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TECHNICAL MEMORANDUM

AUTHOR(S): R. R. Jay

TITLE: ANALYTICAL DEVELOPMENT WORK ON BIS-(PHENOXYPHENYL) ETHERS, MIX 4P3E

ABSTRACT

Analytical procedures were developed for the characterization and quality control of Mix-4P3E. A high temperature (300°C) gas chromatographic method employing a silicone oil partitioning liquid was developed for resolution of the six isomers of Mix-4P3E and for determination of volatile contaminants. Characterization of impurities was performed by infrared and nuclear magnetic resonance spectroscopy, and by chemical testing. Specific tests were also developed for total halogens and phenolic contaminants.

This TM is a reissue of a report to F. H. Cassidy, SNAP-8 Materials Section, from M. L. Moberg, Dept. 311, dated 24 September 1964.

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To: F. H. Cassidy⁽²⁾

30 September 1964
RRJ:sl

From: M. L. Moberg

Subject: Analytical Development Work on Mix 4P3E*

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I. INTRODUCTION

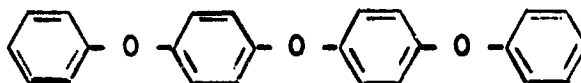
The following is a report on the development of analytical methods for quality control of Mix 4P3E*. The major portion of this effort involved the adaptation and development of gas chromatographic procedures for determination of volatiles and isomer distribution in Mix 4P3E with due cognizance of earlier work in this field performed at other organizations. In other work, methods were developed for the analyses of halogen and phenolic contaminants. In addition, a limited investigation of the infrared and nuclear magnetic resonance spectra of Mix 4P3E was performed.

II. SUMMARY

A. GAS CHROMATOGRAPHIC ANALYSIS OF MIX 4P3E

1. Evaluation of a number of column materials including several recommended by other organizations led to the selection of a gas chromatographic column using a methyl-phenyl silicone (SE-52) liquid phase on a Chromosorb W support. With this column and a conventional thermal conductivity detector, procedures for both volatiles and isomer distribution in Mix 4P3E were developed.

*This is a short hand designation for a mixture of the six isomeric bis-(phenoxyphenyl) ethers, where the 4P and 3E designate 4 phenyl groups, and 3 ether oxygens. For example, the p,p-isomer:



is named p,p-4P3E, or bis-(p-phenoxyphenyl) ether. Similarly, the next lower and higher members of the polyphenyl ether homologous series are Mix 3P2E, and Mix 5P4E, respectively.

2. Isomer identification in Mix 4P3E was confirmed through the use of pure isomers graciously furnished by the Shell Development Company at Emeryville, Calif.

3. The identification of volatiles including phenol, diphenyl ether, m-phenoxyphenol, m-3P2E, and p-3P2E was accomplished by infrared characterization of chromatographically separated fractions and confirmed by comparison with known pure compounds.

B. CHARACTERIZATION OF IMPURITIES IN MIX 4P3E

A brief NMR examination of several different lots of Mix 4P3E showed little or no significant differences between liquid and solid phases and no evidence of side chain branching. The separation of solids is now known to be due to a high fraction of the m, m-isomer. Identification of volatile impurities has been presented in the previous section.

C. DETERMINATION OF PHENOLS

A rapid nonaqueous titrimetric procedure, AGC 3003 - Method 5106.1, was developed for monitoring the acidity of Mix 4P3E. Background investigations and correlations with gas chromatographic data indicate that the acidity of typical samples of the polyphenylethers is due almost exclusively to phenol and phenoxyphenol.

D. HALOGEN ANALYSIS

Total halogen content of Mix 4P3E is determined by refluxing a sample in a hydrocarbon solvent with metallic sodium in the presence of n-butanol to convert the organic halides to inorganic sodium salts, which are then determined by titration with silver nitrate. AGC-STD-3003 Method 5604, a modification of ASTM 1317-57T, was developed and evaluated for application to Mix 4P3E. In supporting studies attendant with the development of the method, it was determined that chloride was the only halogen present in Dow ET-378.

