies, *et al.* /51/, who discovered that NTA is bound onto Dowex-1 resin in the formate form and can subsequently be eluted quantitatively with formic acid, several analysts /9, 11, 15, 16, 18, 20/ have refined this technique to form the basis of a sensitive and precise determination at trace levels. Recovery studies based on formate-resin columns confirm quantitative yields /9, 18, 20/.

Warren and Malec /14/ extracted the butyl ester of NTA in dimethyl chloride leaving most inorganic salts and polymeric material in the aqueous phase, while Rudling /12/ extracted interfering compounds in chloroform. The displacement of NTA from metal complexes by the addition of a more powerful chelating agent was suggested by Stolzberg and Hume /17/ although they achieved a detection limit of only 1 mg l^{-1} with a 1.0 ml sample. Rotary evaporation was suggested /17/ to improve this detection limit, but no quantitative recovery studies were undertaken. Prior to esterification, lyophilization /10, 14/ or evaporation /9, 11, 12, 15, 17, 18, 21/ have been advocated to achieve the completely anhydrous conditions necessary. The esterifying reagents and solvents, although the n-butyl ester is formed most frequently /14, 15, 18/. A summary of methods, detection limits and statistical data is included in Table I.

The method of Aue *et al* /15/ as modified by Williams *et al* /19/ has achieved the highest recorded sensitivity of all GLC methods reported, and is based on anion exchange preconcentration /51/, and subsequent derivatization to the n-butyl ester in acetone; coupled with the use of an NPD (nitrogen sensitive detector) /19/, which is said to improve the signal-to-noise ratio by markedly decreasing solvent interference. Aue *et al*'s /15/ claimed detection limit of $1.0 \text{ } \mu\text{g l}^{-1}$ (Table 1) was improved to $0.2 \text{ } \mu\text{g l}^{-1}$ by the use of an NPD (nitrogen and phosphorus detector) /19/, although a recent survey of drinking water by Malaiyandi *et al* /20/ suggests that such sensitivity may only be achieved by purification of the ion exchange resin with redistilled formic acid, until the washings (after derivatisation) are free of interfering nitrogen-containing compounds. Fortification studies carried out by Malaiyandi *et al* /20/ on potable waters indicate an average recovery efficiency of 94.7% between 1.0 and $25.0 \text{ } \mu\text{g l}^{-1}$

TABLE I

Principle, detection limits and statistical data on the determination of NTA by gas-liquid chromatography

Author	Principle	Source of Water Sample	Sample Volume, cm ³	Limit of Detection $\mu\text{g l}^{-1}$	Relative Standard Deviation %
Chau and Fox /9/	AEC n-propyl ester	Lake	200	0.5	6.5 ($\times 40$) ^a
Murray and Povedo /10/	methyl ester electron capture detector	Lake	10	25	4.12 ($\times 22$)
Rudling /11/	AEC 2-chloroethanol ester	Lake, Sewage	100	10	
Aus <i>et al.</i> /15, 16/	AEC n-butyl ester	River, Sewage	50	1	11 ($\times 30$) River 14 ($\times 10$) Sewage
Rudling /12/	methyl ester	Potable, Sewage	10	200	4.7 ($\times 5$)
Warren /14/	n-butyl ester	River, Sewage	10	25	8.7
Solzberg and Hume /17/	methyl ester	River, Medical	1	1000	9.6 ($\times 10$)
Larson <i>et al.</i> /18/	AEC n-butyl ester nitrogen detector	Artificial Stream	50	10	
Williams <i>et al.</i> /19/	AEC n-butyl ester nitrogen detector	Surface, potable	50	0.2	
Malayandi <i>et al.</i> /20/	AEC n-butyl ester	Potable	50		4.2 (1-25 $\mu\text{g l}^{-1}$)
Means <i>et al.</i> /14/	methyl ester		2	300	
Reichert and Linckens /21/	propyl ester	River, Potable	50	4	

^a = number in brackets denotes concentration at which relative standard deviation was determined relative to the limit of detection

AEC = anion exchange concentration

with a relative standard deviation of 4.2% (average of 8 determinations). This is the only reported relative standard deviation close to the detection limit for this procedure.

