FISHERY WASTE EFFLUENTS: A METHOD TO DETERMINE RELATIONSHIPS BETWEEN CHEMICAL OXYGEN DEMAND AND RESIDUE

JEFF COLLINS AND RICHARD D. TENNEY[1]

ABSTRACT

Researchers and the fishing industry have experienced difficulty in applying the Environmental Protection Agency's standard tests to industrial fishing waste effluents, especially for total suspended and settleable solids, and oil and grease.

The relationship between chemical oxygen demand and residue was determined on a limited number of samples from four types of screened waste effluents from November 1973 to September 1974: shrimp using fresh or salt water processing, snow crab, and canned salmon. In addition to chemical oxygen demand and residue, tests for settleable solids, total suspended and settleable solids, oil and grease, protein, and salt were also performed. Based on these relationships, a method is suggested to develop a system for the analysis of pollutants that will be more economic and give more meaningful data than currently obtainable under Environmental Protection Agency's methods. The method requires that base data on a plant be obtained to relate chemical oxygen demand with residue values using regression lines and equations. A subsequent routine monitoring program need only test for total residue and chemical oxygen demand of the filterable residue. Substitution into the equations gives the other residue fractions and their chemical oxygen demand values, i.e., total chemical oxygen demand, chemical oxygen demand of the particulate matter, filterable residue, and nonfilterable residue.

This laboratory has modified and studied in detail a number of analytical techniques to measure pollutants (Tenney)[2]. We have considered the methods of testing specified by the Environmental Protection Agency (EPA) to monitor fishery pollutants and are of the opinion that the monitoring program and analytical methods specified under the National Pollutant Discharge Elimination System (NPDES) program could be improved for application to seafood-processing effluents (Pojasek 1975). The purpose of this paper is to suggest different tests for monitoring effluents with certain prerequisites that would satisfy the intent of the law, yet recognize both the technical and economic problems associated with the fishing industry's efforts to comply with the monitoring regulations.

Since laboratory space, equipment, and labor necessary to conduct a waste-monitoring program are quite expensive to the fishing industry, economics suggest the use of a minimum number of tests to do the job, and where possible, the use of inexpensive equipment. In some analyses, the time required to complete any analysis is important, as in the 5-day test for biological oxygen demand (BOD). In this instance, the chemical test (chemical oxygen demand–COD) provides quick results and has better application. The limited level of laboratory experience and equipment generally found in seafood-processing plants and their diverse and often remote locations also suggest that the regulations and permit system should reflect these limitations and require only fairly simple tests to measure pollutants. At the same time, however, analytical techniques used to measure pollutants must be accurate, have good precision, and be a meaningful measure of pollutants.

In this study we have evaluated the relationship between COD and residue of the screened effluents of four plants. Based on these correlations, a monitoring system is suggested that enables the results of two analyses to provide data on six pollutant parameters.

EXPERIMENTAL

Identification and Definition of Terms

BOD (*Biochemical oxygen demand*): oxidation by bacteria.

[1]Pacific Utilization Research Center Kodiak Utilization Research Laboratory, National Marine Fisheries Service, NOAA, P.O. Box 1638, Kodiak, AK 99615.

[2]Tenney, R. D. 1972. COD for Industrial Waste Water, Tech. Rep. 97, 5 p.; 1972. Chemical Oxygen Demand, Tech. Rep. 101, 12 p.; 1973. Shrimp Waste Streams and COD, Tech. Rep. 104, 3 p. Unpublished, intralaboratory reports, Kodiak Utilization Research Laboratory.

Manuscript accepted April 1976.

COD (*Chemical oxygen demand*): oxidation by potassium dichromate.

Residue: This term does not necessarily mean solids, rather it is the results of or the substance remaining from a separation process such as filtering or drying. For example, if a solvent is evaporated from oil, the resulting residue is a liquid, not a solid.

TR (*Total residue*): is the weight of material remaining from a sample of the original screened effluent after overnight drying at 103°C.

