Determination of Ethylene Oxide Based Nonionic Detergents in Sewage

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Abstract

A sensitive analytical method has been developed for the determination of ethylene oxide based nonionic detergents in sewage. After suitable cleanup procedures, which are described, the detergent is complexed with phosphotungstic acid in the presence of excess reagent. The excess reagent is then decomposed by raising the pH to 5 while the complex remains stable for a short period. The complex is separated from reagent decomposition products by partition between methyl ethyl ketone and dilute sodium chloride solution buffered to pH 5. Quantitative assay is made for tungsten since the amount of tungsten bears a stoichiometric relation to the ethylene oxide chain length.

Introduction

A NUMBER OF METHODS for quantitative assay of ethylene oxide based nonionic detergents are in the literature; all suitable for consideration in microanalysis are based on the formation of complexes with the polyether chain.

At present the most widely used analytical method is based on the cobaltothiocyanate complex $[Co(SCN)_4]^=$. Two variations are in use. Crabb and Persinger (1) concentrate the detergent by countercurrent ether extraction and measure the absorbance of the complex at 620 mμ. Greff, Setzkorn and Leslie (2) use only 100 ml of aqueous sample but achieve comparable sensitivity by measuring the absorbance at 320 mμ. These methods were apparently developed principally for use in laboratory biodegradability studies. When applied to sewage, however, they lack the sensitivity for use at the 0.1 ppm (parts per million) concentrations to be expected in some sewages. For example, the calibration curves of Greff, Setzkorn and Leslie all show absorbances of about 0.100 or less at the 5 ppm level (0.5 mg per 100 ml), while the phosphotungstic acid (PTA) method described in the present paper is sensitive enough to give the same absorbances at 0.1 ppm.

The well-known complex with the heteropoly acid of tungsten forms the basis of the proposed method. At pH $\geq$ 5 excess reagent (phosphotungstic acid) decomposes rapidly while the complexes with polyethers are sufficiently stable to permit separation by partition between methyl ethyl ketone and molar NaCl. The solvent is then evaporated and the complex hydrolyzed. The amount of tungsten present bears a stoichiometric relation to the ethylene oxide chain length and is determined (as $WO_4^=$) by the very sensitive dithiol colorimetric procedure.

Interferences require cleanup. High speed centrifugation for removal of fine solids, followed by filtration through a mixed-bed ion exchanger for removal of ammonia and amines, was found adequate for purification of the samples reported here.

Experimental

Reagents

All reagents are of Analytical Reagent grade except as specified.

Phosphotungstic Acid (PTA) solution: Dissolve 0.5 g PTA and 1.0 g $BaCl_2 \cdot 2H_2O$ in 100 ml of 0.5 N HCl. If turbid, let settle overnight and decant the supernatant.

pH 5.0 buffer: Dissolve 25 g citric acid monohydrate and 58.5 g NaCl in 250 ml of 1 N NaOH, and dilute to slightly less than 1 liter with distilled water. Add NaOH to bring to pH 5.0 and dilute to 1 liter. This buffer is stable at room temperature for at least 2 weeks.

Methyl ethyl ketone (MEK), practical or reagent grade: Add 30–40 g of powdered activated carbon to 4 liters of MEK and stir for 30 min. Filter and distill. About 20 g of Fuller's earth may be added during the carbon treatment as adsorbent and filter aid. Some lots of solvent are suitable for use without purification; this can be determined only by running a blank on each lot.

MEK solution for ion exchange: Mix 3 volumes of the purified MEK with 10 volumes of distilled water.

NaCl solution: Dissolve 58.5 g NaCl in a liter of distilled water.

NaOH solutions: 0.5 N and 1.0 N.

Acid mixture: Mix 120 ml of concentrated sulfuric acid with 120 ml distilled water, and cool to room temperature. Add 200 ml of concentrated HCl and a few drops of 85% phosphoric acid.

$TiCl_3$: 20% solution.

Dithiol (Toluene-3,4-dithiol): 10 mg/ml in 0.25 N NaOH. Add about 5 drops mercaptoacetic acid per 100 ml as a preservative. Keep refrigerated.

CCl_4

Ion exchanger: Mixed-bed. Amberlite MB-1 or equivalent.

Procedure

Centrifuge a convenient volume of sewage in a high-speed centrifuge at 10,000 to 15,000 g.

Prepare an ion-exchange column by weighing 10 g of resin (moist) into a beaker, equilibrating 30 min in 3:10 MEK/H_2O solution, adding to a column, and washing with 100 ml of additional 3:10 solution.

