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# Conversion of Six Chemical Water Tests from Manual to Automated Methods

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## ABSTRACT

Water quality assessments were made by a Technicon Basic Auto Analyzer system equipped with a Sampler II. This method replaced manual methods used during the first year of testing. Several problems were observed and corrected during the undertaking. It was necessary to modify manifolds, to increase sensitivity, to correct problems of turbidity, and to assure reagent stability.

## INTRODUCTION

This paper concerns automation of procedures used in assessing water quality in Lake Dardanelle and some of its tributaries as it is affected by poultry effluents, and the effect of buildups of these pollutants on the zooplankton populations.

Samples came from eight stations on Lake Dardanelle and five stations on feeder tributaries. The stations ranged from points close to the lake itself to points approximately 20 miles from the lake. Testing started on 3 June 1970 and continued until 21 October 1970 for the first year. The second year of testing ran from 1 June 1971 to 16 November 1971. During both years, sampling was generally on a weekly basis for the first three months of testing and on a biweekly schedule for the remaining period.

The Chemistry Department at Arkansas Polytechnic College acquired a Technicon Basic Auto Analyzer with a Sampler II prior to the starting date of sampling for the second year of the project. This device made possible the automation of several water quality tests which had been performed by manual methods during the first period of testing. These tests had been performed on the Hach DR "Direct Reading" colorimeter and with Hach titration methods (Hach, Methods Manual, 5th Ed.).

Tests performed with the Hach kits included chloride (mercuric nitrate method), nitrate (nitrogen cadmium reduction method), phosphate (stannous reduction method), and total hardness (EDTA method). During the first year of the project ammonia levels were not determined and the determination of uric acid concentrations proved unsuccessful.

## MATERIALS AND METHODS

The samples were labeled as they were collected. In the laboratory they were filtered through a Millipore filtering apparatus with a 0.45-micron pore size. The filtrates were stored in the refrigerator at a temperature of approximately 4C on the day they were collected. Several tests were performed on the samples before filtration and storage.

The chemical analyses of nitrate-nitrite, chloride, ortho-phosphate, ammonia, total hardness, and uric acid were performed on a Technicon Basic Auto Analyzer equipped with a Sampler II and a 15-mm flow cell.

During the second year of testing a colorimeter equipped with a 50-mm flow cell was used in some procedures. The modules of the basic system used included:

1. sampler
2. proportional pump (with specific manifold),
3. heat bath (used in NH<sub>3</sub> & nitrate-nitrite procedures),
4. colorimeter (with specific filters), and
5. recorder.

The principles of the reaction in the procedures for nitrate-nitrite, chloride, phosphate, ammonia, total hardness, and uric acid come from Technicon Auto Analyzer methodology (Technicon, Vol. II, III). All tests performed on the Auto Analyzer were color-producing reactions.

The platen manifolds for the ammonia, nitrate-nitrite, and total hardness tests were industrial manifolds and required only minor adjustments. The manifolds used in the chloride, phosphate, and uric acid tests were clinical manifolds and required modification.

In the chloride procedure, the color reagent consisted of the following chemical composition:

1. saturated aqueous mercuric thiocyanate (900 ml),
2. ferric nitrate solution (100 ml), and
3. mercuric nitrate solution, approximately 3.5 ml.

The mercuric nitrate solution was used to adjust the sensitivity of the color by reacting with the chloride ion first. The more Hg(NO<sub>3</sub>)<sub>2</sub> that is added, the greater the reduction of chloride ions present in the sample. It therefore is recommended that the Hg(NO<sub>3</sub>)<sub>2</sub> be omitted from the color reagent when samples of low chloride-ion content are being tested.

In the phosphate procedure the stannous chloride-hydrazine reduces the phosphomolybdic acid which is formed, producing a color reaction which is then measured colorimetrically. The stannous chloride-hydrazine sulfate working solution had the following chemical composition:

1. stannous chloride (200 mg) and
2. 0.2% hydrazine sulfate in 1.0 N H<sub>2</sub>SO<sub>4</sub>, q.s. (1000 ml).

The stability of this reagent must be checked! The recommended duration for stability, at room temperature, is two weeks. The writer found that this reagent could be used for longer periods; however, as the reagent aged, a decrease in peak size was noted.