FR (*Filterable residue*): is the residue of the filtrate (GF/A glass filter) dried at 103°C. Drying seafood effluents at 180°C (Environmental Protection Agency 1974) produced results that could not be related to the TR and nonfilterable residue.

NFR (*Nonfilterable residue*): is the residue remaining on the glass filter after drying at 103°C. Since the three residue terms are related and provided drying conditions are the same, NFR can be determined indirectly, i.e., TR - FR.

SS (*Settleable and floatable solids*): This term has caused considerable trouble to the industry and researchers. By custom, the volume of the settled portion in the Imhoff cone is measured and considered SS. However, this measurement does *not* actually measure SS, because floatables are not included in the reading. The term only has correct meaning when SS is determined in milligrams/liter by difference: the NFR minus the NFR of a sample taken from near the center of the Imhoff cone after 1 h of settling.

Sus. Sol. (*Suspended solids*): are the particulate matter suspended in the center of the Imhoff cone, i.e., the NFR of that area.

TSS (*Total suspended nonfilterable solids*): This term has also caused confusion. It means the dry weight of all particulate matter (settleable, suspended, floatable), i.e., the NFR. For both technical and grammatical reasons, NFR is the preferred term.

O&G (*Oil and grease*): content was determined by a method in which the precipitated, filtered-solids material plus Celite[3] (used as a precipitation aid) is extracted directly under anhydrous conditions, using 2-propanol and petroleum ether (Collins 1976). This technique extracts all lipidlike material, including carotenoids.

Protein: The nitrogen content was determined by the macro-Kjeldahl method on 100- to 200-g samples and expressed as protein by multiplying N by 6.25 (Horwitz 1965:273).

Salt: Chloride was determined by the standard $AgNO_3$ method and expressed as NaCl (Horwitz 1965:273).

Subscripts: In this paper, we use subscripts to identify the particular portion of the sample tested. For example, COD_{TR} is the COD of the screened waste effluent, and COD_{FR} is the COD of the FR, i.e., the filtrate, not the actual dried FR. If no subscript is used, we are referring to the test in general or to the test on the original screened sample, i.e., COD is the same as COD_{TR}.

Industrially screened shrimp and crab effluents were obtained from November 1973 through February 1974 and from salmon effluents July through September 1974. Since our purpose was to compare data rather than characterize the level of pollution in a plant, we took grab samples at specific times during the production to get a useful range of values. The following analyses were made: COD_{TR}, COD_{FR}, TR, FR, NFR (i.e., TSS), SS, protein, O&G, salt, and the COD of a sample from the center of the Imhoff cone after 1 h of settling.

In conducting these analyses we used the methods of the Environmental Protection Agency (1974), unless otherwise indicated. The particulate matter in our samples of fishery waste was so high that the filter clogged frequently before the entire sample had been filtered. For this reason, sample sizes were reduced, where necessary, to 25 ml.

The degree of pollutant in an effluent is affected by the processes employed, species processed, and the use of fresh or salt water in varying degrees during processing. Mechanical shrimp peelers use about 7 gallons of water per pound of shrimp. Salt water from wells close to the shore or from the ocean is sometimes used on the mechanical peelers. The two main types of peelers vary in their relative waste load. The Model A peeler peels raw shrimp and generally has a higher waste load than the Model PCA peeler that peels a steam-blanched shrimp.

RESULTS

Study 1—Shrimp: Analyses of effluents from a shrimp plant processing with fresh water and mechanical peelers (Model A).

