

**DETERMINATION OF DISSOLVED OXYGEN IN  
WATER BY FLOW INJECTION ANALYSIS**

by

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## MANAGEMENT PERSPECTIVE

This report presents the results of the continuation of the study dealing with the problems related to the determination and monitoring of Dissolved Oxygen in natural waters. It describes the development and the function of the continuous flow injection system based on the "Winkler chemistry" using the spectrophotometric detection of Iodine. The difficulties of the absorption of colloidal particles and the diffusion of the ambient air into the system have been resolved. The method is suitable for automated analysis of large number of samples and limits the human error of other methods. The equipment is relatively inexpensive, the consumption of the reagent is very low and the system conducts all data handling, statistical calculation as well as data storage. Proposed method fulfills all requirements of the sensitivity, selectivity and efficiency. Practical application of the procedure should improve the quality of DO data as well as the economy of environmental analytical laboratories.

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## PERSPECTIVE-GESTION

Ce rapport présente les derniers résultats de l'étude sur les problèmes reliés au dosage et au contrôle continu de l'oxygène dissous dans les eaux naturelles. On y décrit l'élaboration et le fonctionnement d'un dispositif d'analyse par injection en phase mobile fondé sur la méthode de Winkler. Le dosage de l'oxygène dissous est effectué par détection de l'iode au moyen d'un spectrophotomètre. Les problèmes d'élimination des particules colloïdales et de diffusion de l'air ambiant dans le système ont été résolus. Cette méthode permet d'analyser de façon automatisée un grand nombre d'échantillons et comporte moins de risques d'erreurs humaines que les autres méthodes. Ce dispositif consomme très peu de réactif, l'équipement requis est relativement peu dispendieux et le système permet d'effectuer tous les traitements de données, les calculs statistiques et les opérations de stockage des données. Cette méthode est pleinement satisfaisante à tous égards; sensibilité, sélectivité et efficacité. Ce système devrait améliorer la qualité des données d'O.D. et s'avérera économique pour les laboratoires d'analyse.

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## ABSTRACT

A continuous flow method for the determination of dissolved oxygen in fresh water samples is described. The method is suitable for the analysis of large number of samples as well as for continuous monitoring. It utilizes Flow-Injection principle with in-line Winkler chemistry and spectrophotometric detection. Up to 120 samples/hour can be analysed with relative standard deviation of ca 2% and the detection limit of 0.1 ppm. The turbidity and colour of the samples do not interfere with the measurement. The operation of the system including calibration, calculation and statistical evaluation as well as data storage in main frame computer is governed by a PC work station.

## RÉSUMÉ

Nous décrivons une méthode d'analyse par injection en phase mobile permettant de doser l'oxygène dissous présent dans des échantillons d'eau douce. Cette méthode permet d'analyser un grand nombre d'échantillons et remplit les exigences des programmes de contrôle continu. La réaction de Winkler et le dosage par spectrophotométrie sont effectués en circuit au cours du processus d'injection en phase mobile. Jusqu'à 120 échantillons peuvent être analysés en une heure. L'écart-type relatif se situe aux environs de 2 % et le seuil de détection est de 0,1 ppm. Le dosage n'est pas perturbé par la turbidité et la couleur des échantillons. L'étalonnage, les calculs, l'évaluation statistique et le stockage des données dans l'unité centrale de traitement sont effectués au moyen d'un micro-ordinateur.

## INTRODUCTION

The availability of reliable data and values of dissolved oxygen is of great importance in aquatic environment diagnosis, water quality assessment and water management. Large numbers of water samples are being analysed for the content of dissolved oxygen. Most widely used methods are the titrimetric or spectrophotometric versions of the Winkler procedure (1-4). Voltametric methods using membrane electrodes are also frequently applied (5). Previously developed method of continuous flow and Flow-Injection systems require manual sample preparation and treatment (6). Several attempts to develop the continuous flow system including Winkler chemistry were not successful mainly due to the absorption of manganous hydroxide on tubing walls during the basic stage of the sample treatment procedure and due to the diffusion of the air through the tubing into the analytical system (7). The Flow-Injection system described in this paper is free of these problems.