III. TECHNICAL DISCUSSION

A. GAS CHROMATOGRAPHIC METHODS DEVELOPMENT

1. Description of Developed Method

a. The high temperature (300-400°C) operation required for convenient analysis of Mix 4P3E severely limits the choice of a liquid partitioning agent in gas chromatography. The material selected must provide adequate resolution with very low volatility to prevent contamination of, or "bleeding" into, the eluted sample components. A thorough experimental evaluation of several materials, taking into account methodology and techniques employed at other organizations, led to the ultimate selection of a high molecular weight low volatility methylphenyl silicone, SE-52, a product of General Electric Silicones Division. This material exhibited good resolution of components without excessively long elution times, produced no bleeding, gave symmetrically shaped peaks, and permitted column operation at only 285°C, which is considerably lower than the 300° + temperatures required with other materials.

b. The gas chromatographic procedure developed and recommended for the analysis of Mix 4P3E is given in detail in AGC Standard 3003, Method 6103*. Essentially, a 10' x 1/4" stainless steel column packed with 15% SE-52 on a Chromosorb W fire brick support is operated at 285°C with a conventional thermal conductivity cell detector to yield complete resolution of five of the six possible isomers of Mix 4P3E. The retention time data are presented in Table I and a typical chromatogram is presented as Figure 1.

The o,p- and m,m- 4P3E isomers are only incompletely resolved because of the small difference between their relatively long retention times coupled with the fact that in current lots of commercial Mix 4P3E the o,p- isomer is present in very low concentrations (of the order of 1%) in comparison with much larger amounts (ca. 70%) of the m,m- isomer. While no

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*This method is available in Preliminary Draft form pending corporate approval for official issue.

extensive study of the degree of resolution possible with more equitable concentrations of o,p- and m,m- was made, it is quite certain that any sizeable increases in the o,p- isomer concentration in Mix 4P3E would be detected inasmuch as an analysis of a synthetic mixture of all six isomers in nearly equal proportions did give definite resolution of the o,p- and m,m- components. The samples of pure isomers were generously furnished by the Shell Development Co., Emeryville, Calif. These materials were analyzed separately and in known mixtures to obtain relative retention times. Comparison with Mix 4P3E chromatograms then easily established identity of the isomers in the sample.

c. A good approximation of the total volatiles content is obtained along with the isomer distribution on the same run. However, for a more precise determination of the individual volatiles, another determination is made at 275°C at an increased sensitivity in order to expand the peak areas and facilitate differentiation. Five major volatile contaminants have been identified in samples of Mix 4P3E: phenol, diphenyl ether, m-phenoxyphenol, m-3P2E, and p-3P2E. Quantitative determinations of these specific volatiles are now performed on a routine basis.

The identification of the volatiles was accomplished by infrared identification of chromatographically separated fractions. A sample of Mix 4P3E containing several percent of volatiles was fractionally distilled to separate and concentrate the volatile fractions from the heavier tetraphenyl-ethers. The volatiles were then separated on the gas chromatograph SE-52 column operated at 150°C to obtain the individual components (peaks) which were collected in cold traps. The five materials corresponding to the major peaks were identified by their infrared spectra and confirmed by correspondence in gas chromatographic retention times with known pure compounds. Several other very minor peaks were observed in the chromatograph of the distilled volatiles, but no identifications were attempted because of insufficient material for infrared examination. If, in the course of future analyses, these or other contaminants should be noted in significant quantities, further efforts to identify them may be warranted.

d. Some typical data for a series of Mix 4P3E samples are presented in Table II. This and other data obtained routinely for a number of experimental samples from environmental testing indicates that satisfactory precision is readily attainable.

2. Experimental Development

The following paragraphs present a more detailed description of the chromatographic equipment and summarize some of the more significant considerations and experimental work leading to the development of the analytical methods described above.

a. Of the several types of detectors available, thermal conductivity cells were selected because of their linear response over a wide range of concentrations, which is not the case with the flame ionization detector for instance. Furthermore, the thermal conductivity detectors are readily available, rugged, and generally ideal for repeated analyses with a minimum of maintenance. Tungsten wire sensors were used because of their superior high temperature characteristics. In order to execute the program within the allocated time, two chromatographs, each fabricated with stainless steel columns and fittings, were employed. The isomer work was performed with a modified Consolidated Electrodynamics Corp. Model 26-014 Analyzer, the volatiles studies with an Aerograph Model A-90-P manufactured by Wilkins Instrument and Research Inc.