To a 100-ml aliquot of centrifuged sewage add 30 ml MEK, and pass through the ion-exchange column. Wash the column with 20 ml of 3:10 MEK/H_2O, and add to the eluate. Transfer to a separatory funnel with 20 ml of MEK, and add 23 g NaCl. Shake for 1 min and discard the aqueous layer. Transfer to a 100-ml beaker with 10 ml MEK. Evaporate to dryness in the hood at room temperature or in a constant-temperature bath at 30C with an air stream.

Add about 4 ml water to the residue in the beaker, followed by 1 ml of PTA solution. Allow to stand overnight. Approximately neutralize the HCl from the PTA solution with NaOH, and buffer at pH 5. This is best done by pipetting 1 ml of 0.5 N NaOH into approximately 25 ml of pH 5.0 buffer and adding the resulting mixture to the sample. Immediately transfer to a 125-ml separatory funnel. Rinse the beaker with 35 ml MEK and add to the separatory funnel. Shake 1 min. Once the buffer has been added, the extraction must be carried through quickly and with the least possible variation in time. Discard the

aqueous layer. Wash the MEK twice with 20-ml portions of NaCl solution. Transfer the MEK to a 125-ml flask, and boil down to incipient dryness. Remove the flask from the heat, and evaporate the last traces of solvent with an air stream.

Add 10 ml of 1 N NaOH, and heat in a water bath or on a hot plate at low heat for 10 min. Remove from the heat, and add 25 ml of acid mixture and 2 ml of $TiCl_3$. Cover with a watch glass, and heat 30 min at 90–100C. Add 2 ml of dithiol solution, and heat 30 min longer. Cool to room temperature.

Extract with 25 ml CCl_4 in two portions; filter through a small plug of glass wool wetted with CCl_4, and catch in a 25-ml volumetric flask. Dilute to volume with CCl_4.

Determine absorbance at 625 mμ in 1-cm cells with a spectrophotometer.

Results and Discussion

Phosphotungstic Acid Assay Method

The heteropoly acid complexes with ethylene oxide polymers have been used by a number of authors for analytical purposes. Oliver and Preston (3) used phosphomolybdic acid (PMA); Shaffer and Critchfield used PMA and phosphotungstic acid (PTA) (4) and silicotungstic acid (5). Barber, Chinnick and Lincoln (6) used PTA. Stevenson (7) formed the PMA complex, which was then dissolved in concentrated sulfuric acid to produce a color read at 520 mμ. Etienne (8) filtered the PMA precipitate with Celite and determined C_2H_5I after treatment with HI. Heatley and Page (9) dissolved the complex in HCl/methyl ethyl ether and read the absorbance at 310 mμ. These methods all depended on separation of the insoluble complex from the mixture, centrifugation being preferred by all except Etienne.

Wurtzschmitt (10) has explained the reaction by assuming that quaternary-like oxonium derivatives form and then react with suitable anions.

No data are available as to the proportions in which *pure* polyglycol derivatives would react (11); therefore, for high accuracy, calibration runs with known detergents are necessary. The situation in sewage or surface waters is more complex since many different types of polyglycols may be present, with variations in chain lengths and in the nature and sizes of the hydrophobic groups. Laboratory biodegradation studies, on the other hand, present no such problem because the detergent to be analyzed is known and reference samples are available for calibration.

The initial work here employed precipitation with PMA and purification by centrifugation or filtration with Celite. Sensitivity was good, but precision was poor and methods based on precipitation were abandoned. It was observed, however, that PMA was decomposed at pH's where the complexes appeared stable. PTA was selected for further work since it is less subject than PMA to reduction by impurities in the air of the laboratory (12). There is little doubt, however, that the latter can be employed if it is desired to use an instrumental technique such as atomic absorption spectrometry or polarography for assay instead of colorimetry.

After some trials methyl ethyl ketone (MEK) was found to be an adequate solvent for the complex while the decomposition products from the excess PTA partitioned into the aqueous phase (M NaCl, pH 5). NaCl was used to reduce solubility of the MEK in the aqueous buffer. The complex itself decomposes at pH 5.0, but the rate is low; PTA and PMA decompose almost instantly.

The time allowed for complexing is not critical. Periods of from 10 min to 48 hr have been tried; yields are somewhat smaller at the extremes, but any time from 1 to 18 hr is satisfactory as long as the samples are handled uniformly.