## EXPERIMENTAL

### Reagents

All chemicals used were of analytical-reagent grade. Stock solutions prepared by weight were standardized by appropriate standard analytical procedures. Standard and working solutions were prepared from respective stock solutions by dilution with distilled-deionized water. Fresh water samples were collected from Hamilton Harbour (Lake Ontario) area. The calibration solutions containing known concentration of dissolved oxygen (DO) were prepared by bubbling the water with appropriate mixtures of oxygen-nitrogen gases at the constant temperature. The concentrations of DO ranged from 0.1 to 10 ppm.

### Apparatus

Sampling procedures and equipment used are described in "Standard Methods for Analysis of Water and Wastewater" (2). Spectrophotometric

measurements were performed on Hewlett Packard HP 8451A Diode Array Spectrophotometer. The "Winkler Chemistry" of the sample treatment was based on the procedure recommended by Strickland and Parson (8). The absorbance was measured at 287.5 and 349 nm in a 1 cm long and 2 mm ID silica flow-through cell. Sample containers were 100 mL glass bottles furnished with rubber and aluminum foil septa. The FIA system comprised a sample changer (modified Fisher Titralyser) capable of handling sample bottles and piercing the septa. A Multiflow Injector AMI-103 (Control Equipment Corp) provided the timing, pumping and injecting functions. The HP 8451A spectrophotometer conducted the data recording as well as all calculations, calibration and statistical evaluations. A Cole Parmer Ultrasonic Cleaner and a Haake Constant temperature bath were also incorporated in the system. In order to minimize the diffusion of the air into the system the PharMed tubing was used.

## Results and Discussion

The major problem of the development of the FIA method for the determination of DO was to eliminate the absorption of the colloidal manganous hydroxide on the walls of the tubing in the segment where the reaction with oxygen takes place. This has been achieved by the combined effect of the ultrasound and flushing of the tubing by a plug of sulphuric acid. These two operations created variations of the temperature and therefore the incorporation of the temperature bath was imperative.

## Description of the Continuous Flow System

During the "stand-by" situation (no sample in the system) the carrier liquid (1 M H<sub>2</sub>SO<sub>4</sub>) flows through the injector and is mixed with the manganous (0.1 M) reagent. After passing through 100 cm long mixing coil the solution of alkaline iodide (NaOH, 0.1 M, NaI, 0.5 M) is added. A second reaction coil (100 cm) is immersed in the ultrasonic bath. The next step is the addition of

0.5 M sulfuric acid followed by the passage through the constant temperature bath (25°C). Finally the stream enters the spectrophotometric detector and flows to the waste.

During the "sample in" situation the carrier stream is diverted to the waste and a preselected volume of the sample enters the system. Because the previously existing overall acid conditions do not exist within the sample segment, the "Winkler chemistry" reactions take place. The liberated iodine corresponding to the DO concentration in the sample is detected by the spectrophotometer. The peak height is directly and linearly related to the concentration of dissolved oxygen in the sample. Due to the linear response of the detector to the concentration of DO, a two point calibration is adequate.

The experimental arrangement suitable for analysing turbid and/or colored samples is illustrated in Fig. 1. It consists of the addition of the thiosulfate solution after the detector and of the incorporation of the second detector. The thiosulfate reacts with the iodine destroying the color and exposes the original color and turbidity of the sample. The subtraction of the signal of the second detector from the signal of the first detector gives the peak height corresponding to the actual concentration of DO.

The in-line continuous flow chemistry eliminates the process of the sample dilution (in the acid stage) which is required during the manual spectrophotometric procedure. This contributes to the better precision of the measurements. The Multiflow Injector AMI-103 used in this study generates the flow of all fluids by the nitrogen gas pressure instead of commonly used peristaltic pumps. It means that all solutions are oxygen free and are under the nitrogen atmosphere and the danger of air diffusing into the system does not exist. Due to the dark color of the PharMed tubing and connectors, the possibility of the photooxidation of the iodine has also been minimized.

