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# MONITORING FOR LAS IN NORTHERN CALIFORNIA SLUDGE DIGESTERS



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MONITORING FOR LAS IN NORTHERN  
CALIFORNIA SLUDGE DIGESTERS

by

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## I. INTRODUCTION

### NEED FOR INVESTIGATION

The investigation reported herein was performed in response to a rash of operational difficulties arising at many treatment plants in the Northern California area in 1963 and continuing for several years thereafter. An unprecedented number of digester failures and upsets were occurring for no apparent reason. These problems were also being experienced in other sections of the United States as well as in the United Kingdom, and the universality of these complaints suggested a universal cause.

Synthetic detergents were considered by many to be a possible causative agent despite the 1965 industry-wide conversion from the biologically resistant alkyl benzene sulfonate-based detergents (ABS) to the more easily biodegradable linear alkylate sulfonate-based detergents (LAS). Although LAS is highly biodegradable in aerobic sewage treatment processes, it does not degrade to an appreciable extent in anaerobic systems [1].

ABS was found by the author [2] to cause digester failure at a level of 750 mg/l. Other investigators [3-7] have reported similar findings in the 600 to 900 mg/l range. Since ABS and LAS differ only slightly in chemical structure and physical behavior, it was thought that their critical levels might be nearly the same.

The critical level would be reached sooner in the United Kingdom where per capita water use is less and the detergent concentration in wastewater is approximately twice that found in the United States.

Whether or not detergents were responsible, there was indeed prior concern in the United Kingdom over digester problems. This concern was serious enough that in 1961 the Water Pollution Research Laboratory at Stevenage began a series of investigations into the causes of digester failures. Based on these laboratory studies Swanwick, Bruce, and Vandyke [8] reported that a 2 percent detergent concentration (dry weight total solids basis) in sewage sludge could cause severe inhibition of sludge digesters, although it was possible to operate above this level provided careful operating conditions were observed. It was further found that initiation of digestion was hampered by a concentration as low as 1 percent. A survey of twenty-five failed digesters revealed that the concentration of detergents in the digester sludge ranged from 0.6 to 1.8 percent, but it was not determined that detergents caused these failures.

A more recent survey by Swanwick, Shurben, and Jackson [9] of 142 sewage works with a total of 342 mesophilic digesters indicated that only 5.2 percent of digester problems were attributed to detergents. The majority of difficulties were attributed to inadequate design or operation (56.2 percent), and 37.2 percent of the difficulties were attributed to trade wastes.

To assess the United States position more carefully with respect to the levels of synthetic detergents present in digesters, in 1968 a monitoring program was established at five Northern California sewage treatment plants. This program was designed to provide baseline information during normal operation which should prove useful if an upset occurs in the future. In that event the relationship between detergent concentration and digester performance can be evaluated,

and the role of synthetic detergents as a primary cause of the digester difficulty in question might then be established.

#### NATURE AND SCOPE OF INVESTIGATION

A year-long study was initiated in June of 1968. Of the five treatment plants selected for inclusion in the study, four had experienced severe and recurring digester problems for several years while the fifth, Stege Sanitary District Wastewater Treatment Plant, remained relatively free of operational difficulties. It was of interest then to determine whether there was a significant difference in detergent concentration between Stege and the other plants which might be correlated to digester upsets.

The Stege plant is located on the east side of San Francisco Bay and serves an estimated population of 45,000 persons. The district is largely residential in nature, with only a small number of light industries in the area.

Largest of the plants monitored is the East Bay Municipal Utility District Water Pollution Control Plant which serves a population of 600,000. Also in the East Bay area are the City of Richmond Sewage Treatment Plant serving a population of 75,000 and the Central Contra Costa Sanitary District serving a population of 200,000.

The only West Bay plant studied was the North San Mateo County Sanitary District Sewage Treatment Plant serving approximately 50,000 residents of Daly City, California.