The complex is formed in a solution containing 0.1% PTA and 0.2% $BaCl_2 \cdot 2H_2O$ in 0.1 N HCl. Concentrations can be varied somewhat without observable effect; the amounts stated can be increased severalfold with less than 10% increase in the blank but loss in sensitivity may be considerable if they are decreased substantially. Small amounts of NaCl are of no importance.

Alcohols, ketones, and similar organic solvents should not be present in significant amounts because some, e.g., isopropyl alcohol, cause heavy increases in the blank. This may be observed by adding $NaHCO_3$ solution to dilute PMA in water and in 35% isopropyl alcohol. The aqueous solution decolorizes almost instantly; the alcoholic solution only very slowly.

No special cleaning of glassware is required. An ordinary anionic-type household detergent followed by a distilled water rinse is adequate.

The pH of the buffer is preferably about 5.0. At lower pH the sensitivity is slightly greater, but there is a considerable increase in the blank. There is relatively little difference in the pH range 4.5–6.0, but it is recommended that a blank and control be prepared along with each group of samples.

Although the complex is sufficiently stable at pH 5.0 for the present purpose, it does decompose. Table I shows the change occurring with time, the time being measured from the addition of buffer to the beginning of shaking with MEK. A relatively long contact period may be chosen, but this is unnecessary and inconvenient. The operator soon develops a cadence so that the time variation between replicates is negligible. All results reported were obtained with a 25- to 30-sec buffer-complex contact time. The complex becomes quite stable after addition of MEK.

Citrate is preferable to phosphate for the buffer as the latter may precipitate with Ba from the complexing step. Saturating the solution with NaCl gives no improvement, nor does increasing the citrate concentration.

A colorimetric assay for tungsten was preferred. In general, the dithiol procedure of Hobart and Hurley (13) is followed except that the steps relating to removal of molybdenum are omitted and a commercially available $TiCl_3$ solution is used. Times for $TiCl_3$ reduction and dithiol complexing should be at least 5 min each. Excess times does no harm, and 30 min was customary in the work reported here. The flasks should be covered with watch glasses and the temperature kept about 90C so that evaporation may

TABLE I

Reaction Time of Complex with Buffer

Time	Absorbance [a]		
	Blank	Sample [b]	Average [c]
25 Seconds [d]	0.010	0.451–0.460–0.441	0.441
5 Minutes	0.009	0.419–0.404–0.400	0.399
20 Minutes	0.006	0.367–0.352–0.327	0.343
1 Hour	0.005	0.331–0.325–0.336	0.326
2 Hours	0.005	0.318–0.351–0.331	0.328

[a] Absorbance in 1-cm cells at 625 mμ in 25 ml CCl_4 versus CCl_4 reference, 0.06-mm slit.
[b] Surfonic N-95 (Jefferson Chemical Company), 41.2 μg.
[c] Corrected for blank.
[d] Average time for the operation carried out without pause.

TABLE II

Precision of Assay Method

	Absorbance [a]
Blanks	0.019–0.020–0.020
30.2 μg BC-720	0.400–0.430–0.403

[a] Absorbance in 1-cm cells at 625 mμ in 25 ml CCl_4 vs. CCl_4 reference, 0.06-mm slit.

be kept to a minimum; if this is not done, significant losses may occur.

Basic hydrolysis of the PTA complex is required for the dithiol reaction to take place; 10 min at about 100C was the usual time, although 30 min at room temperature in N NaOH was equally effective. Care should be taken to evaporate all the MEK before hydrolyzing the complex since small amounts of residual solvent can cause serious interference.

Precision is satisfactory. Table II shows the results obtained in several replicate determinations. In all cases, pure CCl_4 was used as a reference in order to keep records of the blanks. Beer's Law was followed by a group of eight detergents (Table III) over the range of 5–40 μg. One curve (Emulphogen BC-720) was checked at higher concentrations and proved to be linear up to at least 120 μg.

Sensitivity is limited primarily by the blank. The absorbance at 625 mμ (in 25 ml CCl_4) varied from 0.012 to 0.017 per μg of detergent in 1-cm cells for the detergents in Table III. The actual value obtained varies somewhat with different lots of buffer and MEK, and a control should always be run.

