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TABLE OF CONTENTS

Ozone Generation

Drinking Water Treatment

Ozone Contacting

Ozone in the Air

Ozone and Food

Hazardous Wastes

Muncipal Wastewater and Sludge Treatment

Ozonation Kinetics

Organic Oxidation Products

Biological Activated Carbon

Aharon Netzer, James L. McNutt, Robert P. Smith

Engineering Performances at Operational Ozone Water and Wastewater Treatment Plants

Municipal Wastewater

TECHNICAL AND ECONOMICAL ADVANTAGES
OF PRODUCING AND APPLYING OZONE AT HIGH CONCENTRATIONS

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For practical reasons high ozone concentrations are desirable. Nevertheless most of the ozone generators present in operation produce ozone at concentrations of only 1 to 1,5 wt % in air and 2 - 3 wt % in oxygen. From the point of view of application this is unsatisfactory. The reasons are technical and economical. Higher ozone concentrations cause a higher specific energy consumption. Therefore the production capacity of an ozone generator decreases, when the ozone concentration is increased. The output reaches zero at the cut off concentration, which again is a function of the specific energy consumption and the gas temperature at which the ozone is produced.

Prerequisites for high ozone concentrations are therefore a high production density, a low specific energy consumption and a high cut off concentration.

The production density is a function of the energy supplied per unit of the discharge surface or expressed in other terms, the resulting power density. The higher this is, the greater the ozone production. The power density of an ozone generator is given by the formula

$$P = 4\, f\, C_D \cdot U_B \left[\hat{U} - \frac{C_D + C_G}{C_G}\, U_B \right]$$

According to this relationship, the power density increases with an increase in peak voltage $\hat{U}$ and in frequency f. Since the allowable peak voltage is restricted by the occurence of sparking and breakage of the dielectric to values below about 20 kV corresponding up to 14 kV rms, the attainable production density is limited. Much higher outputs at reliable continous operation can only be obtained with high frequencies and corresponding low voltages. The appropriate frequencies of 600 Hz to 1000 Hz are easily achieved by power electronics. A modern ozone generator working on this basis runs with a power density of 3 to 4 kW/m2 and a production density of 0.2 to 0.25 kg/h m2 with an electrode voltage of not more than 10 kV rms. This is an multiple of that of classical ozone generators with an operational frequency of 50 Hz. Simultaneously a low specific energy consumption is obtained when an efficient cooling of the ozone generator elements is provided. An essential requirement for intensive cooling of the gas is a narrow gap.

As a result ozone concentrations of up to 3.5 wt % can be produced with a good yield. For higher concentrations the production decreases sharply and reaches zero at the cut off concentration of 5 wt %. In oxygen ozone concentrations of up to 7 wt % are obtained with good production yields.

The advantage of the high ozone concentration for the application in water treatment as well as chemical industries are obvious.

In general the ozone reactions are carried out in a liquid medium in which the substances are dissolved. Therefore the first step, before the ozone may react, is the mass transfer from the gas phase into the liquid phase. The driving force for the mass transfer is the concentration gradient. A higher ozone concentration therefore gives a faster and more efficient mass transfer.

Due to Henry's law the maximum concentration in the liquid is proportional to the concentration in the gas phase. Since the reaction rate depence on the concentrations of the respective reactants, a higher ozone concentration in the liquid results in a faster reaction. A concequence of the higher ozone concentrations is a smaller reactor volumen and a simultaneously more complete utilisation of the ozone. Therefore the usage of ozone generators producing high concentrations is increasing.

In drinking water treatment plants the high mass transfer efficiency combined with the better disinfection guarantees a safer and more economical operation. According to this facts the Los Angeles Water Works will be equiped with an ozone plant producing ozone from oxygen at a concentration of 6 wt %. The high efficiency in ozone production and its utilisation allows even a once through process without a recirculation of the oxygen not transfered to ozone.