Over a 10-day period in December 1973, eight samples of waste effluents were taken from the underflow of the Bauer Hydrasieve (tangential screen, 0.04-inch) and analyzed (Table 1). Averages for COD by analysis are as follows:

[3]Reference to trade names does not imply endorsement by the National Marine Fisheries Service, NOAA.

a. COD, screened effluent 3,257 mg/liter
b. COD, center of Imhoff cone 3,043 mg/liter
c. COD, filtrate of NFR test 1,616 mg/liter

By calculation, the COD of the particulate matter and its percentage contribution to the total COD are:

COD of NFR (a - c) = 1,641 mg/liter 50.4%
COD of SS by weight (a - b) = 214 mg/liter 6.6%
COD of Sus. Sol. [(a - c) - (a - b)] = 1,426 mg/liter 43.8%

By analysis and calculation, data were also obtained for the means of other residue tests:

By analysis:
d. Total residue (TR) 2,381 mg/liter
e. Filterable residue (FR) 1,577 mg/liter
f. Settleable solids (SS) 5.6 ml/liter
g. Nonfilterable residue (NFR) 769 mg/liter

By calculation: NFR, i.e., (d - e) or TR - FR = 804 mg/liter.

By weight, the FR was 66.3% of the TR, but the COD of the FR was only 49.6% of the total COD. The NFR, however, contributed only 33.7% to the TR by weight but contributed 50.4% as COD.

The standard deviations (SD) in Table 1 show relatively large values in agreement with practical experience. The higher average concentration and lower SD for the NFR determined by difference suggests that this is a better method for determining the concentration of NFR than is the direct analysis.

Study 2—Shrimp: Analyses of effluents from a shrimp plant processing with salt water and mechanical peelers (Models A and PCA).

Ten samples of waste effluent were taken from the underflow of the 0.7-mm Dorr-Oliver screen. The individual results are given in Table 2, and the average analytical data are as follows:

a. COD, screened effluent 2,643 mg/liter
b. COD, center of Imhoff cone 2,338 mg/liter
c. COD, filtrate from NFR test 1,519 mg/liter
d. Settleable solids (SS) 7.8 ml/liter
e. Nonfilterable residue (NFR) 684 mg/liter

TABLE 1.—Analyses of shrimp waste effluents from a plant processing with fresh water and mechanical peelers (Model A). All values are in milligrams per liter except SS in milliliters per liter.

Date of sample	Screened effluent		Filtrate (glass filter)		By difference		Center Imhoff	SS	Direct analysis
Dec. 1973	COD_{TR}	TR	COD_{FR}	FR	COD_{NFR}	NFR	COD	Vol	NFR
11	3,070	2,370	1,492	1,640	1,578	730	2,856	8.0	880
12	3,364	2,660	2,040	1,990	1,324	670	3,212	7.0	840
13	3,068	2,290	1,580	1,540	1,488	750	2,912	3.0	656
14	2,516	1,970	1,240	1,350	1,276	620	2,312	7.0	796
18	3,353	2,280	1,405	1,360	1,948	920	2,956	11.0	892
19	2,660	1,790	1,080	1,010	1,580	780	2,418	2.0	120
20	2,962	2,040	1,588	1,420	1,374	620	2,841	2.5	660
21	5,065	3,650	2,500	2,310	2,565	1,340	4,836	4.0	1,308
Mean	3,257	2,381	1,616	1,577	1,642	804	3,043	5.6	769
SD	789	578	455	407	428	238	781	3.2	332

TABLE 2.—Analyses of shrimp waste effluents from a plant processing with salt water and mechanical peelers (Models A and PCA). All values are in milligrams per liter except SS in milliliters per liter.

Date of sample	Screened effluent		Filtrate (glass filter)		By difference		Center Imhoff	SS	Direct analysis
	COD_{TR}	TR	COD_{FR}	FR	COD_{NFR}	NFR	COD	Vol	NFR
18 Nov. 1973	3,264	33,500	—	—	—	—	2,915	8.0	993
27 Nov.	4,050	—	2,690	—	1,360	—	3,883	3.0	—
7 Dec.	2,090	25,550	1,212	25,360	878	190	1,882	4.0	580
10 Dec.	3,161	34,090	1,729	33,780	1,432	310	2,935	9.0	1,212
2 Jan. 1974	3,143	27,730	1,733	—	1,410	—	2,849	8.0	1,008
9 Jan.	2,364	23,314	1,353	—	1,011	—	2,021	9.0	180
1 Feb.	2,890	23,300	1,363	23,100	1,527	200	2,487	10.0	616
4 Feb.	1,948	26,610	1,100	—	848	—	1,640	9.5	476
7 Feb.	2,442	23,940	1,659	—	783	—	1,806	9.5	896
15 Feb.	1,080	25,240	828	25,200	252	40	960	8.0	192
Mean	2,643		1,519		1,056		2,338	7.8	684
SD	836		534		415		839	2.4	367