The monitoring program consisted of sampling influent raw sludge and circulating digester sludge on a once-per-week basis. The plants involved in the program followed their customary routine of

analyzing the sludge samples for pH, total solids, volatile solids, alkalinity, and volatile acids. Results of these analyses and other pertinent data on hydraulic and organic loading were recorded on data sheets. This information, together with a portion of the sludge samples, was submitted to the Sanitary Engineering Research Laboratory for analysis of synthetic detergent concentration reported as Methylene Blue Active Substances (MBAS).

#### ORGANIZATION OF STUDY

The monitoring program was conducted by the Sanitary Engineering Research Laboratory of the University of California at Berkeley under the terms of Research Grant No. 442418-52600-K by the Soap and Detergent Association to The Regents of the University. Professor P. H. McGauhey served as Faculty Investigator and Mr. S. A. Klein as Project Engineer.

Mr. Glenn Davis, Superintendent of the Operation Section of the East Bay Water Pollution Control Plant, selected and organized a steering committee. It consisted of plant operators or delegated personnel from the participating treatment plants and was established to coordinate and guide the study. The committee members were as follows:

Glenn Davis, Committee Coordinator  
 David Niles, Central Contra Costa Plant  
 Bob Bernicchi, North San Mateo Plant  
 Ed Macdonald, Richmond Plant  
 Fred Lowell, Stege Plant  
 S. A. Klein, SERL

Under the guidance of this committee the research program was established and carried out.

#### ACKNOWLEDGMENTS

The project staff is indebted to the committee members and other personnel of the participating plants for their cooperation in collecting, analyzing, and transporting samples to SERL and to Mr. Paul Graham of the SERL staff for conducting MBAS analyses.

II. MATERIALS AND METHODS

DATA COLLECTION

Sample data sheets (see Figure 1) were provided to participating plants for ease of data transmittal. Each week the information indicated was recorded and submitted to SERL along with raw and digested sludge samples. At SERL these data were transferred to a master sheet (see Figure 2) and results of MBAS analyses were added.

Several departures from the normal sampling schedule were made. Starting in January of 1969, two additional digesters were sampled each week at the Central Contra Costa plant. This was done to compare the MBAS levels in different digesters of the same plant. Also, one digester (Digester A) functioned at an unusually high volatile acids concentration, which led to speculation regarding its general condition and whether its MBAS concentration was measurably different.

The operation of the Stege plant was severely impaired by winter rain storms, and the added burden of making repairs forced the plant personnel to withdraw from the program in February of 1969.

At the conclusion of the monitoring period, bottom sludge samples were collected from the East Bay and Central Contra Costa plants. This was done in order to determine the MBAS content of this thick, sandy material which accumulates and may have an effect on digester performance.

SAMPLE PREPARATION

Due to the extremely high viscosity of raw sludge samples, an initial 1:1 dilution had to be made before an aliquot could be pipetted.

Date \_\_\_\_\_

Weather \_\_\_\_\_

Average Daily Flow, mgd \_\_\_\_\_

Flow at Time of Sampling, mgd \_\_\_\_\_

Digester Loading

    Total, lb solids/cu ft/day \_\_\_\_\_

    Volatile, lb VS/cu ft/day \_\_\_\_\_

Raw Sludge

    Time \_\_\_\_\_

    Total Solids, % \_\_\_\_\_

    Volatile Solids, % \_\_\_\_\_

Circulating Digester Sludge

    Time \_\_\_\_\_

    Total Solids, % \_\_\_\_\_

    Volatile Solids, % \_\_\_\_\_

    pH \_\_\_\_\_

    Volatile Acids, mg/l HOAc \_\_\_\_\_

    Alkalinity, mg/l CaCO<sub>3</sub> \_\_\_\_\_

FIGURE 1. SAMPLE DATA SHEET





## III. RESULTS

In Appendix C a complete tabulation of plant data and MBAS results for each week is presented. Had a digester upset occurred during the monitoring period the plant data on loading and pH equilibrium response would be helpful in determining the exact cause. Inasmuch as all the digesters functioned normally, this information serves as a background to be relied upon should a future incident occur. In this event, samples will be taken and comparisons of the current data to background data will be made.

