A RAPID, SENSITIVE METHOD FOR THE DETERMINATION OF THE CHEMICAL
OXYGEN DEMAND OF POLLUTED WATERS.*

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ABSTRACT

A rapid, sensitive cerate oxidative method for measuring the chemical oxygen demand (COD) of waters is described. The pollutants are oxidized with perchlorato-cerate reagent and the resulting cerium(III) is determined fluorometrically. Analysis requires only a few minutes for determinations at levels as low as 100 μ g oxygen demand per liter.

Results of tests on solutions of known organic compounds, various industrial waste streams, and natural waters show that the method compares favorably with the dichromate reflux procedure recommended by APHA. However, the new method is considerably faster and easier to use, and is a hundred times more sensitive. An analytical system which is suitable for use as either a continuous COD monitor or as an analyzer for multiple samples in series is also described.

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INTRODUCTION

The chemical oxygen demand (COD) of waste waters and natural streams is one of the important parameters of the water quality. The standard method for determining COD (1) is frequently used to estimate the efficacy of waste treatment systems or the polluttional potential of waste waters. Although this method has been in use for many years and was selected by the APHA because dichromic acid "has advantages over other oxidants in oxidizability, applicability to a wide variety of samples and ease of manipulation", it has the disadvantages of requiring significant manual attention and approximately 3 hours to complete. These drawbacks have been somewhat overcome by automating the procedure and measuring the change in oxidant colorimetrically instead of by back titration (2). Another improvement which drastically reduces the time required and also cuts chemical costs by a factor of four, is the rapid COD test developed by Jeris (3).

However, all of these methods suffer somewhat when they are used to determine the COD at levels below 100 mg/l. In an attempt to increase the sensitivity of the COD test without yielding the advantages of rapid analysis and automation, the previously rejected method using cerate oxidation (4) was reexamined.

Cerate oxidimetry has been in general use in volumetric oxidimetry for several decades (5), and its use in the analysis of COD in polluted waters was suggested as early as 1941. For valid reasons, this method was not adopted as the standard in the United States, but the intrinsic fluorescence of trivalent cerium coupled with recent advances in fluorescence analysis and cerate oxidimetry made another look at cerate oxidation methods for COD analyses seem warranted.

Many of the organic compounds normally found in sewage and industrial wastes are not oxidized as efficiently with ceric sulfate (sulfatoceric acid) as with dichromic acid particularly when silver is used as a catalyst with the dichromate. This is understandable when one compares the available oxidation

potentials as shown in Table 1; as can also be seen from the table, perchloratoceric acid provides oxidation potentials approaching that of silver catalyzed chromic acid, and thus should also oxidize many of the same organic compounds.

The other attractive feature of a cerate oxidation method is that the trivalent cerium which results from any redox reaction with compounds in the water sample is strongly fluorescent (Figure 1). Concentrations of cerium (III) from 10^{-8} to 10^{-4} molar can be readily determined fluorometrically by excitation with ultraviolet light (254 nm) and measuring the 90° light emission at 350 nm (6).

With this information in mind, a method which requires only a few minutes for measuring the COD of waters at levels as low as 100 μg per liter was developed. The method is quite amenable to automation and can be used for continuous, remote stream analysis.

EXPERIMENTAL

The following is a brief description of the proposed method which can be used either as a manual laboratory procedure for batch samples or as an automated instrumental procedure for discrete or continuous samples. A detailed list of chemicals and procedures are given in the appendix.

To test the method for its applicability, several organic compounds representative of the various constituents of waste and natural waters were analyzed with the method. The classes of such compounds included carbohydrates, alcohols, amino acids, surfactants, straight chain acids, volatiles, and others. In addition, samples of sewage plant effluents and a river water sample were analyzed.

The "perchloratoceric acid" method involves the mixing of the waste sample with 10^{-3} to 10^{-2} M perchloratoceric acid reagent and heating at 100°C for five minutes. The reagent concentration and the ratio of reagent to sample is

chosen so that about 10-50% of the cerium (IV) will be utilized. After this the mixture is diluted to a total of about 10^{-3} M cerium with cold 0.2 N sulfuric acid to halt the reactions. The fluorescence of the mixture resulting from trivalent cerium is then measured.

This procedure was established using conventional laboratory glassware and a Perkin-Elmer Model 203 fluorescence spectrophotometer. However, once the general procedure was worked out, the following continuous flow apparatus was assembled, and the reported results were obtained using this equipment.

Apparatus

The continuous flow apparatus which was used to test the "perchloratoceric acid" COD method consisted of two pressurized reagent reservoirs, a sample pump (peristaltic), two jet mixers, a boiling water bath, a flow fluorometer, and a strip chart recorder (Figure 2). This apparatus can be used as a continuous stream monitor, or as was used here, as a discrete sample analyzer. In this mode of operation, it is capable of analyzing about 10 samples per hour.