By calculation, the COD of the particulate matter and its percentage contribution to the total COD are:

COD of NFR	(a - c) =	1,124 mg/liter	42.5%
COD of SS	(a - b) =	305 mg/liter	11.5%
COD of Sus. Sol.	[(a - c) - (a - b)] =	819 mg/liter	31.0%

Some figures were also collected on the concentration of residues by direct analysis and are included in the table to illustrate the problems associated with monitoring plants that process with salt water. Residue values were not determined by calculation because of the high and variable salt content. It is questionable that meaningful data for NFR can be obtained because of errors that can occur when the salt values of about 25,000 mg/liter are subtracted from the mean TR values of about 27,000 mg/liter.

Study 3—Snow Crab: Analyses of effluents from a plant processing both meats and sections in fresh water.

Over a 2-wk period in February 1974, six samples of waste effluent from a plant processing snow crab using fresh water were taken from the underflow of Dorr-Oliver 0.4-mm screen and analyzed (Table 3). Average values by analysis are as follows:

a.	COD, screened effluent	1,426 mg/liter
b.	COD, center of Imhoff cone	1,332 mg/liter
c.	COD, filtrate from NFR test	824 mg/liter
d.	Total residue (TR)	1,393 mg/liter
e.	Filterable residue (FR)	1,086 mg/liter
f.	Settleable solids (SS)	4.2 ml/liter
g.	Nonfilterable residue (NFR)	277 mg/liter

By calculation, the mean values for COD of the particulate matter and its percentage contribution to the total were:

COD of NFR	(a - c) =	602 mg/liter	42.2%
COD of SS	(a - b) =	94 mg/liter	6.6%
COD of Sus. Sol.	[(a - c) - (a - b)] =	503 mg/liter	42.2%

By calculation, the mean value for NFR is: (d - e) = 307 mg/liter.

Study 4—Salmon: Analyses of effluents from a plant processing canned salmon.

During the summer of 1974, ten samples of

TABLE 3.—Analyses of snow crab waste effluents from a plant processing both meats and sections in fresh water. All values are in milligrams per liter except SS in milliliters per liter.

Date of sample Feb. 1974	Screened effluent		Filtrate (glass filter)		By difference		Center Imhoff	SS	Direct analysis
	COD_{TR}	TR	COD_{FR}	FR	COD_{NFR}	NFR	COD	Vol	NFR
6	680	880	506	770	174	110	599	1.3	126
8	888	960	650	850	238	110	868	0.5	41
11	1,056	1,230	746	1,030	310	200	974	5.0	143
14	1,560	1,590	870	1,280	690	310	1,408	4.0	462
19	1,988	1,900	1,077	1,500	911	400	1,889	7.5	540
25	2,383	1,800	1,093	—	1,290	—	2,254	7.0	348
Mean	1,426	1,393	824	1,086	602	226	1,332	4.2	277
SD	668	433	235	303	442	127	640	2.9	202

TABLE 4.—Analyses of salmon waste effluents from a plant processing canned salmon. All values are in milligrams per liter.