The ozone treatment of waste water for disinfection as well as removal of organics needs large ozone doses of 10 mg/l and more. A reduction in the gas to liquid ratio allows a reduction in the contactor volume and simultaneously better reaction conditions. Consequently a high ozone concentration is preferable for a waste water treatment plant and e.g. has been proposed for the Jeddah waste water treatment plant.

In the chemical industries ozone is used as a reagent. Due to the stoichiometry of the reactions large amounts are needed. A reduction of the gas flow rate and the size of the reaction vessel by applying higher ozone concentrations is a basic requirement for a break through in large scale operation. This has been confirmed by different chemical plants, which could only achieve economical ozonation with an ozone concentration of 3 wt % in air.

A COMPARISON OF ANALYTICAL METHODS FOR RESIDUAL OZONE

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SUMMARY

Eight analytical methods for the determination of residual ozone in water are compared on the validity of the ozone titer, the stability of the titer of the ozonated reagent solutions, the stability of the reagent solutions, and the ease of calibration of the reagent solutions. Four are iodometric methods based on the reduction of ozone by iodide ion: the standard iodometric method (1), the amperometric method (1), the arsenic(III) back titration method (2), and the DPD method (3). Four are non-iodometric methods: the indigo method (4), the arsenic(III) direct oxidation method (5), the Delta electrode (6), and the direct measurement of UV absorption at 259 nm (4). Two or more analytical methods are compared by simultaneous measurement of the decay curve of ozone in water and aqueous solutions. This kinetic technique minimizes sampling errors due to concentration changes, and allows a direct comparison of methods under conditions of rapidly changing ozone concentration.

The ozone titers differed among methods only when changes in the ozone-reductant were involved. Differences between iodometric and non-iodometric methods are not directly caused by iodate ion formation or hydrogen peroxide formation. Conditions which reduce ozone decay prior to reaction with reductant reduced the scatter observed within a single method and reduced the differences observed among the analytical methods. The indigo method minimizes ozone decay by operating at pH 2. Buffers which slow ozone decay increase the ozone concentration determined by arsenic(III) direct oxidation. Multiple analyses on tap water or acid stabilized ozone solutions show few differences.

All methods occassionally give a point 30-50 percent removed from that calculated on an otherwise smooth decay curve. This makes single point analysis for residual ozone untrustworthy.

Convenient laboratory analysis demands stable ozonated reagent solutions. With the DPD method, the ozone titer changed so rapidly with time both for ozone in purified water and for ozone solutions with added hydrogen peroxide that the method cannot be recommended for routine ozone analysis. The arsenic(III) back titration titer steadily increased for ozone solutions with added hydrogen peroxide. The ozone titer by the amperometric method with excess sodium thiosulfate increased 4 percent in 9 minutes with ozone in purified water. The ozone titer determined by the arsenic(III) direct oxidation method and the Indigo method varied less than 3 percent over 3 hours even with added hydrogen peroxide.

The arsenic(III) stock solutions used for the arsenic(III) direct oxidation method are stable standard solutions readily prepared by weight. Dilute working solutions should be prepared daily. Stock Indigo disulfonate would need replacement at least every four weeks. The Indigo trisulfonate stock solution is more stable and would require replacement only every ten weeks. Calibration of the Indigo dyes is essential, is time consuming and is based on Iodometry. These problems could be avoided if higher purity dye were readily available and calibration could be based on weight.

The direct measurement of the absorbance of aqueous ozone at 259 nm is the most straightforward and simplest ozone procedure. However, in waste water many impurities absorb in the critical UV region and produce a large background absorption thus making the method applicable only to very pure solutions free from bacteria, turbidity, and other absorbing materials.

The Delta electrode promised continuous, specific ozone analysis. Unfortunately, the electrode failed to respond linearly over a 10 mg/L ozone range and rarely maintained calibration on switching from one ozone solution to another.

In conclusion, no iodometric method is recommended. The Indigo method and the arsenic(III) direct oxidation method are the methods of choice.

