United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-84-036 Mar. 1984

EPA

Project Summary

Improved Techniques for Residual Ozone

Gilbert Gordon and Joyce Grunwell

This project responds to the need for accurate, acceptable analytical procedures for residual ozone in treated water. The standard iodometric method is compared with three iodometric modifications: The amperometric method, the arsenic(III) back titration method, and the N,N-diethyl-p-phenylenediamine (DPD) method. In addition, the study evaluates four analytical methods based on the reaction of ozone with a reductant other than iodide ion: The indigo method, the arsenic(III) direct oxidation method, the delta electrode, and the direct measurement of the UV absorption at 259 nm. Comparisons are made of all eight methods regarding the validity of the ozone titer, the stability of the titer of the ozonated reagent solutions, and the ease of calibration of the reagent solutions.

Also discussed are four exploratory methods based on new ozone-reductant reactions: The chlorite ion method, the iodate method, the iron(II) terpyridine method, and the cerium method.

Results were that no iodometric method was recommended. The indigo method and arsenic(III) direct oxidation were the methods of choice and were recommended as replacements for the standard iodometric method currently in wide use. None of the four exploratory methods gave reliable residual ozone values.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In the past 80 years, chlorine has been widely used for disinfection of municipal and industrial wastewaters in the United States. But recent concerns over the toxic effects of chlorinated organic byproducts produced during chlorination of potable water and wastewater have renewed interest in the use of ozone for water treatment. Experience in Europe has shown that in addition to serving as an effective disinfectant, ozone acts as an oxidant to remove taste, color, odor, and organic matter from water. If ozonation is to achieve wide application for water purification in the United States, accurate analytical procedures acceptable to technicians and water treatment plant operators are necessary.

The nature of ozone makes its residual analysis difficult. The element is usually generated by passing a stream of dry oxygen through an electrical discharge that converts only 2 to 5 percent of the oxygen to ozone. The instability of pure ozone precludes the preparation of weighted reference samples. Large analytical errors can result from volatilization of ozone from solution, its rapid decomposition in water, and its reaction with any trace contaminant in the water, the reagents, or the glassware.

In the current standard method for the determination of ozone in water, ozone oxidizes iodide ion to iodine in a 2-percent neutral, phosphate-buffered potassium iodide solution; then the pH is adjusted to 2 with sulfuric acid, and the liberated iodine is titrated with sodium thiosulfate to a starch endpoint. The ozone:iodine stoichiometry has been extensively studied and found to range from 0.65 to 1.5. The factors affecting the stoichiome-

try include pH, buffer composition, buffer concentration, iodide ion concentration, sampling techniques, and reaction time. The pH during the initial ozone-iodide reaction and the pH during the iodine determination can alter the ozone:iodine stoichiometry. The formation of iodate ion and hydrogen peroxide have been specifically implicated as factors affecting the ozone:iodine stoichiometry. Modifications in the iodine determination include changes in endpoint detection, pH, and back titration techniques.

This project compares the standard iodometric method with three iodometric modifications: The amperometric method, the arsenic(III) back titration method, and the DPD method. Also evaluated are four analytical methods based on the reaction of ozone with a reductant other than iodide ion: The indigo method, the arsenic (III) direct oxidation method, the delta electrode, and the direct measurement of the UV absorption at 259 nm.

All eight methods are compared as to 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 exploratory methods based on new ozone-reductant reactions are discussed: The chlorite ion method, the iodate method, the iron(II) terpyridine method, and the cerium method. The failure of these potential new methods is discussed.

Experimental

Ozone was generated from dry oxygen by an OREC Model 03V9-0 ozonator.* Ozone solutions were prepared in a 3000-ml contactor (Figure 1) equipped with a medium-porosity glass frit and a sampling stopcock with a Leur tip. Additional stopcocks allowed the inclusion of a closed-flow loop for mixing and for the Delta electrode. A Cole-Parmer Model 7149-10 all-Teflon pump provided circulation.

A multi-stop Silverman syringe was designed to minimize sampling time for multiple analyses (Figure 2).