Date of sample 1974	Salmon	Screened effluent					Filtrate — glass filter				By difference	
		COD_{TR}	TR	Protein	O&G	Salt	COD_{FR}	FR	Protein	Salt	COD_{NFR}	NFR
30 June	Red	5,716	3,695	2,197	1,190	574	1,365	1,513	1,044	545	4,351	2,182
7 July	Red	2,908	2,076	1,500	330	373	1,212	1,135	656	273	1,696	941
8 July	Red	4,069	2,368	1,453	918	253	1,131	1,078	744	247	2,938	1,290
11 July	Chum	2,070	1,125	1,179	308	—	797	350	531	453	1,273	775
14 July	Chum	6,294	4,450	2,980	—	728	2,687	2,560	1,775	436	3,607	1,890
17 July	Pink	9,513	7,102	—	—	596	4,020	3,655	3,346	465	5,493	3,447
30 July	Chum	9,101	6,315	3,346	1,407	397	3,420	2,813	—	—	5,681	3,502
13 Aug.	Pink	5,236	3,595	2,378	845	493	1,462	1,465	1,009	459	3,774	2,130
14 Aug.	Pink	2,647	2,148	1,518	226	344	1,822	1,570	1,168	292	825	578
22 Aug.	Mixed	6,219	4,874	3,263	924	642	2,615	2,722	1,938	556	3,604	2,152
Mean		5,377	3,775	2,201	769	489	2,053	1,886	1,357	414	3,324	1,889
SD		2,557	1,937	840	437	157	1,078	1,007	885	115	1,664	1,026

salmon cannery waste effluent were taken from the underflow of a Bauer screen (0.03-inch) (Table 4). The average values by analysis and calculation are as follows:

a.	COD, screened effluent	5,377 mg/liter
b.	COD, filtrate of NFR test	2,053 mg/liter
c.	COD, of NFR (a - b)	3,324 mg/liter
d.	Total residue	3,775 mg/liter
e.	Filterable residue	1,886 mg/liter
f.	Nonfilterable residue (d - e)	1,889 mg/liter
g.	O&G, screened effluent	769 mg/liter
h.	Protein, screened effluent	2,201 mg/liter
i.	Salt, screened effluent	489 mg/liter

The NFR is 50% of the TR, but the COD of the NFR is 62% of the total COD.

DISCUSSION

The following discussion is concerned with monitoring parameters previously suggested or currently in effect under EPA effluent limitations for seafood processing and with the suggestion of a more precise and simpler monitoring system. The present EPA requirements, however, for use of alternative analytical methods must be considered. Under EPA rules (Title 40 "Code of Federal Regulations," Parts 136.4 and 136.5), any person wishing to use alternative analytical methods for the parameters listed must follow variance procedures specified under the NPDES permit system.

Current permits require monitoring for SS, COD (i.e., COD_{TR}), TSS (i.e., NFR), O&G, flow, and pH. SS is imprecise and contributes so little to the pollution load in seafood processing that it has relatively little value as a measure of pollution, although it has merit as a check on the efficiency of screen operation. As discussed later, total COD can be determined more accurately in an indirect manner. The O&G analysis is difficult to do, and this value, too, can be obtained more accurately through calculation. Data in this paper suggest that the indirect analysis for NFR (i.e., TSS) was more accurate than the direct method. The FR is an important parameter because this fraction contributed about 50% to the total COD or TR and will need to be considered in the design of future treatment systems.

To develop an improved monitoring system, we plotted the COD and residue data of Table 1 to illustrate the correlation between the COD of the residue and the concentration of the residue (Figure 1). The regression lines and equations were determined by the method of least squares. The TR and FR regression lines were obtained through direct analyses, and the NFR line was obtained by difference. The maximum deviation of any COD value from the regression line was 260 mg/liter. This is slightly less than the possible error of the analytical method (± 8%) (Moore et al. 1949). On the average, the individual values were within 107 mg COD of the regression line.

The correlations shown in Figure 1 can be used to calculate COD and residue values. In the following, the first three equations are the regression lines of Figure 1 and the next three are derived equations to solve for residue rather than for COD. Of course, these equations are valid only for this group of data and for this particular plant. If the TR and COD_{FR} are determined by analysis, the other values can be derived from the equations or the regression line and from the expression TR = FR + NFR.

$$COD_{TR} = 1.32\,TR + 113 \quad (1)$$
$$COD_{FR} = 1.08\,FR - 96 \quad (2)$$
$$COD_{NFR} = 1.78\,NFR + 210 \quad (3)$$

