CANADA

TECHNICAL BULLETIN NO. 40

# *Use of Ultraviolet Irradiation in the Determination of Nutrients in Water with Special Reference to Nitrogen*

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OTTAWA, CANADA, 1971

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# *Use of Ultraviolet Irradiation in the Determination of Nutrients in Water with Special Reference to Nitrogen*

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## MANUAL METHOD FOR THE DETERMINATION OF SOLUBLE NITROGEN

The role of nutrients in natural waters is very well known (Jenkins, 1968). One such nutrient, nitrogen, occurs in natural waters in inorganic as well as organic forms. The differentiation of various forms of nitrogen is of considerable value in the study of some specific biological aspects of pollution (Jenkins, 1968) and, to further our understanding of this phenomenon, the Water Quality Division has undertaken to monitor the total nitrogen content and the concentration of various forms of nitrogen that might be present in natural waters. As the concentration of total nitrogen in slightly polluted natural waters does not exceed 0.5 - 1.0 mg/l, a method had to be developed which could detect individual forms of nitrogen with concentrations as low as 25-50 ug/l. There are already excellent methods for determining nitrate, nitrite (Brewer and Riley, 1965) and ammonia (Sawyer and Garisley, 1967) which are routinely used in the Water Quality Division's laboratories. However, a convenient, reliable and sensitive method for determination of low levels of organic nitrogen has not yet been found. The classical digestion method first proposed by Kjeldahl (1883) and its automated version (Tenny, 1966) do not give reproducible results below 0.5 mg/l. Furthermore, certain compounds are known to resist reduction to ammonia using the Kjeldahl method. Therefore, attention was given to developing an alternative method which could give accurate and reproducible results and which also could convert all known organic nitrogenous compounds, normally present in natural waters, to some measurable form.

The use of irradiation with UV below 250 mμ to oxidize different soluble organic compounds containing carbon, nitrogen and phosphorus was first reported by Armstrong and Tibbitts (1968) and Armstrong, Williams and Strickland (1966). Also developed was a manual method for the determination of organic nitrogen in sea water (Strickland and Parsons, 1968) However, certain organic compounds, especially urea, were not oxidized quantitatively. Later, after converting organo-phosphorus compounds to orthophosphate by UV-irradiation, Grasshoft (1966) developed an automated method for the determination of organic phosphorus compounds. Therefore, in the Water Quality Division's laboratories, a detailed study was undertaken to investigate the potentialities of using UV-irradiation to oxidize different organic compounds, including compounds such as organo-mercuric compounds (Goulden and Afghan, 1970) and develop the analytical procedures for their determination.

EXPERIMENTAL

Apparatus

Photolysis reactor: The reactor is set up as shown in Figure 1, with the 550-watt photochemical lamp placed inside the fused quartz lamp protection jacket which is plugged at the bottom with 1-inch asbestos tape and mounted axially in the centre of the galvanized iron cylindrical body of the reactor. Samples for irradiation are contained in ten 60-ml glass-stoppered fused quartz sample tubes. These are set in the reactor parallel to the lamp and equidistant from it. The fan at the lower end of the cylinder operates at high speed and forces cool air up through the cylinder. This arrangement ensures that the temperature of samples does not exceed 60°C even after 2 hours of photolysis. The inside of the cylindrical tray at the bottom of the reactor is painted black with a standard matt oil paint which acts as a radiation baffle and reduces the intensity of scattered ultraviolet radiation. To remove the ozone produced by the action of the UV-irradiation on the oxygen in the air, an exhaust hood is placed over the top of the reactor.

Standard Technicon AutoAnalyzer parts: The Technicon AutoAnalyzer is set up as shown in Figure 4A. The rate of sampling is 20 per hour with a ratio of wash to sample of 2 to 1. A colorimeter with a 550-mμ filter assembly, No. 5 apertures and a 15-mm flow cell, is used during the investigations.

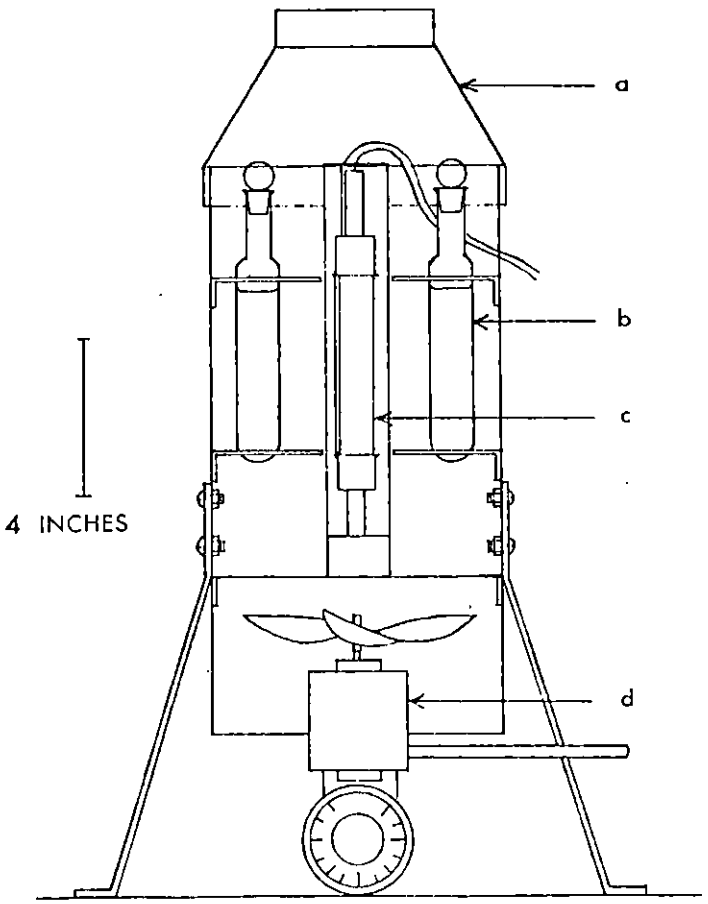


Figure 1. Cross-sectional view of photolysis reactor a) chimney b) sample tube c) UV-lamp d) cooling fan.

Reagents

a) Technicon reagents:

EDTA - Dissolve 25 g of the disodium salt of ethylene diaminetetraacetic acid in about 900 ml of deionized water, adjust pH of the solution to 6.5-7.0 with sodium hydroxide, and dilute to one litre.

Sulfanilamide solution - Dissolve 5.0 g of sulfanilamide in a mixture of 450 ml of deionized water and 50 ml of concentrated hydrochloric acid.

Naphthylethylenediamine solution - Dissolve 0.5 g of N-1- naphthylethylenediamine dihydrochloride in 500 ml of deionized water. Filter the solution through a 0.45μ "Millipore" filter and store in an amber bottle. The reagent is stable for several weeks but should be discarded when it turns brown.

Cadmium coil - Fill a 24-inch length of 1/8-inch I.D. tygon tubing (R-3603) with cadmium metal filings which are larger than 20 mesh. Plug each end of the coil with a small quantity of fine glass wool.

Stock nitrogen solution, 100 mg/l - Dissolve 0.7220 g of potassium nitrate in deionized water and dilute to one litre.

Working nitrogen solution, 5 mg/l - Dilute 25 ml of stock nitrogen solution to 500 ml with deionized water. Prepare the above solution fresh each week.

b) Photolysis reagents:

Buffer solution (pH 6.2, I=0.05) - Dilute a mixture of 320 ml of solution (A) and 60 ml of solution (B) to one litre with deionized water.

Solution A - Dissolve 13.6 g of potassium dihydrogen phosphate in deionized water and dilute to 250 ml with deionized water.

Solution B - Dissolve 3.6 g of disodium hydrogen phosphate in deionized water and dilute to 250 ml with deionized water.

Removal of nitrogenous impurities from buffer solution:

Wash 50 g of ion exchange resin Rexyn (R) 101 (H) with deionized water and transfer to a 100-ml column. Pass approximately one litre of 20% sodium chloride through the resin column until the effluent is neutral. Then wash the column with deionized water. Pass the buffer through the column at a rate of approximately two drops/seconds. Discard the first 200 ml of effluent and collect the rest.

