

# The Continuous Determination of Low Level Iron, Soluble Phosphate, and Total Phosphate with the AutoAnalyzer

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The Wahnbach Reservoir Authority, whose job it is to prepare the drinking water for the Bonn Siegburg area utilizes a reservoir of 33,740 cu ft capacity. At the moment this authority is engaged in a research project to develop methods to stem eutrophic development in the reservoir.

In this research project it was desired to ascertain how far the plant growth in the reservoir could be reduced when the total phosphate content of the Wahn River, which is the main feed water for the reservoir, is treated with iron salts to reduce the phosphate content to less than 10  $\mu\text{g/liter}$  of phosphorus. In order to carry out this phosphate removal and to develop methods for dephosphating the water, an experimental plant was set up at the mouth of the Wahn River.

In the course of these experiments it was necessary to perform continuous analyses for total iron, soluble ortho-phosphate and total phosphate on samples of river water, and on samples from the dephosphating plant. In order to check the efficiency of phosphate removal by the experimental plant, continuous analyses are required for the estimations of iron and phosphate in the water after treatment. From the iron content, conclusions can be drawn about the quantity of undissolved phosphate that is present in the treated water. When the iron content is under 0.05 mg/liter, then the concentration of undissolved phosphate is less than 5  $\mu\text{g/liter}$  of phosphorus.

The demand for continuous iron and phosphate analyses and the need to examine daily a large number of water samples for their iron, soluble phosphate and total phosphate content made the installation of some form of automated analytical equipment essential. In order to achieve this automation a Technicon AutoAnalyzer was used. We have developed for the AutoAnalyzer a new iron method and also a digestion procedure for the determination of total phosphate.

## Methods

The existing methods for soluble phosphate have been modified so that a continuous determination

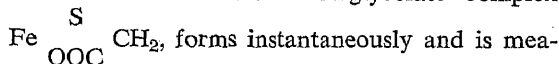
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of phosphate down to 2  $\mu\text{g/liter}$  of phosphorus can be performed in the plant.

### 1. Continuous Total Iron Determination with the AutoAnalyzer

The continuous determination of iron with the AutoAnalyzer is based on the thioglycolic acid method for total iron described by Klump *et al* (1). The pump tubes were so chosen that the ratio of reagents: sample is correct after the 2 concentrated reagents have been diluted 1:10 (Fig. 1).

The air-segmented water sample is mixed with thioglycolic acid to reduce the trivalent iron to ferrous iron. After the addition of ammonia the red colored ferrous thioglycolate complex



The calibration graph obtained from this method is shown in Fig. 2. Using the sampling rate of 20 samples/hr there was no carryover from one sample to the next even when high and low samples followed one after another.

The standard deviation calculated from 100 measurements from a standard solution of 50  $\mu\text{g/liter}$  iron was  $\pm 7 \mu\text{g/liter}$  iron for a single measurement. Hardness up to 890 mg/liter  $\text{CaCO}_3$  (50°d), sulfate ions up to 200 mg/liter and sulfide up to 1 mg/liter do not interfere with the determination of 50  $\mu\text{g/liter}$  iron. Larger quantities of manganese do not have a negative influence on the process, if the reaction time is prolonged.

The following reagent solutions were used:

*Thioglycolic Acid:* prepare an 8% v/v solution in 2X distilled water.

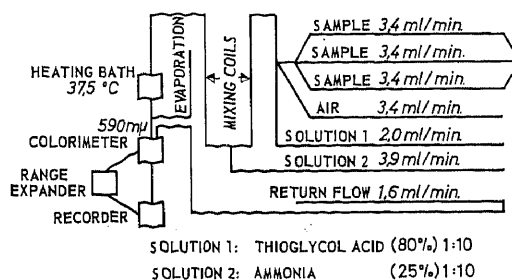


Figure 1

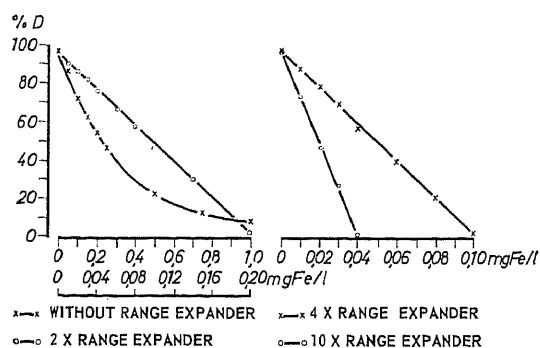


Figure 2

**Ammonia Solution:** dilute AnalaR ammonia solution such that the final solution contains 2.5% w/v ammonia.

## 2. Phosphate Determination

The separation of soluble ortho phosphate from undissolved phosphate is normally carried out by membrane filtration using an MF 15 membrane filter (pore size 270  $\mu$ ). In the filtrate from the membrane filtration the phosphate has been determined by the manual method of Ohle (2).