The basic "Winkler" chemical reactions involved in the DO determination are given in Figure 2. Figure 3 is a typical strip chart record of increasing concentrations of DO at the sampling rate of 60 samples per hour.



The precision achieved with the described method was better than that of manual titration or of manual spectrophotometric procedure. Representative results are summarized in Table 1.

The presented method provides a fully automated, precise, sensitive and cost effective system of the determination of dissolved oxygen in large number of water samples. It is also well suited for monitoring and shipboard operation. The comparative summary of the three methods for DO determination (manual titration, manual colorimetry and colorimetry by FIA) is shown in Table 2.

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TABLE 1

Precision of DO determination (n = 10)

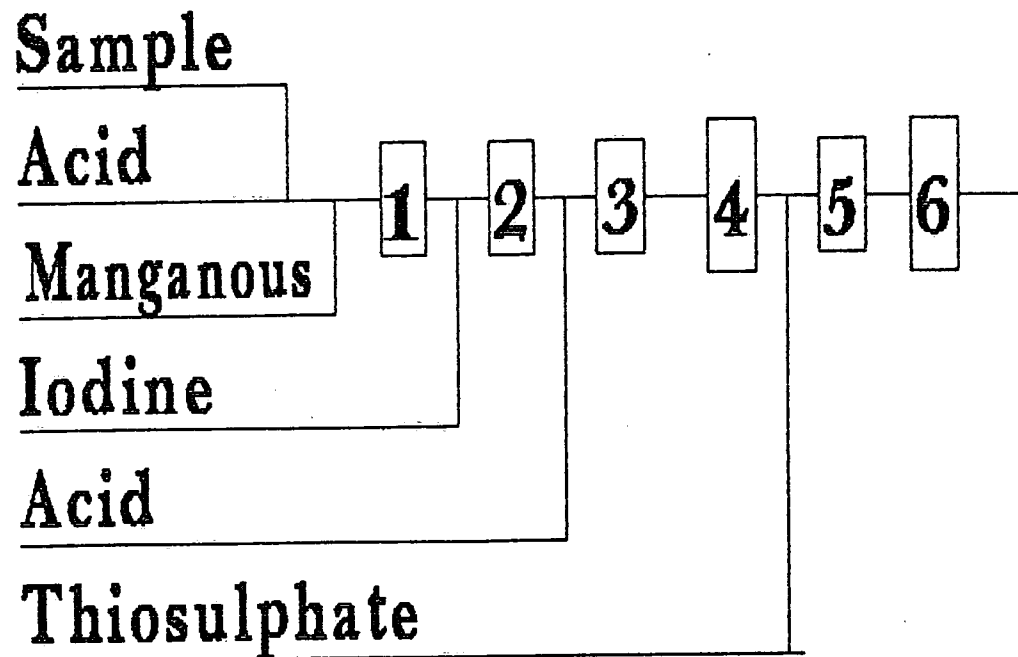
Concentration (Sample)	Mean	RSD %	Recovery %
10.0 ppm	10.09	2.3	n.a.
7.5 ppm	7.48	1.8	n.a.
5.0 ppm	4.93	2.3	n.a.
2.5 ppm	2.54	2.5	n.a.
1.0 ppm	1.04	3.4	n.a.
0.5 ppm	0.52	4.2	n.a.
Sample No. 1	6.33	2.1	98
Sample No. 2	5.72	1.9	102
Sample No. 3	4.92	2.5	104
Sample No. 4	8.76	1.5	101
Sample No. 5	3.45	3.1	103

n.a. = not applicable

TABLE 2  
A COMPARISON OF THE 3 METHODS OF DO DETERMINATION

	MANUAL TITRATION	MANUAL COLORIMETRY	COLORIMETRY BY FIA
Precision	± 0.1 mg/L	± 0.1 mg/L	± 0.05 mg/L
Complicated to use	Tedious	No	No
Operator Skill	High	Low	High
Sampling Rate	Low	Low	High
Automation	Difficult	Possible	Automated
In-Situ Analysis	No	Possible	Possible
Cost of Equipment	Low	Low	Medium
Human error factor	High	Medium	Low