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Evaluation of Analytical Methods for Dissolved Ozone in Natural Waters and Wastewater

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INTRODUCTION

Recent reviews describe the various analytical techniques available for the measurement of dissolved ozone in water (1,2). These methods involve either the direct measurement of molecular ozone or an indirect approach using an intermediate step such as the oxidation of iodide to iodine. However, the selectivity and detection sensitivity requirements in many practical ozone applications limit the choice of methods to be employed. Selectivity for molecular ozone, O_3, can be a major problem because many methods such as DPD, the direct colorimetric measurement of I_3^-, and iodometric titrations with reducing agents (phenylarsine oxide or thiosulfate) have systematic errors due to the presence of interferences which, like ozone, oxidize iodide. These interferences, such as peroxides, manganese(IV), and other oxidants, are produced by ozone's reactions in natural waters. Detection sensitivity at microgram per liter (ppb) concentration levels is also a requirement in many applications. In monitoring disinfection in practical situations, residual concentration levels are usually maintained at or below 500 micrograms per liter since the concentration of ozone required to produce 99% inactivation of E. coli is reported to be below 30 micrograms per liter(3).

In consideration of these analytical problems, this report compares the sensitivity, selectivity, and applicability of several methods in natural surface water and wastewater. These observations have been made in conjunction with continuing efforts to improve the detection sensitivity and further evaluate new applications of an amperometric ozone membrane electrode.

ANALYTICAL METHODS

Several methods were employed in the applications examined. Each method is described briefly below.

(a) UV Absorbance (4) - The absorbance of UV by the ozone molecule is measured at 259 nm (Σ = 2900 1 mole^{-1} cm^{-1}. The absorbance of the solution after ozone decomposes (reacts) is compared in a differential method to the same sample containing ozone.

(b) DPD-colorimetric (5) - The oxidation of 2% potassium iodide at pH 7.0 produces iodine. The iodine is then reduced by the oxidation of N,N-diethyl-p-phenylenediamine (DPD) added under acidic conditions (final pH 6.3). Oxidation of DPD indicator results in formation of a red colored product in solution that obeys Beer's Law to 2.5 mg/l (Σ= 19,900 1 mole^{-1} cm^{-1}).

(c) Indigo oxidation (6) - Indigo trisulfonate, a blue colored aromatic compound is oxidized to a colorless product under acidic conditions. The decoloration obeys Beer's Law at 600 nm (Σ= 20,000 1 mole^{-1} cm^{-1}).

(d) Amperometric membrane electrode (7,8) - Current is measured from the electrochemical reduction of ozone at a noble metal electrode in a cell isolated from test solutions by a semi-permeable polymeric membrane.

(e) Iodide oxidation-amperometric titration (9) - Ozone oxidizes excess iodide at pH 4.0. The iodine produced is measured by titration methods with a reducing agent using a bare amperometric electrode cell for endpoint detection.

APPLICATION RESULTS

Methods were examined in two independent studies conducted with surface waters obtained from Lake Griefensee, Switzerland and at the Tar River Regional Wastewater Facility, N.C., U.S.A.

Griefensee Study

Four methods (indigo, DPD, UV absorbance, and membrane electrode) were examined using surface water samples obtained from Lake Griefensee (3.8 milligrams per liter dissolved organic carbon, less than 0.5 micrograms per liter Mn^{+2}, pH 8.4). Ozone concentrations from 1 to 2 milligrams per liter were obtained by adding aliquots of a 25 milligrams per liter stock ozone solution to a 500 ml sample. Ozone concentration levels in the sample were then monitored over a period of one to six minutes as the ozone reacted with the solution.