## ORGANIC LOADING

Organic loading of the digesters is shown in Table I with average monthly values indicating seasonal variation - particularly at the East Bay plant which receives cannery wastes. The overall average loading values indicate the digesters surveyed represent a broad range of rates. Notable are low rates at Stege, Richmond, and North San Mateo; an intermediate rate at Central Contra Costa; and a fairly high rate at East Bay.

The results of MBAS analyses are summarized in Table II in terms of the monthly average as percent MBAS of total solids on a dry weight basis.

## MBAS CONCENTRATION OF RAW SLUDGE

The overall average indicates that concentrations are similar at all five plants. The minimum value was 0.48 percent MBAS at Stege and the maximum value was 0.63 percent MBAS at Central Contra Costa.

TABLE I  
MONTHLY AVERAGES OF DIGESTER LOADING  
Volatile Solids, lb/(cu ft/day)

Plant Month	Stege STP	Richmond STP	East Bay STP	North San Mateo STP	Central Contra Costa STP		
					Digester A	Digester B	Digester D
Jun 68	0.0374	0.0412	0.2670	0.0487			
Jul 68	0.0470	0.0425	0.0997	0.0478		0.0632	
Aug 68	0.0465	0.0975	0.1655	0.0492		0.0750	
Sep 68	0.0475	0.0725	0.1240	0.0485		0.0740	
Oct 68	0.0512	0.0782	0.0930	0.0465		0.0770	
Nov 68	0.0538	0.0550	0.0772	0.0398		0.1470	
Dec 68	0.0486	0.0572	0.0884	0.0460		0.0750	
Jan 69	0.0636	0.0472	0.0860	0.0450	0.0600	0.0900	0.0500
Feb 69	0.0450	0.0350	0.0715	0.0480	0.1790	0.0860	0.0852
Mar 69		0.0550	0.3030	0.0430	0.0692	0.0775	0.0880
Apr 69		0.0500	0.1364	0.0428	0.0862	0.0774	0.0704
May 69		0.0570	0.1320		0.0875	0.0850	0.0933
Jun 69		0.0850			0.0980	0.0543	0.1010
Avg.	0.049	0.059	0.137	0.046	0.097	0.079	0.081

TABLE II  
MONTHLY AVERAGES OF MBAS CONCENTRATION  
(% MBAS of Total Solids, Dry Weight Basis)

Plant Month	Stege STP		East Bay STP		Richmond STP		Central Contra Costa STP		North San Mateo STP	
	Raw Sludge	Digester Sludge	Raw Sludge	Digester Sludge	Raw Sludge	Digester Sludge	Raw Sludge	Digester Sludge	Raw Sludge	Digester Sludge
Jun 68	0.49	1.24	0.65	1.24	0.63	1.32	0.76	2.33	0.61	1.80
Jul 68	0.53	1.24	0.64	1.27	0.85	1.28	0.74	1.68	0.55	2.05
Aug 68	0.60	1.19	0.56	1.08	0.62	1.03	0.63	1.75	0.67	1.91
Sep 68	0.46	0.96	0.70	0.89	0.46	0.84	0.62	1.59	0.54	1.55
Oct 68	0.62	1.33	0.54	1.00	0.70	0.73	0.67	2.05	0.62	1.78
Nov 68	0.55	1.30	0.60	1.10	0.59	0.87	0.54	1.70	0.36	1.55
Dec 68	0.36	1.16	0.48	0.93	0.49	0.91	0.55	1.10	0.45	1.45
Jan 69	0.23	1.11	0.34	0.90	0.34	0.79	0.32	1.47	0.46	1.34
Feb 69	0.51	1.22	0.44	1.24	0.50	0.86	0.46	1.50	0.55	1.68
Mar 69			0.62	1.16	0.52	0.83	0.94	1.13	0.62	1.58
Apr 69			0.47	1.02	0.66	1.03	0.68	1.29	0.51	1.41
May 69			0.60	1.04	0.63	0.85	0.68	1.25		
Avg.	0.48	1.19	0.55	1.07	0.58	0.95	0.63	1.57	0.54	1.65

