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CONTINUOUS ON-LINE MONITORING OF TOTAL ORGANIC CARBON

WATER AND SOLID RESOURCES
ENVIRONICS DIRECTORATE
AIR FORCE CIVIL ENGINEERING CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32401

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→Continuous on-line monitoring of total organic carbon was performed at an Air Force sewage treatment facility using an Ionics Total Organic Carbon Analyzer. This instrument was installed and operated to determine its potential use in Air Force monitoring programs and the validity of a total organic carbon (TOC) to biochemical oxygen demand (BOD) correlation for the wastewater analyzed. Information was obtained →

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on the operation and required servicing for proper instrument application. Analysis of data collected during this study indicated that a valid long term correlation of TOC:BOD could be used to effectively monitor treatment plant performance.

FOREWORD

This report summarizes work done under job order 20543W08 between January 1975 and April 1975. Capt Brian D. Bennett was project engineer. The author wishes to thank 1st Lt Patrick Fink and MSgt Bennet Lamm for their assistance in support of this study.

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SECTION I

INTRODUCTION

The requirement for timely analysis of wastewater streams has become increasingly important with the advent of more stringent water quality discharge standards. These standards require the removal of organic matter to levels which require efficient treatment plant operation and improved sampling and test procedures for monitoring plant performance. Typical municipal and industrial wastewater may vary rapidly in both quality and quantity, suggesting continuous monitoring of the waste stream in order to insure effective treatment.

Several methods for determining the level of organic content in wastewaters have been developed. The laboratory methods commonly used include biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and total oxygen demand (TOD). The BOD test has been the standard for measuring oxygen consumption for over 40 years. This test, however, takes 5 days to complete and presents a time delay problem for effective treatment plant operation. The precision of the BOD test leaves much to be desired. A ±20 percent standard deviation has been reported for tests run by 34 water analysis laboratories on a test solution of 1.5mg glucose and 1.5mg glutamic acid (Reference 1). To supplement and possibly replace the BOD test, the chemical oxygen demand test has been used. This test takes 2 hours to accomplish but results in an increased reproducibility of ±8 percent (Reference 1). Because of the time involved with these analyses, considerable attention has been given to the development of quick, reproducible methods which would be relatable to the BOD test. One method developed which has been applied to continuous on-line operation is total organic carbon.

When considering routine plant monitoring of a wastewater characterization program, BOD is not the most useful test of waste load because of the long incubation time required to obtain a meaningful result. It is therefore important to develop a correlation between BOD, COD, and TOC. Once the correlation has been established, the TOC measurements can be translated in terms of BOD (Reference 2).

The use of accurate and dependable on-line TOC analysis at Air Force wastewater treatment facilities would improve the ability to meet current and future discharge standards with reduced laboratory analysis time. The field of on-line monitoring equipment is rapidly expanding, offering new techniques and products for measuring organic pollutants. The Air Force must maintain a knowledge of developments in this field in order to improve and expand current environmental monitoring programs.

SECTION II

ANALYZER OPERATION

The Ionics Inc. Model 1218 Total Organic Carbon Analyzer (Figure 1) is designed to automatically determine the carbon concentration of the process or wastewater streams. Analysis for TOC is routinely performed on-line at 5-minute intervals, thereby maximizing process control capabilities. The instrument contains a selectable dual range measurement scale of 10:1. One scale is for the range of 0 to 100 ppm carbon, and the other is for 0 to 1000 ppm. The data output from the analyzer is obtained either as a continuous spectrum or trend stripchart recording. The spectrum output displays the peak concentration for each analysis followed by a distilled water wash cycle. Trend output is displayed as a continuous line output showing the peak values updated for each successive analysis.

Continuous on-line operation requires the water sample to flow through an external, vertically mounted, Hallikaienen filter containing a 165-micron element in an upward direction at a minimum flow of one gallon per minute and 5 to 10 psig. This is designed to promote a self-cleansing wash of the inner filter walls using the normal sample flow. A 200-milliliter portion of the continuously flowing sample is drawn off from the filter and passes through the acid wash system and sample injection valve to the drain. When the dual channel injection valve is activated by the timing mechanism, a 40-microliter aliquot of the acidified purged sample is injected into the high temperature reactor by the nitrogen carrier gas. When returned to its original position, a 100-microliter distilled water sample is injected to clean the reaction chamber. Customer-supplied prepurified compressed nitrogen gas from a standard 1A cylinder is used as the carrier and purge gas. The nitrogen gas enters the analyzer through an in-line filter, pressure regulator, flow restrictor, and flow indicator. Nitrogen delivery pressure is set at 50 psig at the cylinder and is further regulated at the instrument to about 30 psig and a flowrate of 100 cubic feet per minute (CFM). The carrier gas stream flows continuously through the reaction chamber, gas-liquid separator, and infrared analyzer to the vent. Loss of nitrogen pressure below 15 psig will result

