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**ANALYSIS FOR DISSOLVED OXYGEN IN
NATURAL WATER, INCLUDING SAMPLE PRESERVATION**

by

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MANAGEMENT PERSPECTIVE

This report presents the results of the study of the problems related to the determination and monitoring of Dissolved Oxygen (DO) in natural water. The problems of sample preservation prior to analysis were investigated and a procedure preserving the DO for up to 70 days was developed. Two detection methods have been studied and the spectrophotometric approach was found to be superior to the titration one.

The practical application of the conclusions and recommendations contained in this report should improve the quality of DO data as well as the efficiency in the operations of environmental laboratories.

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PERSPECTIVE-GESTION

On présente dans ce rapport les résultats de l'étude sur les problèmes liés au dosage et au contrôle de l'oxygène dissous (OD) dans les eaux naturelles. On a examiné les problèmes que constitue la conservation des échantillons avant l'analyse, et on a mis au point une méthode permettant de conserver pendant une période pouvant atteindre 70 jours les échantillons dont la teneur en oxygène dissous sera déterminée. Deux méthodes de détection ont été étudiées: la technique spectrophotométrique s'est révélée supérieure à la méthode par titrimétrie.

La mise en application des conclusions et des recommandations formulées dans ce rapport devrait permettre d'améliorer la qualité des données relatives à la teneur en oxygène dissous, ainsi que l'efficacité des laboratoires s'occupant de l'analyse d'échantillons environnementaux.

ABSTRACT

A sample preservation procedure as part of the determination of dissolved oxygen (DO) in natural water by a modified Winkler method is described. The procedure involves the "in situ" treatment of the samples to the acid stage of the Winkler procedure. DO in preserved samples was stabilized for at least 70 days. Colorimetric and titrimetric methods for the quantitation of dissolved oxygen were evaluated and colorimetry was found to be a superior method. A simple flow injection analysis method for the determination of dissolved oxygen in large number of samples is described. Up to 120 samples/h can be analysed with a relative standard deviation of 2% and a detection limit of 0.5 ppm.

Key words - Natural water, dissolved oxygen, preservation, determination

RÉSUMÉ

On décrit une méthode de conservation d'échantillons utilisée dans le cadre du dosage de l'oxygène dissous (OD) dans les eaux naturelles par la méthode modifiée de Winkler. Cette méthode de conservation comporte le traitement in situ des échantillons jusqu'à l'étape de l'acide dans la méthode de Winkler. L'oxygène dissous dans les échantillons ainsi conservés est stabilisé pendant au moins 70 jours. On a évalué le dosage de l'oxygène dissous par colorimétrie et par titrimétrie, et on a constaté que la méthode colorimétrique était supérieure. On décrit une méthode simple par injection en courant de réactif permettant de doser l'oxygène dissous dans un grand nombre d'échantillons. Cette méthode, dont la limite de détection est de 0,5 ppm, permet d'analyser 120 échantillons à l'heure avec un écart-type relatif de 2 %.

Mots clés - eaux naturelles, oxygène dissous, conservation, dosage

INTRODUCTION

In water quality characterization, the analysis for dissolved oxygen (DO) is extremely important. DO levels in water are dependent on the physical, chemical, biochemical and biological activities occurring in the water body; therefore DO is used as a primary indicator in pollution abatement and is a vital parameter of water treatment. The Winkler method with its modifications (1,2) is widely used for DO analysis and is generally accepted as the standard method. A solution of manganous sulphate and an alkaline solution of potassium iodide are added to the sample, forming a precipitate of manganous hydroxide, with part of it reacts with oxygen to give manganic hydroxide. Upon acidification, a quantity of free iodine is released. The amount of iodine released is equivalent to the oxygen originally present in the sample. The free iodine is measured either by titrating the sample with a sodium thiosulphate solution using starch as an indicator or by spectrophotometric determination of light transmission at 287.5 (3), 349 (4) or 450 (5,6) μm . Voltametric methods, including membrane electrodes (7), were not included in this study.