The range for individual monthly values was 0.23 to 0.94 and, as would be expected, the higher concentrations occurred during the dry season of the year.

It is evident then that the normal concentration of MBAS in raw sludge is considerably less than the 1 percent level, which Swanwick *et al.* [8] stated could inhibit digester recovery from upsets. Only very occasionally did individual samples approach this level, and two samples were higher with one sample at 1.02 percent (the 24 September sample from the East Bay plant) and surprisingly the other sample even exceeded 2 percent (the 11 March sample from the Central Contra Costa plant, see Appendix C). The MBAS concentration is also expressed on a wet basis as mg/l in the tables presented in Appendix C. Reporting MBAS in terms of mg/l is not as meaningful as percent of total solids when applied to sludges, since MBAS concentration is largely a function of total solids concentration, i.e., surface-active materials adsorb readily on solids. Expressed in terms of mg/l, the concentration was in several instances near 1000 mg/l (see Appendix C) but usually this simply indicated an unusually thick raw sludge, i.e., high total solids.

#### MBAS CONCENTRATION OF DIGESTED SLUDGE

The MBAS content of the digested sludges proved to be similar for three plants (Stege, East Bay, and Richmond) at approximately 1 percent of total solids, but the Central Contra Costa and North San Mateo plants had an overall average of over 1.5 percent. Individual monthly averages for the latter plants rose to over 2 percent on three occasions.

Information is not abundant on the critical levels of MBAS in digested sludges. A large-scale survey in England, Scotland, and Wales [9] indicated that out of 92 cases of digester difficulties only 5 were considered to be caused by anionic detergents, and one of these sewage works reported a concentration of 2.5 percent in the digested sludge, the other 2.6 percent. The literature dealing with laboratory studies generally report MBAS concentration on a wet basis which is subject to the limitations mentioned previously, and unfortunately solids concentrations are seldom given, thus preventing conversion of results to the dry basis. It has been established by laboratory studies that values ranging from approximately 600 to 900 mg/l (reported as ABS) cause retardation of anaerobic digestion. The range of values determined in this survey (see Appendix C) generally show concentrations of 200 to 400 mg/l, which indicates that all five digesters are well below this retardation level.

#### IN-PLANT VARIATION IN MBAS CONTENT

Three digesters at the same plant were sampled because of two unique circumstances. One of the digesters at the Central Contra Costa plant had not been cleaned in the past fifteen years and would be expected to contain a large quantity of ABS-bearing bottom sludge in addition to more recent deposits of LAS-bearing sludge. This digester (designated as Digester A) also operated at an unusually high volatile acids concentration — often the concentration exceeded 2000 mg/l. In contrast to Digester A, two digesters (B and D) functioned normally and have been cleaned in recent years.

As part of the investigation, these three digesters were sampled to determine if there were an observable difference in MBAS content resulting from their differing histories.

For a period of three months from February through March of 1969, each of these digesters was sampled on a weekly basis. The circulating digester sludge was examined for MBAS during this period and the results are given in Table III. (Samples of bottom sludge were later analyzed and these results are reported later.)

