BIODEGRADABILITY OF SOME DYE CARRIERS

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Jose Roberto Rodriguez Soria

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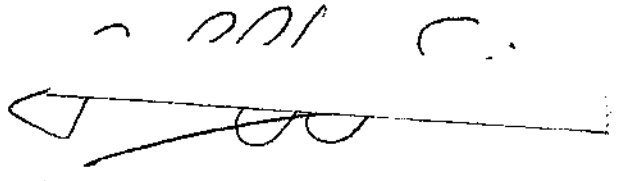

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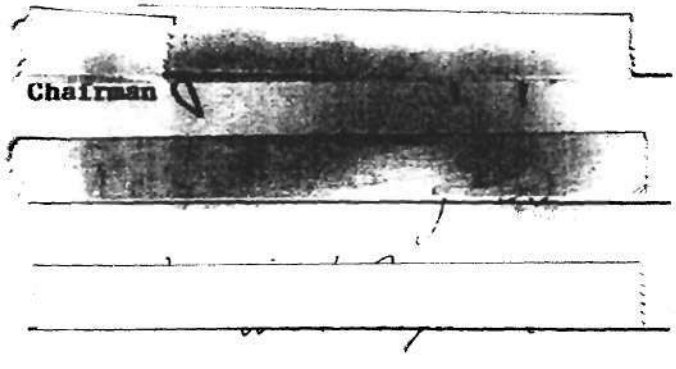

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DEDICATION

In memory of my father, Jose Rodriguez Diaz, whose love and counsel through the years guided me.

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SUMMARY

Dyeing auxiliaries or "carriers" covered in this study were resistant to degradation in conventional activated sludge waste disposal plants. Where bacteria were acclimated to the chemicals and treatment times were extended, degradation did occur.

Metabolites for some carriers were recovered from the activated sludge digesters by solvent extraction techniques and separated by thin layer chromatography. Attempts to identify the structure of the metabolites by infrared spectroscopic techniques were unsuccessful.

Toxicity of the carriers and their resistance to degradation in the digesters as determined by chemical oxygen demand for digester effluent is discussed.

CHAPTER I

INTRODUCTION

Statement of the Problem

Effluent from processes in use today for dyeing hydrophobic fibers, coupled with the increasing usage of those fibers and the concentration of the textile dyeing industry along a few streams, is a cause of grave environmental concern. The pollution potential from the dyeing of hydrophobic fibers, particularly polyesters, is great due to the large amount of auxiliary chemicals or "carriers" necessary for dyeing those fibers.

Vickerstaff (1) noted that in order to achieve a significant improvement in dyeing, the quantity of carrier required was quite high, ranging up to 20 per cent of the weight of the fiber for some of the carriers used. He also noted that removal of the carrier was desirable, if not essential, since many carriers which are effective are also toxic or dermatitic. Fabrics are after-scoured in order to completely remove the carrier, making the concentration of this compound in the dyehouse effluent extremely high since all of it would be in the effluent.

The results of bacterial degradation of carriers, many of which are toxic, are important since the possibility of formation of metabolites, more toxic than their precursors, could have disastrous effects on aquatic and human life.

History Leading to the Problem

Secondary cellulose acetate fibers were the first commercially successful hydrophobic man-made fibers. Prior to their appearance, prevailing technology had dealt only with hydrophilic natural fibers such as cotton, wool, silk, and others. Direct cotton dyes and most acid dyes did not dye acetate fibers.

Thus, the need arose for developing dyes which would be capable of yielding good color in acetate. Dyes of the aminoanthraquinone and aminoazo types were developed and became known as disperse dyes because, although insoluble in water, they could be applied to the fiber from aqueous dispersions.

The appearance of truly synthetic fibers, all hydrophobic, presented dyeing difficulties also. The discovery that disperse dyes had an affinity for the synthetic fibers as represented by polyester proved invaluable. Although disperse dyes had an affinity for the polyester fiber, diffusion rate of dye into the fiber was extremely slow. The carrier method of dyeing was developed to accelerate the diffusion rate.

A carrier is an organic compound that, when added to the dyebath, accelerates the absorption of the dyes by the fibers.

Many classes of compounds can act as carriers: esters, ketones, alcohols, aldehydes, ethers, hydrocarbons, amines, phenols, and halogenated compounds are widely used.

Arnold (2) states that much research has been done in the field of water pollution from textile processing with primary interest in the natural fiber segment. Cotton textile waste, relatively free of toxic substances, was readily biodegraded in conventional waste disposal systems because of the high content of natural nutrients. When the new synthetic fibers appeared,

industry simply continued using the same conventional methods for waste treatment without regard to the change in chemical character of the effluent. The principal parameter for evaluating the success of the treatment was the biochemical oxygen demand test (BOD) (3) (4). This method, although useful in determining residual biodegradable organic matter in an effluent, could not distinguish between compounds so it may not be reasonable to assume that the non-biodegradable residue is identical to the original pollutant (5).

Purpose of the Research

The objective of this research was to determine if certain dye carriers used by the textile industry could be effectively degraded in conventional waste treatment plants and, if so, what their degradation products were and if those degradation products were known to be hazardous to the health of the public.

Review of the Literature

Masselli, et al., (4) stated that Dacron scouring and dyeing represents a severe pollution problem because of the large amounts of carriers necessary for proper dyeing. These carriers are used in amounts ranging from 6 to 40 per cent based on the weight of the fiber. The BOD load from carriers alone could range from 50 pounds to 700 pounds per 1,000 pounds of cloth depending on the type of carrier used. The use of biological oxidation processes for treatment of wastes containing carriers has been recommended.

Alspaugh, et al., (6) reported that textile wastes are no longer considered to constitute a difficult treatment problem provided they contain no

toxic materials and contain adequate nutrients. As such, biological processes could be used to treat the waste satisfactorily in the same manner as domestic waste.

Conventional waste treatment plants have proved ineffectual in the treatment of certain chemical pollutants. Malaney, et al., (7) showed that 27 chemicals known to produce cancer in animals, due to their refractory chemical structure, were resistant to biological oxidation within normal detention times. Also tested were other hydrocarbons, many of which could be used as carriers with similar results.

Bogan (8) and Hammerton (9) carried out research on synthetic detergents and linked biodegradability to chemical structure. The greater the degree of branching of alkylsulphonates, the more resistant to degradation the synthetic detergents became.

Young, et al., (10) in developing tools for measuring biodegradability, worked with chemicals reported to be toxic or biologically resistant and confirmed that these compounds were oxidized only to a small extent. It is quite possible that bacteria present in waste treatment processes may encounter difficulties degrading some of the carriers presently in commercial use. This could be due to their inertness or even toxicity.

Raw or partially treated textile waste laden with chemicals and dyes could be ecologically disastrous to the streams that receive it. Chlorinated biphenyl derivatives, present in many proprietary commercial carriers, have been found in tissue extracts of fish, mussels, and birds from the Rhine River. As such, fatal concentrations were thought not yet developed, but regular environmental monitoring was suggested (11).

The carcinogenic activity of other biphenyl derivatives were investigated by Walpole (12). The compounds investigated were mainly 1, 2, or 3 methyl substituted derivatives. After injection into rats, tumor localization was shown to be dependent on the number and position of substituent chemical groups on the biphenyl nucleus.

A study of the possible effects of biphenyl on the liver has shown that the liver microsomes from the rabbit, rat, guinea pig, fox, and man bring about conversion to 4-hydroxybiphenyl (13). However, another study on the liver of rabbits showed no impairment of liver function after cumulative doses up to 7.5 grams (g.) biphenyl had been administered. The urine was examined and the following compounds detected, 2-biphenylol, 4-biphenylol, 3,4-biphenydiol, and 4,4'-biphenypdiol (14).

In a toxicological study of biphenyl, albino rats were placed on a diet containing biphenyl from 0 to 1.0 per cent. Hemoglobin levels in the blood stream were lowered, growth and weight were affected and longevity decreased when the diet contained from 0.50 to 1.0 per cent of biphenyl. Also the kidneys exhibited irregular scarring, lymphocytic infiltration, tubular atrophy, and dilatation (15).

Rabbits receiving subcutaneous injections of chlorinated biphenyl exhibited hyperlipemia and hypercholesterolemia. A single injection increased liver fat and liver weight; repeated injections caused liver hypertrophy (16).

Rats subjected to chronic or acute poisoning with biphenyl showed liver, kidney, spleen, thyroid, and intestinal tract damage (17).

Studies of the toxicity of dimethylterephthalate showed that inhalation caused marked effects while ingestion in mice of 10 milligrams per kilogram (mg/kg) caused only excitation (18). Cutaneous applications provoked

dermatitis and pigmentations. The maximum permissible concentration was suggested at .0001 milligram per liter (mg/l).

Numerous studies have shown naphthalene to be toxic. Zulzer reports severe hemolytic anemia and hemoglobinuria, resulting from its ingestion (19). Welsh (20), reporting on the toxicity of chloronaphthalene on cattle, disclosed that it resulted in symptoms resembling those of severe Vitamin A deficiency. General weaknesses as draggy walk and night blindness were observed. Pathological changes included keratosis and necrosis of the mucous membranes of the gastrointestinal tract. Ribeliu (21) states that ingestion of naphthalene by rats produced lesions of the testes.

Toluene, another chemical used as a carrier, has also been reported as being toxic. Acute poisoning in rats from toluene lowers the glycogen content in liver, heart, and skeletal muscles (22). Guinea pigs treated with daily subcutaneous injections of 0.25 ml. of toluene showed in some organs hemorrhagic and hyperemic changes as well as degenerative and necrotic processes and medullary hyperplasia. Most affected were the lungs and kidneys, then the liver, spleen, and adrenal glands (23). A Russian study for the maximum permissible concentration of toluene in water establishes the limiting factor as its odor and suggests a maximum concentration of 1 mg/l (24).

Salicylates as well as salicylic acid have been reported to be toxic when ingested in high concentrations. Warkany (25) studied the effects of methylsalicylate upon pregnant rats and reported it caused death, fetus absorption, and external as well as internal congenital abnormalities on the newborn. Studies on dogs after administration of 0.6 to 4.7 g/kg of methylsalicylate caused nausea, vomiting, excitation of the central nervous system and diarrhea. Two dogs recovered and two died after 8 and 18 hours (26).

Studies on rabbits after successive injections of salicylic acid for 3 to 4 months caused increase in the number of leucocytes, significant decreases of erythrocytes and hemoglobin as well as fatty acid degeneration of the liver (27).

Harvey, et al., (28) investigated the interaction between hydrocarbons and nucleosides. Reported were donor-acceptor complex formation between polycyclic aromatic hydrocarbons, both carcinogenic and noncarcinogenic, with compounds of biological importance such as adenosine uridine, riboflavine, and others. A study on the biochemistry of cancerous growth gives evidence that cancer results from a genotype, that is defects in the reproduction of certain types of genes due to combinations of carcinogens with nucleic acids or proteins (29).

A study of carcinogens in the drinking water supply (30) discusses the possible additive effects of carcinogens from different sources and, as such, the water should be kept as free as possible from them. Borneff (31) dismisses this idea as it applies to humans indicating that the additive effects might cause carcinoma in animals over the years. No evidence could be found that linked carcinoma in people to carcinogens in public water supplies.

CHAPTER II

INSTRUMENTATION, EQUIPMENT AND CHEMICALS

Laboratory Scale Digestion Units

The activated sludge process was used for biological degradation of the carriers. In this process, biologically active growths are in continual motion and kept in contact with the waste in the presence of air. To this end, air is injected at the bottom of the tanks.

Domestic sludge was collected from the South River Waste Treatment Plant in Atlanta, Georgia. A static system where the sludge was contained in one-gallon jars was used, because it permitted better control of concentrations and was better suited for acclimation of waste. The jars also served as settling basins.

Analytical Instruments

The ultraviolet (uv) spectra of the effluent was monitored on a Beckman DB-G Grating Spectrophotometer with recorder using ether as a reference standard.

Thin layer chromatography was used to separate the metabolites from carrier digestion. Both 5 x 20 cm. and 20 x 20 cm. glass plates were used. A Desaga spreader was used to spread a film of silica gel 250 microns thick on the glass plates. The metabolites were collected for infrared analysis.

Infrared spectra of the recovered metabolites and carriers in chloroform were charted on a Beckman IR-10 recording spectrophotometer using potassium bromide cells. The pH measurements were made using a Corning Model 12 pH meter.

Carriers Covered in This Study

1. Salicylic acid--Baker analyzed reagent grade.
2. Benzoic acid--Baker analyzed reagent grade.
3. Benzyl alcohol--Fisher certified reagent grade.
4. Methyl salicylate--Fisher certified reagent grade.
5. Naphthaline--Fisher certified reagent grade.
6. Biphenyl--Reagent grade from Eastman organic chemicals.
7. o-phenylphenol--Reagent grade from Eastman organic chemicals.
8. p-phenylphenol--Reagent grade from Eastman organic chemicals.
9. Toluene--Reagent grade from Merck.
10. Xylene--Reagent grade from Fisher Scientific Company. Meta-xylene makes up the largest percentage of the mixture.
11. Dimethylterephthalate--Reagent grade from Eastman organic chemicals.
12. Methylnaphthalene--Reagent grade from Eastman organic chemicals.
13. 1,2,3,4-Tetrahydronaphthalene--Fisher reagent grade.
14. Butyl benzoate--Reagent grade from Eastman organic chemicals.
15. Methyl salicylate carrier--Commercial proprietary product.
16. Orthophenylphenol carrier--Commercial proprietary product.
17. Butyl benzoate carrier--Commercial proprietary product.
18. Biphenyl carrier--Commercial proprietary product.

CHAPTER III

PROCEDURE

Choice of Carriers

The carriers used in this study are all of commercial importance and representative of most classes of compounds employed as carriers. Reagent grade chemicals were of primary interest in this investigation. Commercial carriers were investigated to a limited degree only due to the variability in formulations encountered. Four commercial carriers were selected for comparison purposes. No attempt was made to isolate and identify the metabolites from the commercial carrier. Effects of the carriers on the bacterial population in the digestion tanks was covered.

The concentration of carrier used was 125 mg/l since that concentration was representative of the concentration encountered in total effluent from dyeing processes.

Degradation Studies

A static degradation system was selected. It is believed this model resembles more closely the conditions actually present in the textile waste treatment plants because it includes shock loading effects as one of the operating parameters.

The sludge from the Atlanta, Georgia South River Treatment Plant was acclimated to laboratory conditions by feeding 1.0 g/l of a 3:1 mixture of glucose and peptone daily for four days. The sludge was aereated for 23

hours and allowed to settle. Fifteen hundred milliliters (mls.) of effluent were removed and replaced with tap water containing the daily feeding mixture.