For many applications, the Winkler method lacks the necessary accuracy and precision (3). The problems have been related to photochemical oxidation of iodine, loss of iodine by volatilization (8), and difficulties with the definition of the titration end-point. Great care is required in collecting water samples for DO measurement as the samples must not remain in contact with air, nor be agitated. The time lag between sampling and performing the analysis is of great significance. Errors and difficulties associated with the sampling can be minimized by analyzing for DO "in situ". The other possibility is to use a preservation procedure which stabilizes the sample with respect to DO for the time period between sampling and analyzing. The aim of this study was to establish a preservation procedure adequate for a 10 weeks time interval between sampling and analysis. Another objective of the study was to evaluate and compare the performance of titrimetric and colorimetric methods. Furthermore, the flow injection technique was investigated as part of our efforts to develop

a method suitable for analysis of a large number of samples, in a cost effective, efficient and precise way.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent grade. Stock solutions prepared by weight were standardized by appropriate standards analytical methods. Standards and working solutions were prepared from respective stock solutions by dilution with distilled-deionized water. Natural water samples were collected from Hamilton Harbour (Lake Ontario) area. Ten calibration concentrations of DO (0.1 to 10 ppm) were prepared by bubbling the distilled water at a constant temperature with appropriate mixtures of nitrogen-oxygen.

Apparatus

The sampling procedures and equipment used in this study have been described in "Standard Methods for Analysis of Water and Wastewater (4)". The spectrophotometric measurements were performed using a Hewlett Packard HP8451A Diode Array Spectrophotometer. Samples treatment prior to spectrophotometry followed the method described by Strickland and Parsons (10). The adsorbance of each sample was measured at 287.5 and 349 nm in 1 cm silica cells.

The "Winkler" manual titration procedure recommended by Carritt and Carpenter (8) was chosen. The flow injection analysis (FIA) system comprised a sampler changer (ISCO-ISIS), a peristaltic pump (Lachat), two pneumatically operated Rheodyne six-port valves and a Lachat-QuickChem four channel spectrophotometer equipped with 1 mm diameter flow through cells. The timing of the system was governed by a Xanadu Programmable Timer. The signals of the

detectors were recorded by a Philips PH8252A two line recorder. Two versions of the FIA assembly (serial and parallel detectors) are shown in Fig. 1 and 2.

Preservation Procedures

Three versions of bottles used for Biological Oxygen Demand (BOD) determinations were used to collect and store samples, namely a set of standard BOD bottles, a set of black BOD bottles and a set of black bottles equipped with air tight plastic caps. The samples were divided into three groups: group A consisted of three sets of untreated samples, group B, samples treated by the addition of manganous, iodide, azide and hydroxide solutions (basic stage of Winkler procedure) and group C, samples treated to the full extent of the "Winkler" procedure (Mn^{2+} , I^- , N_3^- , OH^- - mixing - H_2SO_4). BOD bottles were stored at the laboratory temperature ($22^\circ C$). Each group was divided in three subgroups and stored in clear BOD, ($A_1B_1C_1$) black BOD ($A_2B_2C_2$) and black BOD bottles with sealing caps ($A_3B_3C_3$). Determinations of DO were performed at one week intervals by the manual titration as well as by the colorimetric method. After each determination the samples were discarded.

RESULTS AND DISCUSSIONS

Preservation Study

The results of the preservation study are summarized in Fig. 3. The definition of the stability of the samples in regard to DO was derived arbitrarily as the deviation from the initial DO value by more than $\pm 5\%$ taking into account the reproducibility of the methods of determination. From Fig. 3, it is obvious that the samples without treatment are not suitable for DO

determination unless the analysis is performed immediately after sampling. The samples treated to the basic stage of "Winkler" procedure showed better stability of DO, whereas the full treatment (acid) stage produced the best stability of DO.

With respect to results obtained with the different BOD bottles used, the maximal stability was achieved in the samples kept in black bottles with air tight seal caps.

In summary, the optimal preservation procedure is to use black BOD bottles equipped with plastic air tight seal caps and treat the samples to "acid" stage of the Winkler method. However, the "basic" treatment may be considered appropriate for cases where the storage time is shorter than seven weeks and when it is desirable to avoid the the use of concentrated sulfuric acid for the "in situ" preservation step.

EVALUATION OF ANALYTICAL PROCEDURES

The following procedures for DO determination were evaluated:

1. The azide modification of the Winkler method where the free iodine is titrated with sodium thiosulfate using starch as the indicator.
2. A spectrophotometric method involving the colorimetric determination of liberated iodine at 287.5 and/or 349 μm , with the correction for turbidity and color of the sample by three-point difference in adsorbance or by addition of thiosulfate (6).
3. The automated version (FIA) of procedure No. 2.