**Figure 1**



**1-Mixing coil**

**4-Detector 1**

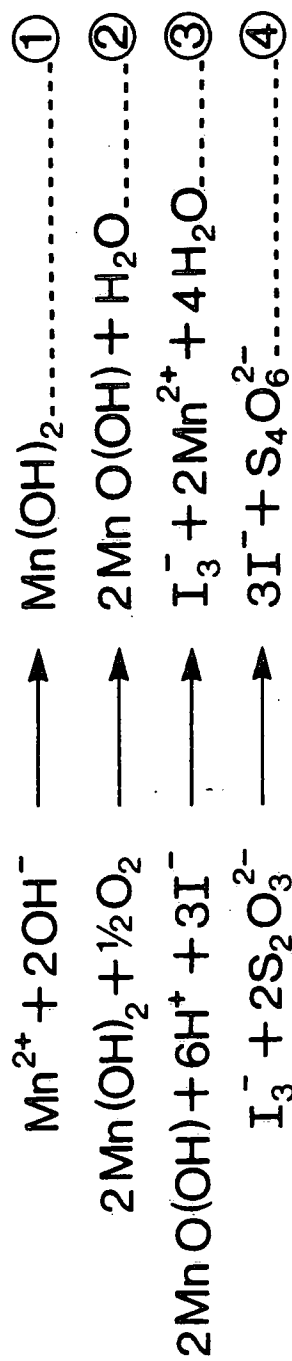
**2-Ultrasound**

**5-Coil**

**3-Const. Temp.**

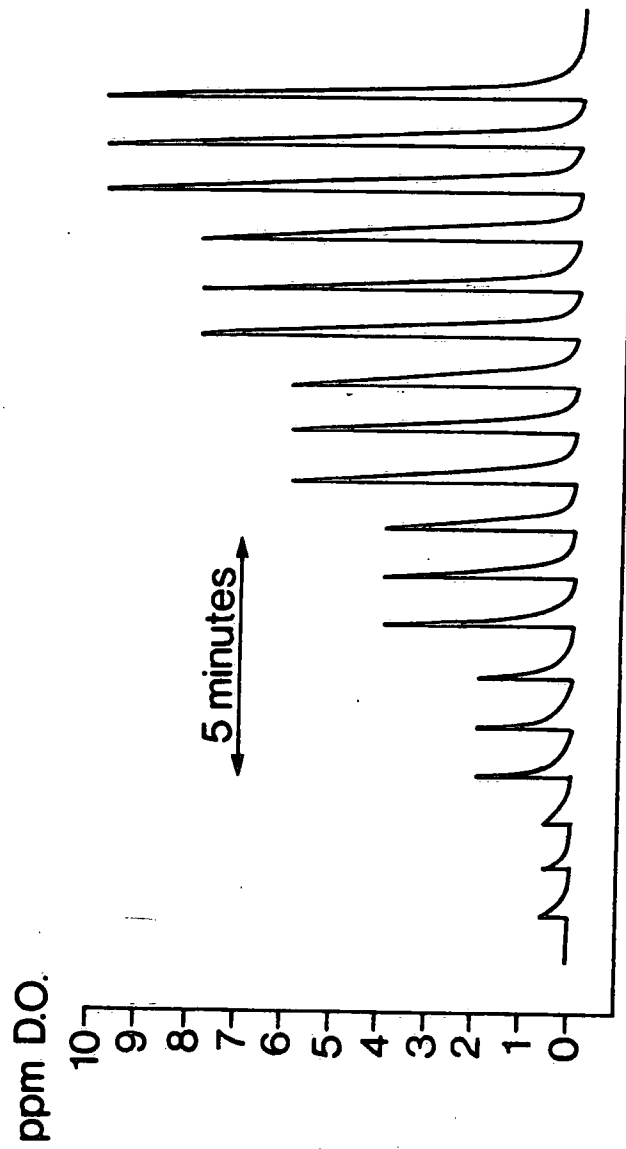
**6-Detector 2**

Figure 2.



Basic "Winkler" chemistry of DO analysis:

Figure 3.



A strip-chart record of different D.O. concentrations  
at the sampling rate of 60 s/h.