At that point in the acclimation period, where the settled solids volume reached 1,500 cubic centimeters (cc.) at the end of one hour, the feeding of the carriers began. The carriers were fed to the system at a concentration of 125 mg/1 at the beginning of the aereation period only. Those carriers not soluble in water were dissolved in five mls. of acetone and submitted to degradation. The acetone acted as a food source and at the same time increased the carrier solubility. No attempt was made to supply mineral nutrients or to buffer the pH of the aereation mixture.

The digestion mixture was held in one-gallon jars calibrated at 250 ml. intervals. Each jar contained 3,000 mls. of aereation mixture.

Daily measurements were taken of temperature, pH, and chemical oxygen demand (COD) of the supernant liquid withdrawn from the mixture. At intervals, bacterial counts were taken as a measure of toxicity. The counts were made in nutrient agar in Petri dishes at 10^3, 10^4, 10^5 dilutions. The colonies were counted after 48 hours incubation at 37°C. in a Quebec counter.

After the carriers had been fed at the end of zero (0) day, four extractions of the digestion mixture were made at points illustrated by X in Tables 1-19 in the Appendix. The volumes withdrawn from the digestion mixture were not replaced. In the first three extractions, 500 mls. of digestion mixture were extracted with 500 mls. of ethyl ether anhydrous. The fourth extraction, on the tenth day, was made on 1,500 mls. of digestion

mixture. The ether extracts were concentrated on a steam bath using a Büchi Rotavapor vacuum distillation apparatus. The extracts were examined in the (uv) region of the spectrum. Thin layer plates were also made from the concentrate. The jars were monitored for a 10-day period; each day jars were allowed to settle before samples were taken for measurement.

Isolation of Metabolites

Chromatography was the method chosen for isolating the metabolites. Chromatography is based on the principle that the components of a mixture can be separated from one another and concentrated into zones by passing the mixture through a two-phase system, one of which is mobile and the other is stationary.

The technique used was that of thin layer chromatography. This technique is widely used for separating components in a mixture. The Rf values of the components, which is the distance traveled by the component divided by the distance traveled by the solvent, is characteristic of a given solvent, sorbant and operating conditions. The Rf value aids in identifying the components.

Both 5 x 20 cm. and 20 x 20 cm. thin layer plates were prepared. Thirty grams of E. R. Merck silica gel G were thoroughly mixed with 60 ml. of distilled water for 60 seconds and applied with a Desaga spreader to the glass plates forming a film 250 microns thick.

The plates were air dried for 30 minutes and then activated in an oven at a 130°C. for one hour. The plates were stored in a desiccator. The thin layer plates were spotted 1.5 cm. from the bottom and developed to 15 cm. The solutions of the samples in ether were spotted at the appropriate place with a volume of 50 microliters (ul.) using a micrometer syringe.

Two developing mixtures were used, one consisting of 90 per cent chloroform and 10 per cent acetone and the other 80 per cent benzene and 20 per cent methanol.

Since the substances under study were colorless, the solvents were allowed to evaporate from the plates. The plates were then sprayed with a solution of 50 per cent sulphuric acid, 40 per cent water, and 10 per cent nitric acid. The plates were then baked for ten minutes at 200°C. The Rf's values were then recorded for both solvent systems.

For isolation, collection, and identification of the metabolites, a 5 x 20 cm. and a 20 x 20 cm. plates were prepared of each sludge extract. The 5 x 20 cm. plate was developed with the sulphuric acid, nitric acid, and water mixture; where spots appeared, they were marked in the 20 x 20 cm. plate. The plates were observed under ultraviolet light also and those spots appearing were marked. The areas in the 20 x 20 cm. plates were removed and extracted from the silica gel G with chloroform. The sample was placed between two potassium bromide plates and its spectrum determined using an infrared spectrophotometer.

CHAPTER IV

DISCUSSION OF RESULTS

Ultraviolet spectra for each carrier were taken after one, two or four, six or seven, and ten days in the digestion. A sample of the supernant liquid was removed from the aereation tank and extracted for several hours in an ether extractor. The extracts were concentrated to a few milliliters and an ultraviolet spectrum taken.

Metabolism of Salicylic Acid

Degradation began immediately; rapidly at first, then leveled off at a more gradual rate as shown by the rate of decrease in COD. This correlates with a decrease in the number of organisms present as shown by the bacteria counts, further indicating the chemical to be nontoxic to the bacteria present. The uv spectra taken after ten days of aereation showed the appearance of broad peaks around a wavelength of 250 and 300 mu possibly related to peaks appearing on spectra taken within one hour of aereation, and caused by absorption of the acid by the sludge, since in the last extraction the sludge was also extracted.

A spot appearing under ultraviolet light with an Rf value of 0.54 was considered to be a metabolite. However, as with all other carriers, no spots yielded sufficient extract for a positive identification by infrared spectroscopy.

Metabolism of Benzoic Acid

As in Salicylic acid, degradation proceeded immediately as shown by COD values. Bacteria counts showed the organisms increasing with COD, indicating that the chemical was nontoxic to the bacteria present, and served as a food source. The uv spectrum after two days showed that peaks around 260 mu had disappeared. At the ten day extraction, a narrow peak at 250 mu and a broad peak at 300 mu appeared. The pH dropped from 7.5 to 5.2 on the eighth day and returned to 6.1 on the last day. No spots in the thin layer plates were considered to be metabolites.

Metabolism of Benzyl Alcohol

COD values increased until the third day, decreased at the fifth day of aereation and increased until it reached 309 at the final day. The pH values went from 8.7 to a low of 6.4. Bacteria increased at the beginning of aereation and then progressively declined, reaching a low after ten days when the COD was at the highest. The uv spectrum after the sixth day showed a peak at 275 mu not present before or after. A possible metabolite visible under ultraviolet had an Rf value of 0.27. High COD at the final day indicated the chemical to be persistent in the effluent. It was either toxic or inert.

Metabolism of Methyl Salicylate

Like Benzyl Alcohol, COD for the chemical increased until the third day, decreased to the fifth day, and increased to a maximum of 380 at the final day. The pH declined from 8.7 to 6.4 during the ten day digestion period. Bacterial counts also correlated with this pattern indicating the

possibility of a metabolite. A spot appearing under ultraviolet at Rf 0.67 may be considered to be a metabolite. After ten days, a broad peak appeared from 250 to 300 mu on the uv spectra. Increases in COD indicated that the chemical persisted in the effluent and was toxic to the organisms. Had the chemical been nontoxic, a decline in bacteria count should have occurred.

Metabolism of Naphthalene

In general, COD increased to its highest value of 1,176 by the ninth day of aereation, accompanied by increases in the number of organisms present. The pH dropped to 6.8 in the final day from a high of 8.1 on the third day. The peak around 280 mu, present at the beginning, disappeared by the fourth day. A spot detected by ultraviolet with an Rf of 0.80 could have been for a possible metabolite. The high COD obtained after ten days of aereation indicated that the chemical was persistent in the effluent and perhaps was toxic.

Metabolism of Biphenyl

The COD decreased until the sixth day of aereation with no great increase in the number of organisms present, indicating a possible biostatic effect. However, by the ninth day, both had parallel increases. The high COD at the end of the degradation period indicated the chemical to be persistent in some form in the effluent. The pH decreased to 6.5. A possible metabolite is given by spots with Rf values of .70 and .77, both detected by ultraviolet and charred with H_2SO_4. A peak at 250 mu detected in the uv spectrum was not detectable at the tenth day.

Metabolism of o-phenylphenol and p-phenylphenol

Both chemicals showed high COD's during the first two or three days of degradation with corresponding increases in the bacterial counts. High COD's persisted through the study, indicating the chemical was persistent in the effluent. The pH did not decrease as much with p-phenylphenol ending at 8.0 on the final day. The uv spectra of o-phenylphenol showed disappearance of peaks at 230 and 280 mu by the fourth day. On the other hand, the 250 mu peak of p-phenylphenol was present at the tenth day indicating possibility of absorption of the carrier by the sludge. A possible metabolite for o-phenylphenol had an Rf 0.90 and a metabolite for p-phenylphenol had an Rf 0.80. Both projected metabolites were visible under ultraviolet light. O-phenylphenol is toxic to the organisms but capable of acclimation.

Metabolism of Toluene

The COD increased, in general, over the aereation period, accompanied by increases in the number of bacteria present indicating acclimation to the chemical as required before degradation. The pH went from 8.1 to 6.8. At the end of ten days, the COD's were high enough to indicate that the chemical would be present in the effluent of the treatment plant and, as such, constitute a pollutant. The uv spectra showed a peak at 300 mu not present after four days of aereation. A charred spot at Rf 0.87 could have been a metabolite.

Metabolism of Xylene

COD attained its highest value on the eighth and ninth day of aereation dropping by the tenth day but still was high enough to indicate

that the xylene or a metabolite was persistent in the effluent. The pH dropped to 6.6 by the final day. The uv spectra for the tenth day extraction showed a broad peak around 250 mu, bringing up the possibility of absorption by the sludge. A spot detected by ultraviolet light with an Rf of 0.57 was a possible metabolite.

Metabolism of Dimethylterephthalate

COD values increased, reaching a maximum of 957 on the last day of aereation indicating that the chemical would require acclimation before degradation could be expected. The pH dropped to 6.5 by the last day. Bacteria counts decreased paralleling the increases in COD. A spot detected with ultraviolet light had an Rf value of 0.36 indicating the possibility of a metabolite having been formed.

Metabolism of Methylnaphthalene

COD values for Methylnaphthalene went from a high of 1,414 mg/l to a value of 604 mg/l by the tenth day; this product would be expected to persist in the effluent and perhaps toxic. Bacterial growth paralleled COD; uv spectra showed a series of small peaks around 250 to 300 mu, not in evidence by the fourth day.

A spot detected under ultraviolet light with an Rf of 0.82 is considered as a possible metabolite.

Metabolism of 1,2,3,4-Tetrahydronaphthalene

In general, the COD values tended to increase during the ten days aereation reaching a value of 627 mg/l at the end. The pH values went from 8.1 to 7.1. Bacterial counts reached a high by the sixth day, then

decreased indicating possibility of a biostatic effect. The uv spectra taken at the fourth day showed a peak around 250 mu not present in any of the other determinations. A spot with an Rf value of 0.87 detected both by ultraviolet light and charring with sulphuric and nitric acid is believed to be a possible metabolite. The chemical was either toxic or inert.

Metabolism of Butyl Benzoate

COD values suggested that the chemical would be persistent in the effluent, after ten days of degradation, in sufficient amount to make it a cause for concern. Bacterial counts did not change appreciably. The values obtained in pH measurements remained almost the same, about 8.0 until the last two days dropping to 6.7 by the tenth day of degradation. A possible metabolite was detected under ultraviolet light with an Rf value of 0.77.

Metabolism of Commercial Carriers

COD values obtained for a commercial methyl salicylate carrier were higher than those of the primary compound. Both followed a pattern of increases reaching maximums by the end of the period of aereation. Bacterial counts were also higher for the commercial product and pH values were not as low as for the primary chemical. The carrier was toxic.

It appeared that other chemicals present in the formulation of the commercial product increased its resistance to degradation.

Commercial o-phenylphenol showed higher COD values at the end of the period than the primary compound. Bacterial counts were higher and pH values lower in the commercial product. The uv spectra at four days

showed that o-phenylphenol peaks at 250, 275 to 300 mu still present where they had disappeared in the spectra of effluent from the pure compound.

Commercial butyl benzoate COD values were also greater and the pattern differed slightly with a definite tendency to increase with time reaching a value of 864 mg/l at the end of the tenth day. Bacterial counts were higher following this trend. In general, the commercial product was harder to degrade and more persistent in the effluent.

A commercial biphenyl carrier also followed the pattern of increasing COD values with time as did the bacterial counts. The uv spectra was similar to that for the pure compound.

In general, commercial carriers have a higher COD and carry through into the effluent to a greater degree than the primary compound indicating that other chemicals or impurities present in the proprietary carrier are just as worthy of investigation as the carriers' primary chemical and possibly contribute as much as the carrier to the overall pollution problem.

Data recorded daily during the aereation of each carrier can be found in the Appendix in Tables 1 through 19. Ultraviolet spectra are shown in Figures 1 through 19 of the Appendix. Tables 20 and 21 of the Appendix give Rf values of all spots detected by thin layer chromotography.

CHAPTER V

CONCLUSIONS

1. Salicylic and benzoic acid were readily degraded aerobically in activated sludge; benzyl alcohol, methyl salicylate, naphthalene, o-phenylphenol, methyl naphthalene, and 1,2,3,4-tetrahydronaphthalene were considered toxic or inert to the organisms. Biphenyl, toluene, dimethyl terephthalate, p-phenylphenol, xylene and butyl benzoate could be expected to persist in the effluent from conventional waste treatment plants.

2. Proprietary commercial carriers, for dyeing processes containing chemicals enumerated above as the active agent gave higher COD values and longer acclimation times for digestion than the pure chemicals; dispersants, emulsifiers, and other ingredients in the proprietary product markedly affected the response of the principal chemical to the digestion process.

3. Most carriers investigated were regarded as biodegradable only when the bacterial population of the active sludge has adequately acclimated to the carrier and the digestion time had been extended for beyond the normal holding time for most domestic waste treatment plants. Loss of carrier from the activated sludge digestion process could have resulted from volatilization to the atmosphere, or adsorption on or interaction with the sludge.

4. Metabolites resulting from degradation of the carrier were noted; quantities recovered were inadequate for characterization by infrared spectroscopic techniques.

CHAPTER VI

RECOMMENDATIONS

1. Loss of carriers by volatilization from aereation chambers during digestion should be studied. Volatilization may result in air pollution.

2. Adsorption of chemicals, serving as carriers on activated sludge should also be studied as well as the fate of the carriers under anaerobic digestion.

3. Technology of high temperature of dyeing processes, which obviate the need for using carriers should be further developed.

4. Extraction processes for removal of carriers from spent dyebaths should be investigated in the hope that undesirable chemicals could be scrubbed from textile process effluents before they were presented to activated sludge systems for further treatment.

APPENDIX

Table 1. Salicylic Acid Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	*** Bacteria Total Count No./ml
0	7.0	23	136**		
1	7.1	24	274	X	Y
2	7.1	23	145	X	Y
3	6.8	24	90		
4	7.1	23	75		
5	6.9	23	54		
6	6.8	23	55	X	13×10^5
7	5.2	23	40		
8	5.0	23	55		
9	6.2	23	44		
10	6.6	23	36	X	6×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.
*** Bacteria present in too high a number to be counted where Y appears.