Procedure

a) Calibration curve for total soluble nitrogen:

1. Transfer 0.0, 1.0, 2.0, 4.0 and 6.0 ml of 5-mg/l nitrogen working solution to a series of 50-ml volumetric flasks, add two drops of 3% hydrogen peroxide and dilute to 10 ml with deionized water.

2. Add 40 ml of phosphate buffer to each flask and mix thoroughly.

3. Place the quartz tubes in the reactor.

4. Start the photochemical lamp and allow it to warm up for 3 to 4 minutes. Turn on the fan and irradiate the solutions for two hours.

5. Turn off the lamp and leave the fan running for 15-20 minutes.

6. Remove the quartz sample tubes from the reactor, mix thoroughly, and analyze the samples on the Technicon AutoAnalyzer system as shown in Figure 4a.

7. Subtract the peak height of the blank from each of the peak heights of the nitrate standards.

8. Prepare a calibration curve by plotting the concentration of the nitrate standards in mg/l along the ordinate and the corrected peak heights of the corresponding nitrate standards along the abscissa.

b) Analysis of water sample for total soluble nitrogen content:

1. Transfer 10-ml aliquots of each sample containing 0.1-0.8 ppm of total nitrogen to clean quartz sample tubes and to clean dry 50-ml volumetric flasks.

2. Add 40 ml of buffer (pH 6.2) to the quartz tubes and volumetric flasks.

3. Add two drops of 30% hydrogen peroxide to the quartz tubes only, stopper, and mix thoroughly.

4. Irradiate the samples for two hours as described above.

5. During this irradiation period, the samples in the volumetric flasks are thoroughly mixed and analyzed for nitrate and nitrite content.

6. Remove the quartz sample tubes from the reactor, mix thoroughly and analyze the samples for total nitrogen content using the AutoAnalyzer system in Figure 4a.

Calculations

1. Using the calibration curve, convert the peak heights of all the samples, before and after photolysis, to mg/l nitrogen.

2. Subtract the concentration of nitrogen in the blank before irradiation from the concentration of nitrate obtained for the samples before photolysis. Similarly, subtract the concentration of nitrate in the blank irradiation from the concentration of nitrate obtained for the samples after photo-oxidation.

3. To calculate the concentration of nitrogen which is present in the sample as organic and ammonium nitrogen, subtract the concentration of nitrogen obtained before photolysis from the concentration of nitrate obtained after photolysis.

Safety Precautions

Ultra-violet irradiation can be hazardous. Exposure of the skin and particularly the eyes to the radiation from the photochemical lamp should be avoided.

## RESULTS AND DISCUSSION

Preliminary study of UV-irradiation to decompose different organic nitrogen compounds

In our preliminary experiments, nitrogenous compounds were chosen because their oxidation was relatively slow compared to other compounds (Armstrong and Tibbitts, 1968). A series of solutions containing different organic compounds was prepared in distilled water and lake water. Each solution contained 200 ug/l of nitrogen in the form of different organic compounds listed in Tables I and II; 50-ml aliquots were transferred to quartz tubes and two drops of 30% hydrogen peroxide were added to each quartz tube.

TABLE I

Oxidation of Organic Nitrogenous Compounds in Deionized Water

| Name of Compound | Amount of Nitrogen Photo-oxidized after, (ug/litre)[a] | | | | |
|---|---|---|---|---|---|
| | ½ hour | 1 hour | 2 hours | 4 hours | 8 hours |
| Blank | 5 | 5 | 10 | 10 | 20 |
| Potassium Nitrate | 215 | 210 | 195 | 190 | 195 |
| Adenine | 145 | 150 | 155 | 160 | 175 |
| Albumin | 120 | 130 | 140 | 150 | 150 |
| Ammonium Chloride | 90 | 105 | 130 | 145 | 160 |
| Creatine | 125 | 125 | 140 | 150 | 165 |
| D.N.A. | 130 | 135 | 135 | 145 | 145 |
| Glycine | 120 | 130 | 145 | 160 | 165 |
| Uracil | 185 | 185 | 175 | 180 | 180 |
| Urea | 205 | 200 | 190 | 190 | 195 |

[a] 200 ug/litre of nitrogen was added to each sample listed above.

TABLE II

Oxidation of Organic Nitrogenous Compounds in Lake Water

| Name of Compound | Amount of Nitrogen Photo-oxidized after, (ug/litre)[a] | | | | |
|---|---|---|---|---|---|
| | ½ hour | 1 hour | 2 hours | 4 hours | 8 hours |
| Potassium Nitrate | 215 | 205 | 216 | 205 | 200 |
| Adenine | 115 | 125 | 105 | 115 | 120 |
| Albumin | 90 | 95 | 80 | 95 | 105 |
| Ammonium Chloride | 147 | 194 | 178 | 169 | 180 |
| Creatine | 47 | 82 | 109 | 80 | 80 |
| D.N.A. | 95 | 135 | 115 | 115 | 120 |
| Glycine | 155 | 185 | 170 | 165 | 160 |
| Uracil | 120 | 115 | 135 | 115 | 120 |

[a] 200 ug/litre of nitrogen was added to each sample listed above.

The solutions were then irradiated for ½, 1, 1½, 2, 3, 4, 5, 6 and 8 hours. At each time interval, aliquots of the irradiated solutions were analysed on the Technicon AutoAnalyzer for the resultant nitrate-nitrite mixture using the method of Brewer and Riley (1965), in which the mixture of nitrate and nitrite ions are passed through a cadmium coil. This reduces the nitrate ion to nitrite and total nitrite is then determined colorimetrically by diazotization with sulfanilamide and coupling with naphthylethylenediamine to form an azo dye.

Using deionized water: Of the 8 different nitrogenous compounds investigated, only urea and uracil were oxidized within ½-hour irradiation. Other compounds were oxidized more slowly; however, all other compounds, including ammonium chloride, gave recoveries of between 60-80% at the end of the ½-hour irradiation. Further irradiation to a maximum of 8 hours slightly increased the amount of conversion of these compounds to a mixture of nitrate and nitrite. The pH of all the solutions after 8 hours irradiation was approximately 5. This indicated that urea and uracil were quantitatively oxidized to nitrate-nitrite mixture at this pH while the remaining compounds were not.

Using lake water samples: Table II shows the results obtained when lake water samples were spiked with individual compounds as previously listed. In this case only glycine and ammonium chloride were quantitatively oxidized after one hour irradiation while other compounds did not oxidize completely. Further irradiation of samples resulted in the formation of a film of precipitate on the walls of the sample tubes containing the samples. This was later identified as calcium carbonate. The pH of the lake water samples used in this study was approximately 8. This clearly indicated that the photolysis of different organic compounds is pH dependent and different compounds oxidize at different pH ranges, viz. ammonia and glycine were completely oxidized in neutral or slightly alkaline medium while the oxidation of urea (in Table I) and uracil was quantitative in slightly acidic media.

## Effect of pH

From the preliminary investigations it appeared that the oxidation of different compounds is pH dependent. Therefore, this effect was investigated in detail by oxidizing the different organic compounds listed in Table I and II, between pH 5 to 9. A series of solutions in this pH range was prepared containing different nitrogenous compounds in synthetic lake water. The pH of the solutions was adjusted to the required value by dilute sodium hydroxide or hydrochloric acid. The solutions were irradiated under the same conditions as above, for ½, 1, 2, 3, 4, and 6 hours. Aliquots of the irradiated samples were analyzed for the resultant nitrate/nitrite mixture at each interval. Urea and uracil underwent maximum oxidation at a pH lower than that required for the optimum photo-oxidation of glycine, ammonium chloride, creatine and adenine. In all cases the pH of the solutions changed during irradiation and the final pH was found to be higher than the initial adjusted pH. This was probably due to the thermal decomposition of bicarbonate and lack of buffering capacity of the solutions. It would be possible to remove the bicarbonate from the sample by first acidifying the sample to pH 2 and then either allow it to stand for 16 hours or vigorously stir it for 30 minutes. However, it was more convenient to maintain the pH between 5 and 9 by the addition of phosphate buffer. Other possible organic buffers were not considered because of their susceptibility to photo-decomposition, thereby altering the pH or decreasing the efficiency of the UV lamp used for photo-oxidation.