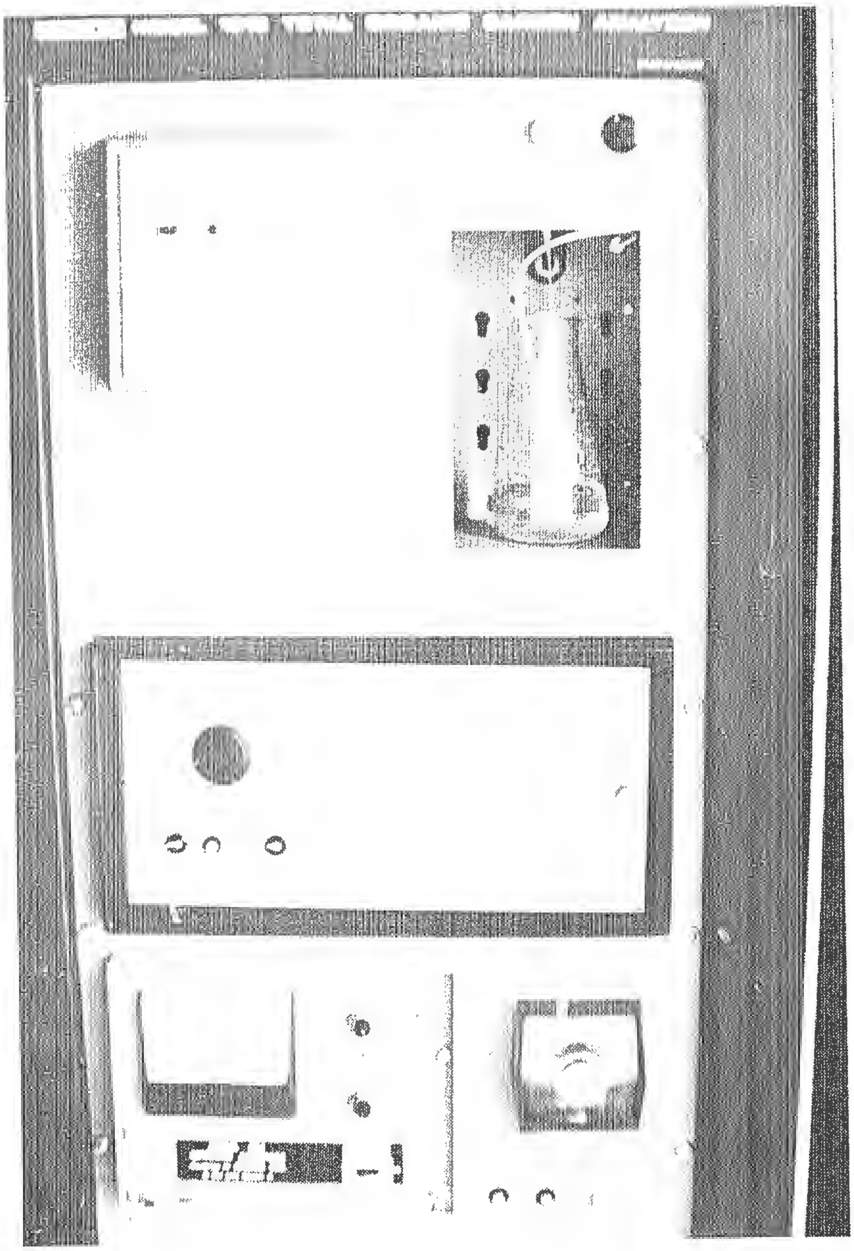

Figure 1. Ionics Total Organic Carbon Analyzer.

in automatic shutoff of the sampling valve. A purge gas stream of 0.15 CFM flows through the acid wash system to remove the inorganic carbon from the sample to be analyzed.

The inorganic carbon fraction is removed prior to sample injection into the high temperature reactor by acidification using a 5:1 solution of hydrochloric acid. The nitrogen purge gas is then used to remove the carbon dioxide formed according to the reaction

$$CO_3^{=} + 2H^+ \rightarrow CO_2 \uparrow + H_2O$$

This procedure to remove the inorganic carbon can, however, also remove certain volatile organic carbon compounds. The effect of sparging with nitrogen can be determined by removing the acid solution, replacing it with distilled water, and noting any difference in readings with and without the nitrogen purge gas. Any difference in readings can be attributed to a loss of volatile hydrocarbons.