Table 2. Benzoic Acid Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	*** Bacteria Total Count No./ml
0	6.5	23	148**		
1	7.5	24	137	X	27×10^5
2	6.5	23	188	X	Y
3	6.5	24	141		
4	6.1	23	74		
5	6.2	23	58		
6	5.8	23	52	X	10×10^5
7	5.9	23.5	55		
8	5.2	23	60		
9	5.8	23	60		
10	6.1	23	55	X	4×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.
*** Bacteria present in too high a number to be counted where Y appears.

Table 3. Benzyl Alcohol Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	*** Bacteria Total Count No./ml
0	8.4	23	232**		
1	8.7	24	169	X	187×10^5
2	8.5	23	212	X	Y
3	8.5	24	255		
4	7.9	23	228		
5	6.4	23.5	210		
6	6.6	23	242	X	60×10^5
7	6.7	23.5	230		
8	6.8	23	257		
9	6.4	23	301		
10	6.5	23	309	X	12×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.
*** Bacteria present in too high a number to be counted where Y appears.

Table 4. Methyl Salicylate Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	8.8	24	200**		
1	8.7	24	196	X	40×10^5
2	8.9	23	216	X	60×10^5
3	8.6	24	357		
4	8.2	23	271		
5	6.6	24	244		
6	6.4	23	277	X	9×10^5
7	6.7	23	317		
8	6.7	23	329		
9	6.6	23	329		
10	6.6	23	380	X	12×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 5. Naphthalene Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.7	23	321**		50×10^5
1	7.3	23	---	X	
2	7.2	23	880		
3	8.1	23	760		84×10^5
4	7.5	23	549	X	
5	7.7	22	933		
6	7.7	22	879		12×10^6
7	7.0	22	998	X	
8	6.7	23	1061		
9	6.6	23	1176		30×10^6
10	6.8	23	721	X	22×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 6. Biphenyl Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.9	22	355**		47×10^5
1	7.3	23	---	X	
2	7.2	23	377		
3	8.1	23	790		50×10^5
4	7.9	22	612	X	
5	7.7	22	620		
6	6.4	22	483		53×10^5
7	6.6	23	622	X	
8	6.6	23	610		
9	6.4	23	713		91×10^5
10	6.5	23	528	X	16×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 7. o-phenylphenol Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.5	22	324**		42×10^5
1	7.7	23	---	X	
2	7.9	23	1592		
3	8.1	23	820		22×10^6
4	7.9	23	267	X	
5	8.7	22.5	353		
6	8.0	22	333		90×10^5
7	7.2	22	352	X	
8	7.5	23	362		
9	7.4	23	384		98×10^5
10	7.3	23	202	X	78×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 8. p-phenylphenol Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.5	22	378**		30×10^5
1	8.1	23	---	X	
2	8.2	23	2490		
3	8.0	23	813		24×10^6
4	8.0	23	1027	X	
5	8.3	23	502		
6	7.9	22	499		76×10^5
7	7.9	22	261	X	
8	8.0	23	281		
9	8.1	23	408		10×10^6
10	8.0	23	334	X	22×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 9. Toluene Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.4	22	370**		30×10^5
1	8.1	23	---	X	
2	7.7	23	400		
3	8.1	23	767		86×10^5
4	7.7	23	557	X	
5	8.0	22	651		
6	7.1	22	840		10×10^6
7	6.8	23	812	X	
8	6.4	23	764		
9	6.9	23	905		83×10^5
10	6.8	23	776	X	20×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 10. Xylene Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.9	23	230**		36×10^6
1	7.2	23	---	X	
2	8.0	23	210		
3	8.0	22.5	---		11×10^5
4	8.2	22	267	X	
5	8.2	22	369		
6	7.0	23	436		94×10^5
7	6.7	23	313	X	
8	6.7	23	511		
9	6.7	23	502		60×10^5
10	6.6	23	272	X	36×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 11. Dimethylterephthalate Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	8.0	23	268**		40×10^6
1	7.1	23	---	X	
2	8.0	23	286		
3	8.1	23	220		5×10^5
4	8.3	22	251	X	
5	8.3	22	301		
6	8.1	23	428		12×10^6
7	7.6	23	503	X	
8	7.0	23	557		
9	6.9	23	671		13×10^6
10	6.5	23	957	X	31×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 12. Methylnaphthalene Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	8.0	23	260**		50×10^6
1	7.7	23	---	X	
2	7.7	23	1414		
3	8.0	22	1004		8×10^7
4	8.3	22	980	X	
5	8.5	22	895		
6	8.3	23	935		13×10^6
7	8.3	23	412	X	
8	8.3	23	1027		
9	8.0	23	558		25×10^6
10	7.7	23	604	X	21×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 13. 1,2,3,4-Tetrahydronaphthalene Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	8.0	23	294**		40×10^6
1	7.7	23	---	X	
2	8.1	23	271		
3	7.8	22	259		16×10^5
4	7.9	22	274	X	
5	8.3	22	384		
6	8.3	23	471		12×10^6
7	7.5	23	436	X	
8	7.3	23	635		
9	7.3	23	411		75×10^5
10	7.1	23	627	X	60×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 14. Butyl Benzoate Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	8.0	23	309**		50×10^6
1	7.3	23	---	X	
2	7.5	23	872		
3	8.0	23	141		4×10^5
4	8.0	22	204	X	
5	8.3	22	285		
6	8.2	23	317		60×10^5
7	8.0	23	261	X	
8	8.0	23	361		
9	7.3	23	276		73×10^5
10	6.7	23	573	X	12×10^5

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 15. Commercial Methyl Salicylate Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.5	23	211**		43×10^5
1	7.8	23	776	X	
2	7.7	23	588		
3	7.9	23	404		56×10^5
4	7.8	23	436	X	
5	7.8	23	420		
6	7.5	23	408		60×10^5
7	7.0	23	629	X	
8	6.8	23	823		
9	7.1	23	1230		40×10^6
10	7.0	23	1072	X	40×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 16. Commercial o-phenylphenol Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.6	23	196**		76×10^6
1	7.5	23	713	X	
2	7.4	23	612		
3	7.7	23	602		41×10^5
4	7.9	23	388	X	
5	8.1	23	345		
6	7.9	23	255		50×10^5
7	7.5	23	155	X	
8	7.5	23	161		
9	7.4	23	561		32×10^6
10	7.4	23	400	X	40×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 17. Commercial Butyl Benzoate Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.5	23	196**		35×10^5
1	7.3	23	376	X	
2	7.7	23	369		
3	7.6	23	317		91×10^5
4	7.8	23	321	X	
5	8.0	23	444		
6	7.1	23	615		15×10^6
7	7.4	23	722	X	
8	7.3	23	502		
9	7.1	23	839		42×10^6
10	7.0	23	864	X	30×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 18. Commercial Biphenyl Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.7	23	222**		55×10^5
1	7.7	22	576	X	
2	7.7	22	353		
3	7.7	22	270		27×10^6
4	7.8	23	396	X	
5	7.8	23	590		
6	6.8	23	705		25×10^6
7	6.9	23	621	X	
8	6.9	23	538		
9	6.9	23	807		18×10^6
10	6.9	23	900	X	10×10^6

* uv spectra monitored where X appears.
** Day prior to feeding carrier.

Table 19. Control Daily Data

Day No.	pH	Temp. °C.	COD mg/l	* uv Spectra	Bacteria Total Count No./ml
0	7.6	23	177**		6×10^5
1	7.4	23	425	X	
2	7.8	22	314		
3	7.7	22	308		30×10^6
4	7.7	23	258	X	
5	7.6	23	196		
6	7.0	23	140		40×10^5
7	7.2	23	120	X	
8	7.0	23	99		
9	6.9	23	50		30×10^5
10	6.8	23	45	X	10×10^5

* uv spectra monitored where X appears.
** Day prior to feeding glucose and peptone.

Table 20. Thin Layer Data For Sludge Extracts

	Rf Values*	
	90% CH C/3 10% Acetone	80% Benzene 20% Methanol
Salicylic Acid		
1st Extraction: 1 hr.	.97	.86
2nd Extraction: 2 days	.97	.86
3rd Extraction: 6 days	0, .6, .97	.6, .86
4th Extraction: 10 days	0, .57, .80, .97	.6, .7(Y), .77(Y), .84(O), .86
Benzoic Acid		
1st Extraction: 1 hr.	1.0	.86
2nd Extraction: 2 days	1.0	.86
3rd Extraction: 6 days	.2, 1.0	.86
4th Extraction: 10 days	.2, .94, 1.0	.7(Y), .77, .86
Benzyl Alcohol		
1st Extraction: 1 hr.	1.0	.66
2nd Extraction: 2 days	1.0	.66
3rd Extraction: 6 days	.40, 1.0	.6, .86
4th Extraction: 10 days	.40, .74, 1.0	.57(Y), .6, .74(Y), .80, .80(O), .86
Methyl Salicylate		
1st Extraction: 1 hr.	1.0	---
2nd Extraction: 2 days	1.0	.87
3rd Extraction: 6 days	.7, .87, 1.0	.6, .87
4th Extraction: 10 days	.33, .6, .87, 1.0	.67(Y), .77, .8, .84(Y), .87(O), .87
Naphthalene		
1st Extraction: 1 hr.	.94	---
2nd Extraction: 4 days	.94	.87
3rd Extraction: 7 days	.94	.87
4th Extraction: 10 days	.10, .33, .94	.66, .70, .87

* Charred spots with concentrated Sulphuric and Nitric Acid Mixture unless otherwise noted: Y= Yellow O= Orange.

Table 20. Thin Layer Data For Sludge Extracts (continued)

	Rf Values*	
	90% CH C/3 10% Acetone	80% Benzene 20% Methanol
Biphenyl		
1st Extraction: 1 hr.	.94	.90
2nd Extraction: 4 days	.94	.87
3rd Extraction: 7 days	.94	.87
4th Extraction: 10 days	.18, .38, .64, .94	.28, .40, .47, .87
o-phenylphenol		
1st Extraction: 1 hr.	.97	.80, .97
2nd Extraction: 4 days	.97	.97
3rd Extraction: 7 days	.97	.97
4th Extraction: 10 days	.18, .80, .97	.84, .97
p-phenylphenol		
1st Extraction: 1 hr.	.77, .97	.74, .94
2nd Extraction: 4 days	.97	.94
3rd Extraction: 7 days	.97	.94
4th Extraction: 10 days	.18, .40, .54, .80, .97	.54, .74, .87
Toluene		
1st Extraction: 1 hr.	1.0	1.0
2nd Extraction: 4 days	1.0	1.0
3rd Extraction: 7 days	1.0	.80, 1.0
4th Extraction: 10 days	.40, .60, 1.0	.60, .94, 1.0
Xylene		
1st Extraction: 1 hr.	1.0	1.0
2nd Extraction: 4 days	1.0	1.0
3rd Extraction: 7 days	1.0	1.0
4th Extraction: 10 days	.06, .33, .64, .7, 1.0	.5, 1.0

* Charred spots with concentrated Sulphuric and Nitric Acid Mixture unless otherwise noted: Y= Yellow O= Orange.

Table 20. Thin Layer Data For Sludge Extracts (continued)

	Rf Values*	
	90% CH C/3 10% Acetone	80% Benzene 20% Methanol
Dimethylterephthalate		
1st Extraction: 1 hr.	.33, 1.0	.64, .87, 1.0
2nd Extraction: 4 days	.74, 1.0	1.0
3rd Extraction: 7 days	1.0	1.0
4th Extraction: 10 days	.84, 1.0	.60, .70, .84, 1.0
Methylnaphthalene		
1st Extraction: 1 hr.	.70, 1.0	.57, .80, 1.0
2nd Extraction: 4 days	1.0	1.0
3rd Extraction: 7 days	1.0	1.0
4th Extraction: 10 days	1.0	.47, .74, 1.0
1,2,3,4-Tetrahydronaphthalene		
1st Extraction: 1 hr.	.74, 1.0	.66, .7, .9, 1.0
2nd Extraction: 4 days	.74, 1.0	.66, .7, 1.0
3rd Extraction: 7 days	.80, 1.0	1.0
4th Extraction: 10 days	.80, 1.0	1.0
Butyl Benzoate		
1st Extraction: 1 hr.	.5, .63, .94	.57, .96, 1.0
2nd Extraction: 4 days	.94	1.0
3rd Extraction: 7 days	.4, .66, .94	.57, 1.0
4th Extraction: 10 days	.66, .94	.57, .96, 1.0
Control		
1st Extraction: 1 hr.	1.0	.80, 1.0
2nd Extraction: 4 days	.66, 1.0	.80, 1.0
3rd Extraction: 7 days	1.0	1.0
4th Extraction: 10 days	.80, 1.0	.80, 1.0

* Charred spots with concentrated Sulphuric and Nitric Acid Mixture unless otherwise noted: Y= Yellow O= Orange.

Table 21. Thin Layer Data For Combined 2nd, 3rd, 4th Sludge Extracts

	Rf Values	
	uv Spots	Charred Spots*
Salicylic Acid	.40	.60
	.54	.80
	.86	
	Color	
	.74 Yellow	
	.80 Orange	
Benzoic Acid	.40	.80
	.47	
	.87	
	Color	
	.84 Orange	
Benzyl Alcohol	.27	.80
	.40	
	.84	
	Color	
	.80 Orange	
	.74 Yellow	
Methyl Salicylate	.47	.80
	.67	
	.90	
	Color	
	.87 Orange	
	.84 Yellow	
Nephthalene	.23	.66
	.74	.74
	.80	.87
	.93	
	Color	
	.84 Orange	
Biphenyl	.20	.70
	.28	.77
	.47	
	.70	
	.77	
	.87	

* Charred spot with concentrated H_2SO_4 and Nitric Acid Mixture.

Table 21. Thin Layer Data For Combined 2nd, 3rd, 4th Sludge Extracts (continued)

	Rf Values	
	uv Spots	Charred Spots*
o-phenylphenol	.43	.94
	.47	
	.77	
	.90	
	.94	
p-phenylphenol	.18	.66
	.20	.94
	.28	
	.33	
	.47	
	.66	
	.80	
	.94	
Toluene	.20	.66
	.23	.80
	.33	.87
	.50	
	.74	
	.94	
	.97	
Xylene	.20	.87
	.47	
	.57	
	.80	
	.87	
	.94	
Dimethylterephthalate	.14	.66
	.21	1.0
	.36	
	.55	
	1.0	

* Charred spot with concentrated H_2SO_4 and Nitric Acid Mixture.