Therefore, the above experiment was repeated with urea and ammonium chloride using phosphate buffer (I=0.05 M) to maintain pH between 5 and 9. Urea and ammonium chloride were chosen for this experiment because they appeared to be most representative of the compounds photo-oxidized in acidic and basic pH ranges respectively. Furthermore, both urea and ammonium chloride have been reported (McLaren and Shugar, 1964) to be the primary photo-decomposition products of amino acids and ureides respectively. Figure 2 shows the effect of pH on the amount of conversion of these compounds using different irradiation times for the oxidation. The optimum pH range lies between 5.9 and 6.5 when irradiation was carried out for 2 to 4 hours. Therefore, unknown samples were irradiated at pH 6.2 (using phosphate buffer) for two hours prior to the determination of total soluble nitrogen. Sometimes phosphate buffer components contain an ammonium ion which gives high colour background. This impurity is easily removed by passing phosphate buffer, containing nitrogenous impurities, through a cation exchange resin in sodium form: this action will remove the ammonium ion which will be preferentially adsorbed by the resin.

## Effect of Calcium

During the analysis of different lake water samples for soluble nitrogen, it was found that when analysed as above, several samples precipitated during UV-irradiation, with low recoveries of nitrogen. The analysis

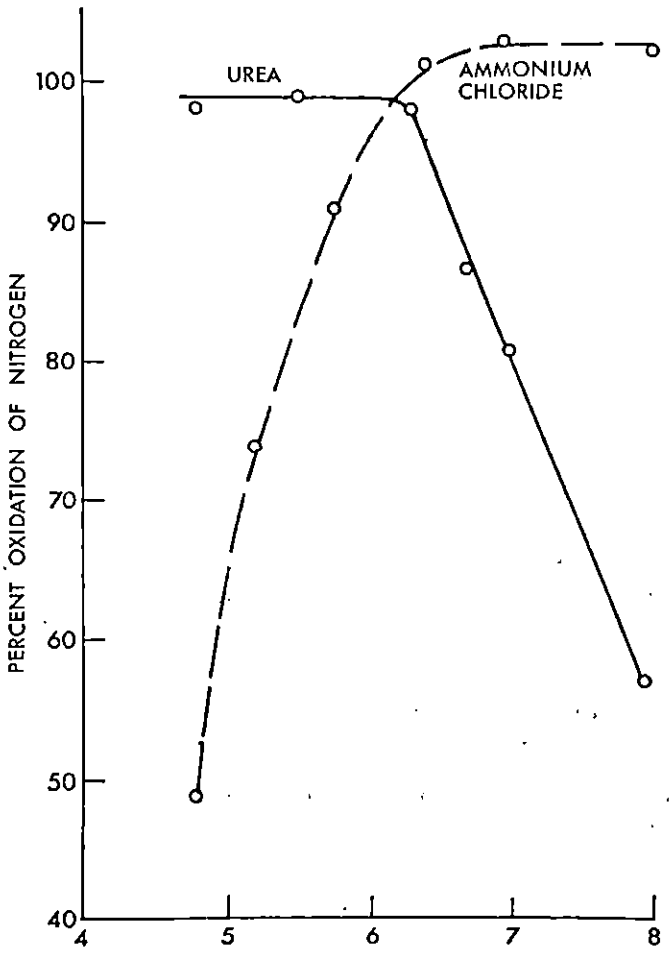


Figure 2. Effect of pH on percent oxidation of nitrogen a) 200 ug/l N as ammonium chloride b) 200 ug/l N as urea.

of major ions in the samples showed relatively higher concentration of calcium. Therefore, it was assumed that calcium phosphate precipitated at the higher temperatures produced during UV-irradiation. To confirm these observations, synthetic lake water containing 200 mg/l bicarbonate and phosphate buffer, was spiked with increasing amounts of calcium, ranging from 10-200 mg/l. These solutions were irradiated as above at 65°C for two hours. Precipitate, later identified as calcium phosphate, was observed when the concentration of calcium exceeded 50 mg/l. The use of hexametaphosphate to prevent the precipitation of calcium phosphate was investigated. However, hexametaphosphate interfered in the colour reaction of nitrite with sulfanilamide and naphthylethylenediamine. It was found, as discussed below, that precipitation can be prevented to some extent by lowering the temperature of the solution. This was accomplished by operating the cooling fan at maximum speed; the precipitation was prevented where the concentration of calcium was not greater than 100 mg/l. At higher concentrations of calcium, precipitation was prevented by diluting the sample, thereby maintaining the calcium concentration below 100 mg/l. The sensitivity of this method is such that dilution does not affect the determination of low concentrations of nitrogen.

## Effect of Temperature

The effect of temperature on the oxidation of nitrogen was thoroughly investigated by irradiating 50-ml aliquots of synthetic lake waters containing 50 mg/l of calcium and 200 ug/l of nitrogen as urea or ammonium chloride at pH 6.2, using phosphate buffer. A thin quartz finger was dipped in the tubes and the temperature of the sample was controlled by circulating distilled deionized water, ranging in temperature from 25-80°C, through the quartz finger. The samples were irradiated at different temperatures viz. 25,35,50,60 and 80°C respectively, and then analysed for resultant nitrate-nitrite mixture after 2 hours of irradiation. The results indicated no significant variation in percent oxidation at the various temperatures. However, above 50°C, the precipitation of calcium phosphate was observed on the walls of the quartz tubes, resulting in lower recovery of nitrogen; to prevent a recurrence during irradiation of unknown samples, the temperature of the UV-reactor was always maintained below 50°C.

## Interferences

A possible interference of different major ions and minor ions such as alkaline earths and heavy metals respectively, was determined separately on both UV-irradiation and colour reaction. None of the major or minor ions interfered except a large excess of iron (III) and trace amounts of silver. The presence of 5 ppm of iron (III) completely bleached the colour due to 50 ug/litre of nitrogen as nitrite. An attempt to remove iron (III) interference by thioglycolic acid was unsuccessful. Thioglycolic acid itself bleached the colour due to nitrite which could be due to the reduction of nitrite with thyioglycolic acid to give nitrogen. Citric acid proved successful in removing iron (III) interference. Interference of other sulfur-containing compounds such as xanthates, mercaptans, etc, on the colour reaction of nitrite with sulfanilamide and naphtylethylenediamine, was also investigated. It was found that, during irradiation, all of these compounds were converted to sulfate and did not interfere in the colour reaction of nitrite. The presence of silver gave a high background and investigations are continuing to explain this effect and possibly develop an analytical method for the determination of trace amounts of silver in water.

Calibration Curve

Identical curves were obtained in the range of 50-250 ug/l of nitrogen as nitrate, glycine and ammonium chloride, using deionized water and synthetic lake water. Standard addition method on the lake water sample also showed the linearity of color formation with increasing concentrations of nitrogen in the sample. The coefficient of variation for 100 ug/l nitrogen was found to be 5.8%. The detection limit of the procedure is 20 ug/l. This limit is not due to the lack of sensitivity of nitrite reaction but rather to the impurities in the reagents used.

## AUTOMATED METHOD FOR THE DETERMINATION OF SOLUBLE NITROGEN

After developing a manual method for the measurement of soluble nitrogen using UV-irradiation, it was decided to investigate the possibility of automating this procedure. It was anticipated that automation of this procedure would result in shorter irradiation time to quantitatively oxidize organic nitrogenous compounds and this has been found to be true. Rather than use quartz tubes, the sample is irradiated in a quartz coil of small internal diameter. The coil gives a greater surface to volume ratio than the tubes; also, the amount of sample irradiated in the automated method is much less.

## EXPERIMENTAL

### Apparatus

The UV-reactor was made from a box 13"x12"x15". A 550-watt photochemical lamp was placed inside a fused quartz lamp protection jacket and mounted axially in the centre of the box. Two quartz coils were placed on top of each other as shown in Figure 3, so that the same lamp could be used to irradiate both coils. Irradiating coils in the UV-reactor are cooled by a high-speed fan fitted on the side of the reactor box and an exhaust is fitted on the top of the reactor. The quartz coils are made of Purcil 453 quality fused silica tubing of 3-mm I.D., 0.6 mm wall thickness and the coil diameter is approximately 5 inches. Prior to entering the manifold, the sample was segmented using purified air which was passed through a scrubber containing 10% sulfuric acid.