Membrane electrode measurements were made in a water-jacketed beaker maintained at 25 $\pm$ 0.2 C. The membrane electrode was immersed in the sample and the current response monitored directly as a function of time using a Metrohm (Model E261) polarograph. UV absorbances were also measured continuously as a function of time. Concentrated stock ozone (25 mg/l) was added directly into Teflon stoppered 10 cm quartz cells containing the sample. DPD and indigo analyses were made using discrete samples from a 500 ml pump pipette at timed intervals directly into the reagents to stop the reaction of ozone. DPD measurements were recorded two minutes after sample addition to the reagents. The indigo measurements were made approximately twenty minutes after sample addition to the indigo reagents. Test runs were conducted at the natural water pH (8.4) and in samples brought to pH 5.0 and 7.0 with 0.5 M H_3PO_4.

The results of one such test run (pH 7.0, ozone dose 1.16 milligrams per liter) are illustrated in Figure 1. From an initial absorbance near 1.46, the molecular ozone content rapidly decreased abruptly reaching a steady state absorbance value due to a background or zero ozone concentration level in approximately two minutes. At the point, where ozone absorbance had reached a steady state value according to the UV measurements, the electrode measurements revealed 42 micrograms per liter, while the indigo and DPD were 60 and 76 micrograms per liter, respectively. By three minutes after the ozone injection, the membrane electrode response had decreased to 2 micrograms per liter and was at zero thereafter. However, after six minutes of contact, the indigo and DPD methods measured low but still detectable levels of 12 and 27 micrograms per liter.
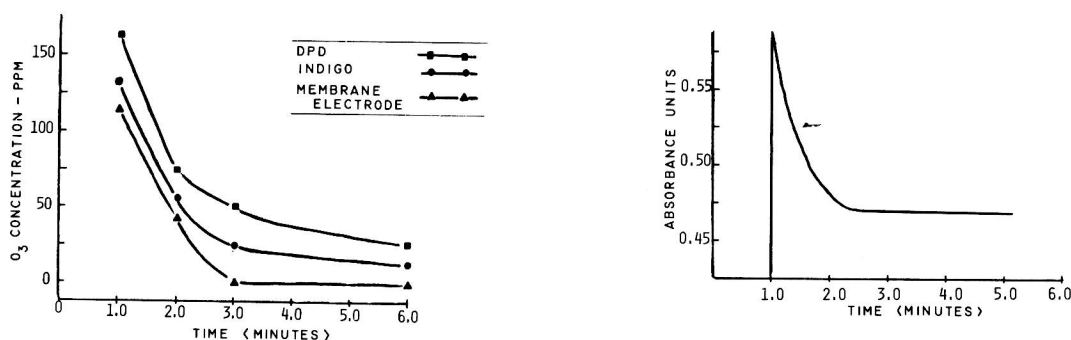

Figure 1. Decay of molecular ozone as measured by DPD (■), Indigo (●), and Membrane Electrode (▲) vs. Differential UV Absorbance Data. Griefensee surface water sample at pH 7.0 dosed with 1.16 mg/lit ozone.

In general, at all three pH levels significant positive interferences were observed with the indigo and DPD methods when compared to the UV measurements. The membrane electrode measurements were also in error because of the mode of operation and the characteristic response time delay (95% in one minute). However, the membrane electrode technique did not suffer from positive interference when the ozone concentration level approached zero, as did the indigo and DPD methods. The DPD method gave interferences generally two times greater than those observed for indigo.