b. Shell Oil Company recommended a column packed with Dow-Corning Silicone Oil 710 (a methyl phenyl silicone) on a Chromosorb W support. However, a brief evaluation of this system in the Von Karman Center Laboratory, using a 10 ft x 1/4 inch stainless steel column packed with 15% DC-710 on Chromosorb W, indicated that column bleeding was a problem. Shell mentioned nothing of this, although operating the column at 365°C, which is considerably higher than the 300°C maximum normally recommended for Silicone Oil 710. The bleeding experienced here took place despite a 300°C vacuum pre-stripping of the silicone to remove the lighter fractions and even after many hours of column conditioning. Nevertheless, fairly good resolution of isomers was obtained with the retention times given in Table I.

c. The gas chromatographic procedure used by Republic Aviation Corp. employed a Dow Corning Silicone Hy Vacuum Grease column. The column investigated for the present work was 15% Silicone Hy Vacuum Grease on Chromosorb P packed into a 10 ft x 1/4 inch stainless steel tube. Although Republic operated their column at 310°C, it was found that 280°C gave better resolution. The isomers were resolved without evidence of bleeding at the retention times shown (Table I). While this technique could have been adopted, later work showed that better results were obtained with the SE-52 presently recommended.

B. CHARACTERIZATION OF IMPURITIES IN MIX 4P3E

1. The presence of volatile impurities has been discussed above. A brief nuclear magnetic resonance (NMR) study was made in an effort to detect any other contaminants. The NMR spectra of liquid and solid phases of Dow ET-378, Batch 12-2P, were virtually identical. As the NMR does not discriminate between the isomers, this indicates only the absence of appreciable quantities of foreign species. A more detailed interpretation by Dr. H. M. Nelson is given below.

2. The 60 mc proton NMR spectra of several samples of ET-378 were obtained using 20 wt-% solutions in carbon tetrachloride with tetramethylsilane (TMS) added as an internal reference. In the following, signal positions are referred to in cycles per second (cps) from TMS.

a. The samples were:

- (1) ET-378, Lot 458-29-13, unused.
- (2) ET-378, Lot 12-2P, 00004A, liquid phase (this sample contained a large amount of crystalline material - the "liquid phase" sample for NMR was taken from the supernatant liquid). This material was subsequently used for the $\text{GN}_2\text{S-1}$ loop degas and flowrate test.
- (3) ET-378, Lot 12-2P, 00004A, solid phase (some of the crystalline material was removed with a spatula and pressed dry on filter paper to obtain the "solid phase" NMR sample). This material was subsequently used for the $\text{GN}_2\text{S-1}$ loop degas and flowrate test.

b. The spectra are virtually identical, consisting of a complicated absorption in the vicinity of 400-430 cps attributable to aromatic protons. The only difference in the spectra is in the relative intensity of the 413 (or 415) cps signal. This signal is strong in sample "-13," of moderate intensity in "4A liquid phase" and not detectable in "4A solid phase." It was thought that this signal was possibly due to phenolic OH but treatment of "-13" with D_2O produced no change in relative intensity thus eliminating this possibility.

c. There is no evidence for any α -methyl impurity in any of the spectra. Such impurities would be expected to produce a signal in the region about halfway between the aromatic absorption and the TMS reference. Integrals of the signal strengths of all the samples were obtained to provide a quantitative estimate of any α -methyl impurity present. In each case the atom % impurity was shown to be less than 1/4% corresponding to less than 2 mole-% impurity on the assumption of one methyl group per impurity molecule. This sensitivity could be increased rather easily to 1 mole-% and probably to 1/2 mole-%.

C. DETERMINATION OF PHENOLS BY ACIDIMETRY

1. One of the more critical and prevalent classes of impurities in Mix 4P3E is the phenols. The acidity of these materials and their propensity to form chelated metallic derivatives renders them inherently corrosive to metals. Fortunately, the phenols may be titrated quite readily in nonaqueous media. While the titrimetric method is not specific for phenols, but responsive to many acidic species, it is valuable for routine control in a case of this type where the phenols are the only acidic species normally encountered. As discussed above, gas chromatography, which may be used as an additional check on the phenol content as well as other components, has confirmed the presence of phenol and phenoxyphenol in Mix 4P3E. In a comparative study, the titrimetric phenol data agreed well with values obtained by gas chromatography as indicated below:

<u>Sample No.</u>	<u>Acid No., Mgs KOH/g</u>	<u>Phenol + Phenoxyphenol, wt-%</u>	
		<u>Titration</u>	<u>Gas Chrom</u>
8	3.72	0.8	0.8
9	3.59	0.8	0.7
3	3.90	0.8	0.8
4	3.40	0.7	0.9
5	3.76	0.8	1.1
11	2.52	0.5	0.5
13	1.5	0.3	0.3

The wt-% titrimetric values above, are calculated from acid equivalents by using the average equivalent weights obtained for the mixture of phenol and phenoxyphenol indicated by G.C. analysis.