Pressuring the reagent reservoirs is a very simple but reliable method of metering a low flow of the reagents. Using a simple gas pressure regulator and a length of capillary tubing provides a constant flow in the range of a few milliliters per hour (7). The sample stream and the perchloratoceric acid stream are mixed in the first jet mixer (Figure 3), the sample entering through the jet and the reagent through the annulus. The cross sections of the jet and annulus are designed so that the fluids' linear velocities at the jet exit are nearly equal, thus minimizing back mixing. From the mixer the stream flows through a coil of thin-wall teflon tubing immersed in a boiling water bath. The residence time in the bath is five minutes. This mixture is then diluted tenfold in the second jet mixer with 0.2 N sulfuric acid, which effectively stops the reaction. The concentration of trivalent cerium in this diluted

stream is continuously measured by the flow fluorometer and recorded on the strip chart recorder.

The key component of the system is the flow fluorometer, which has been described in detail elsewhere (8) but is also briefly described here. The flow fluorometer shown schematically in Figure 4, consists of a fluorometer body, electronics chassis, and a high voltage power supply. The fluorometer body (Figure 5) is a machined aluminum block which contains a low-pressure mercury lamp, a 254 nm interference primary filter, quartz tube flow-cell, two Corning 7-60 secondary filters, photomultiplier tube and housing, and a photoconductor for compensation of changes in lamp intensity. In this situation, nature was exceptionally benevolent, because the excitation *maximum* for trivalent cerium is very close to the most intense emission line of the low pressure lamp, 253.7 nm, and the emission spectrum of cerium (III) corresponds almost precisely with the pass-band of the Corning 7-60 filters. These characteristics plus the S-11 photo response characteristics of the photomultiplier provided an exceedingly low background due to reflected light and allowed the construction of a very sensitive instrument from relatively inexpensive components. The calibration curve for this fluorometer with Ce^{+3} solutions is shown in Figure 6.

As can be seen, the fluorometer has a linear signal output up to about $2 \times 10^{-4} \text{ M Ce}^{+3}$, and a slight decrease in slope up to 10^{-3} M .

Procedure

Using this apparatus in the discrete sample mode, three or more samples of nine organic compounds dissolved in triply distilled water and three polluted waters were run, with a blank of triply distilled water between each sample. Periodically, a calibration standard containing a known amount of trivalent cerium in distilled water was run.

A quantity of each organic compound which would require about 10 mg of oxygen for complete combustion to carbon dioxide and water was weighed out and

dissolved in distilled water. At approximately five minute intervals, the sample tube is placed into one of these solutions and a one-minute sample withdrawn. During the remainder of the cycle the sample tube is inserted into distilled water. The COD of the sample is indicated by the height of a peak on the strip chart recorder ten minutes after the sample is withdrawn. Once each day, usually at the start of the operation, the system is calibrated with three, one-minute samples of a cerium (III) solutions of known concentration (1 to 2×10^{-5} molar or 8 to 16 mg/l oxygen demand). An example of the recorder trace is shown in Figure 7. The results of several series of runs using the selected organic compounds and pollution samples are shown in Table II.

DISCUSSION

Although some compounds were not as completely oxidized as with the catalyzed chromic acid, with the exception of acetone, benzene, and pyridine, all of the samples were oxidized to a sufficient level after 5 minutes at 100°C . Note that under these conditions, pyridine and benzene were oxidized to a greater extent than by the Standard Methods procedure. If greater levels of oxidation are required, longer reaction times or a higher temperature can be used. Temperatures above 125°C should not be used because rapid degradation of the cerate occurs.

The results of the "perchloratoceric acid" method with polluted samples show that the method is indeed rapid and sensitive and should be a useful complement to the Standards Method. For samples containing significant quantities of compounds which are oxidized to a lesser extent than with the Standard Method, a proportionality factor between this method and the Standard Method may be determined by running several samples by each method. This factor can then be applied to later samples run by the perchloratoceric acid method, with an occasional check by the Standard Method.

The major advantages of this method are rapidity, sensitivity and little need for manual attention. Even though no effort was made to optimize conditions for maximum sample throughput, 10 to 12 samples an hour can be analyzed on the apparatus described here. With the addition of an automatic sampler, operator attention would be reduced to about an hour a day, to charge the reagent reservoirs and samples, and to read the chart. The disadvantages of the method are its relative low dynamic range (less than two decades) for a given set of conditions, and that a standard must be run. Since the method also oxidizes chloride quantitatively, the chloride concentration must be considerably less than the organic content and must be determined separately.