The UV method is thought to be selective for molecular ozone when corrected for the background absorbance of the solution and was therefore employed to observe the disappearance or decay of the ozone molecule for comparison with the other methods. In these surface water samples, this approach was possible. But in some waters the UV method is less reliable because of the presence of high concentrations of other UV absorbing constituents which would produce a low signal to background noise level. This phenomenon was observed to a certain extent in the Griefensee samples as illustrated in Figure 2. A background absorbance of 0.7 down to 0.40 to 0.50 was consistently observed in many samples and was also found to shift to the lower values after ozonating the sample due to the oxidation of UV absorbing organics present. The high background absorbance signal also reduces the detection sensitivity of the technique. Sensitivity is a problem for the UV method because of its low absorptivity (1).
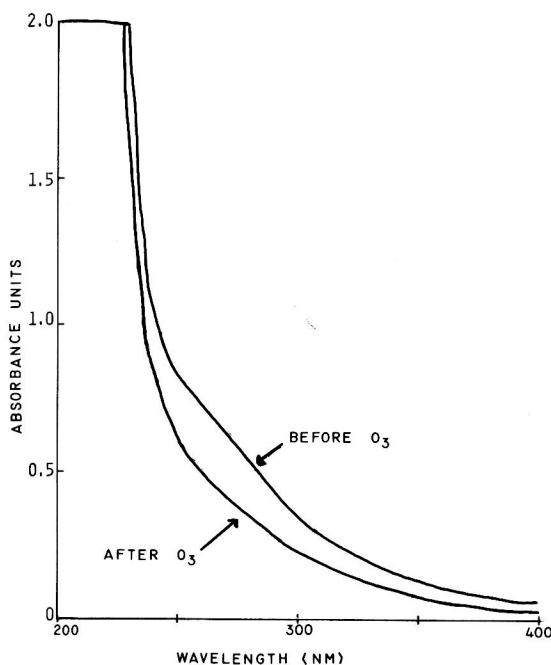
Figure 2. Ultraviolet spectrum of Griefensee surface water sample (200 to 400 NM) before and after ozone dose of 0.9 mg/lit O_3 (pH 5.0).

These results also document the potential improvement in membrane electrode current sensitivity reported with the use of dimethylsilicone membranes (8). The current output of the membrane electrode design employed here was observed to increase approximately twenty fold in comparison with the current output of an identical membrane electrode where a Teflon membrane was employed. This observation is consistent with the fact that silicone rubber and silicone derivative based membranes have oxygen and ozone permeabilities that are considerably higher than Teflon films. In Figure 3, the membrane electrode current response is illustrated for five discrete sample measurements from 3 to 14 micrograms per liter (at 25 C). The current sensitivity is 2.8×10^{-9} amperes per microgram ozone per liter (measured by UV absorbance). Repeated measurements with the membrane electrode over the
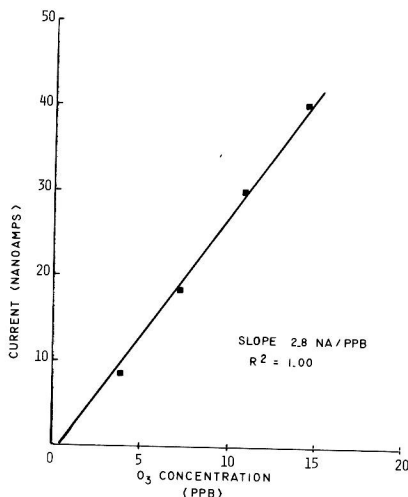
Figure 3. Current response of membrane electrode over 0-20 ppb (μg/lit) ozone concentration range in Griefensee surface water sample (pH 5.0).

two week test period produced an average current response of 2.5 $\pm$ 0.3 x 10^{-9} amperes per microgram per liter dissolved ozone in the concentration range from 3 to 100 micrograms per liter. The increase in current sensitivity resulting from the use of dimethylsilicone membranes has enhanced the current signal to noise ratio and allows for reproducible measurements of ozone concentration levels in the microgram per liter or ppb range. Assuming the detection limit as twice the observed residual current of 1 nanoamperes (i.e., 2 nanoamperes), at the above current sensitivity the detection limit of the electrode is 0.8 micrograms per liter (ppb).

Tar River Study

Three methods (membrane electrode, indigo, and iodide oxidation-amperometric titration) were compared using secondary effluent wastewater obtained from the Tar River Regional Wastewater treatment facility (pH 6.5 to 7.0, NH_3-N 4.8 mg/l, BOD_5 10 mg/l, TSS 30 mg/l). Twenty liter batch samples were ozonated using a gas stream split from the output gas line of an Emery Industries ozone generator (oxygen feed gas) employed at the site for effluent disinfection. The ozonated wastewater sample was then pumped from the reservoir container thru a membrane electrode flow cell (4 l/min flow rate). The membrane electrode was positioned in the flow cell and current measurements were made using a potentiostat/electrometer circuit with a digital voltmeter output. Samples for the iodometric oxidation and indigo measurements were collected from the effluent line of the membrane electrode flow cell directly into volumetric flasks containing the appropriate reagent solution. Similar procedures were employed for measurements made with buffered distilled demand free water.