Table 21. Thin Layer Data For Combined 2nd, 3rd, 4th Sludge Extracts (continued)

	Rf Values	
	uv Spots	Charred Spots*
Methylnaphthalene	.21	.36
	.66	.66
	.82	.93
	.93	
	1.0	
1,2,3,4-Tetrahydronaphthalene	.20	.87
	.27	
	.44	
	.66	
	.80	
	1.0	
Butyl Benzoate	.29	.72
	.43	.97
	.72	
	.84	
	.97	
Control	.13	.66
	.60	.94
	.80	
	.94	

* Charred spot with concentrated H_2SO_4 and Nitric Acid Mixture.

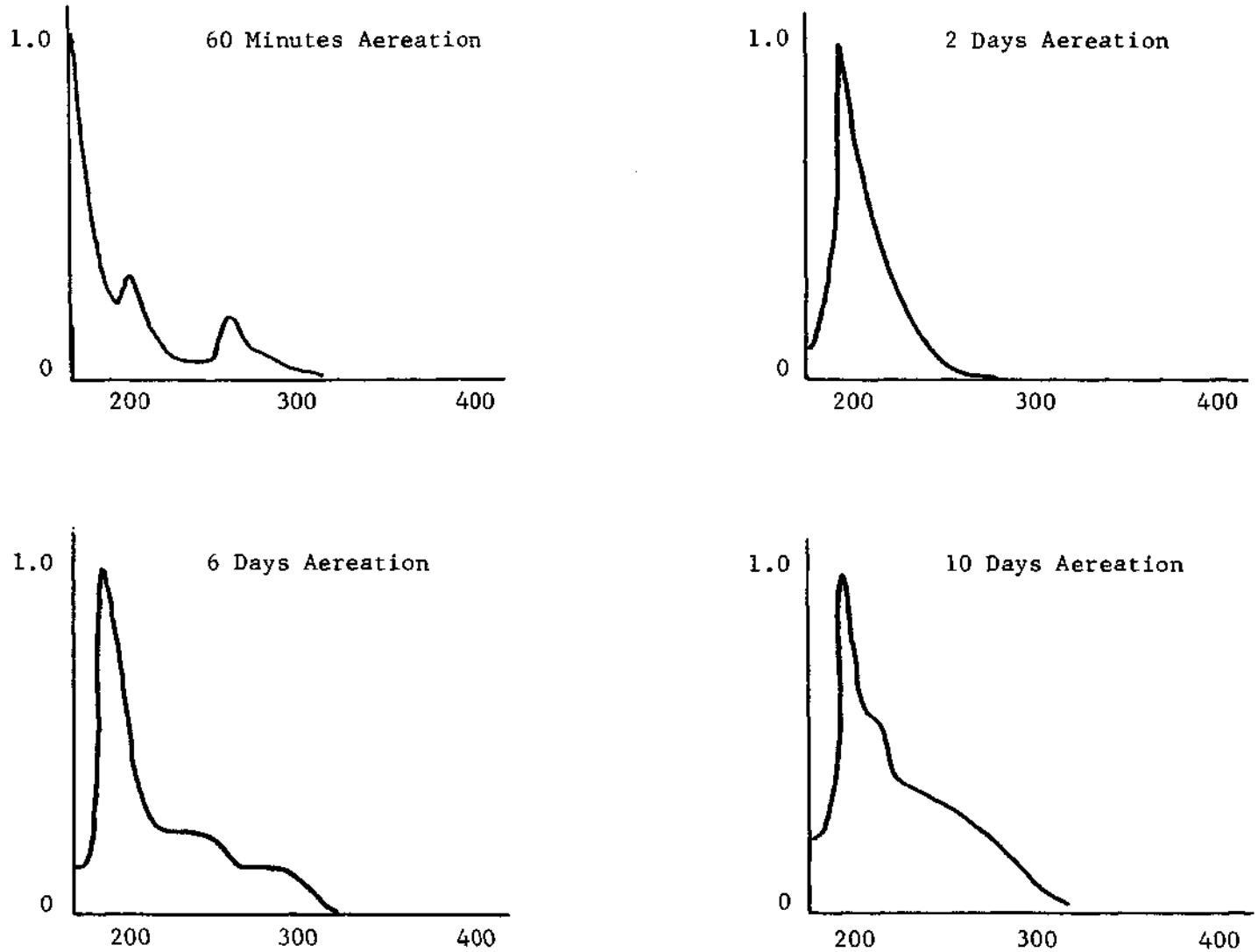
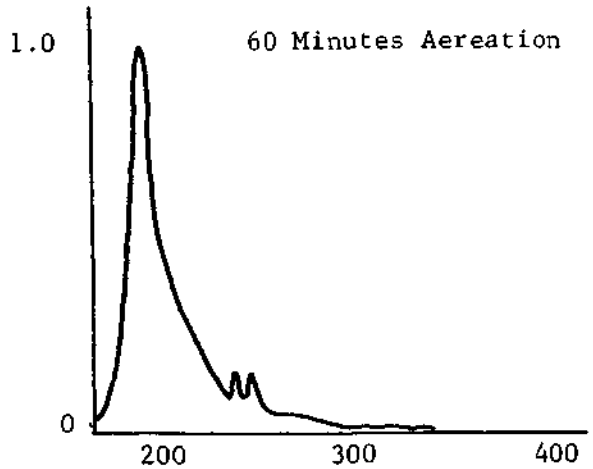
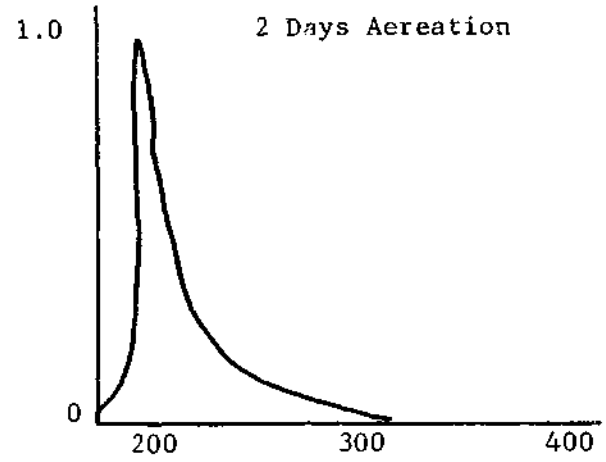
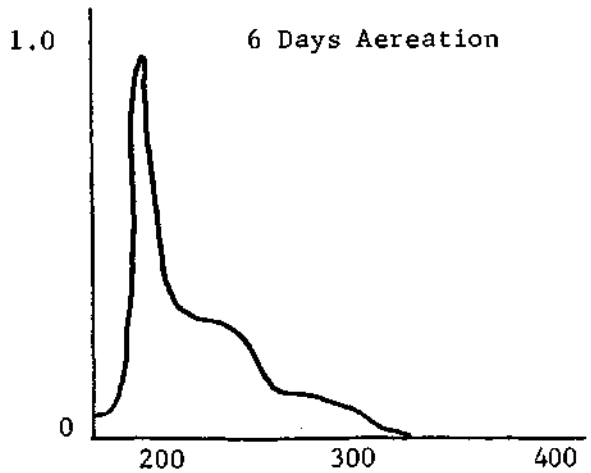