The total organic carbon measurement is performed by analysis of the concentration of carbon dioxide (CO_2) from the combustion of the wastewater sample. Combustion is performed in a high temperature reactor using a palladium catalyst at 900°C. The water fraction of the sample provides the oxygen necessary for combustion. The sample is then carried through the gas-liquid separator to the nondispersive infrared analyzer sensitized for the detection and measurement of CO_2. The output signal is then handled electronically and displayed on the strip-chart recorder.

The instrument also contains a bottle sampling system which permits the analysis of grab samples and calibration solutions. Samples analyzed using the bottle sampler are not filtered and should be free of suspended matter. The procedure for analysis using the bottle sampler is identical to the on-line mode of operation, and the data may be obtained in the same manner.

Calibration of the analyzer is accomplished using known carbon solutions in the bottle sampling system and adjusting the gain controls until the data output agrees with the known concentration. Solutions of potassium hydrogen phthalate (KHP) or sodium carbonate (Na_2CO_3) are used as the carbon standards with a number of different concentrations run for each measurement scale to insure accurate calibration.

SECTION III

INSTRUMENT EVALUATION

SET-UP AND INSTALLATION

The total organic carbon analyzer was installed at the Tyndall AFB sewage treatment plant to conduct field evaluation. Continuous sample flow was provided to the analyzer using 1/2-inch PVC flexible piping from the overflow of the primary clarifiers by gravity feed at a rate of 3 gallons per minute. This line was connected to the 1/4-inch NPT connection of the sample filter, and the overflow continued to drain.

In addition to the sample service connection, the analyzer required electrical and compressed gas service hookups. Electrical power at 115 VAC and 6 amperes was supplied to the unit. Nitrogen compressed gas was provided to the rear of the analyzer from a standard 1A cylinder using 1/8-inch copper tubing and swagelok connectors. The gas feed pressure was regulated at the cylinder to 60 psi. The compressed air required for driving the sampling valve block assembly was generated on site, using a portable air compressor capable of providing the 3 CFM of air required. The compressed air service connection was made to the rear of the analyzer using 1/8-inch copper tubing and swagelok connectors (Figure 2).

ON-LINE OPERATION

An Ionics field engineer performed the necessary instrument checkout required to place the analyzer on-line and provided instruction on its operation and maintenance. Malfunctions in an electronic control card and the strip-chart recorder resulted in limited initial operating capability. Installation of replacement components restored the analyzer to normal operation.

On-line performance during the first weeks of operation was excellent. A continuous recording of TOC was obtained as shown in Figure 3. Both carbon peaks and distilled water peaks are evident in this spectrum chart