The reagent blank also varies slightly with different lots of buffer, dithiol, and solvent, but is ordinarily about 0.020 in 1-cm cells (25 ml). In addition to this, there is a somewhat higher blank because of the usual cleanup for 50- to 100-ml volumes of water. The total blank from ion-exchange cleanup plus reagents may thus be expected to be in the range of 0.070 to 0.110, depending on the type of ion exchanger chosen, and to vary slightly with different lots of reagents. This blank is equivalent to 5–10 μg of a typical detergent and sets a lower limit of perhaps 10 μg of detergent (from 50- to 100-ml of water) for accurate reading. The color intensity is easily great enough for a five- to tenfold increase in sensitivity if the blank can be reduced sufficiently to permit the use of longer cells. The blank appears to depend principally on the amount of MEK used, but not as a straight line function.

Cleanup for Colorimetric Assay

Cleanup is a necessity because the heteropoly acids react with a number of classes of compounds. Since PTA reacts with many nitrogen compounds and with cellulose, all paper, cellular material, and other sewage solids must be removed. A blank to which a few mg of cellulose powder was added gave an absorbance equivalent to 70–80 μg of detergent. Apparently, some nonionic detergents are also adsorbed on the solids; in one trial the centrifuged solids from 900 ml of raw sewage were extracted with MEK at room temperature and assayed by the usual method, including mixed-bed ion exchange. Recovery was 107 μg, corresponding to approximately 0.12 ppm, based on the original volume. The membrane filter was unsatisfactory because of high blanks and possible adsorption of detergent.

TABLE III

Sensitivities of Representative Detergents

Detergent	Structure	Absorbance [a,b] (corrected for blank)
PEG-400	Polyethylene glycol,8-9 EO	0.0145
Emulphogene BC-720	Tridecyl alcohol	0.0128
PEG-4000 dioleate	PEG diester	0.0149
Emulphor EL-620	Vegetable oil derivative	0.0123
Antarox G-100	Alkyl amino amide derivative	0.0123
PEG-4000 monostearate	PEG monoester	0.0172
Emulphor ON-870	Fatty alcohol derivative	0.0143
Triton X-100	Octyl phenol,9-10 EO	0.0120

[a] Under conditions of this test, 1 μg tungsten (as tungstate) gives an absorbance of 0.0052.

[b] Absorbance in 1-cm cells at 625 mμ in 25 ml CCl_4 versus CCl_4 reference, 0.06-mm slit per μg of detergent.

Ammonia and amines react with PTA to give serious interference. When the centrifuged sewage in one trial was assayed without ion-exchange, the apparent detergent concentration was 0.95 ppm, more than 50% greater than the result after ion-exchange cleanup (0.58 ppm). A monobed resin proved satisfactory. Recoveries of 30.2 μg amounts of BC-720 were consistently 85–100%, and column blanks were also consistent. Cetab was removed effectively. ABS was also removed, although in small quantities it does not interfere (90 μg did not increase a blank). Ginn and Church (14) have discussed the use of ion exchangers in detergent analysis at length. Rosen and Goldsmith (11) describe a batch procedure.

Neutral compounds, of course, are not removed by this procedure, but in small quantities do not seem to interfere. Two mg of soybean oil had no effect when added to a blank and to 30.2 μg of BC-720.

MEK extracts of eluates from the ion exchanger must be evaporated near room temperature. Numerous inconsistencies arise if they are boiled to dryness. Placing the solution in a small beaker in the hood and letting it go to dryness was found sufficient. The process can be conveniently hastened by using a stream of clean air while keeping the beaker in a constant temperature bath at about 30C. Evaporation of detergent under the air stream is negligible; the loss was only 16% when 26.2 μg BC-720 was kept in a beaker under a strong stream of air at room temperature for 6 hr. Precision of the evaporation process is excellent. Later work has indicated that the loss from boiling down the MEK extract may actually be due to boiling with the small amount of residual brine partioning into the MEK with the complex. The question has not been settled, and all evaporations reported here were carried out in the temperature range of 25–30C.

Application of Method to Sewage

The combination of centrifugation and ion exchange proved adequate in recovering added detergents from five sewages. The method did not completely remove impurities affecting the infrared spectrum, although the 700–1300 cm^{-1} region of the spectrum was usable. The cleanup procedure also reduced the sensitivity of the assay method because an additional blank was introduced by the ion exchanger. The recoveries obtained after adding known amounts of detergent to sewages from several cities are shown in Table IV. The levels of apparent nonionic detergent concentration found were, in general, sufficient for direct application of this method to 50- to 100-ml samples of sewage.