Rudling /11/ esterified NTA with 2-chloroethanol producing a chlorinated derivative applicable to electron capture detection thereby increasing sensitivity over the usual flame ionization detector. This method was shown to be applicable to raw sewage /11/.

Alternative procedures, such as those employed by Rudling /12/, Stolzberg and Hume /17/ and Reichert and Linckens /21/ appear to exhibit low sensitivity and unknown standard deviation near to their respective limits of detection. Taylor *et al* /13/ experienced problems preparing the special GLC column recommended by Aue *et al* /15/ although Larson *et al* /18/ and Williams *et al* /19/ found that the commercially available OV-210 on Chromosorb W (HP) can be substituted. Aue *et al* /16/ state that a relatively fast and experienced technician can analyse 10 samples per day. GLC has been applied to the determination of NTA by Thayer and Kensler /3/ for a limited survey of potable waters. A comparative survey of NTA in raw, potable and surface waters was undertaken by the Proctor and Gamble Company using the GLC technique described by Aue *et al* /15/ with the modifications of Williams *et al* /19/ and the Canadian Department of Fisheries and the Environment using the polarographic method of Afghan and Goulden /22/. The results obtained by GLC were consistently higher than those obtained by polarography /8/; this is discussed in the following section (polarography).

It appears that analysis time, interference from inorganic salts and inconsistencies when compared with polarography are the main factors limiting the application of GLC analysis to NTA.

POLAROGRAPHIC ANALYSIS OF NTA

Classical and modern techniques of polarographic analysis have been applied to trace determinations of NTA in sewage effluents, raw, potable and saline waters (Table II). The introduction of Linear Sweep Voltammetry (Cathode Ray Polarography) and more recently Differential Pulse Polarography has markedly increased sensitivity and precision; whilst permitting automatic sampling and recording of results. Afghan *et al* /26/ were able to analyse 15 samples per hour with a specially constructed cell using linear sweep voltammetry, while Ha-

TABLE II
Principle, detection limits and statistical data on the Polarographic determination of NTA

Author	Principle	Source of Water Sample	Sample Volume cm ³	Limit of Detection $\mu\text{g l}^{-1}$	Relative Standard Deviation %
Wernet and Wahl /32/	ACP Cd-NTA	Surface, Sewage	1000		
Afghan and Gouldin /22/	DCRP Pb-NTA	Lake	10		5.4 (x5) ^a
Alplan and Wanninen /23/	DCP Cd-NTA	Lake	930		10.4 (x1)
Habeman /24/	DCP In-NTA	River, Sewage	1000	19	42 (x1) 6 (x10)
Afghan <i>et al.</i> /26/	DCRP Bi-NTA	Surface, Sewage	35	10	1.3 (x10)
Taylor <i>et al.</i> /23/	DCRP Bi-NTA	Pure	5		
den Boef <i>et al.</i> /28/	ACP Bi-NTA	Seawater, Sewage	20	500	10 (x1)
Hoover /27/	DPP Bi-NTA		10	10	
Diez /29/	ACP Bi-NTA	Pure	25	100	
Haring and Delft /31/	DPP Bi-NTA	Seawater	10	50	
Stolzberg /30/	DPP Cd-NTA		309		40 (x1) 12 (x3)
Traversy /25/	DCRP Bi-NTA	Surface, Sewage	25	10	3.8 (x5) 8.9 (x10)

ACP – Alternating current polarography
 DCRP – Differential Cathode Ray Polarography
 or Linear Sweep Voltammetry
 DPP – Differential Pulse Polarography
 DCP – Direct Current Polarography
 or Twin Cell Oscillographic Direct Current Polarography

a = number in brackets denotes concentration at which relative standard deviation was determined relative to the limit of detection.

ring and Delft /31/ applied a commercially available sample sequencer to differential pulse polarography.

