The Determination of Ultra-trace Amounts of N,N-Diethylhydroxylamine Residues in Water Used for High-Pressure, High-Temperature Steam Turbines

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Abstract

Oxygen scavengers are usually added to boiler water to stop the steel body of the boiler being oxidized. The choice of an oxygen scavenger must take into account its effectiveness, availability, toxicity and cost. Hydrazine and hydroxylamine are commonly used to inhibit boiler corrosion. Diethylhydroxylamine, (DEHA) has been reported as a useful alternative compound, it is less toxic than hydrazine and hydroxylamine. Consequently the use of this compound as a corrosion inhibitor is likely to increase in parallel with the present-day rising of safety at work standards. Therefore it was decided to develop a method for the determination of diethylhydroxylamine in water samples. The method reported is highly selective, sensitive, and rapid and gives a good reproducibility for the determination of ultra-trace amounts of diethylhydroxylamine residues in boiler water after use of the diethylhydroxylamine as an oxygen scavenger. It allows the diethylhydroxylamine concentrations in water samples to be determined over the ranges 36-460ppb and 178-2140ppb, with a relative standard deviation of less than 1%. The method is based on the inhibition of the bleaching of Remazol Brilliant Blue by oxidation with chloramine-T.

Keywords: Ultra-trace analysis; Kinetic method; Spectrophotometric; Dissolved oxygen; Diethylhydroxylamine.

Introduction

The presence of dissolved oxygen in waters used for high pressure, high temperature turbines in the generation of electricity either from high pressure boilers heated by combustion of fossil fuels or nuclear power is known to have deleterious corrosive effects both on the turbine blades and the boilers used to generate the steam for the turbines. It is essential to remove the dissolved oxygen to avoid corrosion and to ensure that the materials added to remove the oxygen do not cause corrosion either by their effect on the materials of construction of the turbine system or by producing substances which could cause corrosion. It is considered necessary to use the minimum excess of the scavenger and thus it is essential to be able to monitor the residual amounts of scavenger, in the condensates of the boiler system of the various

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reductants that could be used on the scale required for scavenging purposes. Hydroxylamine and hydrazine have found to be favorable for various reasons including their effectiveness, cost, availability and nowadays perhaps more importantly, their low toxicity. Although the reductants themselves must be regarded as being toxic, the majorities of their reaction products are either water or are generally water soluble non-toxic compounds, some are gaseous and non-water soluble and may be vented from the system.

Although hydroxylamine and hydrazine are presently commonly used to inhibit boiler corrosion, various workers [1,2,3,4] have reported that N,N-diethylhydroxylamine should be considered to be useful alternative. It is less toxic than hydrazine and hydroxylamine[5] and consequently the use of this compound as a corrosion inhibitor is likely to increase in parallel with the present day raising of the health and safety requirement standards for industrial situations.

It has been reported that the difficulty of reconciling the handling of hydrazine with European safety regulations has lead to the use of the diethylhydroxylamine in the sugar industry[6] and paper and pulp industries.[7,9]

A survey of the available literature showed no published methods for the quantitative analysis of ultra-trace amounts of N,N-diethylhydroxylamine in industrial waste water.

Thus it was decided to develop a method for the assay of ultra-trace amounts of N,N-diethylhydroxylamine in waste water that have been used for raising steam for high pressure, high temperature steam turbines.

The source water for such purposes is generally of potable quality. In many countries the water have already been purified to legislative requirements, in others where water is obtained from marine sources by reversed-phase osmosis or similar methods the and nature of impurities is well documented. The impurities are usually removed by ion-exchange chromatography. Thus the main impurity for the present purpose may be regarded as the presence of dissolved oxygen, which must be removed by oxygen scavengers prior to using the water in steam raising. Thus the “impurities” in the sample will be the traces of the excess of oxygen scavenger and possibly some ions that have escaped the ion-exchanging process.

Preliminary work related to the determination of hydroxylamine in ultra-trace amounts in boiler water[8] indicated that a kinetic stopped-flow method could be of potential value and the competition of reactions involving the bleaching of suitable dyestuffs by an oxidant and the competitive use of the oxidant by the oxygen scavenger was thought to offer potential for the assay of N,N-diethylhydroxylamine.