Figure 2. Rear Panel Controls of Analyzer

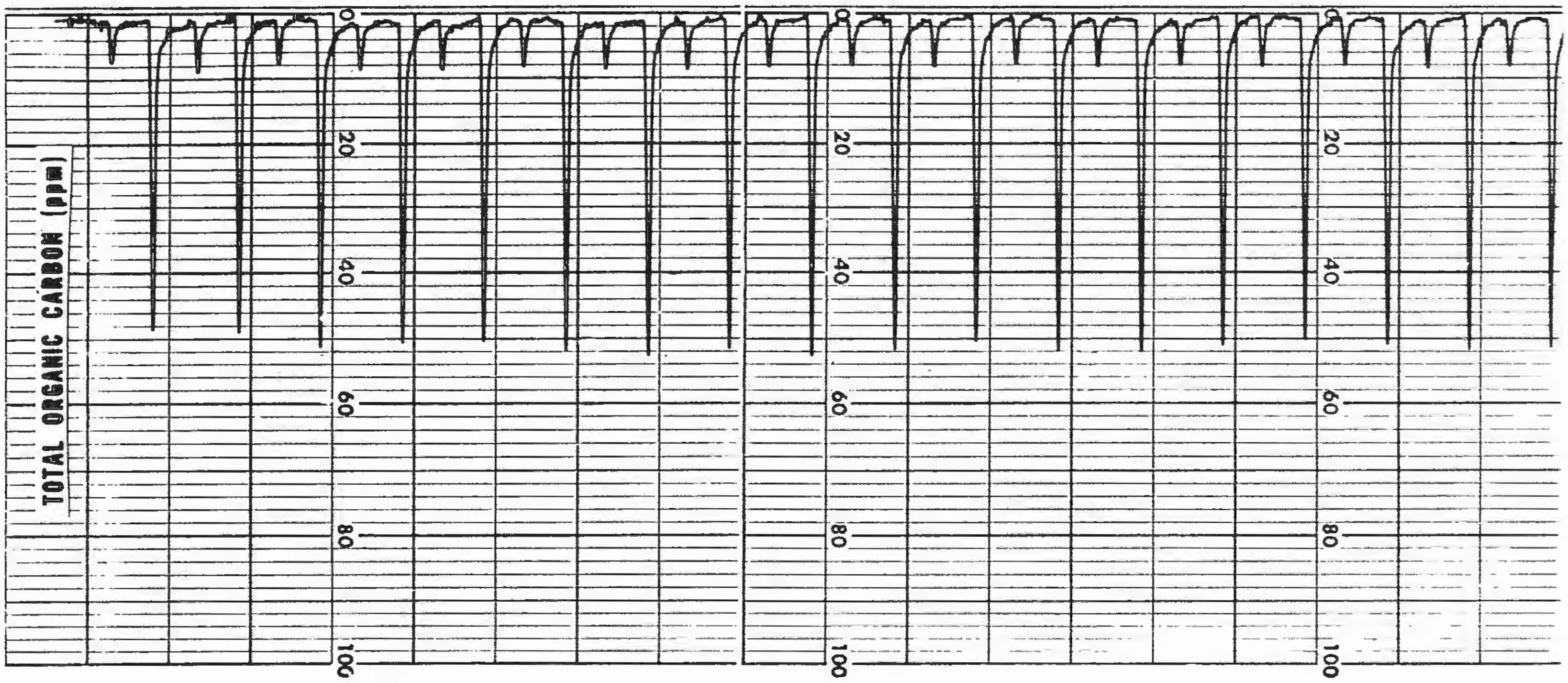

Figure 3. Typical Spectrum Strip-Chart Output

recording, with a TOC of approximately 50 ppm being recorded. During this time only routine servicing and weekly calibration were required. Chart paper required replacement at 5-day intervals, and additional hydrochloric acid was added weekly. Approximately 200 pounds per day of compressed nitrogen was consumed, resulting in a cylinder replacement every 10 days.

Several problems developed during routine operation of the instrument. Severe clogging of the Hallikaienen filter became a recurring problem. Daily removal and manual cleaning of the filter was required in order to operationally maintain the analyzer. Noted decreases in peak heights corresponded to the build-up of solids within the filter and contributed to a decrease in the level of TOC actually reported.

A problem was also encountered with the output signal from the infrared analyzer which became exceedingly noisy and unreproducible. The cause of the problem was traced to a series of power outages at the treatment plant which induced a change in the preamplifier oscillator voltage of the infrared analyzer. A complete optical alignment of the infrared unit was performed. The subsequent data collected showed significant improvement, with an increased level of TOC being recorded of a reproducible nature. This alignment required a general knowledge of electronics and the use of a precision voltmeter to check out the system and obtain accurate settings. Although a relatively simple task to perform, this realignment did result in significant down time.

Fouling of the palladium catalyst was experienced after approximately 6 weeks of operation. Attempts to calibrate the instrument with known solutions of KHP resulted in readings consistently below the standard, even at maximum gain. The cause of this problem was due to a build-up of foreign matter on the surface of the catalyst, thereby reducing its reaction-producing capability. The reaction chamber was removed from the furnace and the catalyst regenerated using boiling concentrated hydrochloric acid. Once the regenerated catalyst was replaced into the combustion tube and the analyzer returned to service, accurate TOC data was again obtained.

The Environmental Protection Agency (EPA) Regulations on Secondary Treatment Information established the authority to permit TOC data to be substituted for BOD data when a long term BOD:TOC correlation has been established (Reference 3). In order to determine if a valid correlation could be developed for this particular treatment plant, 24-hour daily composite samples were collected for BOD analysis. Both total BOD and filtered BOD analyses (using whatman GFC paper) were performed. These analyses determined the oxygen demand resulting from the presence of suspended matter and obtained an indication of the amount of organic matter removed from the wastewater by the filter system used on the analyzer. These BOD data were compared to the average daily TOC obtained using the hourly readings from the on-line analyzer to establish a ratio of TOC/BOD.

Figure 4 presents a typical ratio of TOC/BOD for the effluent of primary domestic sewage treatment plant with a mean of 0.75 and a standard deviation of 0.159 (Reference 4). EPA suggests a mean TOC/BOD_5 ratio of 0.617 for raw domestic waste and a ratio of 2.12 for the effluent from a secondary domestic treatment plant (Reference 2).

Data accumulated during this study are shown in Figure 5 as a ratio of TOC/BOD for both total (BOD_T) and filtered (BOD_F). The ratios exhibited a large degree of variability, resulting to some extent from a variance in sampling and laboratory analysis and the presence of some suspended matter in the samples analyzed for TOC. The variable nature of the data should tend to decrease as an increased number of data points are obtained. The mean TOC/BOD_5 ratio of 0.82 and standard deviation of 0.12 show agreement with data presented previously. Removal of suspended matter resulted in an increased TOC/BOD ratio of 1.43 and an increased standard deviation of 0.17.