APPENDIX

Chemical Reagents

1. Perchloratoceric acid, nominally 0.02 N. Dilute 3 ml of G. Frederick Smith perchloratoceric acid reagent (2 N in 6 N perchloric acid) to 300 ml with 6 N perchloric acid. Electrolyze overnight using platinum gauze anode and platinum wire cathode in a 400 ml reaction beaker.
2. Perchloric acid, 6 N. Dilute 840 g 70% perchloric acid to 1 liter with distilled water. Vycor distilled acid is preferred but ACS reagent grade is satisfactory (causes a slightly higher background).
3. Dilute sulfuric acid. Add 56 ml concentrated H_2SO_4 to 4 liters distilled water.
4. Ce^{+3} standard, 0.001 N. Dissolve 4.34 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in distilled water and dilute to 1.00 liter.

Procedure

1. Mix two volumes sample solutions, diluted to 5 to 20 mg COD, and one volume of 0.02 N perchloratoceric acid.
2. Heat this mixture for 5 minutes in a boiling water bath.
3. Mix 1:5 with dilute H_2SO_4 .
4. Measure fluorescence of mixture to determine concentration of trivalent cerium. Fluorometer calibrated with dilutions of Ce^{+3} standard.
5. Repeat using distilled water for sample.

Calculations

$$\text{COD (mg/L)} = ([\text{Ce}^{+3}]_{\text{m}} - [\text{Ce}^{+3}]_{\text{b}}) \times 8000 \times 9$$

where $[\text{Ce}^{+3}]_{\text{m}}$ = normality of Ce^{+3} from step 4

$[\text{Ce}^{+3}]_{\text{b}}$ = normality of Ce^{+3} from step 5

TABLE LIST

- Table I. Oxidation Potential Available with Various Oxidants in COD Analysis.
- Table II. Oxidation of Organic Compounds and Polluted Waters by Perchloratoceric Acid COD Method.

FIGURE LIST

- Fig. 1. Cerium Fluorescence Oxidimetry.
- Fig. 2. Continuous Chemical Oxygen Demand (COD) Analyzer.
- Fig. 3. Small Jet Mixer.
- Fig. 4. Flow Fluorometer Schematic.
- Fig. 5. Fluorometer Body.
- Fig. 6. Fluorometer Calibration Curve.
- Fig. 7. Recorder Output for COD Monitor.

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TABLE I
OXIDATION POTENTIAL AVAILABLE WITH VARIOUS
OXIDANTS USED IN COD ANALYSIS

$\text{Cr}_2\text{O}_7^{--}$	$\xrightleftharpoons{18\text{ }M\text{ }H^+}$	Cr^{+++}	$< -1.5\text{ v}$
Ag^+	$\xrightleftharpoons{\hspace{1cm}}$	Ag^{++}	-1.98 v
Ce^{+++}	$\xrightleftharpoons{\text{H}_2\text{SO}_4}$	Ce^{++++}	-1.42 v
Ce^{+++}	$\xrightleftharpoons{\text{HClO}_4}$	Ce^{++++}	$-1.70\text{ to }-1.87\text{ v}$

TABLE II. OXIDATION OF ORGANIC COMPOUNDS AND POLLUTED WATERS
BY PERCHLORATO-CERIC ACID COD METHOD

SAMPLE	CONCENTRATION (mg/LITER)	NUMBER OF DETERMINATIONS	OXYGEN CONSUMED (mg/LITER)		% OF THEORETICAL COD
			AVERAGE	RANGE	
ACETIC ACID	10	4	6.1	5.2 - 7.4	57
ACETONE	8	5	3.2	3.0 - 3.3	18
BENZENE	3.3	4	2.8	2.4 - 3.5	26
ETHANOL	7.5	3	11.0	10.8 - 11.1	69
GLUCOSE	14.5	4	17.4	15.9 - 17.9	112
GLYCINE	10	4	3.0	2.8 - 3.2	46
LINEAR ALKYL SULFONATE	5	5	6.9	6.3 - 7.4	105
PYRIDINE	10	6	3.5	3.2 - 3.6	16
SODIUM LAURYL SULFATE	5	5	13.5	12.8 - 14.6	135
SEWAGE PLANT EFFLUENT (INDUSTRIAL PLANT)	19 COD	5	16.5	14.8 - 18.1	
SECONDARY SEWAGE PLANT EFFLUENT (OAK RIDGE, TENN.)	6 BOD ₅	5	25.9	24.2 - 27.4	
CLINCH RIVER WATER	8 COD	3	7.8	7.5 - 8.0	

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CERIUM(IV) + ELUTED COMPOUND →
(NONFLUORESCENT)

CERIUM(III) + OXIDIZED PRODUCTS
(FLUORESCENT)

FLUORESCENCE EXCITATION MAXIMUM: 260 nm

FLUORESCENCE EMISSION MAXIMUM: 350 nm

Figure 1. Cerium Fluorescence Oxidimetry.

Figure 2. Continuous Chemical Oxygen Demand (COD) Analyzer.

Figure 3. Small Jet Mixer.

Figure 5. Fluorometer Body.

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Figure 6. Fluorometer Calibration Curve.

Figure 7. Recorder Output for COD Monitor.