A solution of ozone was prepared, and the ozone concentration was determined at known time intervals by two or more analytical methods. The resulting time and concentration profile for each analytical method was graphed and fitted to the generalized rate law

$$\frac{-d[O_3]}{dt} = k_1[O_3][OH^-] + k_2[O_3]^2$$

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

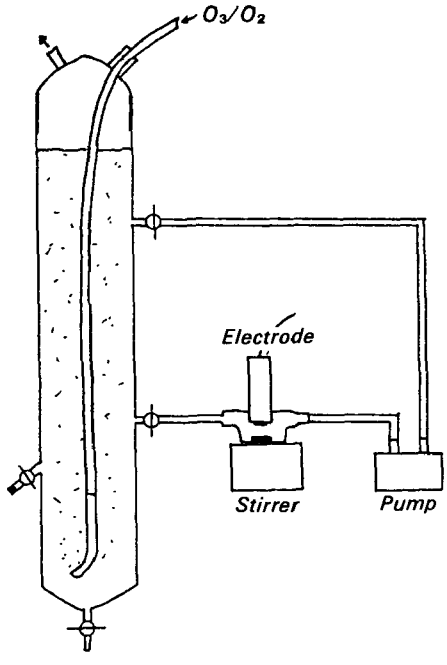


Figure 1. Contactor with flow cell.

using FIT 80. The apparent rate constants were calculated and compared within each kinetic run. Identical kinetic parameters between methods indicated that each method gave the same result. This kinetic technique minimized sampling errors resulting from concentration changes and allowed a direct comparison of methods under conditions of rapidly changing ozone concentration.

Conclusions

Stability of the Titer of the Ozonated Reagent Solutions

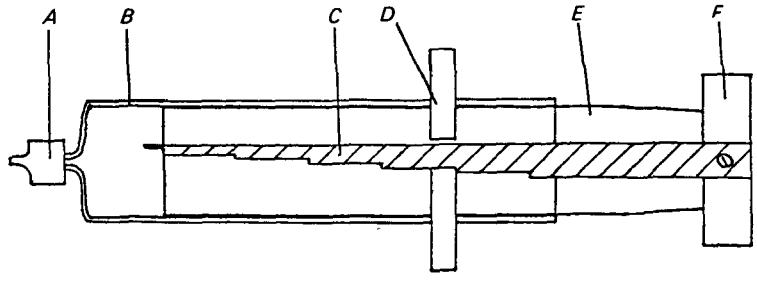
Convenient laboratory analysis demands stable ozonated reagent solutions. With the DPD method, the ozone titer changed so rapidly with time (both for ozone in purified water and for ozone solutions with added hydrogen peroxide) that the method cannot be recommended for routine ozone analysis (Figure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

Stability and Calibration of the Reagent Solutions

The arsenic(III) stock solutions are stable, standard solutions readily prepared by weight. Dilute working solutions should be prepared daily. Indigo disulfonate stock solution would need replacement at least every 4 weeks. The more stable indigo trisulfonate stock solution would require replacement only every 10 weeks. Calibration of the indigo dyes is essential, time consuming, and based on iodometry. These problems could be avoided if higher-purity dye were readily available and calibration could be based on weight.

Accuracy of the Ozone Titer

The ozone titers differed among methods only when changes in the ozone reductant reaction were involved. Differences between iodometric and noniodometric methods were not directly caused by iodate ion formation or hydrogen peroxide formation. Conditions that reduced ozone decay before reaction with reductant reduced the scatter observed within a single method and reduced the differences observed among the analytical methods. All methods occasionally give a point that is 30 to 50 percent removed from that calculated on an otherwise smooth decay



A. Teflon adaptor
B. 50-ml syringe barrel
C. "Five-step" brass rod
D. Plexiglas guide
E. Syringe plunger
F. Brass cap

Figure 2. Multi-stop calibrated syringe.