### Reagents

a) Reagents for total nitrogen and nitrate plus nitrite.

Hydrochloric acid solution: Transfer 38.5 ml of concentrated hydrochloric acid to a volumetric flask and dilute to five litres with distilled deionized water.

Sodium hydroxide solution: Dissolve 34.0 g of sodium hydroxide, 29.8 g of disodium hydrogen phosphate and 5.6 g of potassium dihydrogen phosphate in distilled deionized water and dilute to five litres.

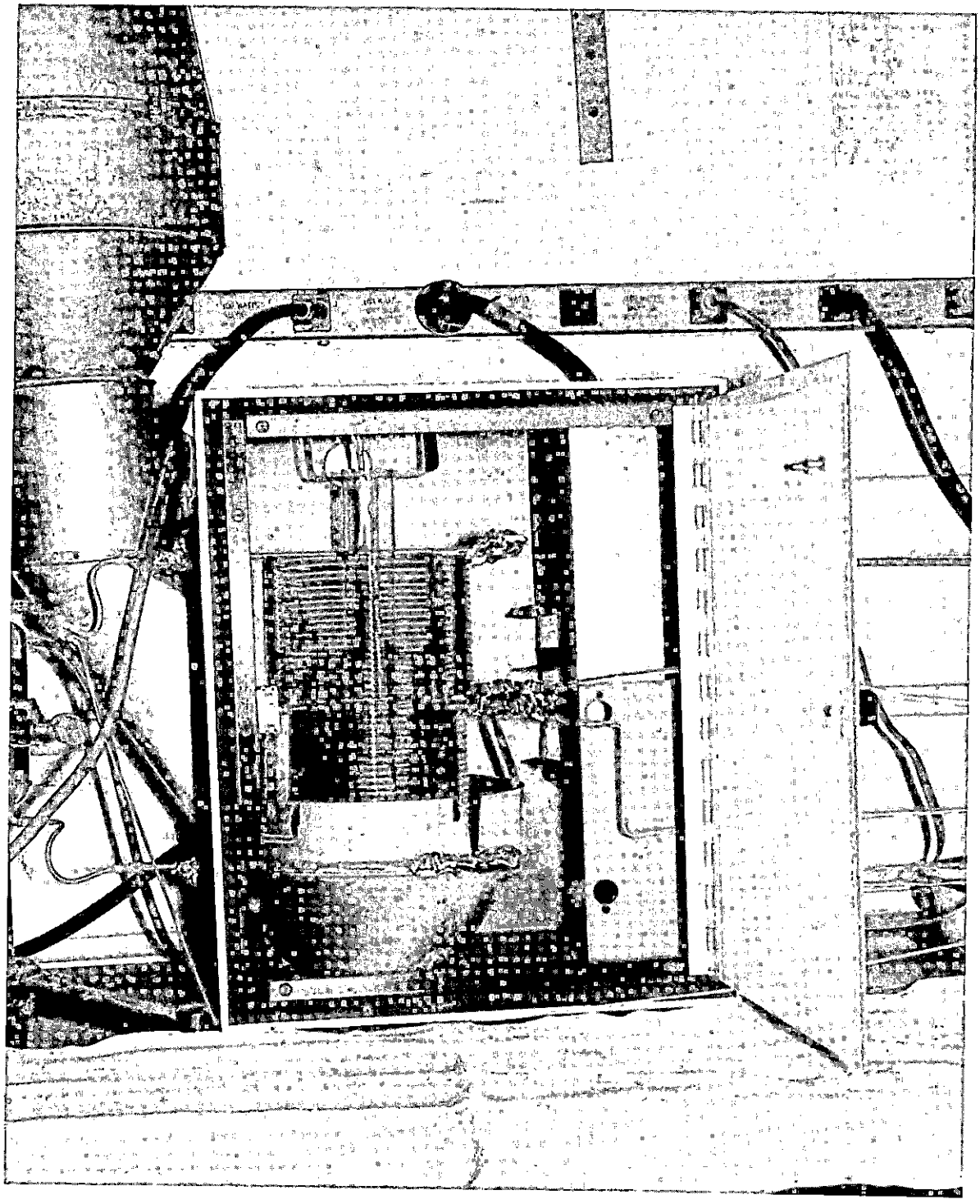

Figure 3. Inside view of UV-irradiator used in an automated method to oxidize different organic compounds.

EDTA solution: Dissolve 50.0 g of the disodium salt of ethylenediamine tetra acetic acid in 700 ml of distilled deionized water, adjust the pH of the solution within the range 6.5 - 7.0 with dilute sodium hydroxide and dilute to one litre.

b) Reagent for ammonia

Alkaline hexametaphosphate solution: Dissolve 40.0 g of sodium hexametaphosphate in one litre of distilled deionized water and 52.0 g of sodium hydroxide in one litre of distilled deionized water. Mix 100 ml of each solution daily.

Buffer solution: Dissolve 89.7 g of disodium hydrogen phosphate hydrated and 10.0 g of disodium hydrogen phosphate in distilled deionized water and dilute to five litres.

Hypochlorite stock solution: Dilute 100 ml of Javex to 500 ml with distilled deionized water and filter through a 0.45-micron fibre-glass filter.

Hypochlorite reagent solution: Transfer 5 ml of hypochlorite stock solution to a 1-litre volumetric flask and dilute to one litre with distilled deionized water.

Reducing agent: Dissolve 40.0 g of oxalic acid and 340.0 g of chloroacetic acid in distilled deionized water and dilute to two litres.

Orthotolidine: Dissolve 1.2 g of o-tolidine dihydrochloride in 500 ml of distilled deionized water. Add 120.0 ml of concentrated hydrochloric acid and dilute to one litre.

Procedure

The manifold AutoAnalyzer equipment is connected as shown in Figures 4 and 4a respectively. This involves two steps: (1) Oxidation of organic nitrogenous compounds to a mixture of nitrate and nitrite; (2) measurement of the resultant mixture thus formed.

The oxidation of some organic compounds is first carried out in acidic medium in one of the coils of the reactor. After leaving the first coil the solution is neutralized with alkali, cooled, and passed through the other coil where oxidation of the remaining compounds takes place. After oxidation, the sample is debubbled, diluted and analyzed for nitrate-nitrite content using the manifold shown in Figure 4. This gives the value for the total soluble nitrogen in the water. The flow diagrams for nitrate-nitrite and ammonia are shown in Figures 5 and 6 respectively. These manifolds are essentially the same as those proposed by Brewer and Riley (1965) and by Sawyer and Garisley (1967) except for the fact that two additional lines containing acid and alkali are added; the results obtained from these manifolds should match the result obtained using the manifold in Figure 4.

The "Technicon" analyzer is set up using the above three manifolds and proportionating pump II. The standard sampler is used and the samples are analyzed at the rate of 20/hr. The sample tray, which holds 40 cups, is filled with the samples and then covered with saran wrap secured with a