2. The recommended procedure for the titrimetric determination of phenols in Mix 4P3E has been issued as AGC-STD-3003 Method 5106.1, which is an adaptation of a more general Von Karman Center method for very weak acids in a variety of materials. The sample is dissolved in pyridine and titrated with an 0.05 N isopropanol solution of potassium hydroxide to an azo violet end point. The method as written will readily detect as little as 0.001% of acids calculated as phenoxyphenol and, if needed, greater sensitivity could be developed by using more dilute reagents and high sensitivity end point detection techniques. In connection with the development of this method it should be noted that any arbitrary titration to some preselected EMF or "pH" is misleading and should be avoided. For instance, titration to pH 11 in a benzene-isopropanol solvent includes only a small and variable fraction of the total phenols.

a. The precise application of the titrimetric method depends upon strict adherence to several points of technique mandatory in handling basic nonaqueous solvents. For instance, rigid exclusion of atmospheric carbon dioxide is essential, and for the potentiometric titration, careful electrode conditioning is required. Nevertheless, in the hands of a trained operator the titration is easily reduced to a simple and rapid routine. Experience indicates that a relative precision and accuracy of about 2% can be readily obtained. Some typical duplicate acid number values (mgs KOH/g) obtained in routine testing are as follows: 0.11, 0.09; 0.01, 0.01; 0.03, 0.03; 0.25, 0.25; 0.30, 0.30; 2.50, 2.53; 3.65, 3.69; 3.37, 3.43.

b. A potentiometric modification using a solvent less basic than pyridine (80/20 benzene/isopropanol, or high purity dimethylformamide) permits differentiation of the very weakly acidic phenols from more strongly acidic species such as carboxylic acids, and the highly ionized mineral acids. However, potentiometric titrations of several commercial Mix 4P3E (ET-378, Dow Chemical) samples in 80/20 benzene/isopropanol indicated only phenols; the range of potentials encountered in the titrations proved the absence of both carboxylic acids and the mineral acid types. In substantiation of this conclusion, addition of carboxylic acids and mineral acids to the same materials yielded three breaks: mineral acid, carboxylic acid, and phenols. In other potentiometric studies in pyridine, it was also proved that both phenol and m-phenoxyphenol are quantitatively determined.

D. HALOGENS IN MIX 4P3E

1. The presence in Mix 4P3E of residual halogens, carried over from the organic halides used in synthesis, is generally thought to be undesirable because of their potentially corrosive nature under adverse operating conditions and their ability to catalyze decomposition of the Mix 4P3E. The analysis of organic halides is usually preceded by a combustion technique to destroy the organic material and convert the halogens to a readily determinable inorganic form. However, for trace analyses, the combustion techniques are inconvenient due to the large sample sizes required to obtain sufficient halide for determination by titrimetric methods. Alternatively, use of smaller samples would yield only minute quantities of halide and thus require more exacting techniques for trace analyses. A practical expedient entails a chemical reduction of the organic halide to the inorganic ions with metallic sodium. In this case, only the very small concentrations of halide are affected, combustion of the bulk of organic sample is avoided, and practically unlimited sample sizes are handled with safety and convenience giving adequate final concentrations of inorganic halides for satisfactory titration.

2. AGC-STD-3003 Method 5604* was developed as a modification of ASTM D 1317-57T especially tailored for convenient analysis of halides in

*This method is available in Preliminary Draft form pending corporate approval for official issue.