### The Continuous Determination of Soluble Phosphate

An attempt was made to adapt the method of Ohle (3) for the determination of soluble phosphate for use with the AutoAnalyzer. This method gave satisfactory results but unfortunately after a while the walls of the flowcell became coated with a basic tin salt, and this resulted in a baseline drift. After the flowcell had been cleaned the same results could be obtained again. However, this method was unsatisfactory for long term use in the plant.

For the same reason it was not possible to apply Grasshoff's method (3) for the AutoAnalyzer according to the method of Murphy and Riley (4) using ascorbic acid as a reducing agent and antimony as a catalyst as described also by Vogler (5), because coating of the cell caused a drift of the zero point over a long time. Henriksen (6) developed a method for the AutoAnalyzer on the basis of the extraction method according to Martin and Doty (4), which is relatively complicated and above all very expensive over a long period (ca. \$560/year). For this reason this method was not good for this purpose.

Good results were obtained with hydrazine sulfate reducing agent as described by Whitley and Alburn (8), with a satisfactory baseline at zero point. This method is also simple and not

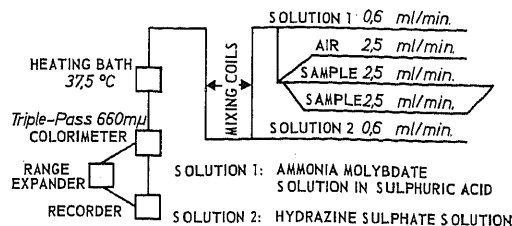


Figure 3

very expensive over a long period (\$60/year).

Fig. 3 shows the flow diagram for this method. The air-segmented sample stream is mixed with acid ammonium molybdate solution. In order to reduce the yellow phosphomolybdate complex to molybdenum blue the solution is mixed with hydrazine sulphate and passed through a heating bath at 37.5°C. The extinction is measured in a 15 mm triple pass flowcell at 660  $\mu$ .

Fig. 4 shows the calibration graph without range expansion and with the scale 2, 4, and 10 $\times$  expanded. With the range expander set at times 10 the transmission for 2  $\mu$ /liter of phosphorus was 94%. This peak can still be measured with a good accuracy.

With the range expander set at times 10 the accuracy of the method is approximately  $\pm 2 \mu$ /liter of phosphorus. Variations in the pH of the sample between 5 and 9 are without effect on the results. We have performed a large number of experiments in order to establish that the presence of up to 10 mg/liter of silica is without effect on the results.

From the results of 100 single measurements of phosphate standard solution of 5  $\mu$ /liter phosphorus we calculated a standard deviation of  $\pm 0.5 \mu$ /liter phosphorus per single measurement.

The baseline is constant over a period of 24 hr and fulfills the requirements necessary for continuous on-stream analysis. The reliability of the AutoAnalyzer procedure was tested over a period