TABLE III  
CENTRAL CONTRA COSTA PLANT DIGESTER STUDY

Date	MBAS, mg/l			% MBAS of Total Solids		
	A	B	D	A	B	D
28 Jan 69	275	380	225	1.78	1.47	1.45
5 Feb 69	400	520	500	2.01	2.44	2.01
11 Feb 69	200	220	290	1.45	1.90	1.57
18 Feb 69	195	175	225	1.48	1.72	1.34
25 Feb 69	175	115	155	1.07	1.07	0.86
4 Mar 69	155	125	200	0.98	1.08	0.83
11 Mar 69	185	155	215	1.29	1.38	1.12
18 Mar 69	185	150	195	0.93	0.72	0.76
25 Mar 69	215	180	230	1.32	1.13	1.10
1 Apr 69	330	230	265	1.32	1.45	1.30
8 Apr 69	345	190	240	1.36	1.17	1.40
15 Apr 69	315	205	170	1.23	1.03	0.70
22 Apr 69	255	215	255	1.13	1.33	1.14
Avg.	248	220	243	1.33	1.38	1.20

The average results of the weekly samples are nearly the same for all three digesters. In fact considering the degree of experimental error that exists in analyzing sewage sludges for MBAS, the results are amazingly close and may be considered identical. On individual test days there were large differences between the three results, but based on the overall values it may be concluded that no significant difference exists insofar as the synthetic detergent content of the circulating sludge is concerned.

#### EFFECT OF BOTTOM SEDIMENTS

In anaerobic digesters sediments are deposited on the bottom and accumulate to such an extent that unless regular maintenance is practiced the effective capacity is significantly reduced. It is not uncommon for the tanks to contain 20, 30, 40, and even 50 percent bottom sludge. Plant operators are well aware of this problem, but cleaning digesters is a cumbersome task and therefore often postponed as long as possible. Digesters which have not been cleaned in the past several years would be expected to contain ABS in the bottom sludges, since ABS does not degrade appreciably under anaerobic conditions.

In 1966 operational difficulties at an East Bay plant digester, which had not been cleaned for 10 years, induced an investigation of the bottom sludge characteristics. The sludge was found to contain a 50-55 percent total solids concentration and an MBAS concentration of 3500 mg/l. Subsequently, the digester was cleaned, restored to normal operation, and no further upsets have occurred. As part of the present investigation samples of this bottom sludge were again analyzed (on 16 July 1969) and indicated reduced concentration of total solids (19.1 percent) and MBAS (900 mg/l).

These reductions in concentrations are not surprising as a shorter time period of accumulation (4 years) is involved. This is explainable in that the organic fraction of sludge degrades leaving the inorganic fraction, i.e., sand, which gradually accumulates or thickens. Similarly, anionic detergents degrade very slowly and as the sand builds up the adsorbed detergents also become more concentrated.

Under equilibrium conditions this detergent probably has little effect on digester operation, but its presence may cause problems if the equilibrium is disturbed. Other investigations by the author [12] on adsorption and desorption phenomena of ABS on soils indicated that anionic detergents are readily desorbed from soil particles by equilibrium changes. It is notable that peak troubles occurred at the East Bay plant digester in the 1966-1967 storm season shortly after a new sludge recirculation system was installed.

In order to determine the quantity of MBAS present in other bottom sludges, depth samples were obtained from a digester at the Contra Costa plant. Digester A, which also has not been cleaned in over 10 years, was sampled at 3 depths. The results are shown in Table IV and indicate that the bottom sludge has a concentration of 1075 mg/l MBAS, but on a percent total solids basis the concentration is only one-half that of the circulating digester sludge. This reflects the distribution of sandy material which is less adsorptive than the silty material predominating in the upper regions.

TABLE IV  
 VARIATION IN MBAS CONCENTRATION OF SLUDGES  
 SAMPLED AT DIFFERENT DEPTHS  
 (Central Contra Costa Plant)<sup>a</sup>

Digester	Sample	Total Solids %	MBAS	
			mg/l	% of Total Solids
A	Circulating Digester Sludge	2.93	320	1.09
A	Thief - Circulate Ring	6.24	690	1.11
A	Thief - Bottom	19.50	1075	0.54

<sup>a</sup> Sampled on 17 June 1969.