Both the sodium carbonate method and the cyanide-urea method for uric acid were tried and proved unsuccessful. The hydroxylamine method using 40% sodium tungstate as a stable alkalizing agent was found to be sensitive enough to produce good results at the low concentrations being tested. The reagents in this procedure included:

1. 0.2% hydroxylamine hydrochloride,
2. 40% sodium tungstate, and
3. phosphotungstate acid.

The use of this procedure with a 50-mm flow cell and 660-nm filters provided reproducible results.

The dialyzer module was not utilized in any of the procedures performed on the Auto Analyzer. Reagents were added directly to the prefiltered water samples.

## RESULTS AND DISCUSSION

When the process of automation was started, four major problems became apparent:

1. The manifolds required modification.
2. The sensitivity of the colorimeter was inadequate.
3. Turbidity had to be eliminated from the samples.
4. Reagent stability had to be assured.

**Manifolds.** Three of the manifolds purchased originally with the machine were designed for clinical analysis of body fluids, in which concentrations are very high in comparison with those generally found in water. This problem was corrected by determining the reagents-to-sample ratio giving the best results; when this ratio had been determined, the manifold was rebuilt to suit the need. In several procedures, an additional sample tube was used to introduce more sample into the system because of the small quantities of certain materials present in the water. This was accomplished easily by use of the proper fittings and tubing on the manifold.

If the amounts of sample and/or reagents being pumped across the manifolds are increased, it is essential that the inside diameter of the air tube be increased also to establish a better bubble pattern. A good bubble pattern is essential for acceptable results in this type of automated system.

Samples collected from streams and tributaries had very low chloride levels. Those taken in the lake proper had very high chloride levels. To retain the accuracy of the low readings the mercuric nitrate was omitted from the color-reagent solution. To accommodate the higher readings, a dilution factor was employed. A dilution factor of three was generally satisfactory. Distilled water was used as the diluent. The saline diluent tube was converted to a sample tube. The two sample tubes were joined by a DO fitting. Sample flow in the two tubes totaled 2.68 ml/min. This was read in a 15-mm flow cell with 480-nm filters. Sampling rate was 60 samples per hour with a 2:1 sample-to-wash ratio.

In the determination of phosphate an increase in sample size was required. This was accomplished by joining the saline diluent tube with the sample tube by a DO fitting. The total amount of sample aspirated across the manifold was 7.80

ml/min. The stream was read in a 15-mm flow cell with 660-nm filters during the first part of the project and then in a 50-mm flow cell with 830-nm filters. The test was run at the rate of 60 samples per hour with a 2:1 sample-to-wash ratio.

The clinical cyanide-urea manifold used in the determination of uric acid required modifications. The sample tube was changed from 0.10 to 0.60 ml/min (Fig. 1, a) and the saline diluent tube was changed from 1.0 to 0.42 ml/min (Fig. 1, b) and was converted to a sample tube by joining the two tubes with a DO fitting (Fig. 1, c). The inside diameter of the air tube was increased from 0.64 to 0.89 mm.

The single tube that was introduced into the stream was converted to a three-tube assembly by an HO fitting (Fig. 1, d). This made it possible to add the reagent  $\text{NH}_4\text{OH}\cdot\text{HCl}$  to the stream of 40%  $\text{Na}_2\text{WO}_4$  (Fig. 1, e) and the air tube (Fig. 1, f). It is important that the stream maintain a bubble pattern that will segment the solution at least once in each turn of the mixing coil to guarantee proper mixing. The double mixing coils were separated in the middle and equipped with a DO fitting to introduce the phosphotungstic reagent at this point (Fig. 1, g). An eleven-turn mixing coil was added to the stream (Fig. 1, h) to allow sufficient mixing. A 3-m delay coil (Fig. 1, i), with an inside diameter of 1.6 mm, was added to the system to allow a greater reaction time. The test was run at a rate of 40 samples per hour with a 2:1 sample-to-wash ratio. This modified system gave reproducible readings.

**Colorimeter.** The sensitivity of the colorimeter, which was equipped with a 15-mm flow cell, was inadequate to detect some of the very low concentrations of certain materials being tested. The problem was corrected when Technicon Instruments Corporation of Tarrytown, New York, made available a colorimeter equipped with a 50-mm flow cell.