Response curves for two sewages were obtained over a range of 0–1.27 ppm added detergent. Several hundred milliliters of sewage were centrifuged, and 50-ml aliquots were withdrawn. A known amount of Triton X-100 (a polyethoxylated alkylphenol) was added to each aliquot, which was then purified by ion exchange, and the total nonionic detergent was determined. Two

TABLE IV

Recoveries of Added Detergent from Sewage

Location	Type of sewage	Volume, ml	BC-720 added, μg	Total detergent found,[a] μg	Added detergent recovered, %
Cincinnati, Ohio [b]	Raw	50	0	15	84
			26.2	37	
Lebanon, Ohio [c]	Sec. effl.	50	0	25	
			26.2	51	100
Loveland, Ohio	Raw	50	0	28	
			30.2	58	100
		50	0	29.5	
			30.2	56.5	89
Grand Rapids, Mich.	Sec. effl.	35	0	31	
			30.2	59.5	94
Archbold, Ohio [d]	Sec. effl.	35	0	3.7	
			30.2	33	97
Hamilton, Ohio	Sec. effl.	35	0	11	
			30.2	41	100

[a] Calculated as BC-720.
[b] Not centrifuged; filtered through Whatman No. 1 filter paper. Sewage is mixed industrial-domestic from area subject to considerable groundwater infiltration.
[c] Not centrifuged; aliquots from 1 liter of sewage filtered through membrane filter; detergent added to sewage *after* filtration.
[d] Detergent concentration was too low for reliable results with the amount of sample available.

blanks and two controls in distilled water were run simultaneously. The results are shown in Figure 1.

The blanks gave absorbances (vs. pure CCl_4 reference) of 0.070 and 0.075. The two controls (25.5 and 51.0 μg) were recovered in 92 and 94% yields, respectively. With the exception of the 51.0-μg addition to Little Miami plant sewage, all recoveries were within the precision of the method. The apparent nonionic detergent levels were 0.62 ppm in primary effluent from the Little Miami treatment plant and 1.04 ppm in raw sewage at the intake to the Mill Creek plant, both in Cincinnati, Ohio.

Controls of centrifuged sewage run without ion-exchange cleanup gave recoveries of 230% (Little Miami) and 195% (Mill Creek) as compared with samples purified by ion-exchange.

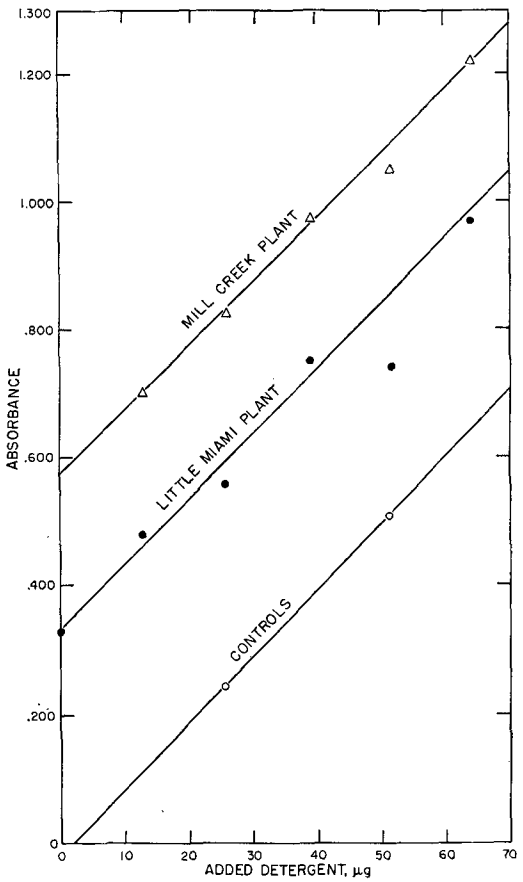

FIG. 1. Recovery of Triton X-100 added to 50 ml of centrifuged sewage.

Infrared Spectra

These tests showed that known pure detergents added to sewage could be recovered in excellent yield, but it remained to be proved that the apparent nonionic detergent content of the sewage was actually determined and not merely an unknown positive interference. Infrared spectrophotometry proved adequate for this purpose.

The spectra of the phosphotungstic acid complexes of pure Triton X-100 and of the detergent recovered from primary effluent from the Little Miami plant, Cincinnati, Ohio, are shown in Figure 2 for the range 700–1300 cm^{-1}.

The corresponding spectra of free Triton X-100 and of the free detergent recovered from the PTA complex with Little Miami sewage are shown in Figure 3.