#### IV. DISCUSSION

Digester upsets generally occur just after storms, apparently due to variable loading conditions, but prompt recovery is expected by plant operators when loading adjustments are made. The period of peak digester problems was characterized by difficulty in restoring upset digesters to normal operation following storms. Had there been less than normal rainfall during the monitoring period of June 1968 to June 1969 it might be expected that little importance could be attached to the absence of sustained digester troubles. However, during this period there was more rainfall than normal and more significantly the winter storms were unusually severe. Therefore, if bad weather was in part responsible for the troubles which instigated this study, then it appears likely that whatever the other contributing factors were have now been eliminated.

If ABS was the culprit in causing digester difficulties, then that problem has been eliminated by the conversion to IAS. Although both IAS and ABS degrade very slowly under anaerobic conditions, it is well known that considerable decomposition of IAS occurs in the sewers. The changeover from ABS to IAS resulted in an approximate 30 percent decrease in synthetic detergent concentrations of raw sewage entering treatment plants. (This figure is, of course, variable depending on the size of individual sewerage systems.) The net result then is a 30 percent decrease in the synthetic detergent concentration of the raw sludge pumped to anaerobic digesters.

the conclusion that the new IAS detergents present no identified problem for sludge digesters in the Northern California area.

## V. CONCLUSIONS

The monitoring program reported herein supported the following conclusions:

1. MBAS levels in raw sludge proved to be on the order of 0.5 percent (dry solids basis), and therefore below the critical level of 1 percent, which has been found to cause digester problems in laboratory studies conducted in England.
2. In the circulating digester sludge the MBAS content was generally in the 200 to 400 mg/l range (or 1.0 to 1.5 percent of dry solids). This is also below the reported retardation level of 600 to 900 mg/l for digester sludge.
3. Bottom sludge samples contained MBAS concentrations of approximately 1000 mg/l, but calculated on a dry solids basis they measured only approximately 0.5 percent MBAS. Therefore, a large accumulation of bottom sludge is probably not significant to performance from the standpoint of IAS detergents, but is otherwise quite significant in that the effective digester capacity is reduced.
4. The cause of the unusual number of digester upsets during the period from 1963 to 1967 remains unknown, but trouble-free digester performance since that period and the data obtained in this study lead to

APPENDICES

- A. Extraction Procedure for Circulated  
Digester Samples and Diluted Raw  
Sludge Samples
- B. Determination of Methylene Blue  
Active Substances
- C. Master Data Sheets



APPENDIX A

EXTRACTION PROCEDURE FOR CIRCULATED DIGESTER  
SAMPLES AND DILUTED RAW SLUDGE SAMPLES

Shake sample well, and rapidly pour 80-100 ml into 150 ml beaker. Stir on magnetic stirrer and withdraw 10 ml (use widetip volumetric pipette). Transfer into 250-ml round bottom flask washing down pipette with a few ml of methanol. Add 10 ml of 0.1 N NaOH in methanol, 150 ml of methanol. Then reflux vigorously for 30 minutes. After refluxing allow sludge to settle, then decant on a methanol-wetted glass-fiber filter paper (Whatman GF/C) on a Buchner funnel. Then transfer entire contents of the flask to the filter paper. Wash the flask out twice with 20-ml portions of methanol, transferring each to filter paper.

The methanolic extract (filtrate) is then transferred to a 500-ml Erlenmeyer, washing with two 20-ml portions of methanol to insure a complete transfer. Add 10 boilozers and place on steam bath. Distill off methanol until a residue of about 10 ml remains in the volumetric flask. Wash the Erlenmeyer 5 times with 25-ml portions of distilled water to insure complete transfer. Make to volume (250 ml). Invert flask completely and slowly 25 times for complete mixing.