The data were analyzed to determine the probability that a correlation existed between the two parameters, BOD and TOC. Figure 6 shows a graph of TOC versus total BOD. A correlation coefficient of 0.87 was calculated for this set of data which resulted in a 99 percent probability of correlation. Total organic carbon versus filtered BOD is plotted in Figure 7. These data also exhibited a 99 percent probability of correlation based on a calculated correlation coefficient of 0.89.

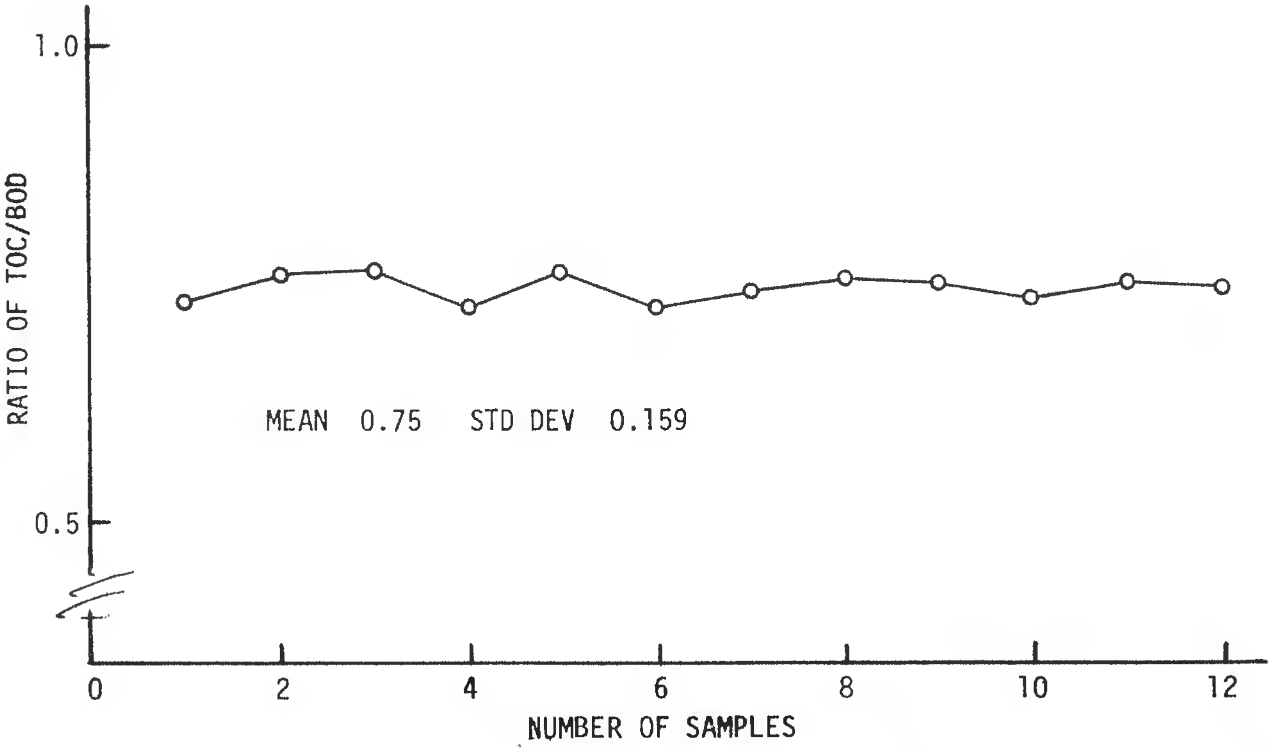

Figure 4. TOC/BOD Relationship for the Effluent of a Primary Sewage Treatment Plant