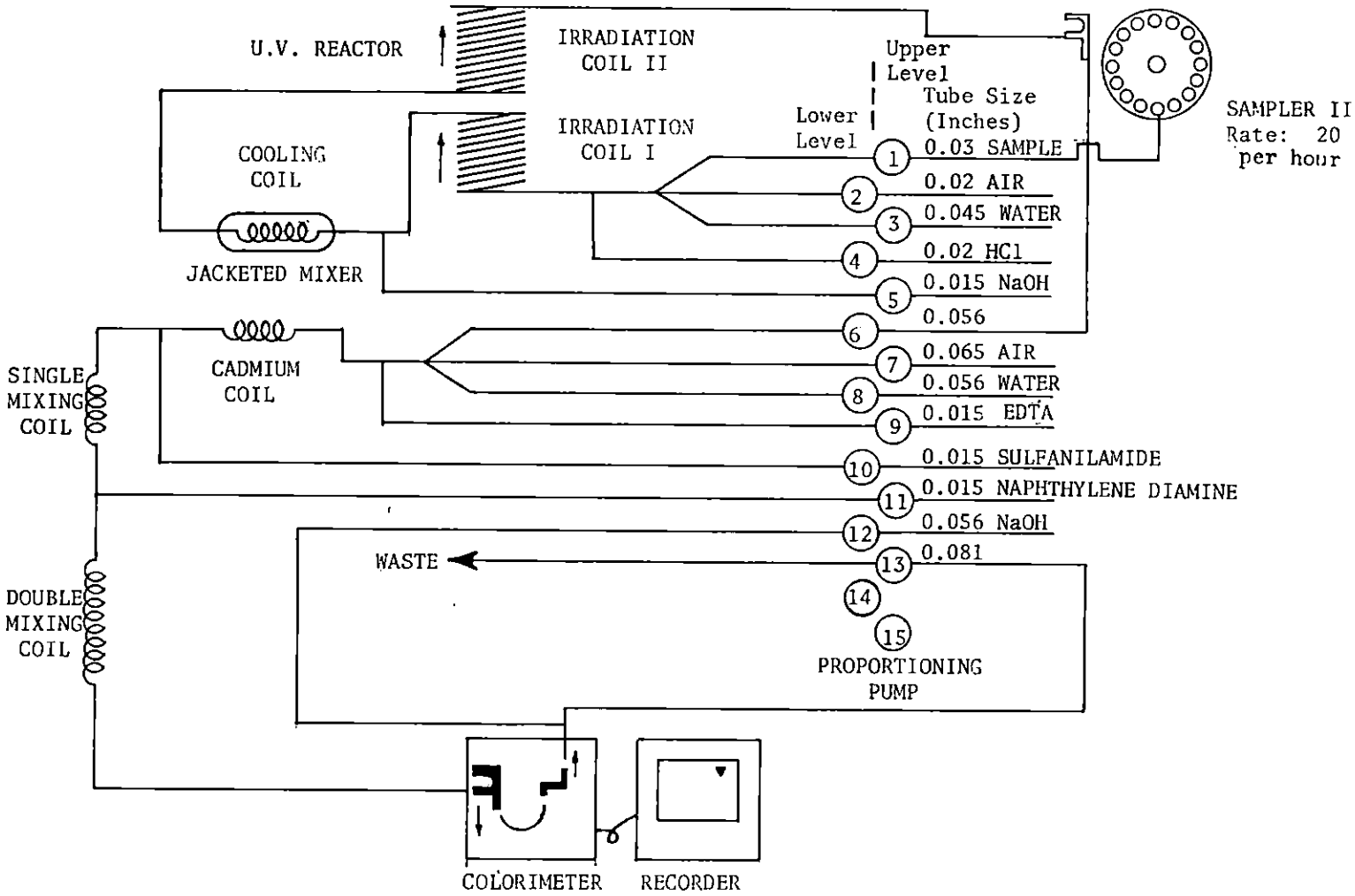


Figure 4. Manifold for total nitrogen.

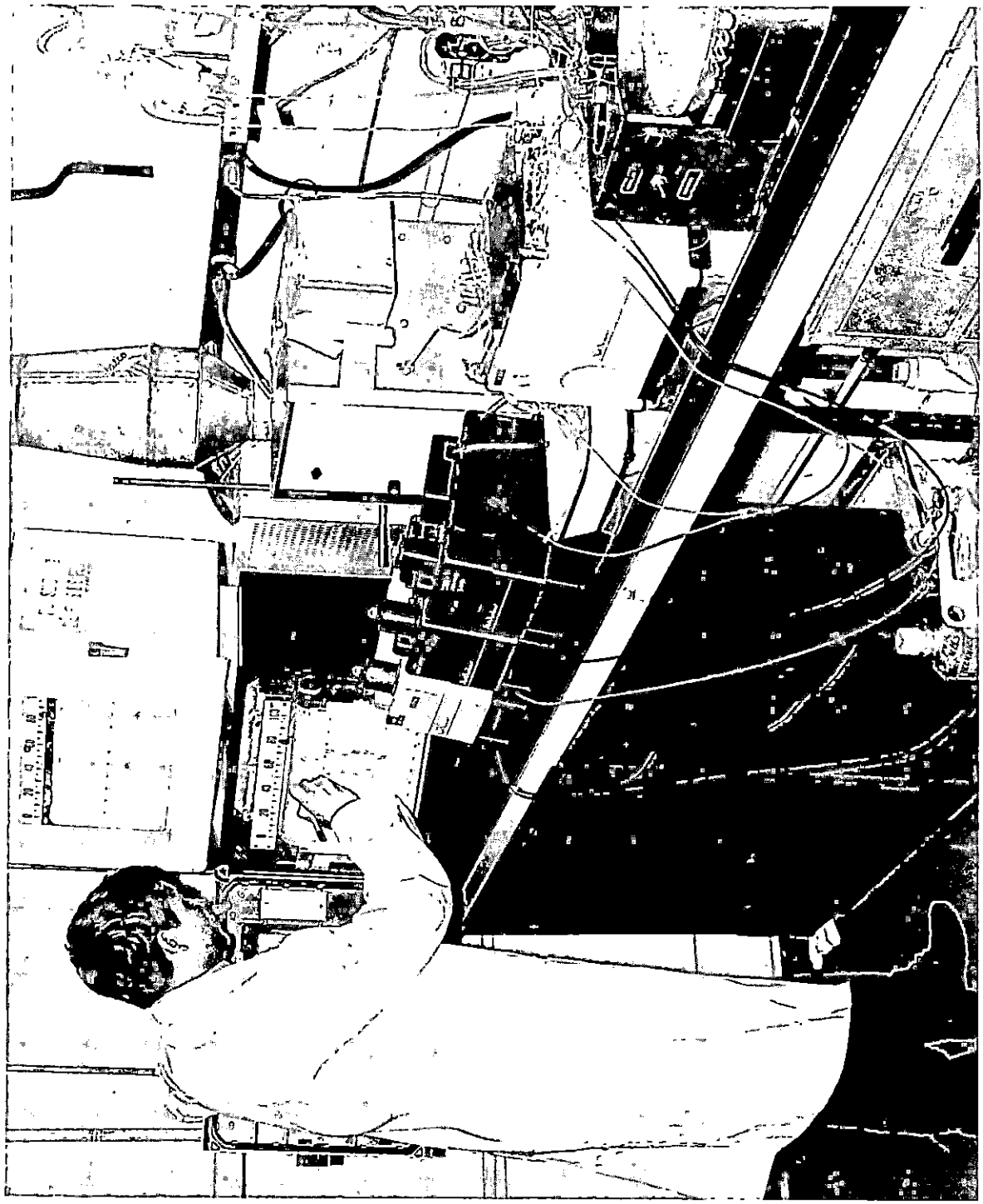

Figure 4a. AutoAnalyzer equipment arranged in the laboratory.