Several dyes with different functionalities were investigated.

Preliminary experiments using a stopped-flow apparatus showed that a quinine dye: Remazol Brilliant Blue. C.I. No. C.I.61200 gave the most potentially promising results when a solution of the dye at pH 3.0 was treated with chloramine-T. There was
a very rapid fall in the absorbance of the dye at 625nm caused by bleaching of the dye. The wavelength of 625nm was chosen because it occurs near a fairly broad peak of the dye spectrum and a low cost optical filter with 625nm as the wavelength of maximum transmission was available.

However, when the dye solution contained ultra-trace amounts of N,N-diethylhydroxylamine, there was a noticeable and significant induction period before the onset of the rapid decolorisation process. This induction period varied with the concentration of the N,N-diethylhydroxylamine and provided an easily measurable parameter of the reaction.

**Experimental**

*Stopped-flow Apparatus*

A block diagram of the experimental layout is given in figure 1.

![Block diagram of the stopped-flow system](image)

**Figure 1.** Block diagram of the stopped-flow system

*Optical system*

Light from a 50 watt tungsten-halogen lamp passes through approximately 1.5cm length of the water in the thermostatted water bath (to act as a heat filter), then through the optical cell and an optical filter (to select the required wavelength),
mounted on the side of the optical cell and then directly on to a focusing lens in front of a photodiode. (Figure 2).

**Signal output**

The progress of the reaction is then followed by measuring the change in absorbance of the beam of monochromatic light.

The electronically amplified signal from the detector may be recorded either on an oscilloscope screen, a mv potentiometric recorder or a simple personal computer. A simple electrical circuit allows the signal to be amplified (sensitivity control) and zeroed on the scale by appropriate “backing off”.

In the present study, after preliminary experiments had been done with the signal being displayed on an oscilloscope, all subsequent readings were recorded using a potentiometric recorder.

From the trace, suitable reaction parameters such as the initial rate of reaction, the rate constant of the induction period before the onset of the main reaction could be measured.

![Arrangement of components along the optical train of the stopped-flow apparatus. These components were mounted on an optical bench of length 90cm.](image)

**Figure 2.** Arrangement of components along the optical train of the stopped-flow apparatus. These components were mounted on an optical bench of length 90cm.

- M mounting for photodiode.
- PD photodiode (BPW21).
- B light-shielding boxes.
- L convex lenses.
- F interference filter (Oriel).
- W water bath.
- S stopped-flow cell (volume 100ml; path length = 15mm).
- T silicon tubes.
- R rotating filter assembly containing neutral density filters.
- I iris.
- Ho housing containing 12V/50W tungsten halogen lamp.

**Dispensing of reagents**

The reagents were contained in stoppered flasks (nominally 100ml) from which they were transferred to the 1ml tuberculin type all-glass syringes fitted with Hamilton stainless steel / Teflon 3-way valves. This enable the syringe to be connected either to the reservoir for filling or to the mixing cell when the solutions were to be mixed. The pistons of both syringes are connected to a block which allows them to be operated
singly or simultaneously. The length of traverse of the piston, i.e. the volumes of liquid
pulled into the syringes, is controlled by means of an adjustable screw stop. In practice
it was found that a volume of ca 0.50 ml, for each syringe, was acceptable volume for
all experiments.

Mixing and reaction cell

The reactants pass through separate coils of thin wall polyethylene delivery
tubing (i.d. nominally 1mm, length approximately 80cm, nominal volume approx.
0.625ml) immersed in the thermostatted bath (±0.5 degree centigrade) and into a
mixing chamber the solutions pass immediately into an optical cell of 1.5cm optical
path length, with an internal volume of approximately 0.14 microliters, permanently
fixed in position. The solutions then pass to waste.