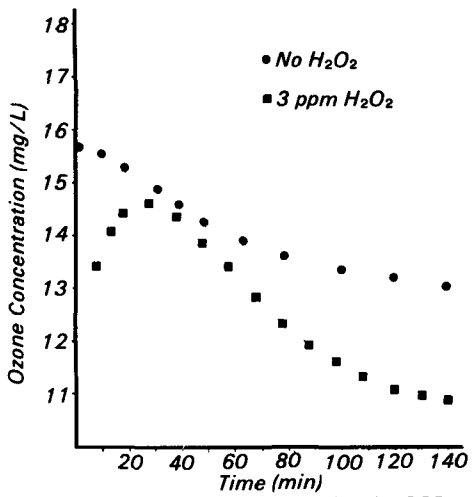


Figure 3. Stability of ozone titer for DPD.

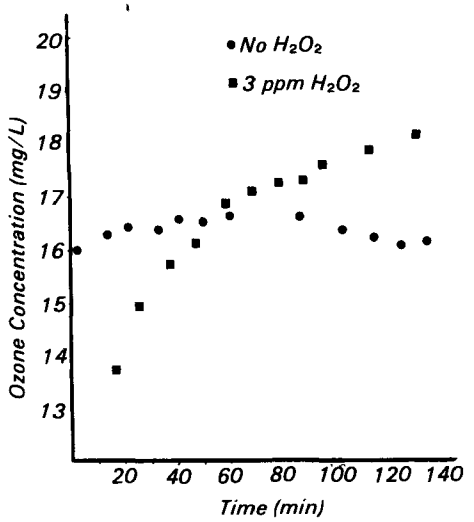


Figure 4. Stability of ozone titer for As(III) back titration.

curve. This fact makes single-point analysis for residual ozone untrustworthy (Figure 5).

The indigo method minimizes ozone decay by operating at pH 2. Buffers that slow ozone decay increased the ozone concentration determined by the direct arsenic(III) oxidation. Multiple analyses of tap water or acid-stabilized ozone solutions showed few differences.

UV Method

The direct measurement of the absorbence of aqueous ozone at 259 nm is the most straightforward and simplest ozone procedure. The absolute ozone concentration is based on the ozone absorption coefficient, which is determined by an iodometric method. Significant differences exist in reported values for the absorption

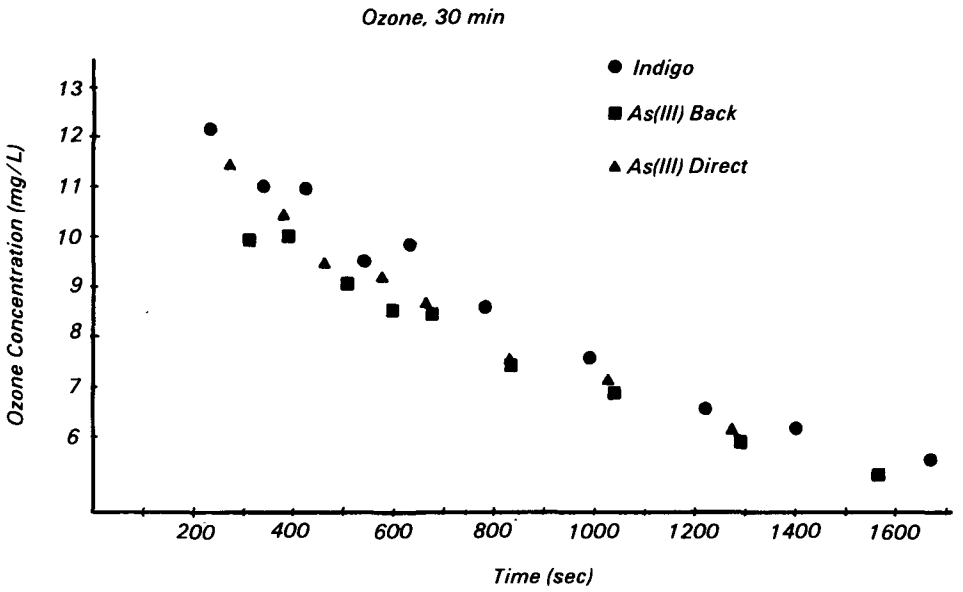


Figure 5. Comparison of indigo, As(III) back, and As(III) direct in phosphate buffer, pH 6.7 : ozone, 30 min.

coefficient. In addition to this fundamental problem, a practical problem exists with regard to the wastewater, where many impurities are absorbed in the critical UV region and produce a large background absorption. The method is applicable only to very pure solutions free from bacteria, turbidity, and other absorbing materials.