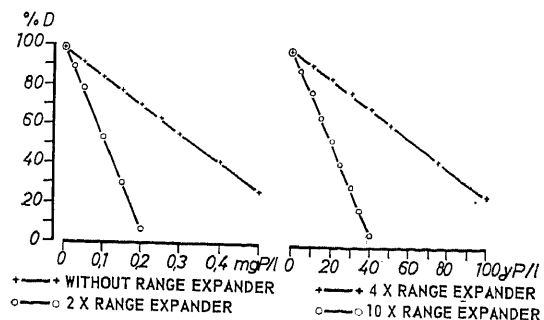


Figure 4

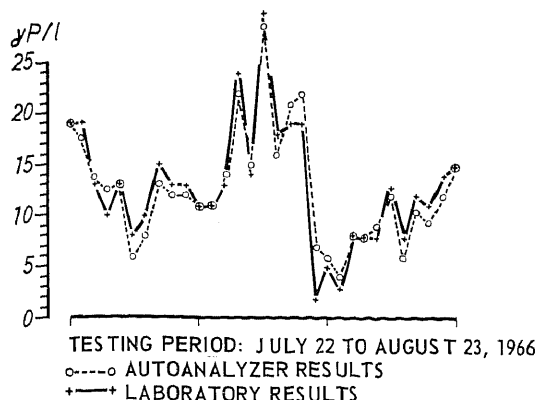


Figure 5

of 4 weeks by taking daily samples and analyzing them in the laboratory by the method of Ohle (2).

A comparison of both results obtained is shown in Fig. 5.

The following reagents were used:

*Ammonium Molybdate/Sulfuric Acid Reagent  
 Soluble phosphate determination*

150 g ammonium molybdate AnalaR are dissolved in 2000 ml of doubly distilled water and this is mixed with 2000 ml of diluted sulfuric acid, and the whole diluted to 5000 ml with water (to prepare the diluted sulfuric acid pour 833 ml of concentrated sulfuric acid into 1000 ml of water and after cooling dilute to 2000 ml with water).

*Hydrazine Solution*

Dissolve 10 g of AnalaR hydrazine sulfate in 5000 ml of doubly distilled water and add 10 drops of Levor IV.

**The Continuous Determination of Total Phosphate with the Digester**

In order to be able to measure total phosphate continuously it is necessary to automate the digestion of the sample with acid. This digestion is normally made with concentrated sulfuric acid and potassium persulfate (2,9). The sulfuric acid is heated until fumes of sulfur trioxide are evolved, care being taken not to heat the solution too strongly as this causes loss of phosphorus (9). After the sulfuric acid digestion the pH of the solution must be brought to exactly the right value with ammonia solution. The intensity of the molybdenum blue complex is influenced firstly by the amount of free sulfuric acid and also by the amount of sulfuric acid that is converted to ammonium sulfate during the neutralization.

For the continuous digestion of the sample we

used the Technicon Digester in combination with the method already described for the determination of soluble phosphate.

During the development of the method we encountered the following difficulties:

a.) The potassium persulfate used for the oxidation of the sample must be totally destroyed before the ammonium molybdate solution is added. In order to test for persulfate the digestate was mixed with silver nitrate and a manganous salt. The formation of the potassium permanganate color in the solution showed that the divalent manganese had been oxidized to the 7 valent state, this indicates the presence of residual persulfate in the digestate. The quantity of persulfate that can be used is controlled by the speed of rotation of the helix and the temperature of the sulfuric acid.

An attempt to replace the potassium persulfate by perchloric acid or nitric acid failed to improve the analytical results. With the first stage heaters set at 3.8 amps and the second stage at 4.8 amps we found after many experiments that the best results were obtained with a 2% solution of potassium persulfate. For the neutralization we used a solution prepared by diluting 25% ammonia solution 1:9 with doubly distilled water.

b.) The neutralization of the strong sulfuric acid in the digestate must be complete and reproducible. Because of the large difference in the specific gravities of the sulfuric acid solution and of the diluted ammonia solution used for neutralization it was impossible to obtain adequate mixing in a mixing coil. Only through the use of a small chamber containing a Sampler II mixer was it possible to get adequate mixing of the 2 solutions. The reproducibility of the neutralization could not be checked with a pH meter but only through titrating the solution with .10 N caustic soda solution using phenolphthalein as indicator.

Fig. 6 shows the manifold. The sample is segmented with air and then mixed with concentrated