Reagents

Stock solutions of the reagents were prepared by dissolving the appropriate
amounts of the reagents in oxygen-free water. They were kept in sealed amber bottles
until used.

\begin{itemize}
\item \textbf{N,N-diethylhydroxylamine, }\text{(C}_2\text{H}_5\text{)}_2\text{NOH} : \text{An aqueous stock solution (1x10}^{-4}\text{M).}
\item \textbf{Chloramine-T, CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N(Cl)Na.3H}_2\text{O} : \text{An aqueous solution (1x10}^{-3}\text{M).}
\end{itemize}

Citrate Buffer

Citric acid/sodium citrate buffer was prepared by mixing aqueous solutions of
citric acid (0.1M) and tri-sodium citrate (0.1M) to give buffer solutions of the desired
pH. The pH of each mixture was checked using a calibrated pH meter.

\textit{Remazol Brilliant Blue, C.I.61200:} An aqueous solution (3.0x10^{-5}M)

Reactions of the dyestuff, chloramine-T and diethylhydroxylamine in buffered system:

The dyestuff, buffer solution and N,N-diethylhydroxylamine were mixed as one
reagent solution, chloramine-T was used as the other reagent solution. Equal volumes
of the two solutions, after thermostating, were mixed and passed into the optical cell.
Typical absorbance traces measured at 625nm are shown in figure 3.
Figure 3. Stopped-flow recorder signals for the mixing of Chloramine-T solution with a solution containing Remazol Brilliant Blue (1.8x10^{-5}M), citrate buffer pH 3 and DEHA. (a) Blank, (b) DEHA (1.2x10^{-5}M) and (c) DEHA (2.4x10^{-5}M).

The effects of variations in the concentration of the reactants, pH and the temperature of the system, necessary to optimize the signal from the system, were investigated.

After the parameters had been determined, calibration curves covering the required ranges of analyte concentrations were prepared and the effects of possible interferences were investigated.

(i) Variations in the concentration of chloramine-T used

A series of solutions containing a fixed concentration of Remazol Brilliant Blue (1.80x10^{-5}M), a fixed concentration of pH 3.0 citrate buffer (0.05M) and a fixed concentration of N,N-diethylhydroxylamine (2x10^{-5}M, i.e. of the order of 2ppm) were mixed in the thermostatted (25°C) stopped-flow cell with different concentrations of chloramine-T in the range 5.0x10^{-4}M to 2.5x10^{-3}M.

The periods of induction, calculated from the chart speed and the appropriate length of the trace, were measured to the nearest second. Typical results are given in table 1.

<table>
<thead>
<tr>
<th>Conc chloramine-T, (10^{-6}M)</th>
<th>5</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (secs.)</td>
<td>250</td>
<td>170</td>
<td>94</td>
<td>60</td>
<td>29</td>
<td>18</td>
<td>13</td>
</tr>
</tbody>
</table>

Concentrations of N,N-diethylhydroxylamine expected in samples are from 0ppb to 5 ppm and thus for the upper range a concentration of chloramine-T of 5x10^{-6}M may be used, but for the lower parts of the range a lower concentration must be used in
order to obtain an induction period of sufficient duration to allow an analytically acceptable precision.

(ii) Variations in the pH of the system

Stopped-flow experiments were done with variation in the pH of the buffered system whilst all other variables were kept constant at those previously indicated except that the concentration of the N,N-diethylhydroxylamine was 1.2x10⁻⁶M. The results are given in table 2.

Table 2.

<table>
<thead>
<tr>
<th>pH</th>
<th>2.8</th>
<th>3.0</th>
<th>3.8</th>
<th>4.6</th>
<th>5.2</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Induction time (secs.)</td>
<td>56</td>
<td>39</td>
<td>12</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The results show that the period of induction is dependent upon the pH of the system. In order to optimize the effect, the system was buffered at pH 3.0. (see discussion).

Obviously small variations in pH can have significant effects on the signal. It is thus necessary to ensure that the buffer capacity of the system is sufficient to maintain the required pH.

(iii) Variations in the concentration of the buffer

The capacity of the buffer must be considered when the buffer is used in low dilutions and thus it is necessary to investigate the effects of variation in the concentration of the buffer.

General conditions with regard to the concentration of the reagent were as in the investigation (i) except that the concentration of the citrate buffer was varied. The results are given in table 3.

Table 3.