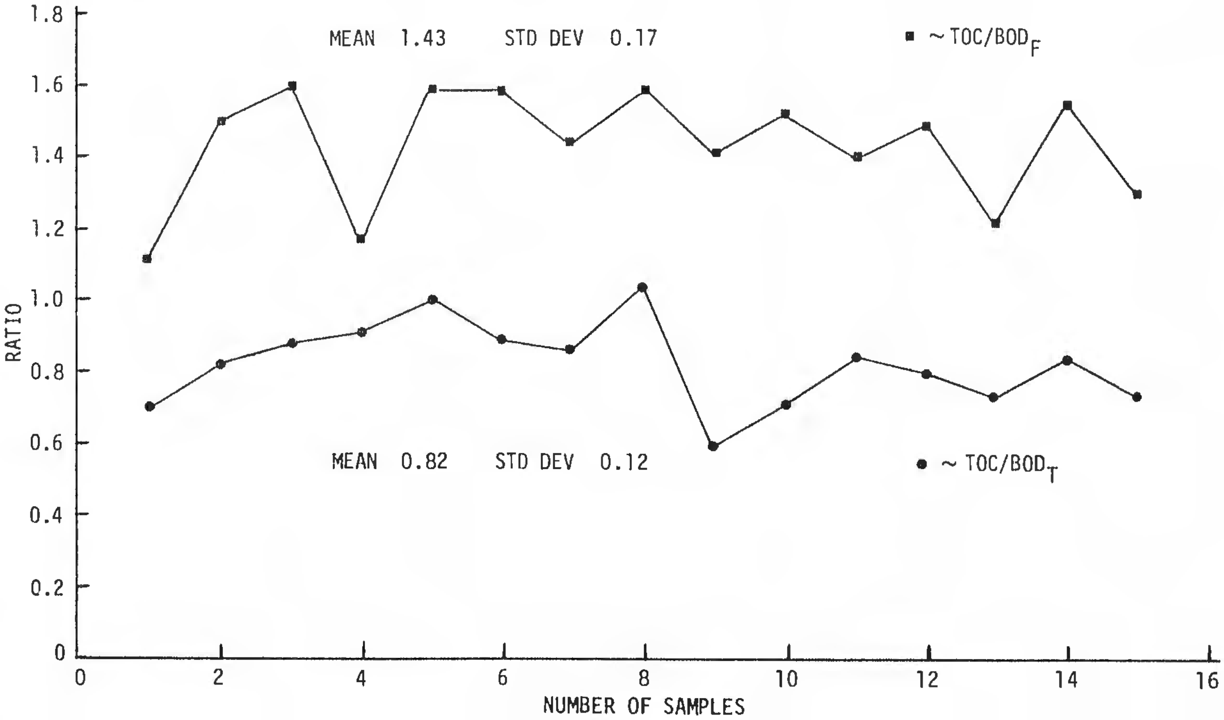

Figure 5. TOC/BOD$_F$ Data and TOC/BOD$_T$ Data

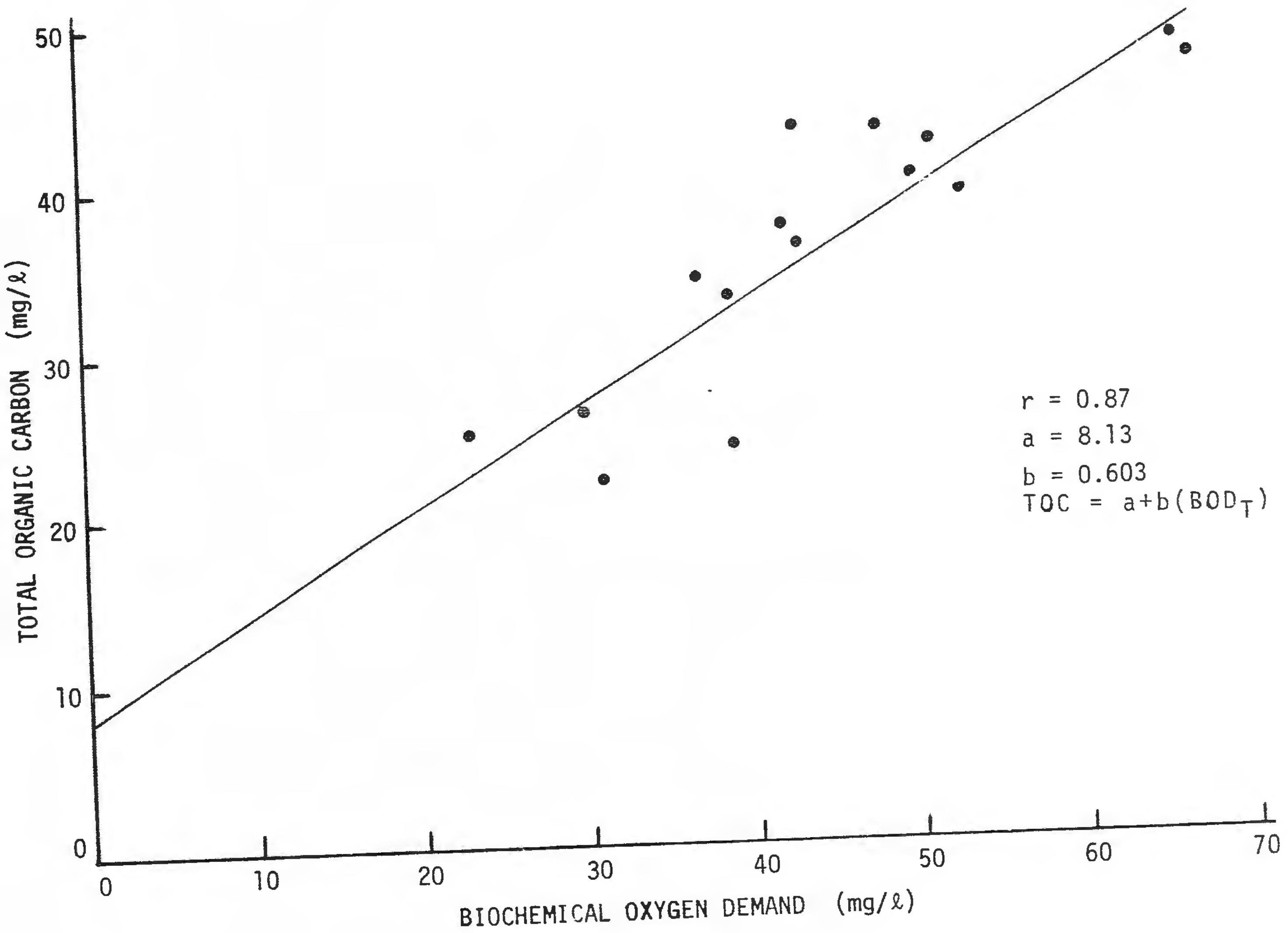

Figure 6. TOC Versus BOD$_T$ Correlation Data

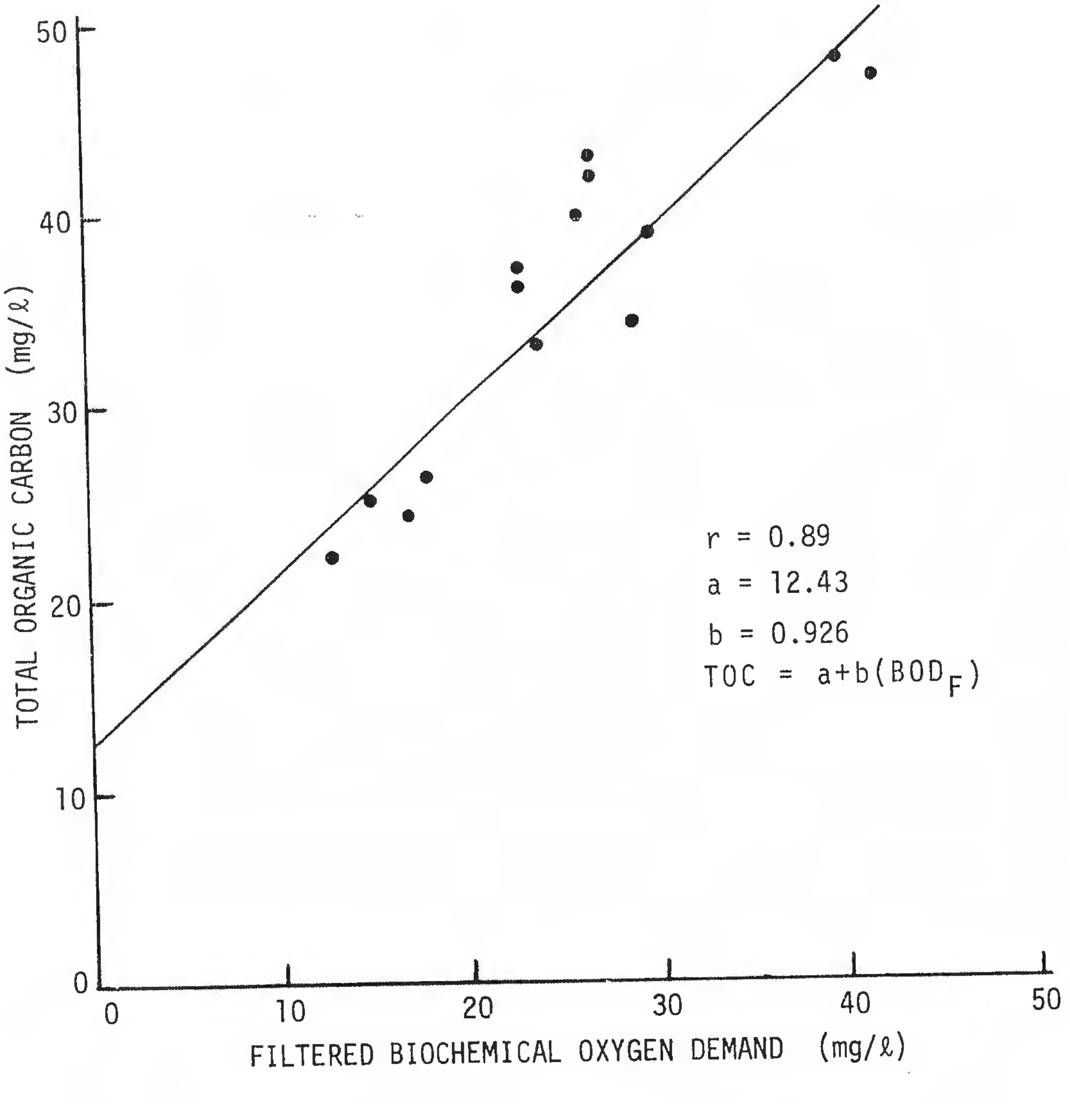

Figure 7. TOC Versus BOD_F Correlation Data

SECTION IV

MAINTAINABILITY

While the Model 1218 TOC Analyzer is designed for continuous on-stream operation, considerable routine attention must be given to various functions within the analyzer in order to maintain it. Normal weekly attention consists of replacing the chart paper and replenishing the hydrochloric acid supply. Unless the nitrogen gas cylinders are manifolded, the cylinders require replacement at approximately 10-day intervals. Periodic replenishment and cleaning of the distilled water wash system is required, in addition to tubing replacement of the acid wash system, depending on the particular operating location and type sample being analyzed. Weekly calibration is suggested in order to insure accurate analysis. However, daily calibration checks should be performed initially in order to determine the variability of the analyzer on a particular waste stream. Maintenance is also required to regenerate the palladium catalyst. The frequency of this servicing will vary depending upon the nature of the waste being analyzed. Catalyst regeneration requires removal of various components in the analyzer and results in significant down time. No special tools are required to perform this maintenance, and the manufacturer's instructions provide adequate technical guidance.