Membrane electrode measurements were recorded one to two minutes after the initial current response stabilized at a constant level to avoid errors due to response time effects experienced above. Amperometric titration measurements of iodine concentrations were conducted with phenylarsine oxide within one minute after sample addition to buffered potassium iodide using a dual gold electrode cell at an impressed cell potential of + 0.2V. Indigo measurements were made within twenty minutes after sample collection.

The membrane electrode design employed in this study produced a higher current sensitivity to molecular ozone (approximately 7 microamperes per mg/l ozone). But, because of greater residual currents approaching 20 nanoamperes, this design possessed a slightly higher detection limit of 5 ppb. The current response over the 0 to 2 mg/l concentration range used for a distilled demand free water and a representative wastewater effluent sample compared to amperometric titration is illustrated in Figure 4. This data demonstrates the
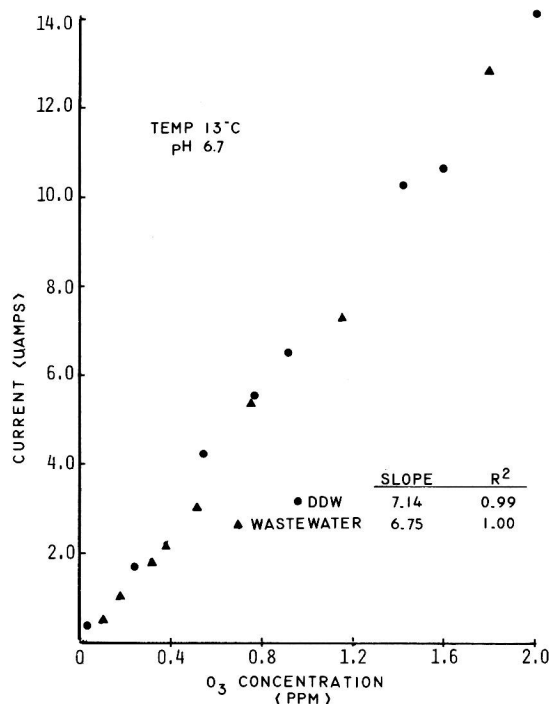
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Figure 4. Comparison of membrane electrode current response in distilled demand free water (DDW) and Tar River wastewater effluent (pH 6.7, temp 13°C).

linearity of the current response over this concentration range. It can also be inferred from comparing the current response data in the two media that the membrane electrode is selective for molecular ozone in the wastewater effluent. This finding has been suggested by others who have employed ozone membrane electrodes in wastewater effluents (8,10).

Because of uncertainty as the the specificity of the iodide oxidation technique, further verification of this conclusion was sought in separate experiments where both the indigo and iodide oxidation techniques were employed as referee methods. The results of one such test are illustrated in Figure 5. The data has been normalized to ozone concentrations in mg/l for comparison purposes. Linear regression fit equations for both relationships are listed below:

(membrane electrode
vs. indigo)

$$(ppm\ O_3)_{electrode} = 1.07\ (ppm\ O_3)_{indigo} + .04$$
$$r^2 = 0.98$$

(membrane electrode
vs. iodometric)

$$(ppm\ O_3)_{electrode} = 1.00\ (ppm\ O_3)_{iodo} - .04$$
$$r^2 = 0.995$$

In this test, the membrane electrode response is nearly identical to the iodometric oxidation - amperometric titration procedure results while showing a positive interference when compared to indigo. Our tests were not exhaustive in comparing the relative errors of each method. It is possible to conclude, however, that the ozone membrane electrode is selective for molecular ozone given some level of measurement error when compared to referee procedures. It is interesting to note also that in this wastewater effluent sample the iodometric oxidation procedure exhibited little or no interference probably due to the low organic and ammonia nitrogen and dissolved organic carbon content of the sample.