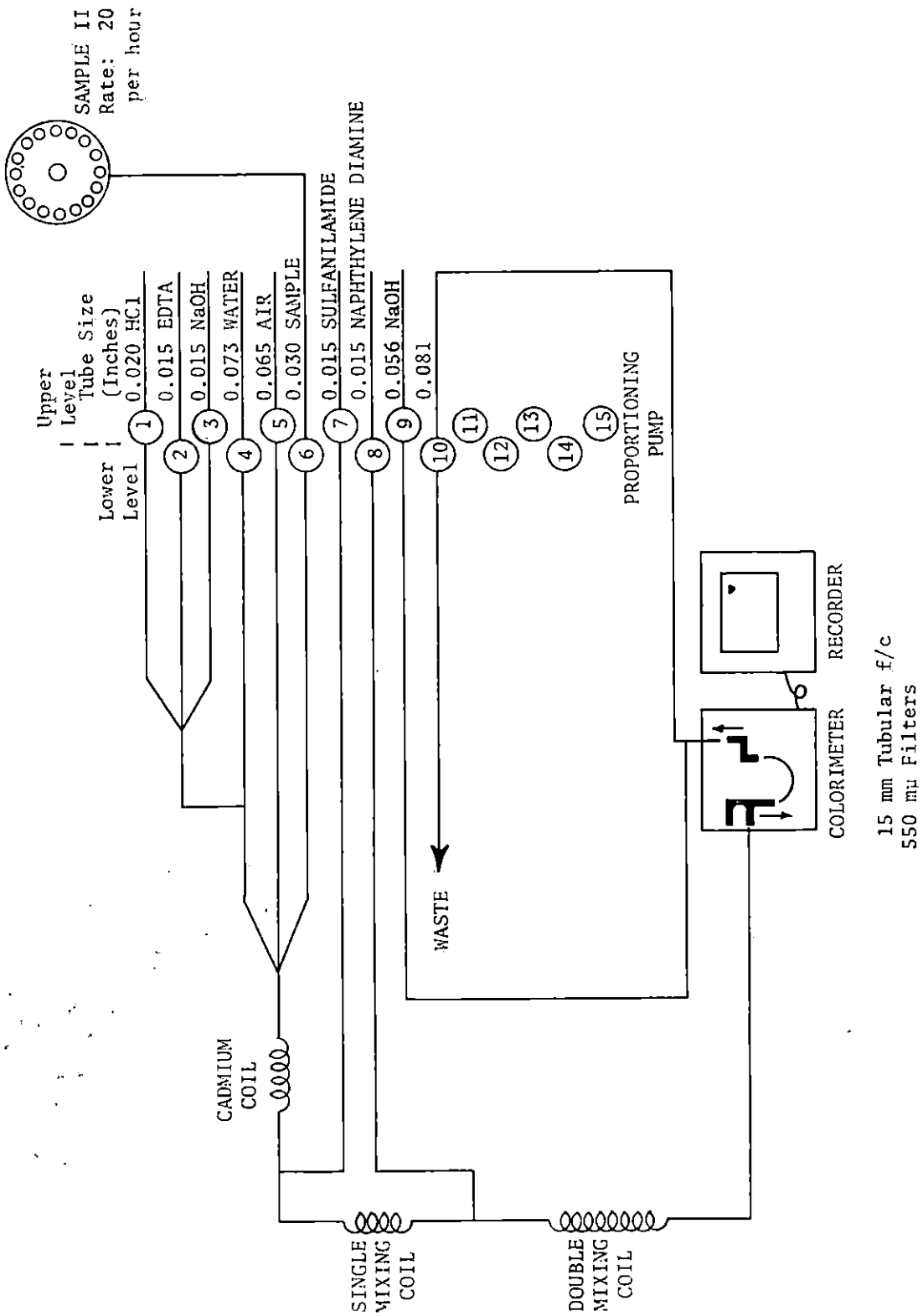


Figure 5. Flow diagram for nitrate plus nitrite.

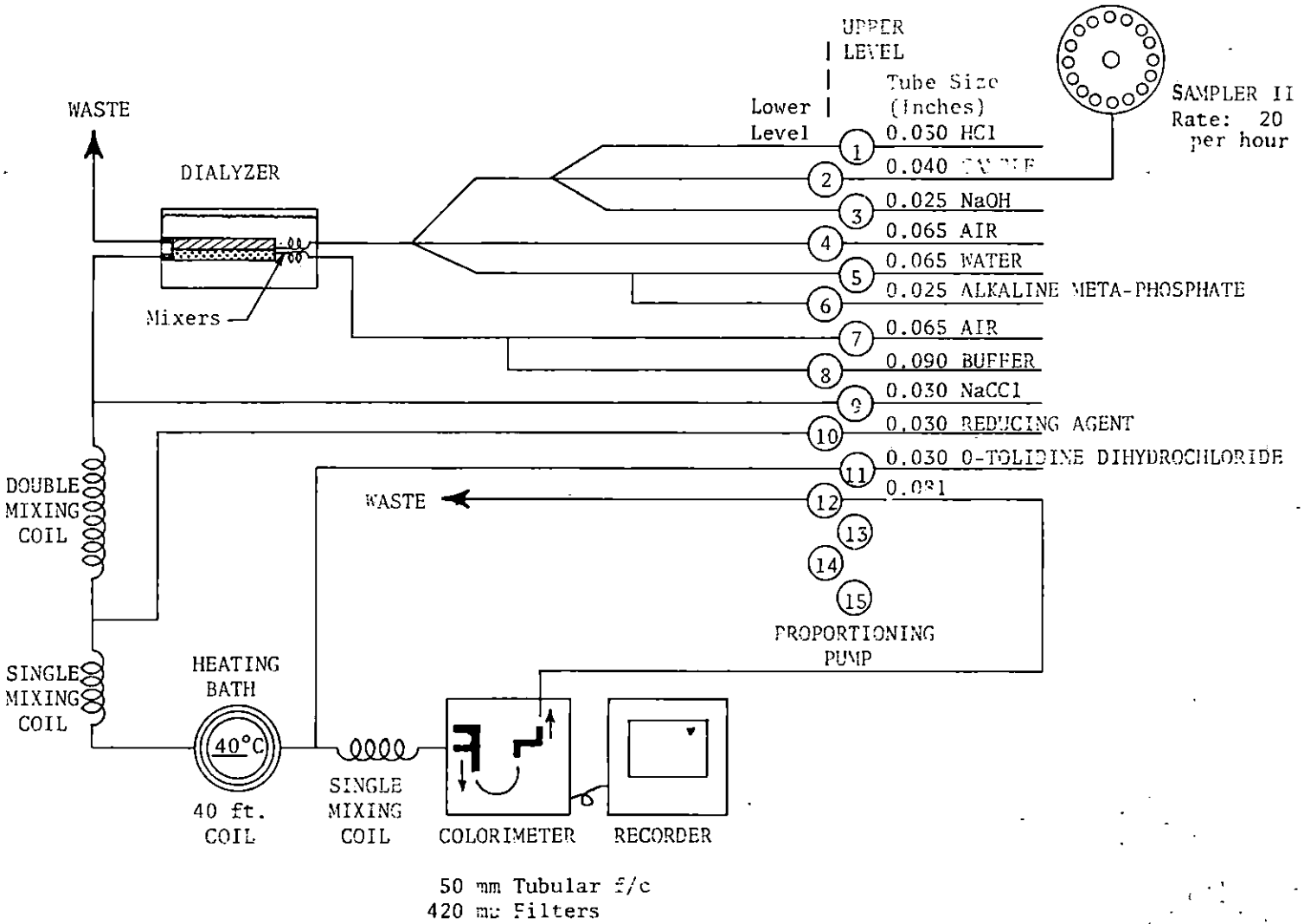


Figure 6. Flow diagram for ammonia.

rubber band to eliminate any contamination from the atmosphere. The probe usually used to withdraw samples from the cups is replaced with an 18 gauge needle which pricks the saran wrap but does not tear it. The withdrawn sample is separated into three, one of which is analyzed for ammonia, the second for nitrate-nitrite content and the third portion is first oxidized by UV-irradiation to a mixture of nitrate and nitrite and then analyzed for total nitrogen content. The concentration of ammonia, and nitrate plus nitrite when subtracted from the total nitrogen content obtained after irradiation gives the organic nitrogen content.

## Results and Discussion

In our preliminary investigations it was observed that the oxidation of organic compounds is pH dependent. Therefore, this effect was investigated further. A series of solutions containing different organic compounds and covering pH range 1-8 was prepared and irradiated using a 550-watt lamp. The solutions were then analyzed for nitrate-nitrite content. The results showed that certain compounds are quantitatively oxidized within a reasonable irradiation time only in acid conditions while others require an alkaline medium. Typical graphs obtained are shown in Figure 7. Urea is quantitatively oxidized in acidic medium while the oxidation of ammonia is quantitative in alkaline medium only. Therefore, for the analysis of unknown samples, the oxidation was carried out both in acid and alkaline media prior to the determination of total nitrogen content in water.

Oxidation of organic compounds also depends upon irradiation time. Certain compounds oxidize readily while others, such as urea, are very resistent to oxidation. Solutions were irradiated under the same conditions as above using different lengths of time. This was achieved by changing the size of the tubes which in turn altered the pumping rate. Aliquots of the irradiated samples were analyzed for nitrate-nitrite content. Results indicated that complete oxidation of the majority of compounds was achieved within one hour of irradiation.