There were no significant losses of iodine from solutions when titration or transmittance measurements were conducted within 20 min. of the acidification and the sample. The precision achieved with the spectrophotometric methods was better than the precision of the titration. The summary of the precision data is given in Table 1.

The advantages of the spectrophotometric method are:

1. The standardization of solutions is eliminated.
2. The time required for the determination is significantly reduced (by 30% over the manual procedure).
3. The method is easier, less cumbersome and more dependable.
4. The method provides more precise results.
5. The automated FIA method is ideal for the routine analysis of a large number of samples.

6. The choice of a manual or automated procedure is possible in covers virtually all situations where the Winkler chemistry is applicable. A comparison of various aspects of the three procedures studied for DO determination is provided in Table 2.

CONCLUSIONS

The optimal procedure of the preservation of samples is the use of black BOD bottles with air tight caps. The "acid" stage treatment assures the longest stability. The spectrophotometric method is superior to the titration for the determination of DO in natural water samples. The automated FIA method is suitable for large number of sample analysis.

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TABLE 1

PRECISION OF DO DETERMINATION

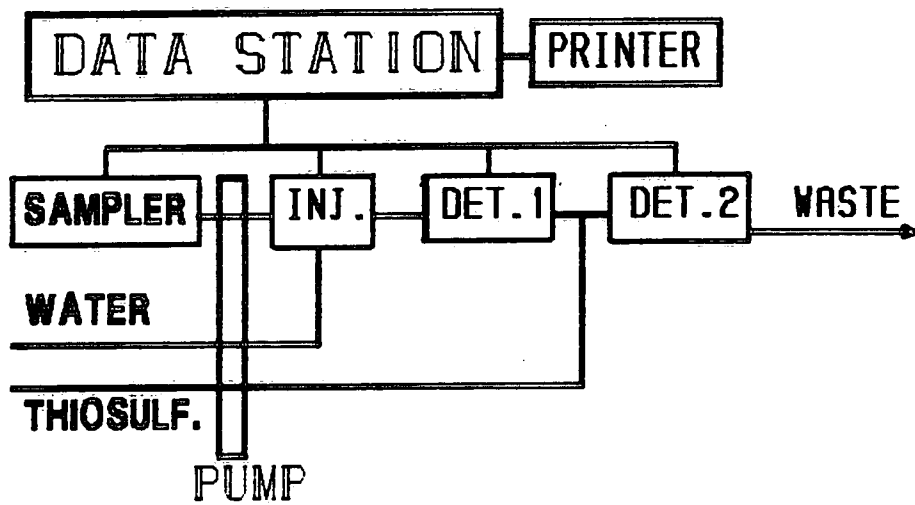
(n = 20)

| METHOD | 1.0 ppm DO | 5.0 ppm DO | 10.0 ppm DO |
|--------------------|------------|------------|-------------|
| | Mean | Mean | Mean |
| | RSD% | RSD% | RSD% |
| Titration | 1.08 | 5.06 | 10.08 |
| | 5.1 | 3.2 | 2.1 |
| Spectrometry | 1.04 | 5.02 | 10.05 |
| | 1.7 | 0.8 | 1.2 |
| FIA Spectrometry | 1.02 | 4.98 | 10.02 |
| Parallel detectors | 1.9 | 1.0 | 1.3 |
| FIA Spectrometry | 1.02 | 4.99 | 10.00 |
| Serial detectors | 1.6 | 1.1 | 1.2 |