DISCUSSION AND CONCLUSIONS

Several analytical procedures for analysis of ozone in water have been compared using surface water (Griefensee, Switzerland) and wastewater effluent (Tar River, N.C.) samples. The selectivities of the methods for ozone in the Griefensee samples was observed to be (in order of decreasing selectivity): membrane electrode, indigo, and DPD. DPD was the least selective of the methods considered, probably as a result of the non-selective iodide oxidation step. In the wastewater effluent examined, all three methods appeared to suffer little or no interferences and the utility of the membrane electrode for molecular O_3 in this medium was confirmed. Estimation of the detection limits of the methods found the membrane electrode, indigo and DPD techniques to be approximately equal. The UV procedure and direct iodometric titration technique were less sensitive at ppb levels.

Of the methods best suited for individual or discrete sample measurements, the indigo procedure is superior to the less selective DPD procedure. Both procedures are equally sensitive and are applicable to the measurement of concentrations from 0.02 mg/l in polluted waters to 0.002 mg/l or 2 ppb in clean water. The membrane electrode and differential UV procedures are much more suited for on-line process analyzers although the UV method is relatively insensitive and in polluted waters requires complex instrumentation for differential measurements. Both of these procedures are much more difficult to apply reliably for single sample measurements.

The membrane electrode is recommended for continuous process analyses and the indigo procedure for individual sample measurements. The indigo method is better suited for calibration of the membrane electrode and other process analyzers than DPD due to interferences with this and similar methods which rely on iodine as an intermediate.
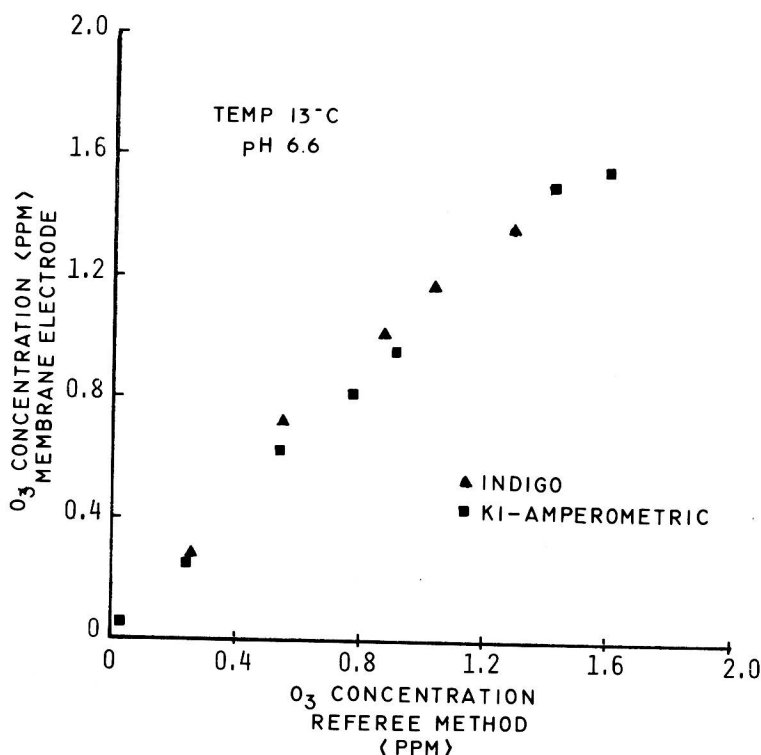

Figure 5.   Comparison of membrane electrode vs. Indigo (▲) and KI-Amperometric Titration (■) methods in Tar River wastewater effluent (pH 6.6, temp. 13°C) over 0 to 2 mg/lit O_3 concentration range.