<table>
<thead>
<tr>
<th>Citrate buffer, (10⁻³M)</th>
<th>4</th>
<th>12</th>
<th>20</th>
<th>28</th>
<th>36</th>
<th>52</th>
<th>72</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Induction time (secs.)</td>
<td>31</td>
<td>48</td>
<td>54</td>
<td>60</td>
<td>63</td>
<td>68</td>
<td>71</td>
<td>73</td>
</tr>
</tbody>
</table>

A citrate concentration of 0.05M was selected for the subsequent determinations (see discussion), in signal. The signal decreases less than 5% of its value at 20°C.
(iv) Variation in the ionic strength of the system

The ionic strength of the medium in any system involving ionic reactions, may have an effect on the rates of reactions in that system(7). Thus variations in the ionic strength could have an effects on the rates of the various reactions in the system under consideration and thus on the period of induction. The effect of increasing the ionic strength was tested by adding various concentrations of potassium chloride to the solutions under test. A concentration of 1.2x10^{-4}M N,N-diethylhydroxylamine was used. All other concentrations and the temperature were as previously reported. The results are given in table 4.

<table>
<thead>
<tr>
<th>Conc. KCl (10^{-4}M)</th>
<th>8</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Induction time (secs.)</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
<td>32</td>
</tr>
</tbody>
</table>

(v) Variations in the temperature of the system

All the parameters except the temperature were fixed. A series of experiments were done with the reaction cell at different measured temperatures. The results are given in table 5.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>18.5</th>
<th>20</th>
<th>23.5</th>
<th>26.5</th>
<th>29.5</th>
<th>34.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Induction period (secs.)</td>
<td>76</td>
<td>70</td>
<td>66</td>
<td>54</td>
<td>39</td>
<td>30</td>
</tr>
</tbody>
</table>

There is a linear relationship between the change in temperature and the change in signal. The signal decreases less than 5% of its value at 20°C for each 1 °C rise in temperature over the range 20-35°C.

Calibration

Construction of calibration graphs

Two series of determinations were done for the concentration ranges of N,N-diethylhydroxylamine:-

(i) from 4x10^{-7}M to 5x10^{-6}M (Range A).
(ii) from 2x10^{-6} M to 2.5x10^{-5}M (Range B)
Experimental conditions

<table>
<thead>
<tr>
<th></th>
<th>Temp. °C</th>
<th>Dye conc. M</th>
<th>pH</th>
<th>Chloramine-T M</th>
<th>Chart speed (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range A</td>
<td></td>
<td></td>
<td>3.0</td>
<td>5x10^-4</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>3x10^-4</td>
<td></td>
<td></td>
<td>See table 6</td>
</tr>
<tr>
<td>Range B</td>
<td></td>
<td></td>
<td>3.0</td>
<td>1x10^-3</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>3x10^-3</td>
<td></td>
<td></td>
<td>See table 7</td>
</tr>
</tbody>
</table>

Table 6

<table>
<thead>
<tr>
<th>Conc. of N,N-diethylhydroxylamine (10^-3 M)</th>
<th>0</th>
<th>4</th>
<th>12</th>
<th>20</th>
<th>28</th>
<th>40</th>
<th>52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Induction time (secs.)</td>
<td>(8 )</td>
<td>3</td>
<td>9</td>
<td>16</td>
<td>22</td>
<td>32</td>
<td>51.5</td>
</tr>
<tr>
<td>(corrected for blank i.e. 8 secs.)</td>
<td>(correlation coefficient for linearity = 0.999)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7

<table>
<thead>
<tr>
<th>Conc. of N,N-diethylhydroxylamine (10^-3 M)</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>12</th>
<th>16</th>
<th>20</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Induction time (secs.)</td>
<td>(5.5)</td>
<td>10</td>
<td>20</td>
<td>29</td>
<td>40</td>
<td>50</td>
<td>59.5</td>
</tr>
<tr>
<td>(corrected for blank i.e. 8 secs.)</td>
<td>(correlation coefficient for linearity = 0.999)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reproducibility and repeatability

To ascertain the reproducibility of the method, calibration graphs for each of the two ranges of concentration of the diethylhydroxylamine (Tables 6 and 7) were obtained weekly over a period of several weeks. The variations in the induction periods for samples assayed over this period were less than 2%. A series of 20 samples of a water containing 0.4ppm of analyte was assayed. The standard deviation of the induction period was 0.46 seconds. on a mean value of 32 seconds. The relative standard deviation of the calculated concentration of analyte was 0.64%.