The effects of different contaminants normally present in water on the oxidation of nitrogen compounds and the colour reaction, were investigated. None of the known constituents in natural waters, such as calcium, magnesium, bicarbonate and traces of heavy metals, interfered with the efficiency of the oxidation and colour reaction which employs coupling and diazotization of resultant nitrate-nitrite mixture obtained after irradiation.

The efficiency of UV-irradiation to oxidize different organic compounds was confirmed by oxidizing these compounds in water and synthetic lake water, and by spiking the same amounts of these compounds in actual lake water. Table III and Figures 8 and 9 show the percent recovery of different organic compounds tested. Of the 17 organic nitrogen compounds tested, only EDTA, hydrazine dihydrochloride and phenylhydrazine hydrochloride failed to give quantitative recovery. Quantitative oxidation of these compounds was achieved by catalytic oxidation using silver. The presence of silver, however, gave high blank and we are not currently using it. Its role in improving oxidation of organic nitrogenous compounds is being investigated and will be discussed thoroughly elsewhere.

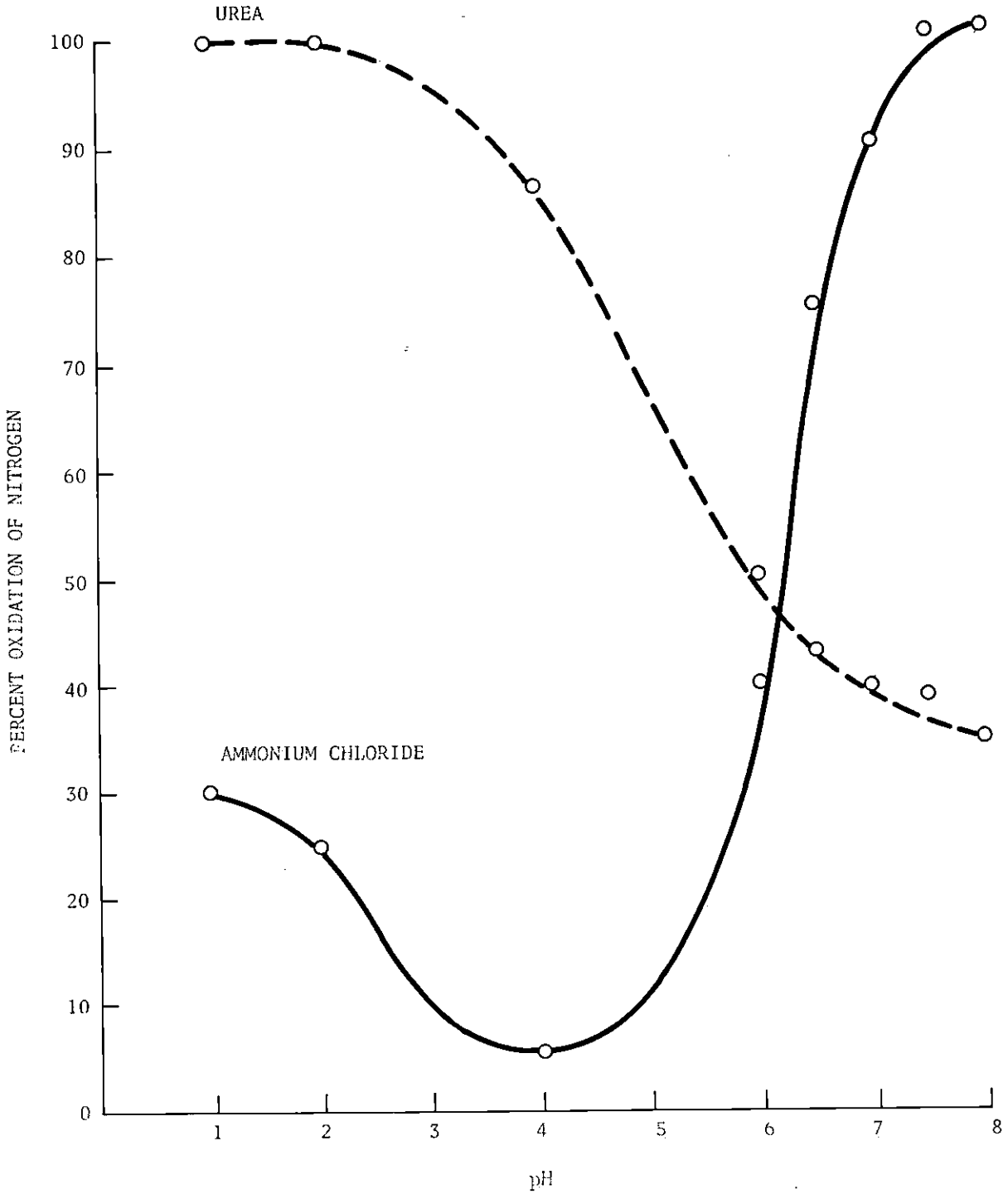


Figure 7. Typical graphs obtained for the oxidation of ammonium chloride and urea.

TABLE III

Percent Recovery of Nitrogen from Different Organic Compounds Using UV-irradiation

| Name of Compound | Known Concentration of Nitrogen (ug/l) | Actual Concentration Found (ug/l) |
|---|---|---|
| Potassium Nitrate | 100 | 100 |
| | 50 | 49 |
| | 100 | 101 |
| Diethylamine hydrochloride | 50 | 50 |
| | 100 | 102 |
| | 200 | 208 |
| Triethylamine | 50 | 49 |
| | 100 | 99 |
| | 200 | 204 |
| Hydroxylamine hydrochloride | 50 | 47 |
| | 100 | 91 |
| | 200 | 96 |
| Uric acid | 50 | 49 |
| | 100 | 92 |
| | 200 | 192 |
| Uracil | 50 | 51 |
| | 100 | 99 |
| | 200 | 198 |
| Nitrilotriacetic acid | 50 | 48 |
| | 100 | 93 |
| | 200 | 202 |
| EDTA | 50 | 20 |
| | 100 | 38 |
| | 200 | 78 |
| al-histidine | 50 | 48 |
| | 100 | 93 |
| | 200 | 190 |
| al-phenyl alanine | 50 | 51 |
| | 100 | 102 |
| | 200 | 196 |
| Acetaldoxime | 50 | 51 |
| | 100 | 109 |
| | 200 | 194 |
| Semicabazide hydrochloride | 50 | 38 |
| | 100 | 65 |
| | 200 | 136 |
| Hydrazine dihydrochloride | 50 | 31 |
| | 100 | 52 |
| | 200 | 110 |
| Phenylhydrazine hydrochloride | 50 | 15 |
| | 100 | 26 |
| | 200 | 54 |
| p-nitrophenol | 50 | 50 |
| | 100 | 99 |
| | 200 | 190 |
| p-nitroaniline hydrochloride | 50 | 49 |
| | 100 | 91 |
| | 200 | 204 |