Polarographic methods are based on the reduction of a suitable metal ion complexed with NTA. The half wave potential for this reduction is shifted reproducibly by specific chelants, making the procedure nearly as specific for NTA as GLC.

To determine total NTA the metal ion must quantitatively displace naturally occurring ions likely to be present in significant concentrations. Several metal ions and pre-treatment methods have been employed to this effect, most notably bismuth /13, 25-29, 31/ although analyses involving cadmium /23, 30, 32/, lead /22/ and indium /24/ have also been reported.

Haberman /24/ employed a complex preparative procedure for a method involving In, while studies by Afghan /33/ and Hoover /27/ indicate that high concentrations of indium are required for complete recovery. Additionally the In-NTA complex has a half-wave potential within 200 mv of that of free In /27/ and indium tends to show polarographic minima /27/ rather than a constant diffusion current.

As with GLC pre-treatment the aim is to displace interfering metal ions from NTA-chelates. Acidification is most generally applied down to pH 2 /26/ or even to pH 1 /28/, usually in sodium/potassium chloride or acetate supporting electrolyte. Ethylenediamine tetraacetic acid (EDTA) masking has been applied by Afghan and Goulden /22/ to Pb-NTA in lake waters. Cation exchange clean-up and anion exchange concentration in conjunction with isotope dilution to correct for incomplete recovery, has found application in the analysis of In-NTA in river water and sewage /24/. A novel clean-up procedure developed by den Boef *et al* /28/ involves the electrolytic stripping of interfering metal ions from solution prior to analysis. However, A.C. polarography was applied to the subsequent determination of Bi-NTA as opposed to differential pulse polarography or linear sweep voltammetry, thereby decreasing sensitivity.

Concentration with associated losses, has not extensively been employed and detection limits utilising differential pulse polarography are cited to be as low as 10 $\mu\text{g/l}$ /27/ in seawater, sewage effluents and potable waters without prior concentration. To achieve these high sensitivities Hoover /27/ recommends a chloride electrolyte for saline waters containing more than 0.1% chloride and an acetate electrolyte for natural and waste waters containing less than 0.1% chloride.

Various interferents have been investigated, most notably metal ions, sulphur compounds, polyphosphates and natural organic chelating agents. Fe (III) has been shown to interfere at pH 2 /22/ resulting in a prewave at -0.23v versus mercury pool, close to that produced by bismuth-NTA. The addition of ascorbic acid or hydroxylamine hydrochloride effectively counters this interference. Other metal interferents cited include Cu (II) /27/; Pb /31/ and high levels (400 mg l^{-1}) of calcium and magnesium /27/.

Afghan *et al* /26/ experienced problems with anaerobic digester effluent due to the presence of sulphur compounds. Oxidation with hydrogen peroxide was suggested as a remedial action, but Hoover /27/ was unable to achieve any improvement in chloride media.

Afghan and Goulden /22/ discovered that sample digestion was required to hydrolyse tripolyphosphate, which interferes by reacting with lead to produce a reduction wave close to that of the Pb-NTA being determined. He also recommended the addition of citrate, oxalate or tartarate to prevent sulphate precipitation of lead.

Hoover /27/ found no interference from sodium tripolyphosphate at 3.68 mg l^{-1} in acetate media. A summary of methods, detection limits and relative standard deviations, where quoted, are presented in Table 2.

Bismuth-NTA appears the most favoured analytical approach with the advantage of high recovery from fresh and saline waters without concentration and small sample volumes (10-25 ml). Relative standard deviations range from 5% to 10% near the limits of detection (Table 2). Taylor *et al* /13/ suggest standard addition to improve the relative standard deviation and reduce the effects of interferents.