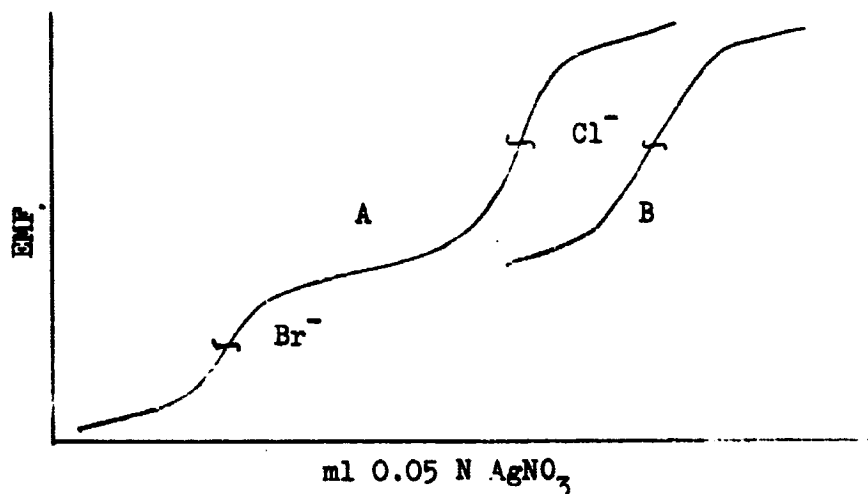
Mix 4P3E in concentrations as low as only a few parts per million. The sample is refluxed in a solution of toluene and isooctane in the presence of metallic sodium and a small amount of n-butanol. This treatment reduces organic halides to inorganic ions. After careful destruction of excess sodium with alcohol and water, the aqueous phase, now containing the halides, is acidified with dilute nitric acid and separated from the organic phase. The halides are then determined by the Volhard* method, in which a slight excess of silver nitrate is added and back-titrated with thiocyanate to a reddish color obtained in the presence of ferric alum.

The major variance from the ASTM method is the use of a toluene-isooctane solvent instead of petroleum naphtha, which was not available at Von Karman Center. In addition, a simplified reflux and separation scheme was developed, which considerably shortens the time required for the analysis without sacrifice of necessary precision or reliability. Procedural details are given in AGC-3003, Method 5604.

3. The method as written determines only total halogen, with no attempt to differentiate chlorides from bromides or iodides. However, a notation is made referring to the fact that differentiation can be accomplished through use of a potentiometric modification of the titrimetric procedure. A sample of ET-378 (Dow Chemical Co.) was shown to contain only chloride, 0.067% as Cl; bromide and iodide were absent. Titrations were conducted with 0.05 N silver nitrate using glass vs silver electrodes.

The reasoning behind the identification and differentiation of the halides in ET-378 is most readily illustrated by reference to the simplified diagram of the actual potentiometric titration curves presented below.

*An excellent discussion of the Volhard method is given by Kolthoff and Stenger, "Volumetric Analysis," V. II, pp 259 ff., Interscience Publishers, New York, New York, 1947, 2nd Ed.



Curve A represents a titration of a synthetic solution of sodium bromide and sodium chloride. The first inflection represents bromide and the second chloride. Curve B is a titration curve for ET-378, in which only one break was obtained, at the EMF corresponding to chloride. When a known amount of bromide was added to the ET-378 sample, two breaks were obtained with the bromide recovered quantitatively at the lower EMF, similar again to Curve A. Conversely, addition of chloride merely shifted the chloride (higher EMF) inflection to the right corresponding to the increased titer. Iodide, if present, would result in an earlier inflection, below that of the bromide. This evidence, conclusively indicates the use of organic chlorides rather than bromides or iodides in the synthesis of this ET-378.

4. The precision of the sodium reflux method is adequate as indicated by the triplicate results 0.067, 0.067, and 0.069% Cl obtained on a sample of ET-378. Satisfactory recovery of a known chlorine compound was indicated by analysis of a halogen free mineral oil to which had been added 0.045% chlorine in the form of orthodichlorobenzene. Duplicate analyses of 0.045 and 0.044% were obtained. This complete recovery of the added chlorine constitutes a severe test of the method because the aromatic chlorides are very resistant to chemical attack.

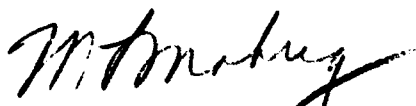
5. It may be noted that a somewhat more rapid method for halogens has been published*, which is based upon the same principles but uses a reagent

*R. L. Menville, and W. W. Parker, Anal. Chem., 31, 1901-2 (1959).

comprised of sodium finely dispersed in a hydrocarbon carrier instead of the massive sodium metal used in the ASTM or AGC procedures. However, for the relatively few analyses contemplated here, it was felt that the added expense of preparing or purchasing the dispersed sodium product would not be warranted. Furthermore, this rather drastic departure from the ASTM method did not appear desirable at this time. Another interesting possibility would be to use NaK for the reduction. Its ready availability at Aerojet, the greater reactivity of potassium as compared with sodium, and its liquid state are favorable considerations; a potential hazard, however, is potassium's propensity to form the superoxide.