The maintenance of the infrared analyzer is specifically detailed by Mine Safety Appliance Company. Routine servicing of the analyzer is fairly straightforward. Realignment of the optics and adjustments to the amplifier can be accomplished using the manual which accompanies the analyzer and a 20,000-ohm/volt high impedance DC voltmeter. Any additional servicing should be accomplished by a qualified electronics specialist due to the complexity of the system.

Periodic servicing of the injection valve assembly and resurfacing of the valve blocks are required. This is a rather extensive procedure which should be accomplished by experienced instrumentation personnel.

SECTION V

CONCLUSIONS

The results obtained during this field evaluation indicated that a valid correlation of TOC:BOD could be established to enhance current monitoring capabilities on the wastewater analyzed. The Ionics On-line Total Organic Carbon Analyzer demonstrated the ability to measure organic carbon in the particular domestic wastewater tested. However, continuous operation of the analyzer was not favorable due to the degree of servicing required to maintain the filtration system. The filter was not capable of handling the level of suspended solids present in the sample, resulting in filter clogging and loss of sample flow to the analyzer. Sample pretreatment would be required for installation on domestic wastes in order to reduce the level of solids reaching the analyzer. This, however, would reduce a significant amount of the organic matter actually reaching the analyzer and would result in reduced values of TOC.