Effect of possible interferences

Dissolved oxygen in reactant solutions

Although it is recognized that the reaction between dissolved oxygen and N,N-diethylhydroxylamine is normally effected at temperatures well above ambient, it was considered advisable in the preliminary work to use oxygen-free water for the preparation of all solutions.

The use of such a solvent has serious industrial disadvantages and thus the calibration experiments were repeated using water which had only been distilled and had not been flushed with oxygen-free nitrogen. There were no significant differences in any of the results. All readings were within experimental error of analogous readings obtained using oxygen-free water.

Thus it is not necessary to use oxygen-free water for the preparation of the solutions and water of the usual analytical quality will be enough.
Possible interference by:

(a) Metallic cations

Since the source water is of potable quality, only ions likely to be present and in the amounts likely to be present were investigated.

The following cations upon a concentration of 200 ppm have no effect: Alkali metals, magnesium, calcium, zinc, cadmium, mercury and iron (III).

Copper and iron (II) interfere at concentrations above 100ppm.

Iron (II) gives a positive interference, i.e. there is an increase in the period of induction. There is also a noticeable change in the shape of the trace immediately before the onset of the bleaching reaction. The onset is much more sharply marked in the presence of iron (II).

(b) Anions

The following anions have no effect when present in concentrations up to 200 ppm:- carbonate, bicarbonate, halides, sulphate, sulphite, nitrate, nitrite, phosphate.

Removal of interferences

(1) Interferences from copper and iron (II) are removed by passing the water through a cation exchanger (Dionex 113) in the acidic form.

A simple syringe cation-exchanger column was devised for the pretreatment of the water sample (see figure 4). The volume of the syringe is nominally 25ml.

![Figure 4. Syringe cation-exchange column devised for the pre-treatment of water samples.](image)

A Glass wool plug.
B Cation-exchange resin, in 5ml glass syringe.
C Plastic stopper from 25ml flask.
D Solution ready for analysis.
E 20ml disposable syringe.

The amount of cation exchanger used is approximately 2g dry-weight of resin.

The larger syringe is filled with sample and connected via the stopper “C” to the ion exchanger. The sample is slowly ejected through the resin into a 25ml flask containing the buffer dye.

The exchanger is originally white and thus acts as a self-indicator for both iron (II) and copper. When the colored part of section B approaches the glass wool plug (A) the column is changed. Or the exchanger is re-generated by slowly drawing 0.1M HCl through the resin and slowly ejecting it to waste. Two or three such washing are
sufficient to regenerate the resin. The resin is then washed with distilled water in an analogous manner.\[^2\] Although it is possible to mask the cations by the addition of EDTA, (up to a concentration of 800 ppm, EDTA has no effect on the determination of the N,N-diethylhydroxylamine) the proposed method does not allow the use of EDTA. (see discussion).

**Proposed method**

**Reagents**

All water used is de-ionized and was distilled before being used to prepare the solutions.

**Chloramine-T solution 10^{-4}M (solution a)**

Dissolve chloramine-T (28.17 mg) in water. Make up to 100ml to give a 10^{-2}M solution. Dilute this to give 10^{-4}M solution. Store in an amber bottle.

**Preparation of buffered dye reagent solution**

Dissolve 0.06g of Remazol Brilliant Blue in water. To an aqueous solution of citric acid (19.6g) and trisodium citrate (2.16g) add 1ml of iron (II) sulphate (10^{-5}M) solution. Mix the dye and the citrate buffer solutions. Make up to 1 liter with water. Store in an amber bottle.

**Stock solution of N,N-diethylhydroxylamine (10^{-2}M)**

A stock solution was prepared by dissolving 0.8914g of diethylhydroxylamine in water made up to 1liter (10^{-2}M). 10ml of this solution was diluted to 1liter of solution to give a working solution of (10^{-4}M).