Figure 1. Ultraviolet Spectra of Salicylic Acid Effluents







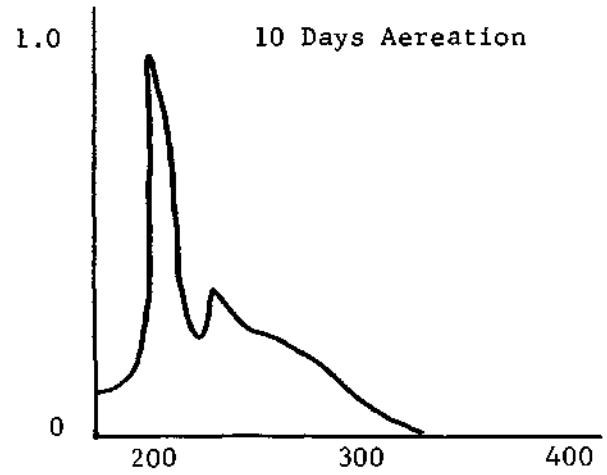


Figure 2. Ultraviolet Spectra of Benzoic Acid Effluents

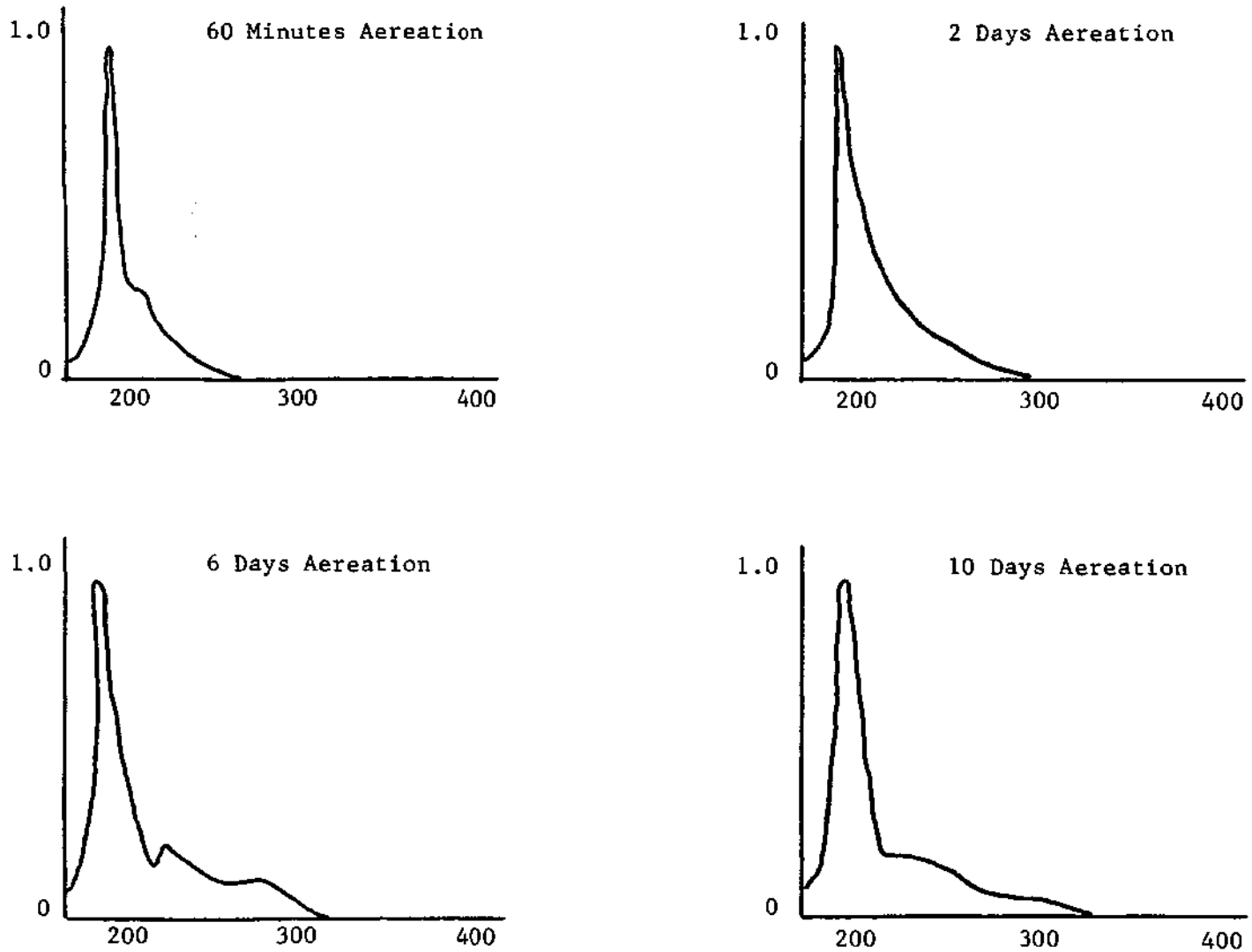


Figure 3. Ultraviolet Spectra of Benzyl Alcohol Effluents

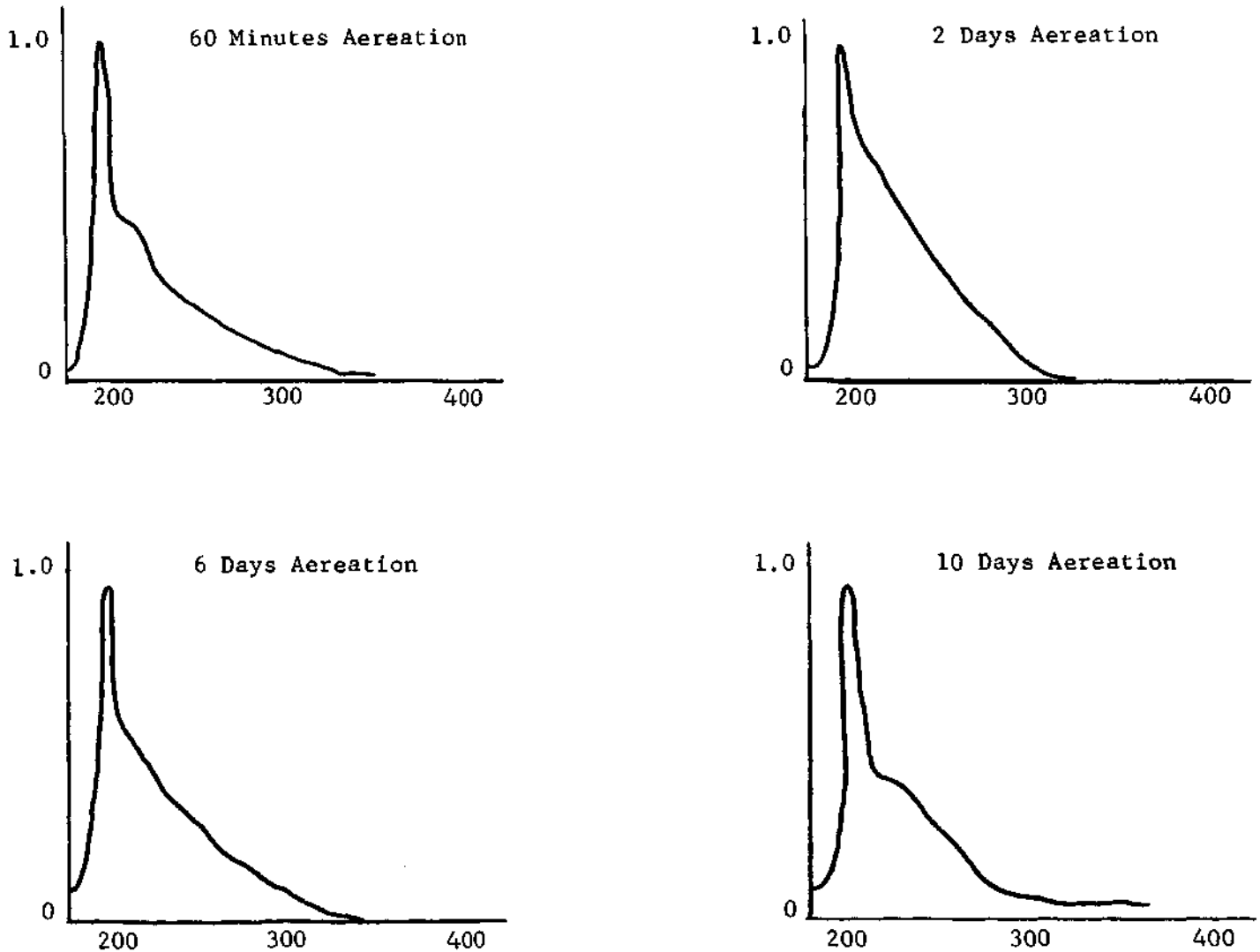


Figure 4. Ultraviolet Spectra of Methyl Salicylate Effluents

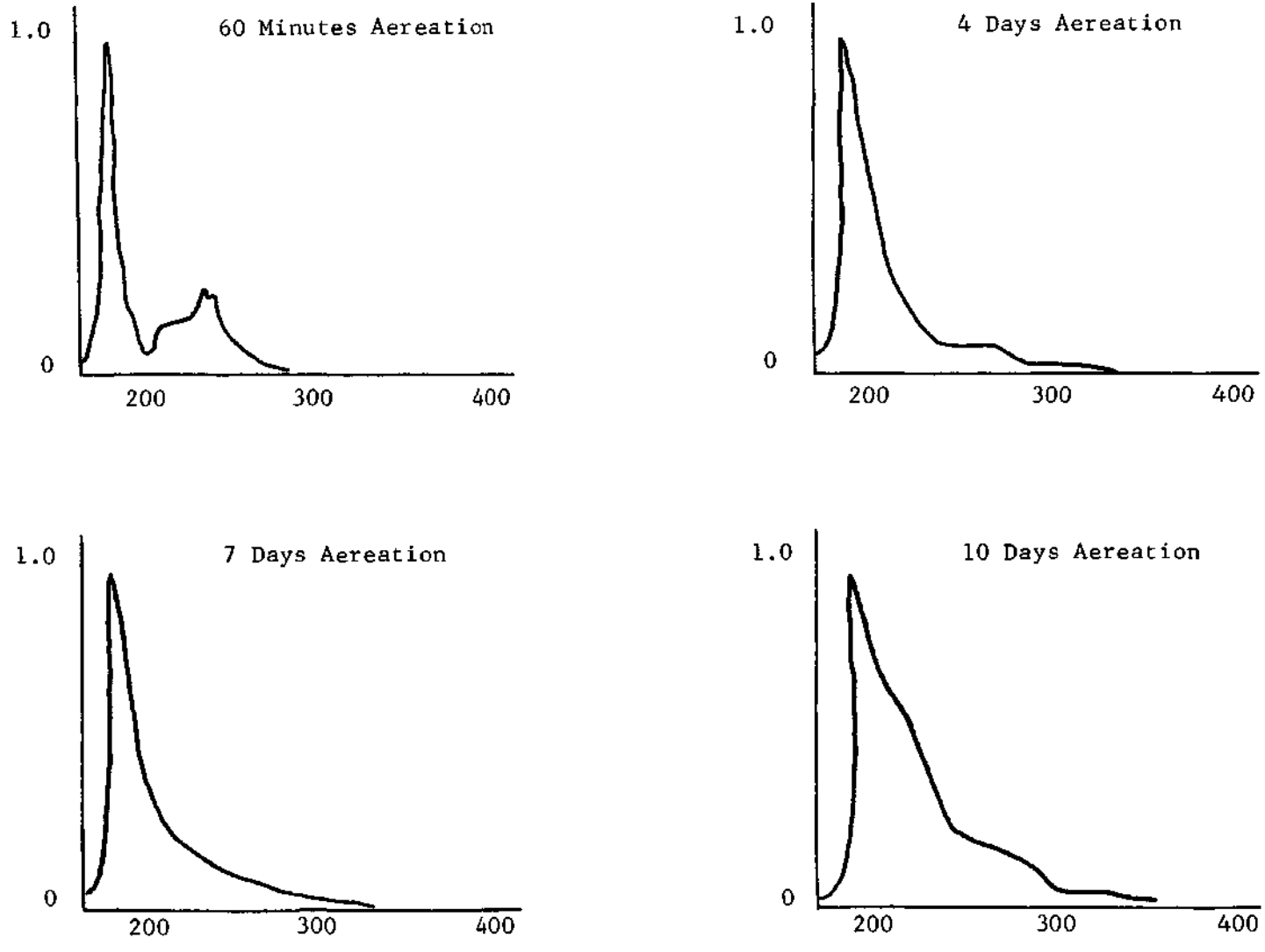


Figure 5. Ultraviolet Spectra of Naphthalene Effluents