Continuous on-line operation required frequent maintenance of the support services: compressed nitrogen, hydrochloric acid wash, and recording paper. The periodic catalyst regeneration, infrared analyzer alignment, and valve block resurfacing require expertise and equipment not normally available at base sewage treatment facilities.

The frequency of total organic carbon analysis performed by the Ionics unit is probably excessive for monitoring domestic wastewater. An analysis time interval of every 30 to 60 minutes instead of every 5 minutes would suffice and would reduce the operational costs and maintenance requirements.

The current list price of this Ionics analyzer is $12,250 which includes start-up assistance and operator training but not the cost of the support services required. The cost of performing related laboratory analysis varies widely, ranging from $10.00 to $15.00 per sample at commercial laboratories for COD and $17.00 to $20.00 per sample for BOD. Prices for TOC analysis range from $9.00 to $25.00 per sample. The costs may be substantially higher for local base analysis due to the low frequency of performance. Current National Pollution Discharge Elimination System (NPDES) permits require weekly analysis for BOD at most Air Force bases. Based on this relatively infrequent analysis requirement, the high initial and operational costs of on-line TOC analyzers and the frequency of maintenance required, wide-scale use of this type instrumentation is not considered practical at this time. Future requirements for more frequent monitoring may necessitate the use of on-line instrumentation requiring additional training for Air Force water and wastewater operators and related maintenance personnel.

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