**Turbidity.** The problem of turbidity in samples was eliminated by preliminary filtration with a Millipore filtration apparatus (Millipore Corp., 1969) equipped with 47-mm HA 0.45-micron pore size filter disk. Results similar to those reported by Kahn (1968) were observed. He found in his determinations of chloride in fresh and salt water that preliminary filtrations negated the need of the dialyzer or continuous filter, which had been employed by other investigators. In an automated procedure, the turbidity factor must be corrected before the samples are aspirated across the manifold. In some manual methods, the problem of slight turbidity of samples theoretically is corrected by the process of "self blanking."

**Reagent stability.** To assure accurate results the stability of reagents must be maintained and a preparation of reagent schedule followed. In projects concerned with the continuous monitoring of water quality in a given body of water, waste of reagents does not occur because of the large amounts of reagents which are consumed. Cananzaro et al. (1968) found in an automatic continuous multiple analysis of water in the Hudson River at Albany, New York, that it was practical to prepare quantities of reagents which would supply a two-week testing period. Quantities larger than this presented problems in storage space and stability, among others.

Some of the major advantages in the use of an instrument such as the Basic Auto Analyzer in water quality testing are the ease of running duplicate samples and standards to check

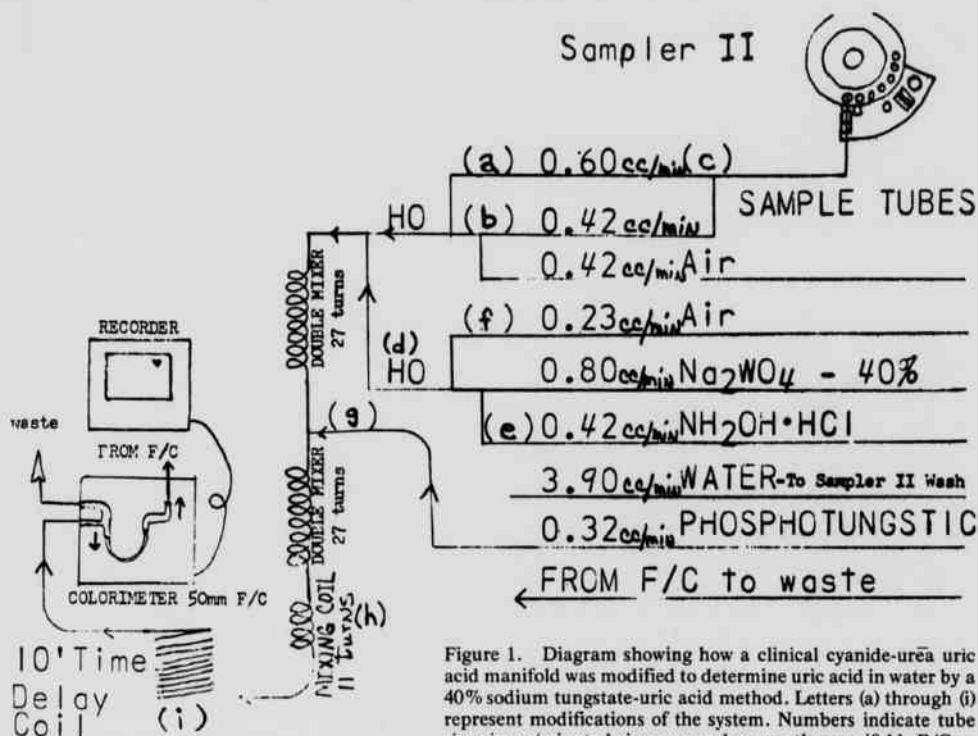


Figure 1. Diagram showing how a clinical cyanide-uric acid manifold was modified to determine uric acid in water by a 40% sodium tungstate-uric acid method. Letters (a) through (i) represent modifications of the system. Numbers indicate tube sizes in cc/minute being pumped across the manifold. F/C = flow cell.

reproductibility of the machine and the convenience in assessing reagent blank readings. The design and arrangement of the manifolds make it possible to adapt many types of modifications to the machine and give the device great versatility.

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