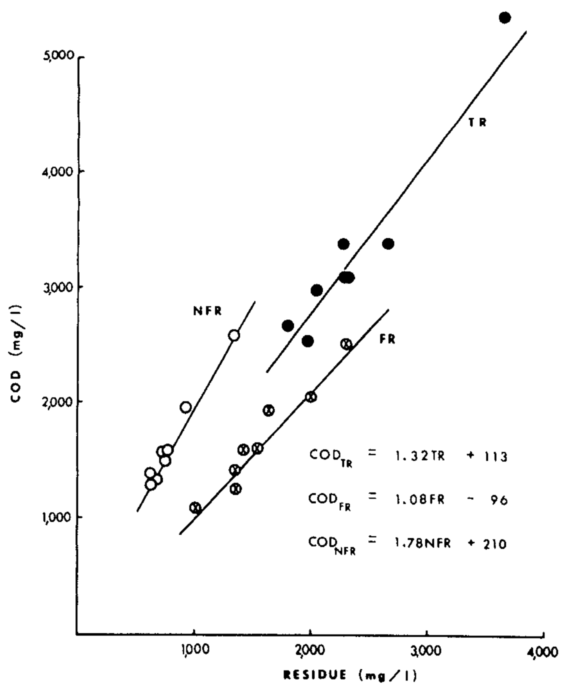

FIGURE 1.–Relationship between the COD of the residue and the concentration of the residue from shrimp processed on Model A peelers using fresh water.

$$TR = 0.76\ COD_{TR} - 86 \quad (4)$$
$$FR = 0.93\ COD_{FR} - 89 \quad (5)$$
$$NFR = 0.56\ COD_{NFR} - 118 \quad (6)$$

When salt water was used in processing, such as in the second plant study (Table 2), the residue values included salt. Since salt values were not determined, COD and residue data were not correlated for this plant.

In the third plant study of snow crab effluent, the data (Table 3) were plotted similarly to the shrimp data (Figure 2). The basic equations for snow crab can also be used to calculate from two analyses the other COD or residue values. The equations are listed in Figure 2.

Data for the fourth plant study of salmon-waste effluents (Table 4) were also plotted, and the regression lines and equations were similarly determined (Figure 3). The regression lines for salmon are less precise because of the variable salt content of the effluent and the high levels of COD and residue. Salt varied because of the erratic operation of the salmon egg-processing room. These regression lines (salmon) should not be used to calculate or interpolate COD or residue values unless a check is first made on salt content. If salt content of the effluent is about normal (500 mg/liter), the calculation is valid since these equations are derived from data with a high standard deviation for salt. A check is made to ensure that the level is not 1 or 2% as it could be if a brine tank were dumped. A routine composite sampling program for the plant, of course, would reduce salt variation.

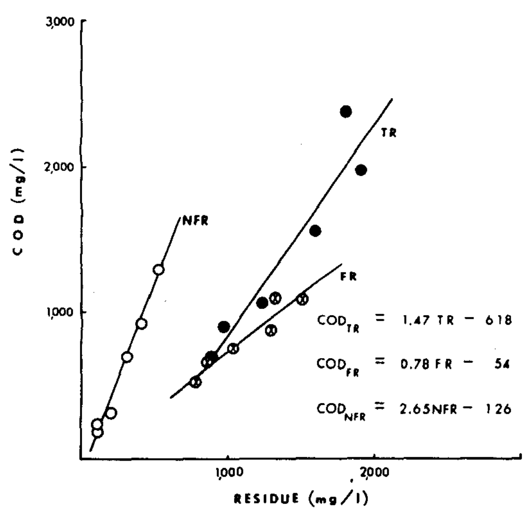

FIGURE 2.—Relationship between the COD of the residue and the concentration of residue from the processing of snow crab meats and sections.