## APPENDIX B

DETERMINATION OF METHYLENE  
BLUE ACTIVE SUBSTANCES

## REAGENTS

1. Alkaline Phosphate Solution. Dissolve 10 g A.R. grade disodium hydrogen phosphate (anhydrous) in about 800 ml distilled water. Adjust the pH value to 10.5 by addition of sodium hydroxide and make up to 1 liter.
2. Methylene-Blue Solution. Dissolve 0.20 g methylene blue B.P. in 1 liter of distilled water.
3. Sulphuric Acid, concentrated.
4. Chloroform. Reagent grade redistilled over silica gel.
5. Manoxol OT Solution. Dissolve 0.100 g of the solid in 1 liter of distilled water to obtain a 100 mg/l solution.

## PROCEDURE

1. The volume of sample taken should be chosen when possible to contain 20 to 150 µg anion-active material. It is generally impracticable to take more than 10 ml of sewage, owing to the degree of emulsion formation on shaking with chloroform, but it is possible to take up to 100 ml of good quality effluent and river water. Highly saline samples, however, should be limited to 20 ml.
2. Place the sample in a 250 ml separating funnel and make up to 100 ml with distilled water. Add 10 ml alkaline phosphate

solution followed by 5 ml methylene-blue solution and 40 ml chloroform.

3. Shake gently and evenly twice a second for 1 minute. Allow to separate, breaking up any emulsion formed by gentle agitation with a glass rod. Now run the chloroform layer into a second separating funnel containing 110 ml distilled water, 0.2 ml sulphuric acid, and 5 ml methylene-blue solution. Rinse the first separating funnel with 2 ml chloroform and run this into the second separating funnel.
4. Shake the second separating funnel as in paragraph 3 above and allow the layers to separate. Run the chloroform layer through a small funnel plugged with absorbent cotton wool moistened with chloroform into a 50-ml standard flask, rinsing with a further 2 ml chloroform.
5. Make up to the mark with chloroform.
6. Before carrying out a further determination, the separating funnels should be rinsed with dilute nitric acid followed by water to remove adsorbed methylene blue.

Sulphide Interference. Sulphide, if present, should be oxidized before extraction. Place the required volume of sample in the first separating funnel, add 10 ml alkaline phosphate solution and 2 ml of 20 volume hydrogen peroxide. Stand for 5 minutes and bulk to 110 ml with distilled water. Add 5 ml methylene-blue solution, 15 ml chloroform, and proceed as before.

Measurement. The optical density of the chloroform extract is measured in a suitable photoelectric absorptiometer or spectrophotometer either at 650 mµ or with an Ilford No. 607 orange

filter. The blank value, determined using distilled water instead of the sample, is subtracted.

Calibration. Suitable volumes of a standard solution of reference IAS material are treated as above and the optical densities of the extracts determined. The optical density of a reagent-blank extract is also measured. The differences between the optical densities of the standards and the reagent-blank are plotted against concentrations to give a calibration curve. The detergent concentration of a sample can then be determined from this curve, which, in practice, is a straight line.

The results are expressed as mg MBAS per liter.

APPENDIX C  
MASTER DATA SHEETS







## REFERENCES (Continued)

9. Swanwick, J. D., D. G. Shurben, and S. Jackson. "A Report on the Water Pollution Research Laboratory Survey of the Performance of Sewage Sludge Digesters Throughout England, Scotland, and Wales," paper presented to Metropolitan and Southern Branch, Institute of Water Pollution Control, 23 May 1968.
10. Longwell, J. and W. D. Maniece. "Determination of Anionic Detergents in Sewage, Sewage Effluents and River Waters," Analyst, London, 80:167, 1955.
11. Slack, J. G. "The Determination of Anionic Detergents in River Water and Sewage Effluents," Analyst, London, 84:193, 1959.
12. Klein, S. A., D. Jenkins, and P. H. McGauhey. Travel of Synthetic Detergents with Percolating Water. First Annual Report. Berkeley: Sanit. Eng. Research Lab., Univ. of Calif., 1961.