TABLE 2
A COMPARISON OF THE 3 METHODS OF DO ANALYSIS

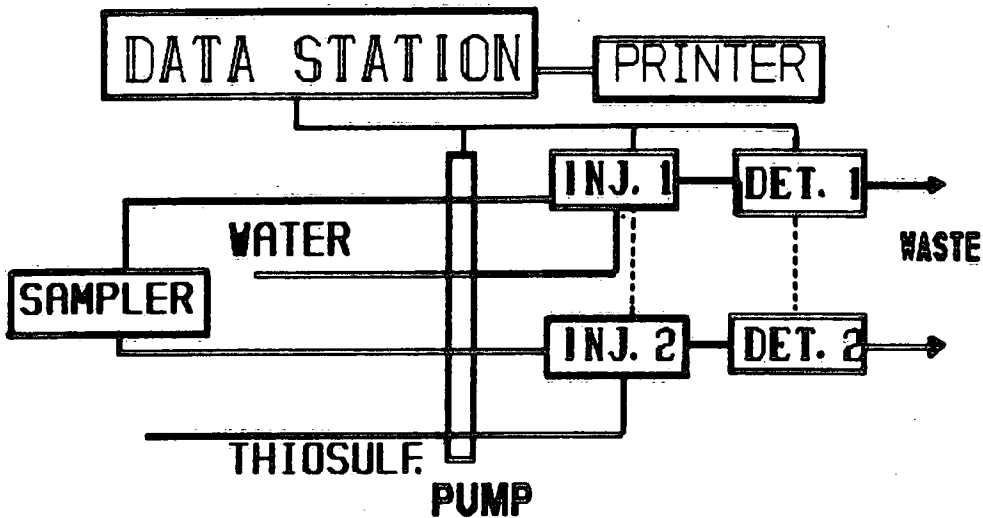
| | MANUAL TITRATION | MANUAL COLORIMETRY | COLORIMETRY BY FIA |
|-----------------------------|-----------------------------|-------------------------------|-------------------------------|
| Precision | ± 0.1 mg/L | ± 0.1 mg/L | ± 0.05 mg/L |
| Complicated to use | Tedious | Simple | Simple |
| Operator;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

FIGURE 1



FIA SYSTEM FOR SERIAL DETECTORS

FIGURE 2



FIA SYSTEM FOR PARALLEL DETECTORS

Stability of DO in respect to Sample Treatment

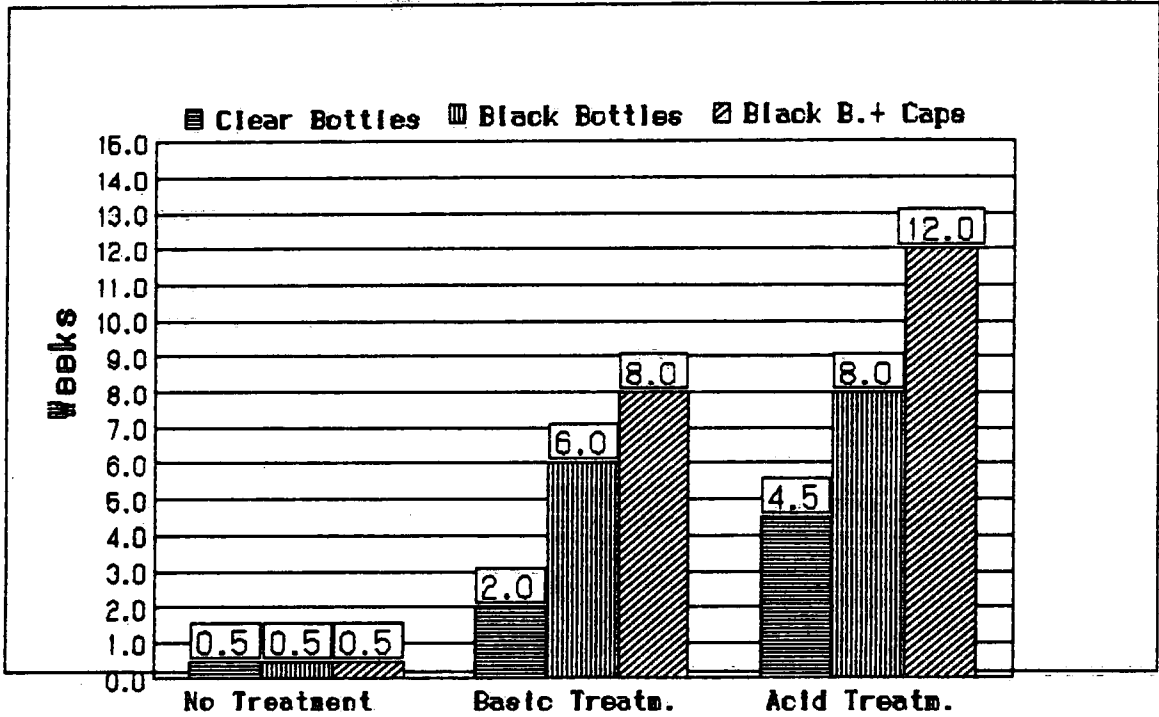


Figure 3 Sample Treatment