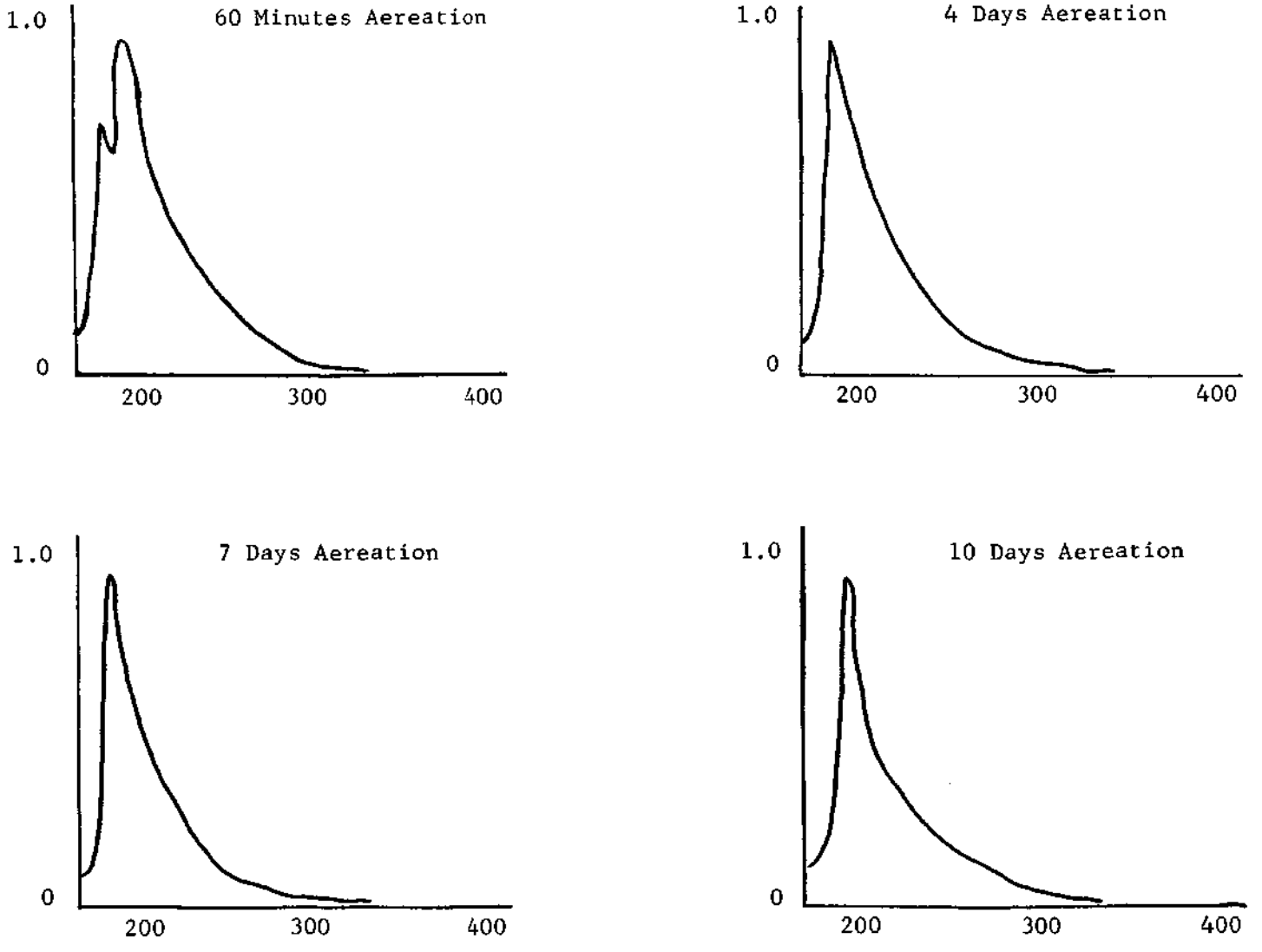


Figure 6. Ultraviolet Spectra of Biphenyl Effluents

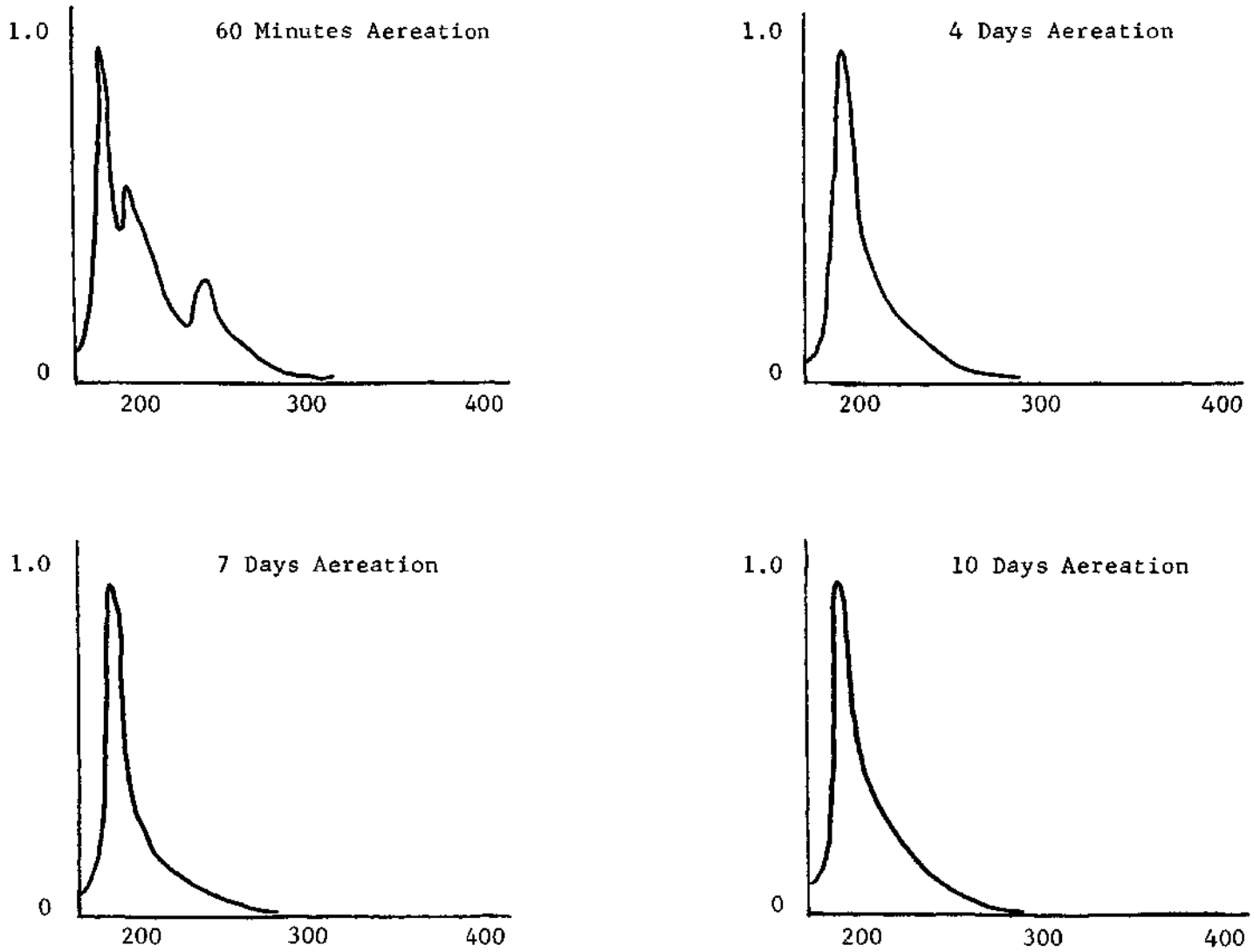


Figure 7. Ultraviolet Spectra of o-phenylphenol Effluents

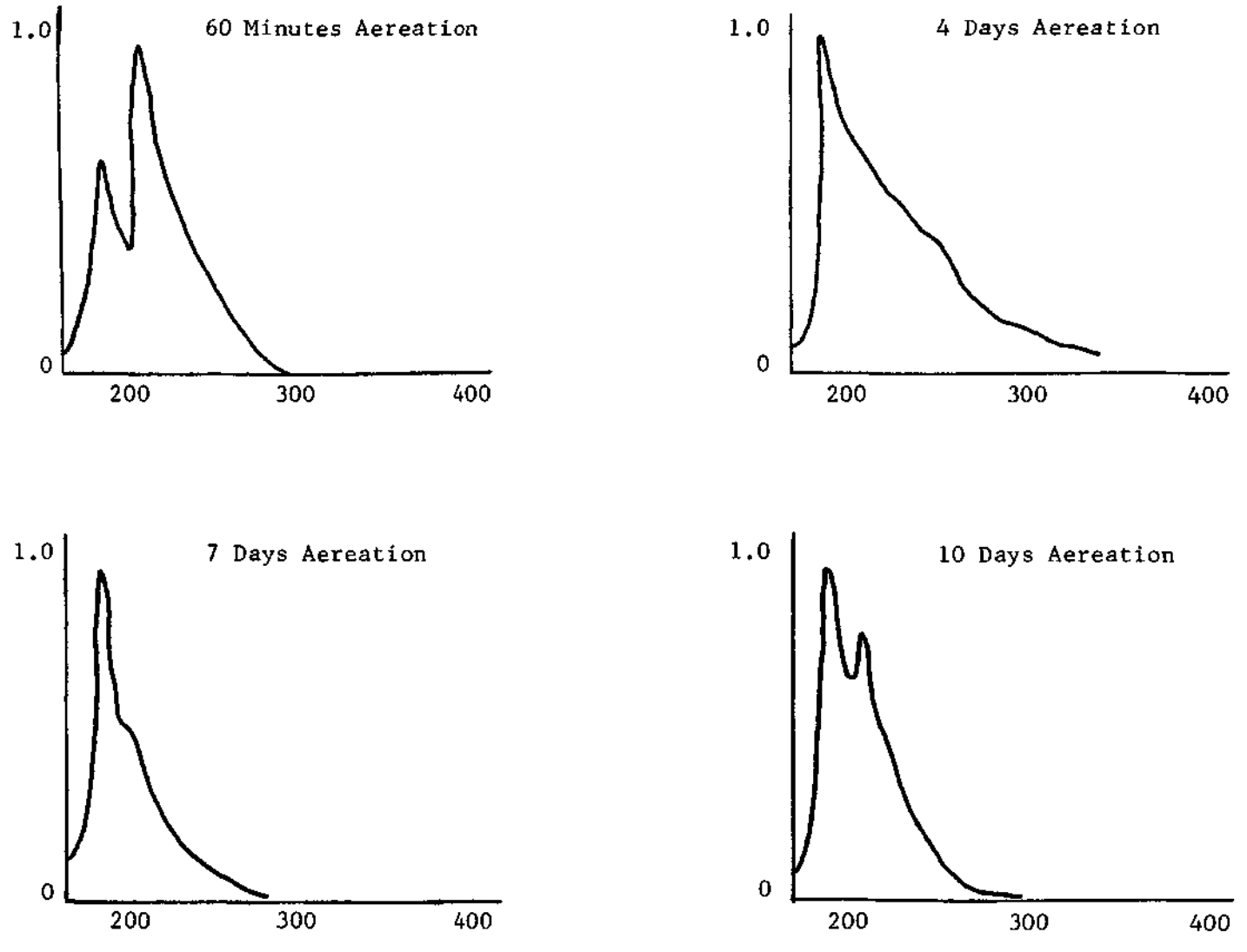


Figure 8. Ultraviolet Spectra of p-phenylphenol Effluents

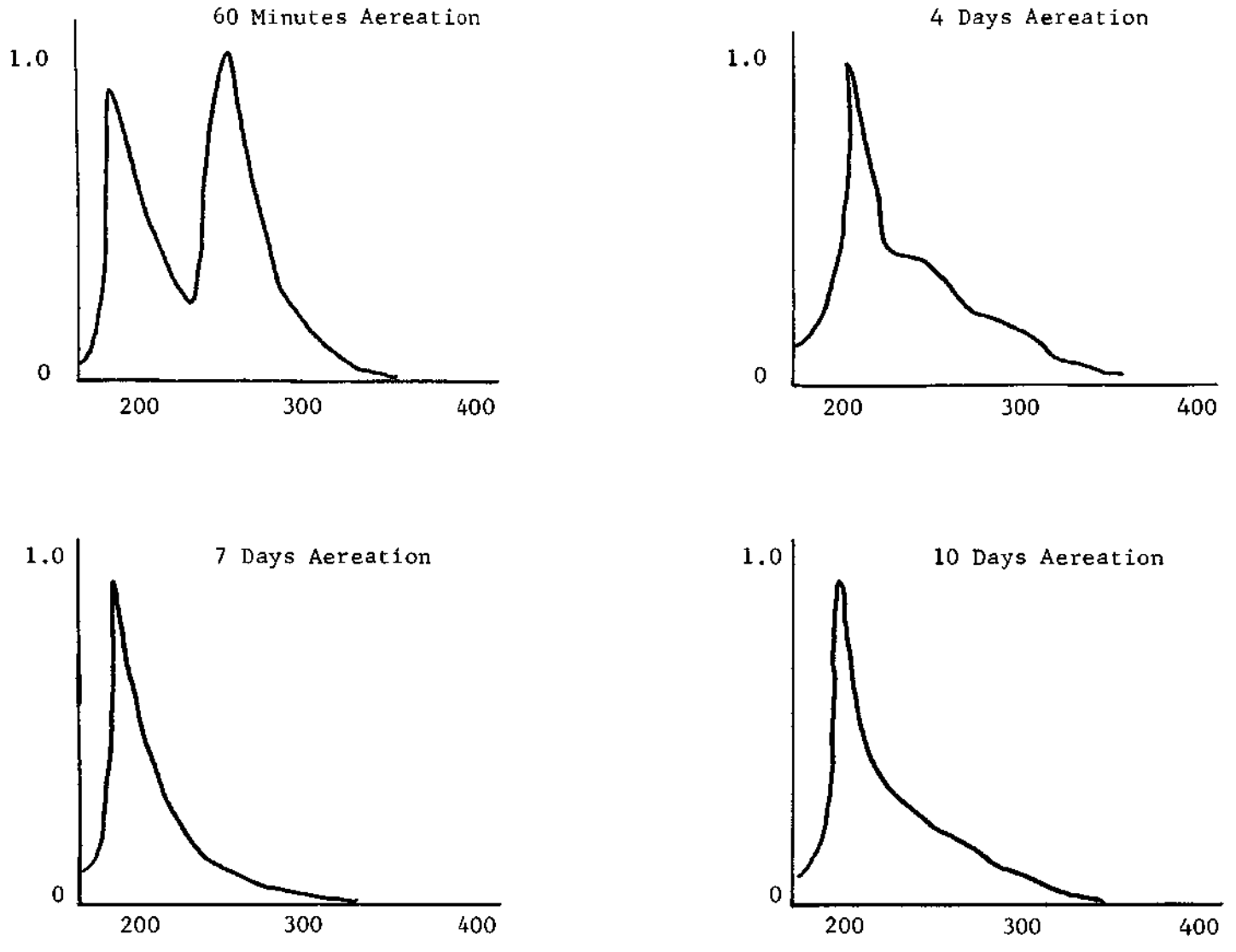
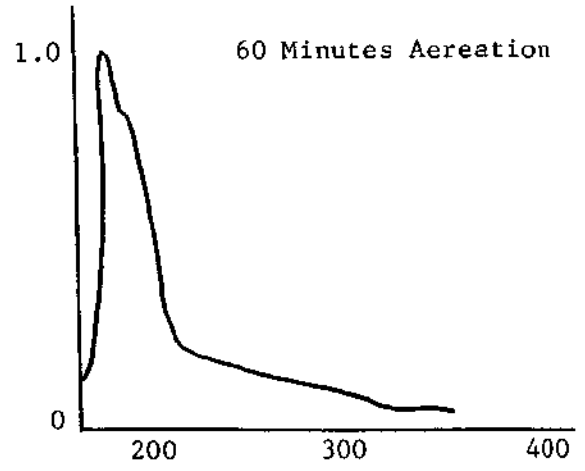
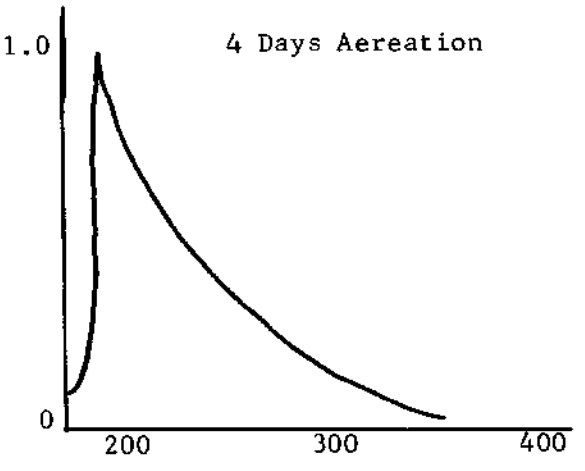
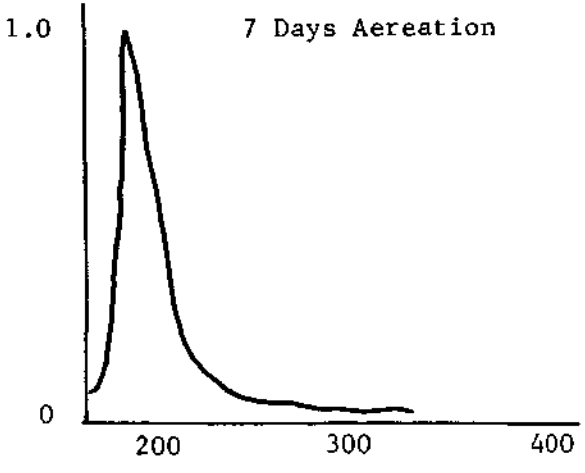