IV. ACKNOWLEDGMENTS

The above work was performed under the supervision of R. R. Jay. The gas chromatographic work was performed by E. A. Tombleson with assistance from H. W. Pust. Infrared and NMR studies were contributed by H. M. Nelson, while the acidimetric titration and halogen analyses were developed by Mrs. Yoshie Kadota and R. R. Jay, respectively. In addition, the helpful suggestions and interpretations of R. J. Bloomfield are gratefully acknowledged.



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TABLE I
RETENTION TIMES (MINUTES) OF MIX 4P3E ISOMERS
RELATIVE TO m-PHENOXYPHENOL

<u>Isomer</u>	<u>Column Partitioning Agent</u>		
	<u>SE-52</u>	<u>DC-710</u>	<u>Hy Vac</u>
o,o	7.8	6.1	6.0
m,o	9.3	7.2	7.1
o,p	11.6	8.9	8.9
m,m	12.2	9.3	9.4
m,p	13.5	10.3	10.3
p,p	15.5	11.1	11.2

Note: Each of the three columns was at its optimum conditions as stated in the text.

TABLE II

TRIPPLICATE ANALYSES OF MIX 4P3E USING SE-52 COLUMN

<u>% Volatiles</u>	<u>% Isomers*</u>				
	<u>o.o</u>	<u>o,m</u>	<u>o,p & m,m</u>	<u>m,p</u>	<u>p,p</u>
2.2	trace	10.2	70.3	16.6	0.7
2.2	trace	10.4	71.3	15.3	0.8
2.1	trace	10.1	71.0	16.3	0.5

*o,p- 4P3E present in approximately 1% concentration not resolved from m,m- 4P3E (see text).

CHROMATOGRAM OF MIX 4P3E ISOMERS ON SE-52 COLUMN

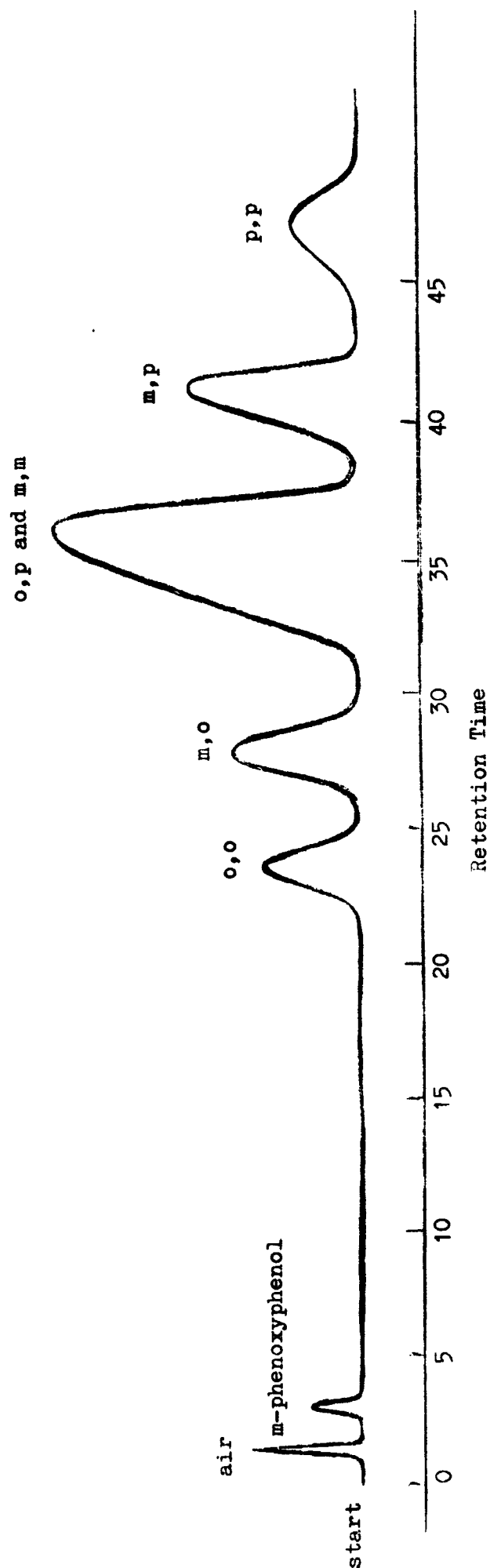


Figure 1