Delta Electrode

The delta electrode did not maintain calibration on switching from one solution to another. The electrode did not respond linearly over a 10-mg/L ozone range, which caused the ozone decay curves determined by the delta electrode to follow rate laws different from the other residual ozone methods (Figure 6).

Alternative Reductants

All four exploratory methods failed to give reliable residual ozone values. The chlorite ion method failed because ozone does not selectively react with the excess chlorite ion to produce the measured chlorine dioxide; ozone also rapidly attacks the chlorine dioxide, thereby producing low ozone titers.

The stable iron(II) terpyridine complexes were oxidized by ozone to the unstable iron(III) state. Reaction conditions could not be found such that the iron(II) to iron(III) conversion quantitatively and consistently reflected ozone titers.

The cerium method failed because the cerium(IV) product seemed to be readily reduced by wastewater impurities and

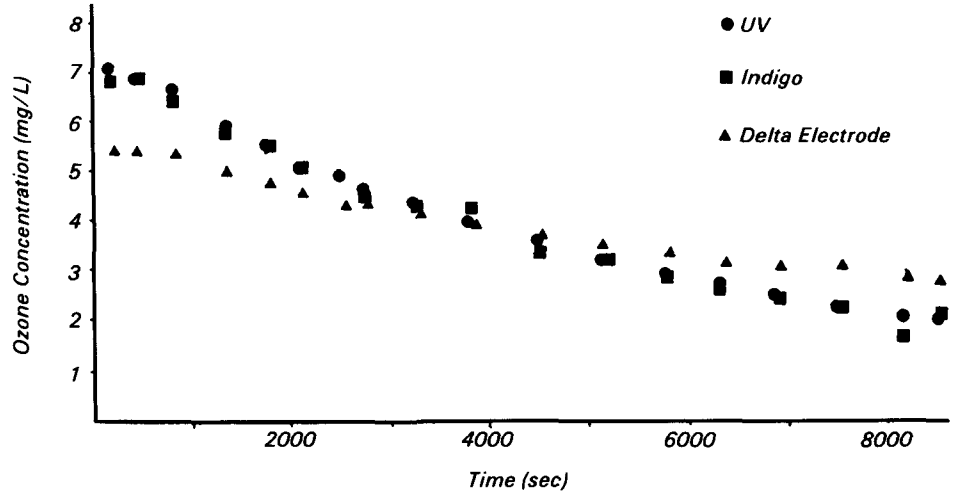


Figure 6. Comparison of UV, indigo and delta electrode in purified water.

ozone decay products. This tendency produced significantly low ozone titers.

The failure of the iodate method was the most puzzling and troublesome. At low concentrations, iodine did not quantitatively disproportionate to iodate ion. Since valid ozone titers demand 100-percent conversion of iodine to iodate ion, the iodate method failed.

Purging Technique

The purging technique is unreliable because of ozone decomposition during the purge and reabsorption steps.

Recommendation

No iodometric method is recommended. The indigo method and arsenic(III) direct oxidation are the methods of choice. The Standard Methods committee should consider replacing the standard iodometric method currently in wide use with either the indigo or the arsenic(III) direct oxidation method.

The full report was submitted in fulfillment of CR-806302 by Miami University under the sponsorship of the U.S. Environmental Protection Agency.

Gilbert Gordon and Joyce Grunwell are with Miami University, Oxford, OH 45056.
***Edward J. Opatken** is the EPA Project Officer (see below).*
The complete report, entitled "Improved Techniques for Residual Ozone," (Order No. PB 84-151 224; Cost: $11.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

☆ U S GOVERNMENT PRINTING OFFICE, 1984 — 759-015/7637