Figure 9. Ultraviolet Spectra of Toluene Effluents







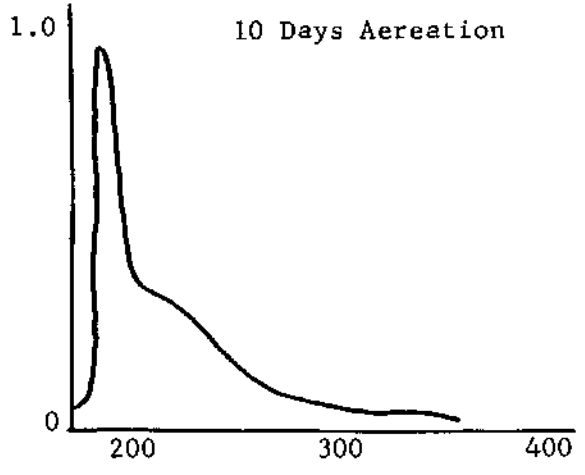


Figure 10. Ultraviolet Spectra of Xylene Effluents

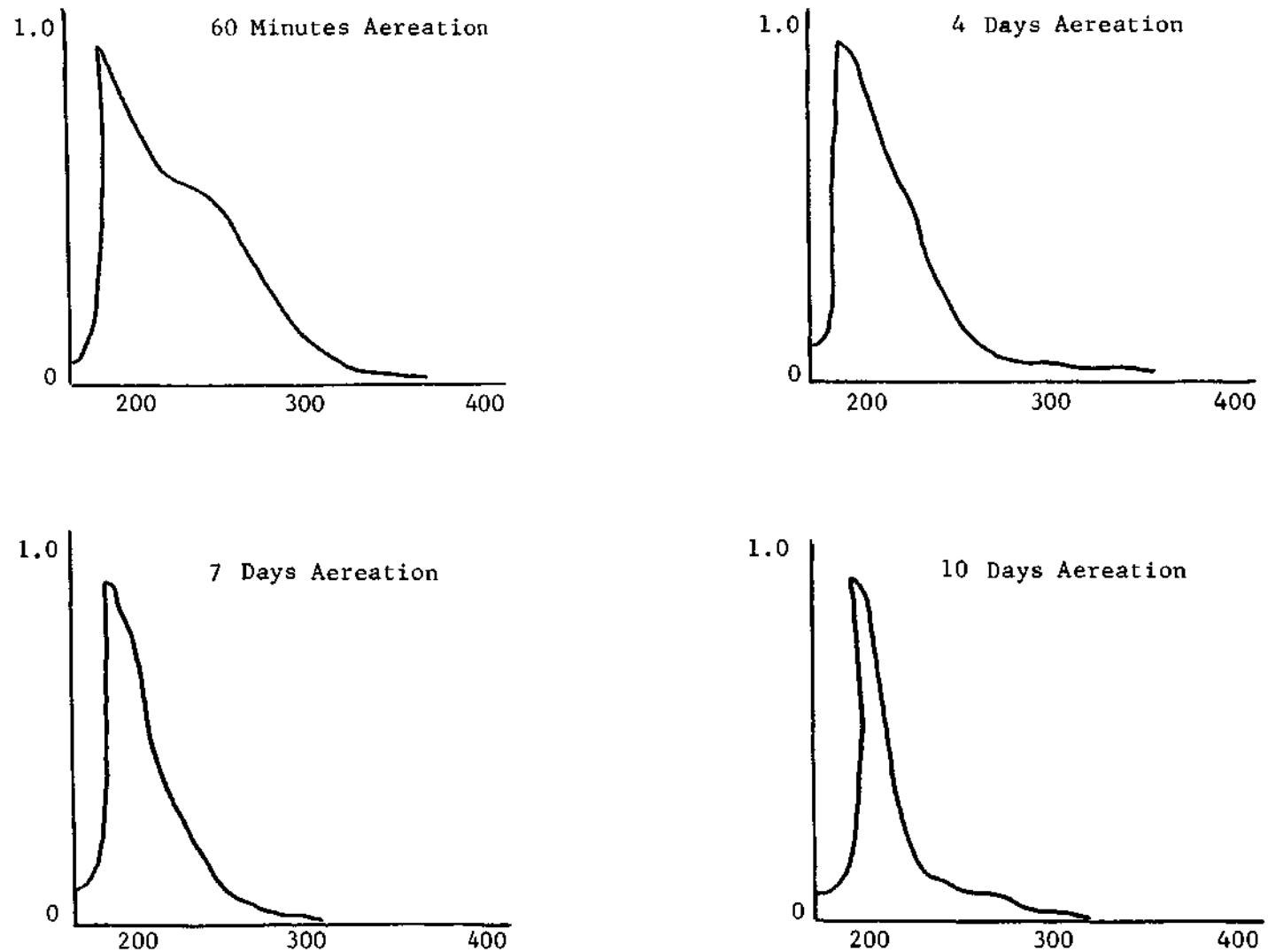


Figure 11. Ultraviolet Spectra of Dimethylterephthalate Effluents

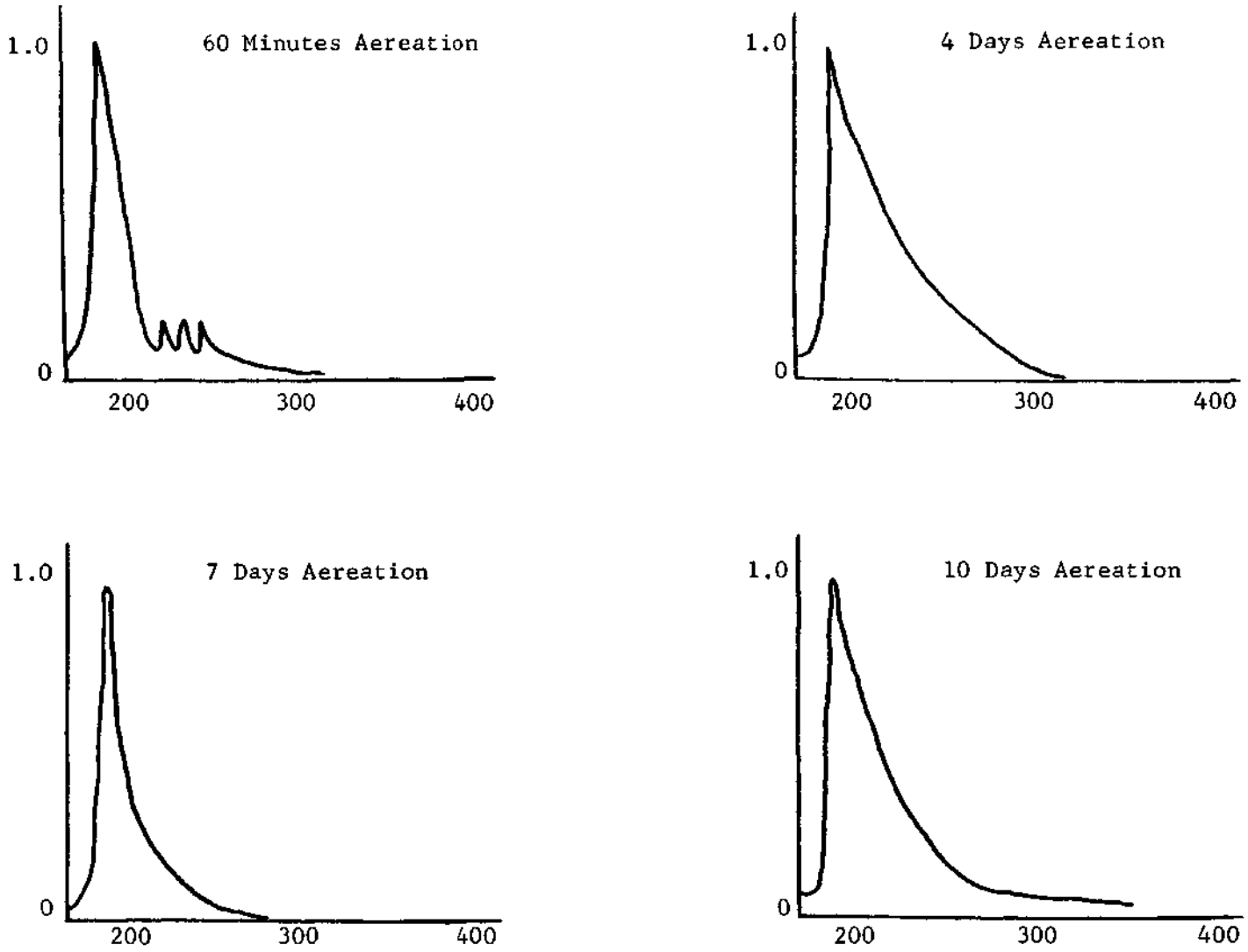


Figure 12. Ultraviolet Spectra of Methylnaphthalene Effluents

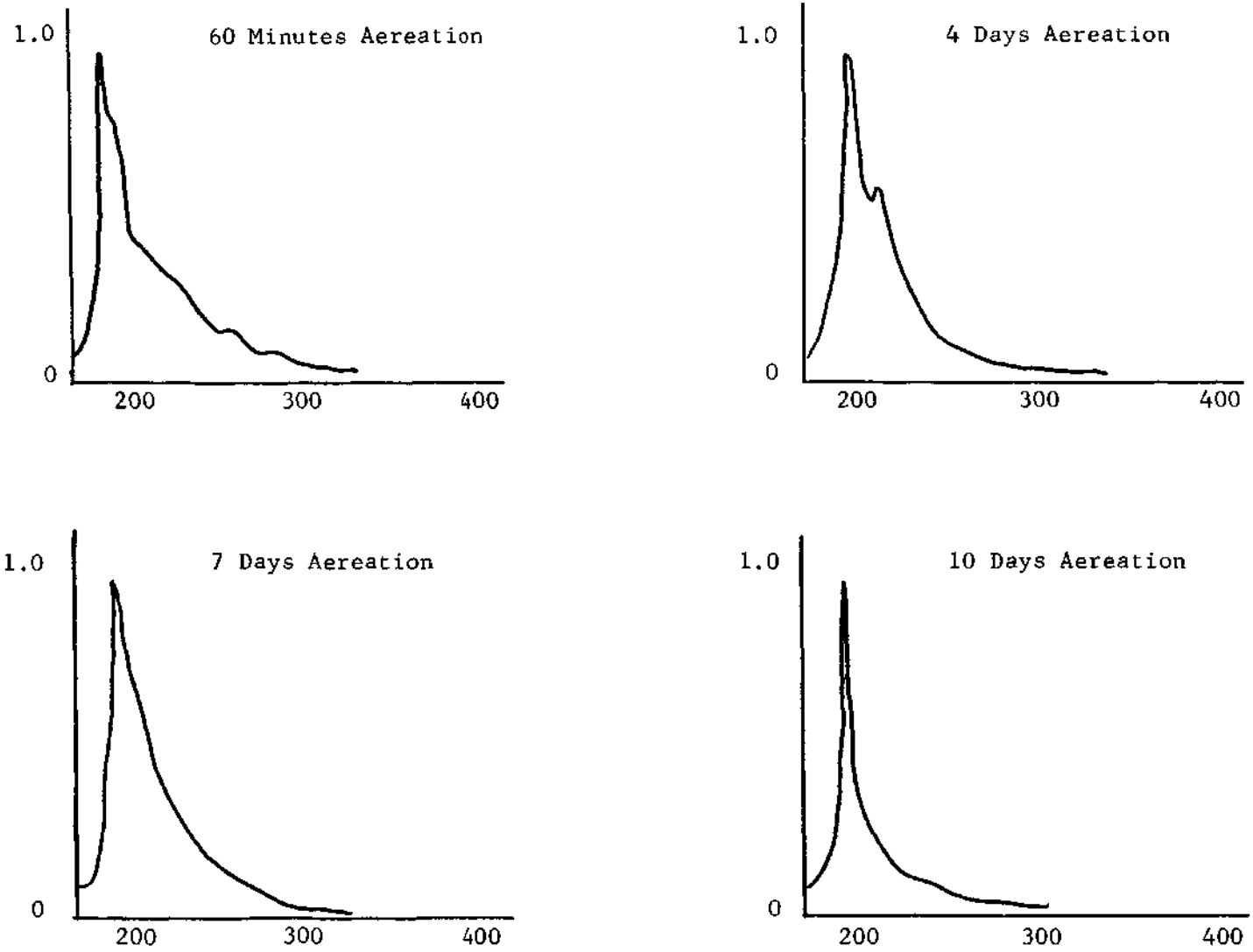
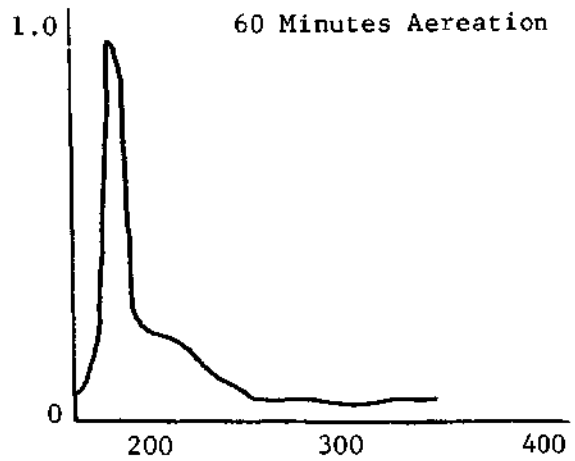
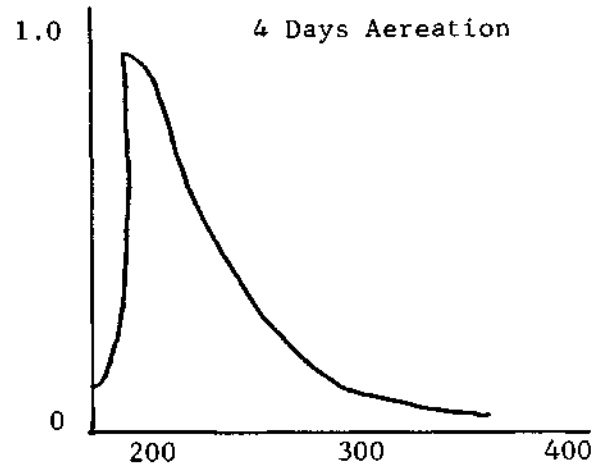
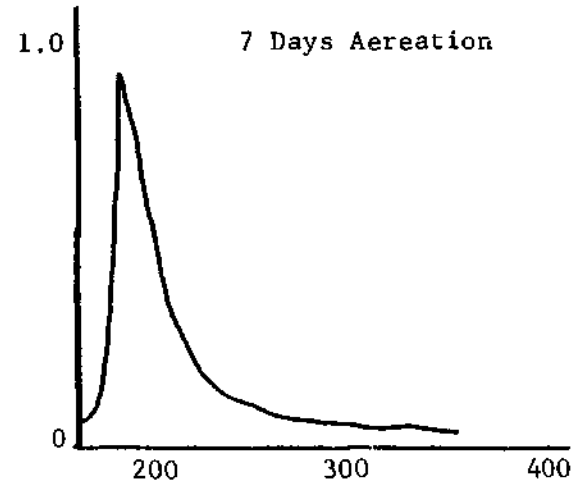