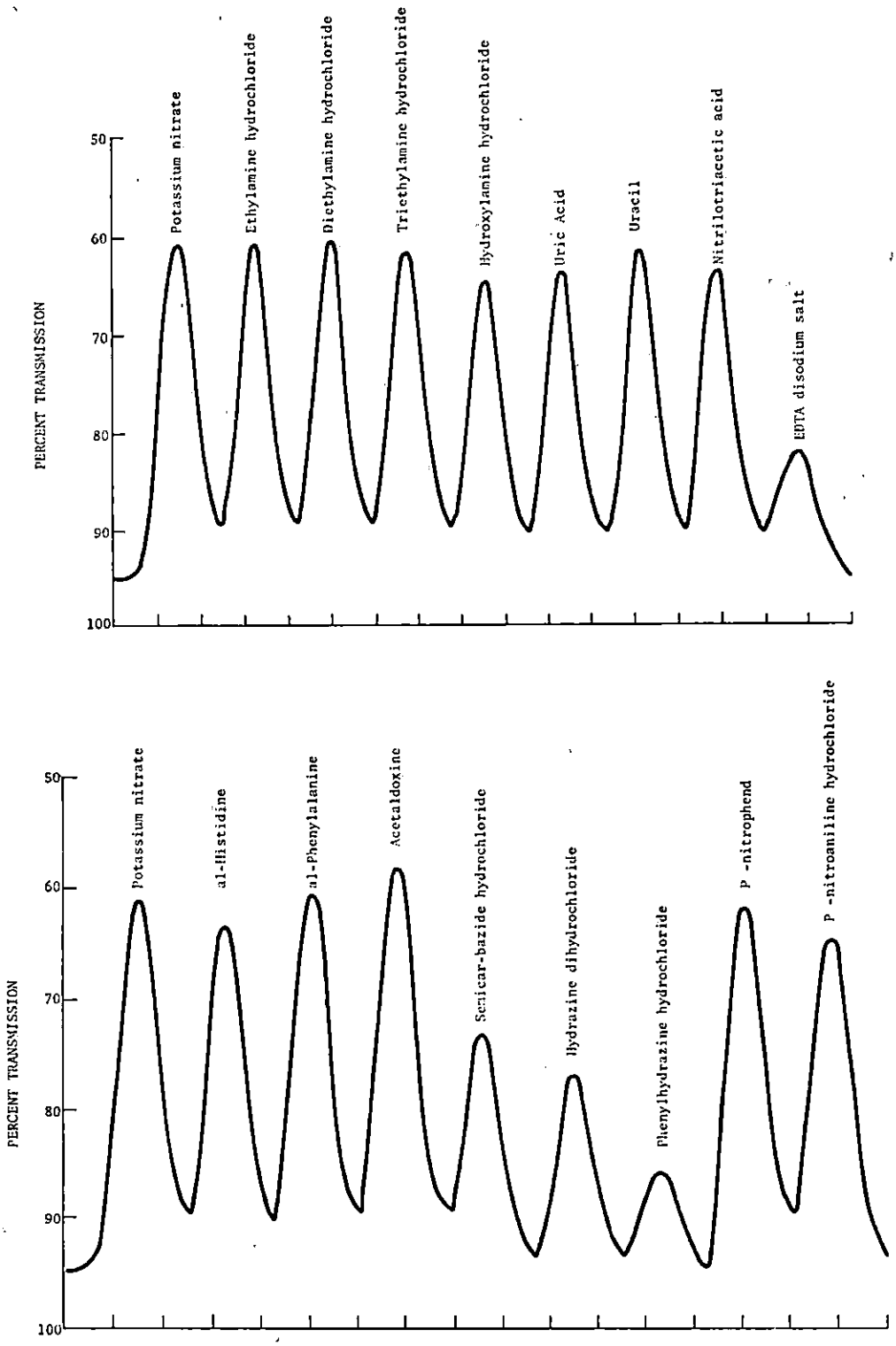


Figure 8, 9. Typical graphs showing the efficiency of UV-irradiation in oxidizing different organic compounds.

Figure 10 shows the calibration curve obtained for organic nitrogenous compounds containing from 0.1 to 0.6 mg/l nitrogen. Since different calibration curves are sometimes obtained in distilled water and natural water, other calibration curves were also obtained using synthetic lake water and lake water spiked with known amounts of nitrogenous compounds. Identical calibration curves were obtained in all cases. The lower detection limit for different forms of nitrogen, using this particular system, was found to be 20 ug/l, provided that relative concentrations of the individual forms of nitrogen are not too different. The precision of the method was calculated by determining the percent standard deviation from multiple analyses of a series of 11 solutions each containing 200 ug/l of organic nitrogen. The coefficient of variation was found to be 2.02 percent.

Table IV shows the typical results obtained for Lake Ontario water from the Burlington area for the total soluble nitrogen content together with the concentration of individual forms of nitrogen.

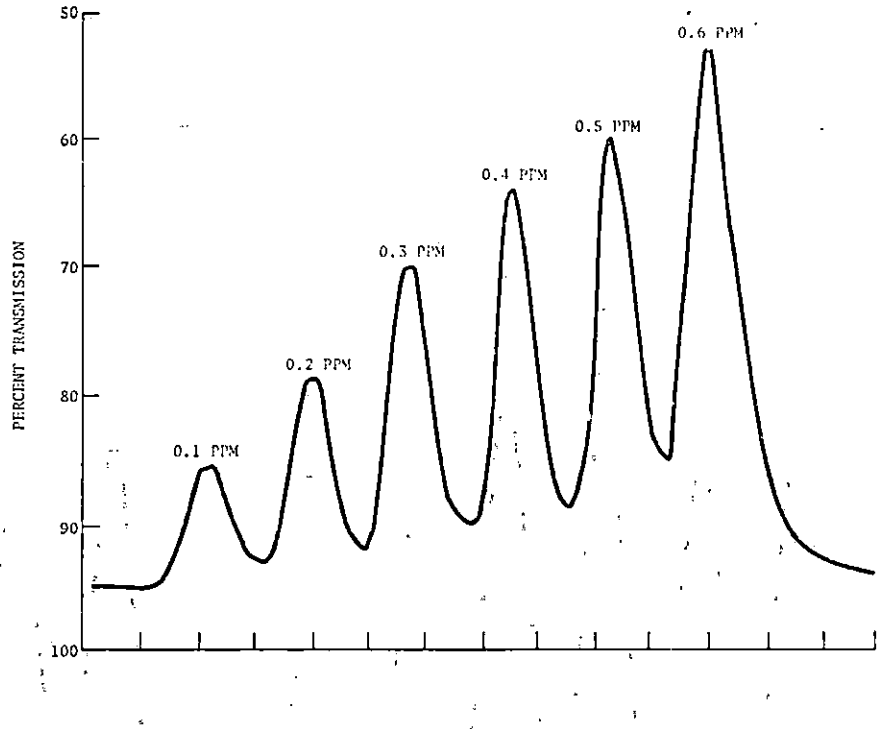


Figure 10. Calibration curve using glycine as standard for organic nitrogen.

TABLE IV

Analysis of Lake Ontario Samples from Burlington Area

| Sample No. | Amount of Nitrogen Added ug/litre | Amount of Nitrogen Found ug/litre |
|---|---|---|
| 1375F | - | As total nitrogen - 780 |
| | - | As nitrate plus nitrite - 275 |
| | - | As ammonia - 295 |
| | - | As organic nitrogen - 210 |
| | As ammonia - 100 | As total nitrogen - 885 |
| | As nitrate - 100 | As total nitrogen - 880 |
| | As glycine - 100 | As total nitrogen - 885 |
| 1311 | - | As total nitrogen - 170 |
| | - | As nitrate plus nitrite - 0 |
| | - | As ammonia - 0 |
| | - | As organic nitrogen - 170 |
| | As ammonia - 100 | As total nitrogen - 270 |
| | As nitrate - 100 | As total nitrogen - 270 |
| | As glycine - 100 | As total nitrogen - 275 |
| 1319 | - | As total nitrogen - 470 |
| | - | As nitrate plus nitrite - 210 |
| | - | As ammonia - 0 |
| | - | As organic nitrogen - 260 |
| | As ammonia - 100 | As total nitrogen - 575 |
| | As nitrate - 100 | As total nitrogen - 570 |
| | As glycine - 100 | As total nitrogen - 555 |
| 1415 | - | As total nitrogen - 660 |
| | - | As nitrate plus nitrite - 430 |
| | - | As ammonia - 0 |
| | - | As organic nitrogen - 230 |
| | As ammonia - 100 | As total nitrogen - 755 |
| | As nitrate - 100 | As total nitrogen - 765 |
| | As glycine - 100 | As total nitrogen - 760 |
| 1439F | - | As total nitrogen - 310 |
| | - | As nitrate plus nitrite - 200 |
| | - | As ammonia - 100 |
| | - | As organic nitrogen - 10 |
| | As ammonia - 100 | As total nitrogen - 400 |
| | As nitrate - 100 | As total nitrogen - 410 |
| | As glycine - 100 | As total nitrogen - 400 |
| 1268F | - | As total nitrogen - 300 |
| | - | As nitrate plus nitrite - 100 |
| | - | As ammonia - 50 |
| | - | As organic nitrogen - 150 |
| | As ammonia - 100 | As total nitrogen - 395 |
| | As nitrate - 100 | As total nitrogen - 400 |
| | As glycine - 100 | As total nitrogen - 400 |

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