**Calibration curves**

A range of solutions containing diethylhydroxylamine (0.0 to 5.0 ml of working solution of diethylhydroxylamine), 5ml of buffered dye reagent solution were prepared and made up to 25ml and shaken to ensure homogeneity. Placed in thermostat at 25°C. (solution B\(_1\) to B\(_n\)).

Switched on the stopped-flow apparatus and allowed to warm up for approximately 10mins.

Syringes and cells were rinsed by pushing water through the system about 10 times. With the lamp shutter in place, using the lockable potentiometer control, adjusted the zero on the photo-diode amplifier until the meter reads zero. Locked the control. With the light on, adjusted the sensitivity control so that a reading of approximately 10 times that required for a full-scale deflection is obtained.

Locked the sensitivity control.

Adjusted the “back-off” control to give a signal on the chart (at say ca 50% of the chart height). Then locked the “back-off” control.
The optical system was then ready for use.

One reservoir was filled with the chloramine-T solution. (solution A) and connected to the appropriate syringe.

Filled the other reservoir with one of the solution B. and connected to the other syringe.

Both syringes were prepared at least twice drawing aliquots (0.5ml) of solutions from the reservoirs into the syringes and ejecting to waste.

This procedure ensured that the reagent solutions in the coils were at thermal equilibrium before being injected into the mixing chamber and the optical cell. Repeated the injection of an aliquot (0.5ml) of a sample, of a standard solution and an aliquot (0.5ml) of the oxidant.

Monitor the reaction.

From the recorder trace were measured or calculated the induction period as indicated. Repeated the process for the series of B solutions and plotted the induction time versus the concentration of diethylhydroxylamine.

**Determination of an unknown sample**

5ml of the buffered dye reagent solution were pipitted into a 25ml flask. Using a 25ml syringe connected to the ion-exchange column, transfer a known amount of the unknown sample solution to the flask making the volume to the mark.

Shake the mixture to achieve homogeneity and place in the thermostat. Connect to the syringe B and flush out the syringe and coil by ejecting 2 aliquots (0.5ml) of the buffered dye and sample mixture through the system.

With both syringes full, inject aliquots of the two solutions into the coils and then to the mixing cell.

Measured the induction period and then calculated the concentration of diethylhydroxylamine in the sample using the previously prepared calibration curve.

**Discussion**

The method was intended to be used in industrial situations and to have the minimum number of manual operations for each assay. Thus the apparatus was designed so that it was not necessary to dismantled when changing samples or reagents. This also meant that maximum stability of the optical system was ensured and hence precise measurement of relatively minute changes in optical density could be made.

The relative volumes of solutions dispensed by each syringe, held in the thermostatted coils and in the optical cell were so arranged to ensure that the reactants were thermostatted before being mixed and the injection of a second aliquot of buffered sample and dye mixture ensured that the first, which had reached thermal equilibrium swept any previous assay material from the optical system. The use of
such a large excess volume of mixed reactants (ca a seven fold excess) being pushed through the optical cell ensured that no memory effects were possible.

One of the most common problems associated with stopped-flow technique was the presence of air bubbles in the flow cell. It was essential to have the optical system completely free of bubbles when in operation; even a small bubble will cause serious changes in the light transmission. The apparatus must be initially purged by pushing solutions rapidly form the drive syringes through the system until the bubbles have been seen to be discharged. With the present apparatus and throughout the present study there was no trouble with air bubbles.

Very small changes in the optical absorbance of the system were easily detected and readily amplified by electronic means. Fixing the cell, light source and photo-diode permanently in position, relative to one another, ensures that there are no changes in optical geometry and hence in absorbance resulting from minute alterations in path length, or changes in the intensity of light from stray light sources.

As expected there is a change in the time of induction of the dyestuff and the chloramine-T with change in temperature. The results (table 5) indicate that it is necessary to control the temperature if analytically acceptable reproducibility is to be achieved.