Figure 13. Ultraviolet Spectra of 1,2,3,4-Tetrahydronaphthalene Effluents







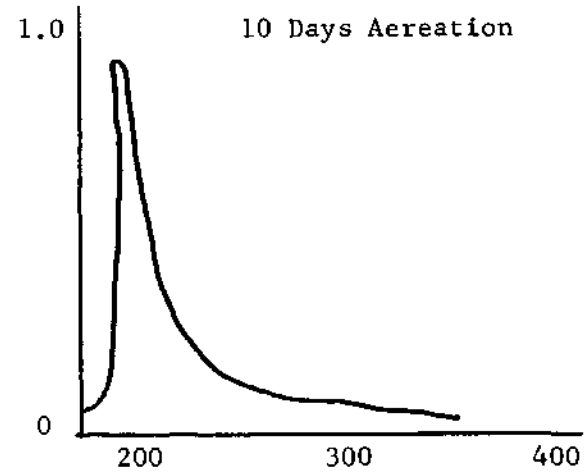


Figure 14. Ultraviolet Spectra of Butyl Benzoate Effluents

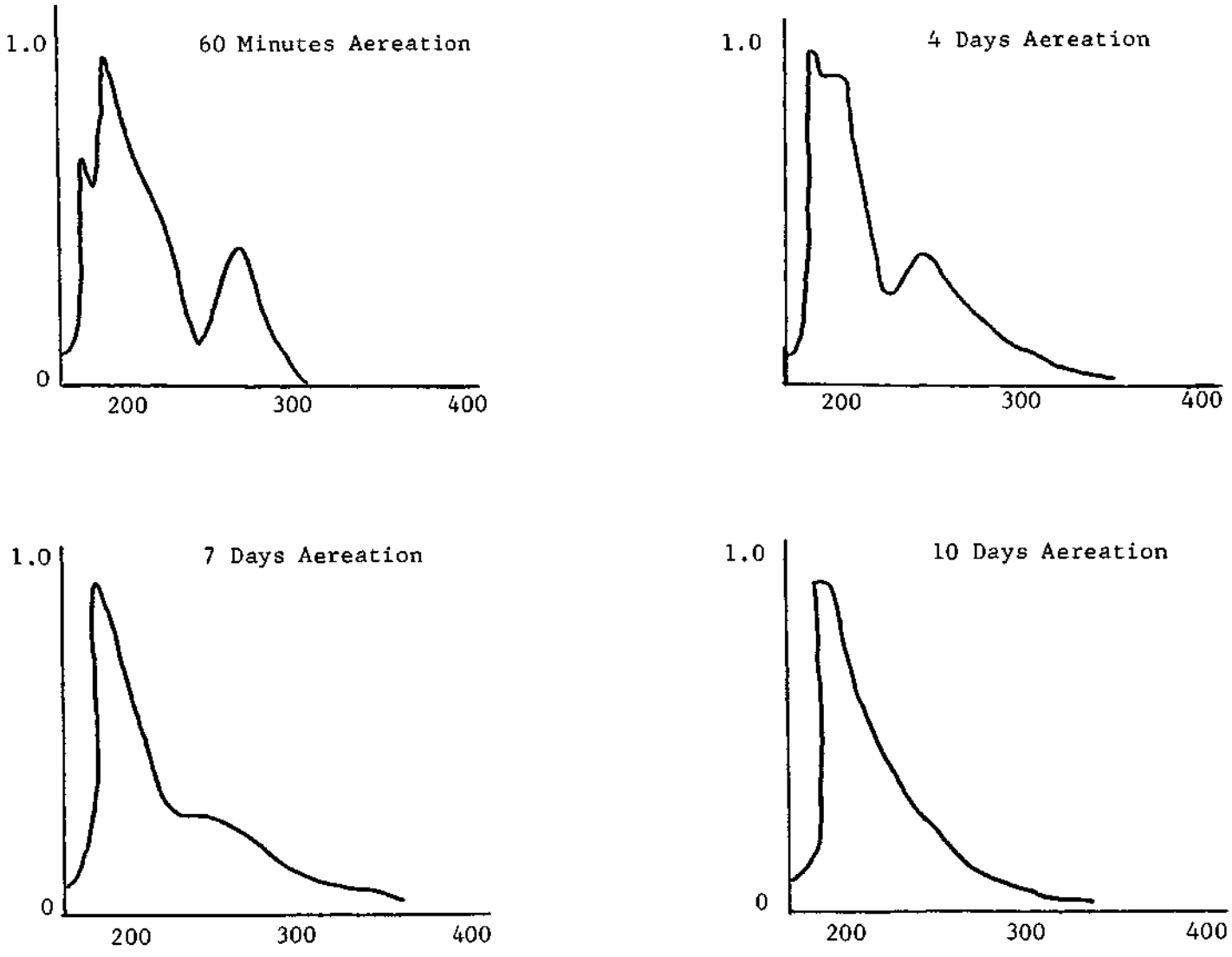


Figure 15. Ultraviolet Spectra of Commercial Methyl Salicylate Effluents

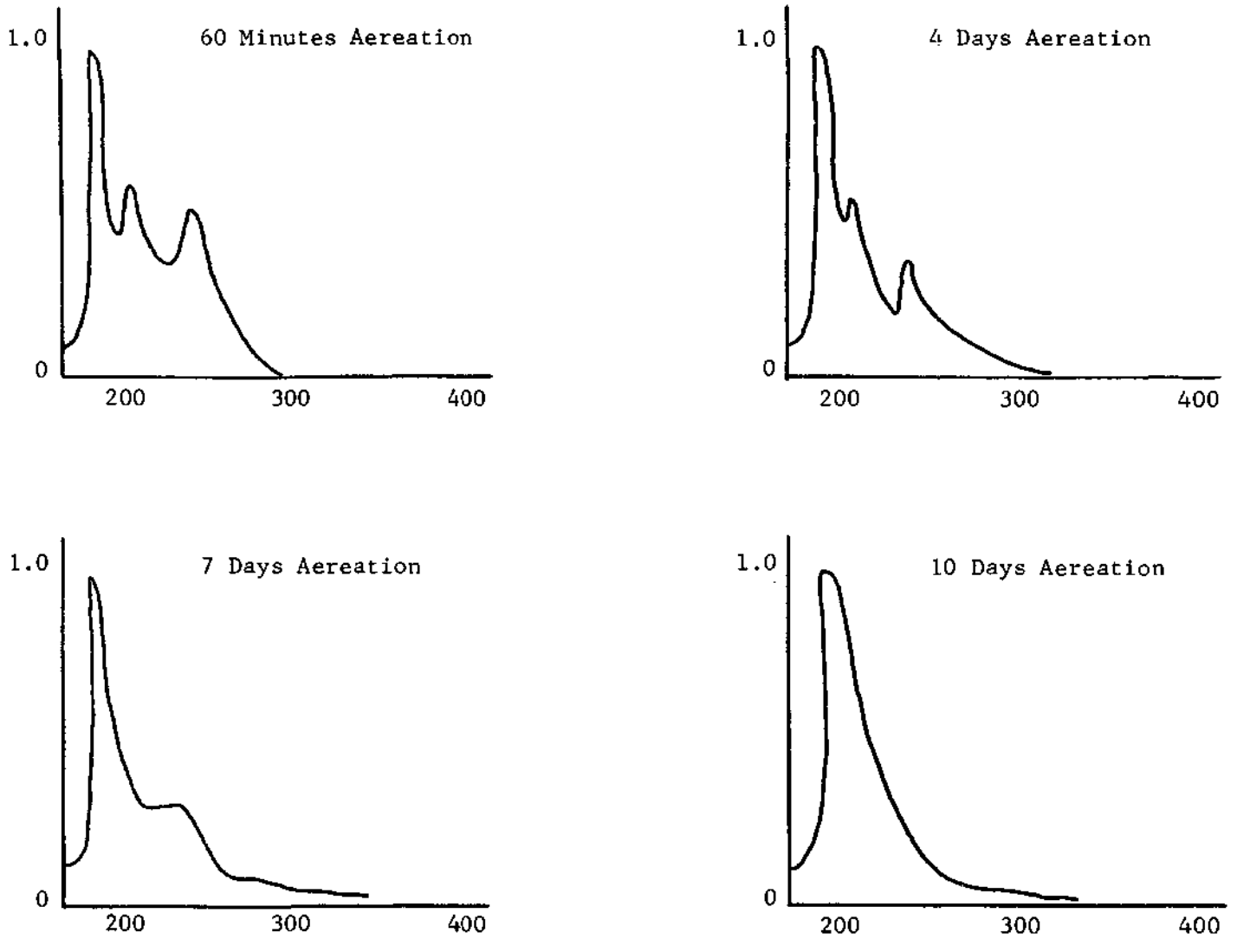


Figure 16. Ultraviolet Spectra of Commercial Orthophenylphenol Effluents

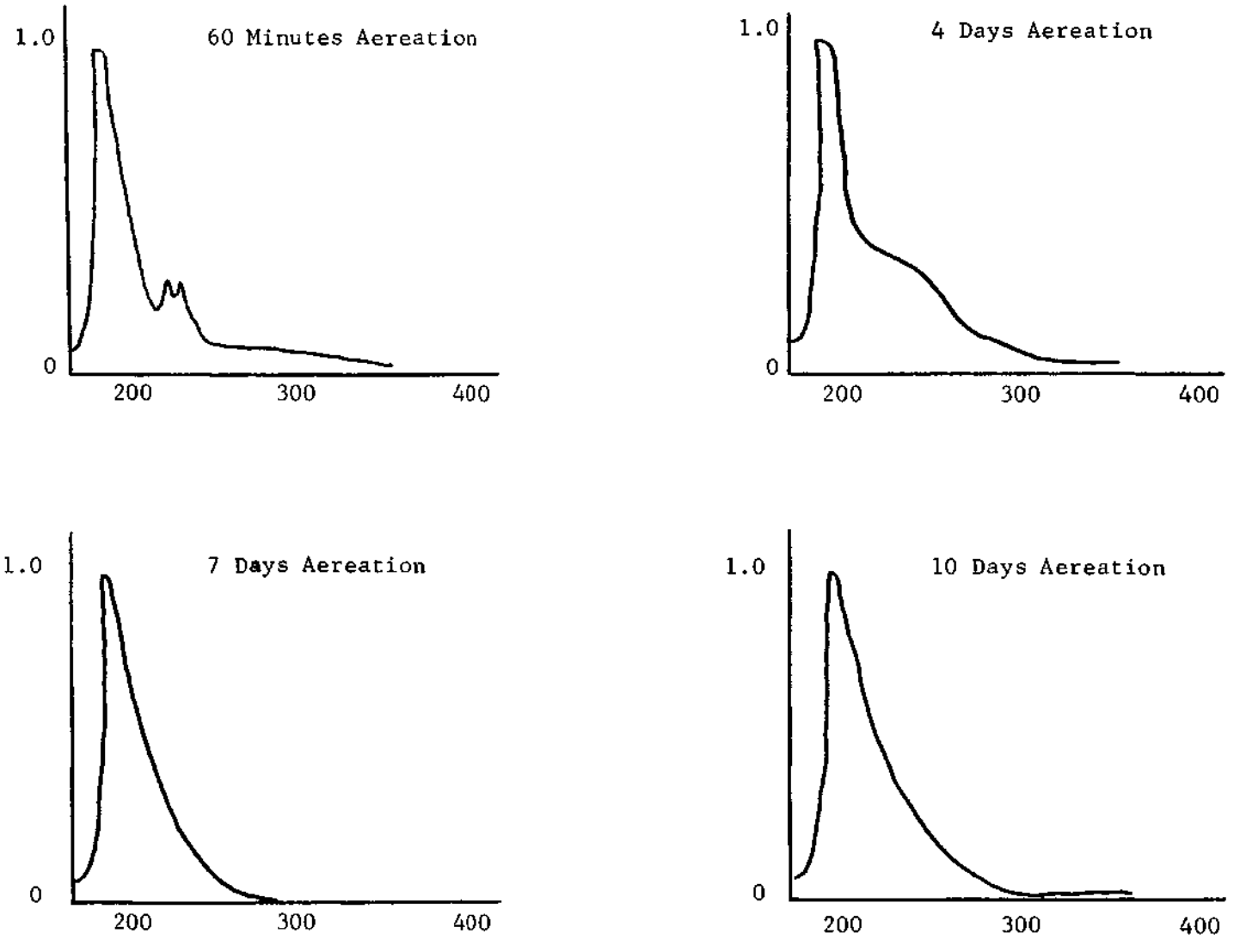


Figure 17. Ultraviolet Spectra of Commercial Butyl Benzoate Effluents

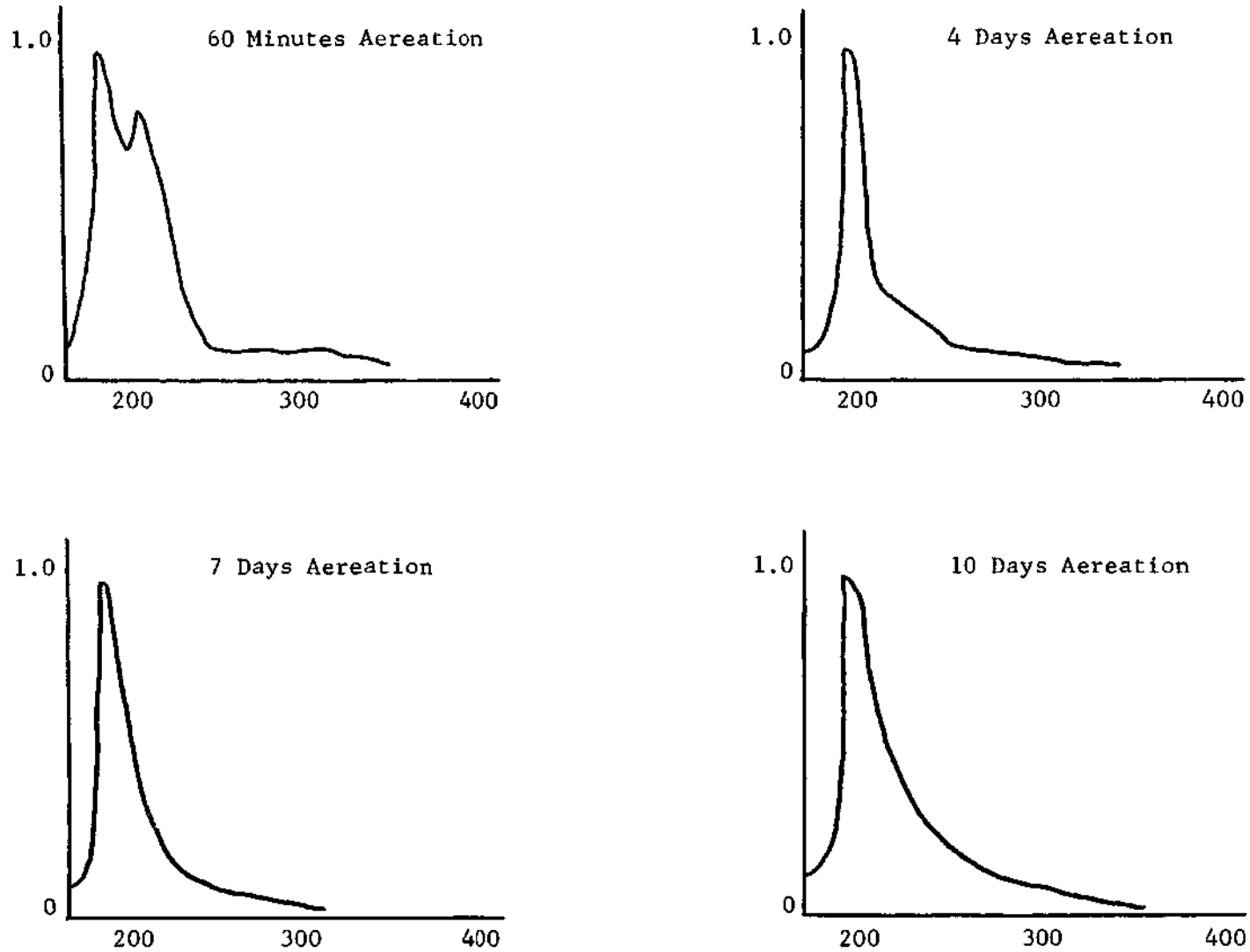


Figure 18. Ultraviolet Spectra of Biphenyl Effluents

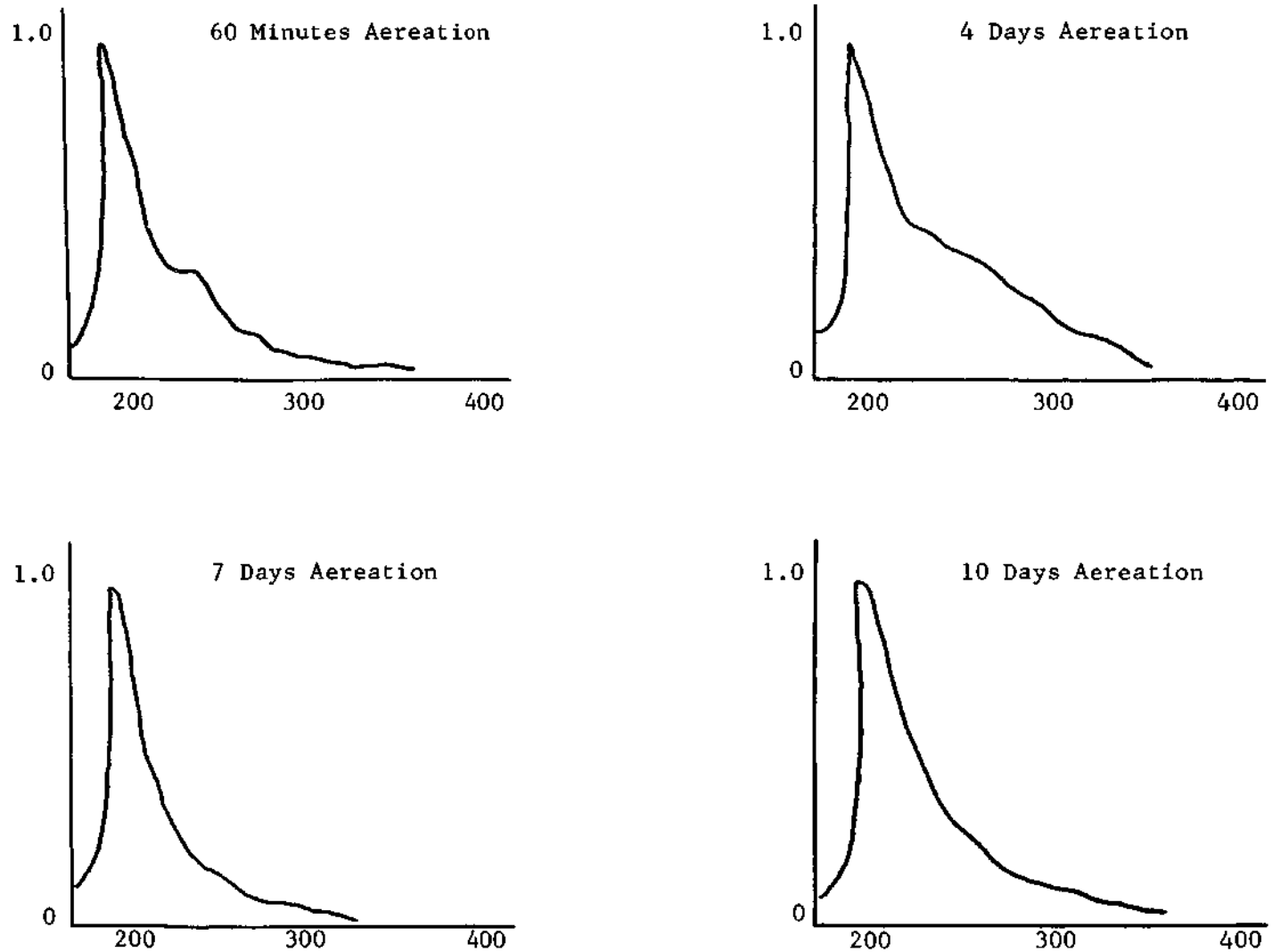


Figure 19. Ultraviolet Spectra of Control Effluents

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