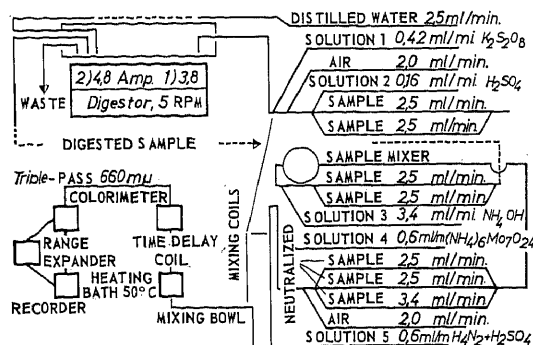


Figure 6

sulfuric acid and a 2% potassium persulfate solution. After flowing through a single mixing coil the analytical stream enters the digester. The digester is set at 5 rpm and the first stage heater current at 3.8 amps and the second stage current at 4.8 amps. On leaving the heating zone of the digester the solution is cooled by a stream of air and diluted with doubly distilled water. This diluted sample is then sampled by the second Proportioning Pump. The excess of sample is sucked to waste using a water pump. After neutralization with ammonia to a pH of 2.8-3.0 the stream enters the bottom of a small mixing chamber and is mixed with a Sampler II mixer. The mixed sample is sucked from the top of this mixing chamber and segmented with air. After the addition of the acid molybdate solution and the hydrazine sulfate solution the determination is the same as for soluble phosphate.

If one short-circuits the digester and sucks the water sample directly into the last part of the manifold, then the same system can be used for soluble phosphate. It has proved desirable to place before the flowcell a capillary mixer and a time delay coil. Only in this way was it found possible to achieve a low enough noise level when the range expander was set at  $\times 10$ .

Fig. 7 shows the calibration graph with  $4\times$  range expansion and  $10\times$  range expansion. With the sampling rate of 10 samples/hr satisfactory accuracy was obtained and with the range expander set at  $\times 10$  it is possible to measure  $5\ \mu\text{g/liter}$  of total phosphate.

The following reagent solutions were used:

*Sulfuric acid:* normal concentrated AnalaR reagent.

*Potassium Persulfate Solution:* prepare a 2% w/v solution.

*Ammonia Solution:* dilute AnalaR ammonia solution such that the final solution contains 2.5% w/v ammonia.

The ammonia molybdate/sulfuric acid reagent

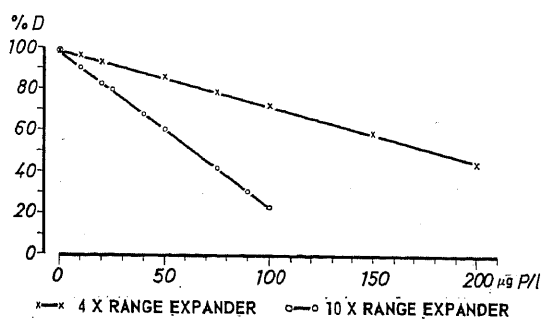


Figure 7

and the Hydrazine solution are the same as those used for the soluble phosphate.

### Accuracy of the Method

The results obtained for the analysis of several water samples with the AutoAnalyzer and by the hand method are shown in Table I. From the table one can see that the 2 methods give similar results. The measurements with the AutoAnalyzer were repeated several times and always gave the same results. The presence of silica up to  $10\ \text{mg/liter}$  does not interfere.

Table I. Comparison of AutoAnalyzer and Manual Phosphate Determination

Sample	AutoAnalyzer $\mu\text{g P/liter}$	Manual $\mu\text{g P/liter}$	Difference $\mu\text{g P/liter}$
1	23	22	+1
2	28	26	+2
3	8	4	+4
4	10	5	+5

A stream water that contained colloidal clay particles was doped with known amounts of soluble phosphate. These samples were then analyzed. The results obtained can be seen in Table II. The results shown for the recovery of added Phosphate from cloudy stream water show a good accuracy, and therefore it seems that the method is suitable for the continuous determination of small amounts of total Phosphate in stream water.

Table II. Phosphate Recovery in Dirty Water

Sample	Added $\mu\text{g P/liter}$	Concentration of $\mu\text{g P/liter}$		Difference $\mu\text{g P/liter}$
		Theoretical	Actual	
1	0	35	35	0
2	7	42	42	0
3	14	49	49	0
4	21	56	56	0
5	28	63	60	-3
6	35	70	66	-4
7	42	77	78	+1

### Conclusion

Methods have been described using an AutoAnalyzer for the continuous determination of total iron and soluble phosphate. Another method is described for the determination of total phosphate using the Digester. These methods allow the determination of iron down to  $10\ \mu\text{g/liter}$ , soluble phosphate down to  $2\ \mu\text{g/liter}$  and total phosphate down to  $5\ \mu\text{g/liter}$ . Details of the manifolds and analysis procedure are described.

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