Buffer systems

The use of the 0.5M citrate buffer was dictated by several considerations. Although the use of a system with a pH of less than 3.0 would give a large increase in the induction period (table 2) and thus the possibility of an increase in precision when very low concentrations of diethylhydroxyamine were being assayed, It may be seen from table 3 that an increase in the molarity of the buffer gives an increase in the time of induction and thus a pH 3.0 buffer, with a molarity greater than 0.05M would be favorable. However, when using buffer solutions more concentrated than 0.05M, problems encountered with the increase in the relative density of these aqueous solutions, causing uneven mixing and optical striations in the cell. As a direct result of the ability of the apparatus to register minute changes (of the order of 0.0001 a.u.) in the optical density of the solution in the cell, these were manifested on the recorder trace as noise. The use of a less concentrated buffer obviated this and thus it was decided to make a compromise by using a less concentrated buffer.

This is also of some importance industrially since the increase in cost of the more concentrated buffer solutions has a bearing on the overall cost of analysis, especially when the assay is used on a routine basis involving large numbers of assays per day.

The addition of a very small amounts of Fe (II) to the buffered dyestuff has no effect on the buffering behaviour of the system or on its keeping properties. Since both copper and iron (II) interfere in the coverall reaction, and it is proposed to use the
effect of the iron (II) to sharpen the “endpoint”, it is essential to ensure that a fixed amount of iron (II) is used in the assay procedure.

Thus it is essential to remove all possible impurities from the sample before mixing it with the buffered dye reagent. This is easily achieved by the use of the proposed ion-exchanger system proposed. The use of EDTA to sequester any Fe, Cu, etc is thus not possible since the metal complexes, especially the Fe complexes, would interfere with the end point.

Other reducing agents such as some sulphur containing anions will be removed either by the process of heating the source water with the N,N-diethylhydroxylamine or by the presence of the excess of chloramine-T. Any oxidizing agents (bromate, chlorate etc) will have either reacted with the N,N-diethylhydroxylamine under the thermal conditions used for the oxygen scavenging or will be incapable of doing so in the assay sequence.

A check was made on whether the monitoring caused any photo-fading of the dye. This was done by inserting the optical shutter after the initial part of a trace had been recorded and removing it before the end of the reaction to record the latter part of the trace. A complete recorder trace, obtained with the monitoring beam on all of the time, showed an exact continuity with the partial traces, proving that the monitoring beam had no effect on the measured absorbance changes.

*Mechanism of the reaction*

The actual cause of the decrease in the induction period has not been ascertained. Although it may be deduced from the experimental results that an increase in the temperature of the system probably causes an increase in the rate of the reaction between the chloramine-T and the diethylhydroxylamine, since the time of delay of the onset of the reaction between Remazol Blue and the oxidant is decreased, it is not possible to state that this is the only reason for the decrease in the induction time. The decrease may also be the result of an increase in the rate of the reaction between the oxidant and the dye. The alteration in the induction period will depend upon the relative increases in the rates of the two competing reactions.

With the conditions of the present experimental study, with the relatively large excess concentration of the oxidant compared to that of the diethylhydroxylamine, it is probable that the increase in the rate of the dye reaction may be the major contributor. However, the increase in the rate of this reaction, for a temperature rise of up to 5°C, calculated from the initial slopes of the appropriate parts of the recorder trace of the reaction, is not sufficient to allow a conclusion to be made.

Since the presence of very small concentration of diethylhydroxylamine in the sample can be measured and is manifested by an induction period, it is considered to be probable that there is practically no diethylhydroxylamine left in solution at the onset of the bleaching reaction sequence.
This bleaching is considered to be the result of oxidation of the dye by the chloramine-T and not by any products of the reactions involving the diethylhydroxylamine. An examination of the spectra produced by the oxidation of the dye by chloramine-T, in the presence and the absence of the diethylhydroxylamine showed them to be practically identical.

The role of the Fe (II) in sharpening the "endpoint" has not been ascertained.

**Range of the proposed method**

The lowest concentration of the analyte that can be determined with an industrially acceptable precision is 2 ppb calculated from calibration curves.

**Conclusion**

The proposed method is highly selective and sensitive and may be used to determine ultra-trace amounts of N,N-diethylhydroxylamine in boiler waters with an industrially acceptable precision and accuracy.

The system is sufficiently low-cost and robust to allow it to form a dedicated method for routine or semi-routine purposes. The time taken for any assay is of the order of 5 minutes from sample reception to calculation of the result from calibration curves.

**References**