The characteristic ether band of the free detergent at 1105 cm^{-1} largely disappears on complexing and is replaced by the typical quadruplet of PTA at 800, 890, 970, and 1075 cm^{-1}.

Furthermore, examination of the spectrum of the complex from sewage shows a very weak 1105 cm^{-1} ether band along with the very strong PTA quadruplet. The detergent recovered from this complex,

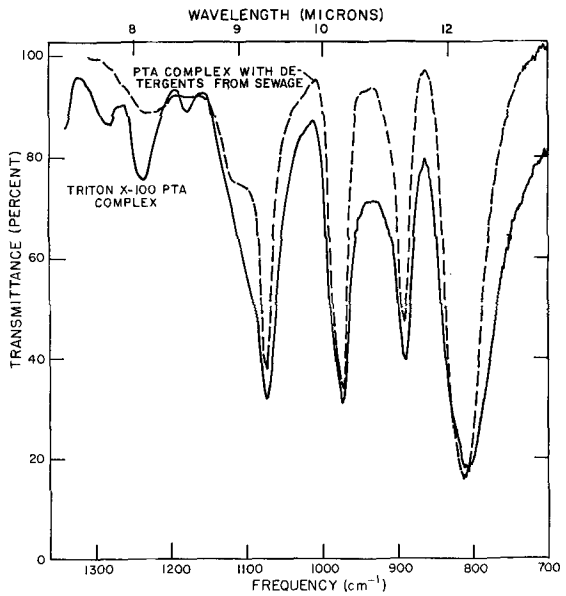

FIG. 2. Infrared spectra of phosphotungstic acid complexes of Triton X-100 and of nonionic detergents recovered from primary effluent, Little Miami Sewage Treatment Plant, Cincinnati, Ohio.

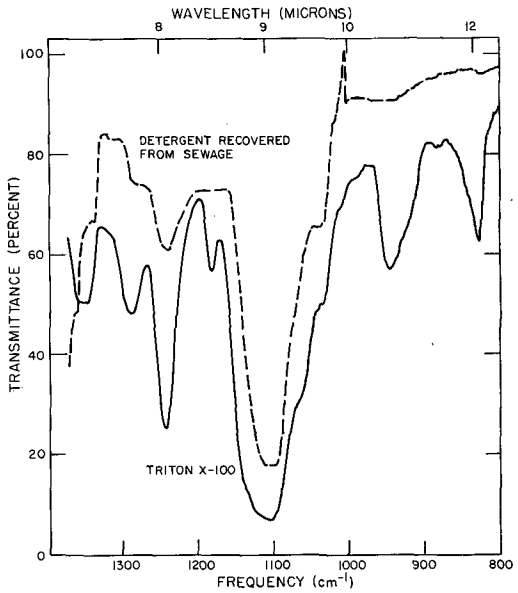

FIG. 3. Infrared spectra of Triton X-100 and of detergent recovered from primary effluent, Little Miami Sewage Treatment Plant, Cincinnati, Ohio.

however, shows only a very strong 1105 cm^{-1} band and no quadruplet. The conclusion follows that there was no significant amount of uncomplexed matter capable of absorbing at 1105 cm^{-1} and therefore, that a large proportion, at least, of the complexed material must be composed of substances with the polyether chain structure characteristic of ethylene oxide polymers.

Preparation of samples for infrared examination is not difficult. A few hundred milliliters of sewage is carried through the analytical procedure until the MEK has been evaporated from the complex. A few drops of MEK are added to redissolve the PTA complex, which is evaporated onto a small amount of KBr. The pellet is pressed, and the spectrum of the complex is obtained in the usual manner. All KBr residues are then collected and dissolved in water. The mixture is hydrolyzed with NaOH to free the detergent, which is then extracted with ether, dried over Na_2SO_4, and evaporated onto KBr. A pellet is pressed, and the spectrum is obtained as before.

The complex may be washed with ether to remove adhering organic matter without any loss; hexane also may be used, but not methanol or other polar solvents.

Sensitivity will vary with the instrument and the technique of the operator. A 1.5-mm KBr pellet and 6X reflectance-type beam condenser were used in the present work with a Perkin-Elmer Model 421 spectrophotometer. With such equipment, the 250–300 μg of sample available from 500 ml of sewage was much in excess of the amount necessary, and only a portion was used. The sample, however, is not decomposed (except possibly for hydrolysis of esters) and may be recovered for chromatographic analysis or for other purposes. The three sewages thus far examined by this method were found almost free of interferences in the 700–1300 cm^{-1} region.

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