The analysis of Bi-NTA by linear sweep voltammetry after the method of Afghan and Goulden /22/ has been adapted and used extensively by the Canada Centre for Inland Waters /2/: An interlaboratory comparison between the polarographic method of Afghan and Goulden /22/ and the GLC technique of Aue *et al* /15/ was undertaken by the Canada Centre for Inland Waters and the Proctor and Gamble company, the results of which are summarised by Matheson /8/. At concentrations exceeding $10 \text{ } \mu\text{g l}^{-1}$ the Proctor and Gamble (GLC) values were found to be significantly higher. A Proctor and Gamble determination of $50 \text{ } \mu\text{g l}^{-1}$ would by regressional analysis be $39 \text{ } \mu\text{g l}^{-1}$ if determined by the Canada Centre for Inland Waters/2/.

It was suggested that these differences may have been due to contamination; differences in the species being identified and changes during storage.

Aue *et al*/15/ recommended the concomitant use of polarography and gas liquid chromatography to improve analytical reliability.

COLORIMETRIC DETERMINATION OF NTA

NTA may be determined indirectly *via* total chelating capacity; and this forms the basis of most colorimetric methods employed. A summary of methods is included as Table III. Such a procedure is open to many sources of error since chelating agents, such as citric acid or natural polyphenolic polycarboxylic acids are often present and many of the high molecular weight acids are themselves coloured. Degradation products of NTA including iminodiacetic acid are also good chelating agents /18/.

Despite these constraints, colorimetric procedures have been applied to the determination of NTA in activated sludge effluents, anaerobic digester effluents, surface and lake waters /34-37, 39/.

Sample pretreatment generally involves the removal of interfering metals or the destabilisation of NTA-metal complexes. Subsequently a specific analyte metal-NTA complex is determined spectrophotometrically directly or via an associated reaction.

Swisher *et al*/34/ utilised acidification to destabilise metal-NTA complexes while Bouveng /35/ extracted interfering metals with oxine in chloroform, the stable Fe (III) and Cu (II) complexes being determined respectively. Swisher *et al* /34/ were only able to achieve a sensitivity of 5.0 mg l^{-1} , while the extraction employed by Bouveng /35/ was prolonged and, according to Longman *et al* /37/, incomplete. Thompson and Duthie /36/ applied anion exchange clean-up to remove interfering metals, and determined NTA by the addition of zinc-Zincon reagent. Zinc forms a blue-coloured complex with { 1-(2-hydroxy-5-sulphophenyl)-3-phenyl-5-(2-carboxyphenyl) formazan } (Zincon) in a solution buffered to pH 9.2. When NTA is added the zinc-Zincon complex is dissociated, reducing the absorbance in proportion to the amount of NTA present. This method was adapted by the United States Environmental Protection Agency /39/ for the manual analysis of surface waters containing more than 0.5 mg

TABLE III

Principle, detection limits and statistical data on the determination of NTA by colorimetric means

Author	Principle	Source of Water Sample	Sample Volume cm ³	Limit of Detection mg l ⁻¹	Relative Standard Deviation %
Swisher <i>et al.</i> /34/	Indirect Fe(III)-NTA Phenanthroline method	Activated sludge	100	5	10
Boueng /35/	Extraction clean-up Cu(II)-NTA determined	Activated sludge	200	0.2	
Thompson and Duthie /36/	Cation exchange clean-up Zinc-Zincon reagent	Activated sludge Anaerobic digester	25	0.2	5
Longman <i>et al.</i> /37/	Chalex 100 clean-up Zinc-Zincon reagent	Activated sludge Settled sewage	100		
Environmental Protection Agency /39/	Cation exchange clean-up Zinc-Zincon reagent	Surface water	25	0.5 (M) 0.04 (A)	7 (x4) ^a ; 34 (x1) 2.2 (x4.5); 10 (x2.5)
Kaiser /38/	Rotary evaporator Co(III)-NTA complex		1000	0.01	7.2 (x20)

M - Manual

A - Automated

a = number in brackets denotes concentration at which relative standard deviation was determined relative to the limit of detection

1^{-1} and for an automated method down to $40 \mu\text{g } 1^{-1}$. No results are quoted for polluted waters.