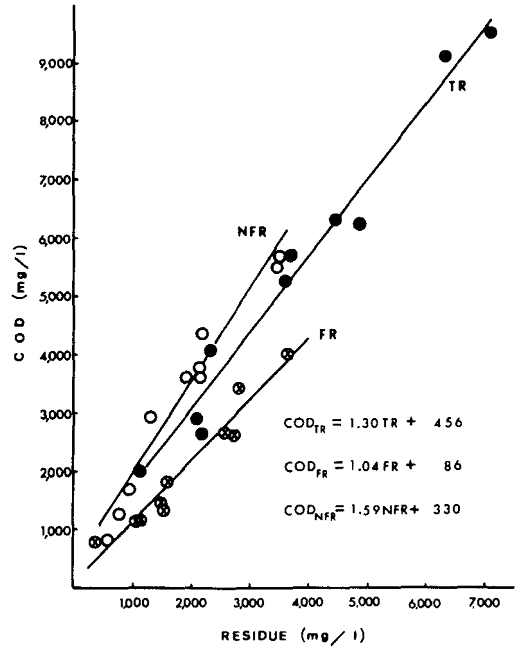

FIGURE 3.–Relationship between the COD of the residue and the concentration of the residue for canned salmon processing.

A SIMPLIFIED MONITORING SYSTEM

The data of the first plant study (Table 1) and the six equations listed earlier may be used to illustrate how a simplified monitoring system can be set up for a particular plant.

Since COD is difficult to determine on the original effluent (particulate matter causes dilution problems) and impractical to determine on a solid sample, COD should be determined on the filterable residue sample before drying. Equation (5) is then used to calculate FR in milligrams per liter. It is not necessary to actually finish the FR test. The next analysis most logically should be the total residue test. It is an easy test to do and is accurate. Equation (1) is used to calculate the COD of the TR, and the previously calculated FR is subtracted from TR to give the NFR in milligrams per liter. Equation (3) is then used to calculate the COD of the NFR. Thus, two analyses plus several calculations give three COD and three residue values.

The two analyses recommended (COD_{FR} and TR) are logically the most accurate of the six possible, thus the other calculated values that are based on an ideal regression line should be more valid than those obtainable by direct analysis. Although this system may suggest doing the FR rather than the COD_{FR}, we believe that one direct analysis for COD is desirable, since the effect of oxygen demand on the receiving water is an important parameter of a monitoring program. Although O&G were not specifically considered except for salmon, for which we had limited data, the COD and residue data imply that O&G are related and that a regression line could be calculated.

In conclusion, it appears that in-plant monitoring for COD_{FR} and TR and the application of proper correlation factors and equations previously determined for the plant effluent will give reportable data on COD_{TR}, COD_{NFR}, COD_{FR}, TR, FR, and NFR. The suggested analyses can be done at reasonable cost with simple equipment, are capable of good precision and accuracy, and can be conducted by quality assurance personnel in the fishing industry. We suggest, recognizing the limitations of our data and obvious and known differences between processing plants and processing methods, that if regression lines or correlations similar to those given in this paper were determined, the resulting monitoring system would be simpler and more accurate than that currently in use.

In a subsequent paper, we will report regression data for protein and O&G similar to that suggested in this paper and a method using a simultaneous equation to calculate protein and O&G from TR and COD data.

LITERATURE CITED

COLLINS, J.
1976. Oil and grease: A proposed analytical method for fishery waste effluents. Fish. Bull., U.S. 74:

ENVIRONMENTAL PROTECTION AGENCY.
1974. Methods for chemical analysis of water and wastes. Environ. Prot. Agency, Off. Tech. Transfer, Meth. Dev. Qual. Assurance Res. Lab., Natl. Environ. Res. Cent. 298 p.

HORWITZ, W. (chairman and editor).
1965. Official methods of analysis of the Association of Official Agricultural Chemists. 10th ed. Association of Official Agricultural Chemists, Wash., D.C., xx + 957 p.

MOORE, W. A., R. C. KRONER, AND C. C. RUCHHOFT.
1949. Dichromate reflux method for determination of oxygen consumed. Anal. Chem. 21:953-957.

POJASEK, R. B.
1975. NPDES permits and water analyses. Environ. Sci. Technol. 9:320-324.