Longman *et al* /37/ evaluated the method of Thompson and Duthie /36/ and discovered that tripolyphosphate interfered at concentrations exceeding $4.0 \text{ mg } 1^{-1}$ and that cation exchange did not remove metals from their NTA complexes. This led to the use of the chelating resin "Chelex-100" /37/ which has a high affinity for metals as a preliminary clean-up step, followed by the zinc-Zincon method. Limits of detection and relative standard deviations for this method are not quoted.

Kaiser /38/ proposed a method in which NTA is determined as the Co(III) complex, following the removal of interfering metals as their insoluble carbonate salts. Rotary evaporation was employed to concentrate the sample and a sensitivity of $10 \mu\text{g}$ was claimed for a one litre sample. The method is said to be applicable to sewage effluents, but recovery studies were only undertaken for lake water samples, a relative standard deviation of 7.2% being found at $200 \mu\text{g } 1^{-1}$. EDTA interferes with the method and is accounted for by first determining the total EDTA & NTA, and then selectively oxidising the NTA, and measuring EDTA alone; the NTA level was calculated by subtraction.

Spectrophotometric determinations can be carried out rapidly and even by an autosampler /39/. Spectrophotometers are also relatively inexpensive and common instruments as compared to gas chromatographs and polarographs. However, sensitivity may be limiting and interference may be expected from turbidity, colour, natural and synthetic chelants, metals, tripolyphosphate and fatty acids. The method is not applicable to saline waters.

OTHER METHODS OF NTA ANALYSIS

The complexing properties of NTA enable complexometric titrations to be carried out, usually based on the cupric ion responsive electrode /13, 43, 44/ or the platinum redox electrode /40, 42/. Bunch and Ettinger /41/ utilised 1-(2-Pyridylazo)-2-naphthol (PAN) as indicator while titrating with Cu (II).

Rechnitz and Kenny /44/ applied a cupric ion activity electrode but only investigated the method in detergent solutions, achieving a detection limit of $2 \text{ mg } 1^{-1}$. Bouveng /43/ applied this technique to

secondary sewage effluents; achieving a detection limit of 0.2 mg l^{-1} ; but this necessitated an extended extraction procedure with oxine to remove interfering metals. This method also fails to differentiate between chelating agents. Taylor *et al* /13/ outline the design of a continuous flow ion activity electrode system in which the Cu(II) is generated coulometrically and then chelates with the NTA in the sample stream. The sample then passes through the electrode system; the uncomplexed Cu(II) being determined. The authors recommend ion-exchanger pre-treatment.

Potentiometric titrations involving various metals and chelants were undertaken by Siggia *et al* /40/ in 1955, who reported that NTA produced a sharp titration break with copper, zinc and lead, the best results being obtained from Cu(II) in a 1:1 water, pyridine mixture at pH 7.0. Sekerka *et al* /42/ adopted the potentiometric technique by utilising two concomitant titrations with Cu(II) and Tl(III) in order to determine NTA. Tl(III) was found to form a 2:1 ratio complex with NTA and a 1:1 complex with all other chelants tested; while Cu(II) formed a 1:1 complex with NTA as well as with all the other chelants. Thus, using the difference in titre values, the concentrations of NTA may be ascertained.

Lautenbacher and Baker /49/ developed a method for NTA determination in tap or river waters down to 4 mg l^{-1} . It is based on the formation of a soluble Pb-NTA chelate, equivalent to the quantity of NTA in the sample. The lead in the chelate is then determined by atomic absorption spectrometry. Interference studies suggest that this method has limited application.

Robinson and Lott /52, 53/ proposed a fluorometric technique based upon the reaction of NTA with the fluorescent Ga-oxine complex. A 95% confidence detection limit of $0.197 \text{ } \mu\text{g l}^{-1}$ for a 100 ml sample is claimed, but the technique was only applied to potable water.

Ion exchange chromatography forms the basis of two methods developed by Longbottom /54/ and Manahan and Jones /55/. Longbottom /54/ employed a Dupont liquid chromatograph at 6900 KPa. NTA was first complexed with Fe(III) after which the anion exchanger separates the components, NTA being detected by ultraviolet absorbance. The method was found to be applicable to sewage and had a detection limit of 1.0 mg l^{-1} with a relative standard deviation of 2%.

Manahan and Jones /55/ applied ligand exchange chromatography, passing the sample through a short column of Chelex 100 in

the copper form followed by direct aspiration into the flame of an atomic absorption spectrometer in order to determine the released copper. A detection limit of 0.188 mg l^{-1} is quoted for pure water with a relative standard deviation of 5%. Ligand exchange chromatography using copper-Chelex 100 was successfully applied to the concentration of amino acids from seawater /56/, but radiometric studies /9/ indicate that recovery of NTA was poor (ca. 15%).

Reaction kinetics have been applied to the determination of NTA. Coombs *et al* /46/ analysed mixtures of aminopolycarboxylic acids *via* the reaction of the cyanide ion with their Ni complexes in a stopped flow spectrophotometer. Untreated water samples required cation exchange clean-up to remove interfering metals. The detection limit is quoted as $10 \mu\text{g l}^{-1}$, but the method does not appear applicable to waste waters.

The effect of NTA on the oxidation of Malachite Green cation by periodate ions has been applied by Mottola and Heath /45/ to the determination of NTA in natural and industrial waters. A variable time kinetic procedure developed by Blaedel and Hicks /57/ was applied to pure water samples containing various chelant and metal interferents. Mottola and Heath /45/ claim a detection limit around $20 \mu\text{g l}^{-1}$ with a relative standard deviation less than 5%, one order of magnitude above the detection limit.

Nikolelis and Hadjiioannu /47/ discovered that NTA activates the reaction between periodate and phosphinate in which manganese acts as catalyst. The time required for the phosphinate to consume a fixed quantity of periodate, accompanied by a decrease in absorbance, was measured with automatic switching. Control of pH was found to be critical for the reaction and other chelates have been shown to interfere. 0.225 mg l^{-1} of NTA could be determined in pure water. NTA was also found to inhibit the copper-catalysed periodatethiosulphate reaction /48/.

SUMMARY

Of the techniques reviewed, colorimetric analysis has been most widely applied for a range of sample matrices down to 0.2 mg l^{-1} without pre-concentration. The analysis may be readily automated but is not specific to NTA and is inapplicable to saline waters.

The determination of trace concentrations of NTA requires the

more complex and costly Gas-Liquid Chromatography and Polarographic techniques. Several Gas-Liquid Chromatographic methods have been used for the determination of NTA in surface, raw, potable and waste waters down to concentrations of $1 \mu\text{g l}^{-1}$ and in surface and potable waters down to $0.2 \mu\text{g l}^{-1}$ /19/. However, Gas-Liquid Chromatographic methods are not applicable to saline waters. Differential Pulse Polarography has been applied to saline and non-saline waters and waste waters down to $10 \mu\text{g l}^{-1}$ while Differential Cathode Ray Polarography has been applied to non-saline, polluted and potable waters down to $10 \mu\text{g l}^{-1}$.

An interlaboratory comparison of Gas-Liquid Chromatography and Polarography has shown that the two methods do not agree and this casts some doubt on the validity of trace determinations of NTA since the two methods produced statistically different results. The recommendation made by Aue that both techniques should be applied for comparative purposes appears advisable.

Other methods of analysis have not been sufficiently investigated and applied to waste waters.

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