

tensile ratio of the individual stocks divided by the tensile ratio for the corresponding control should then be taken as the index of rate of cure.

ACKNOWLEDGMENT

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Determination of Alpha,Para-Dimethylstyrene In the Presence of Para-Methylstyrene, Styrene, and Para-Cymene

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α,p -Dimethylstyrene can be determined in the presence of p -methylstyrene, styrene, and p -cymene by two independent methods. The chemical method depends upon addition of hydrogen chloride or bromide to the styrenes with subsequent estimation of the tertiary halide formed by α,p -dimethylstyrene. The other method involves an analysis of the ultraviolet absorption curve of such mixtures. Results obtained by these independent methods are in good agreement.

NEED has recently arisen for a method for the determination of α,p -dimethylstyrene in the presence of p -methylstyrene, styrene, and p -cymene. Since no satisfactory procedures were available for the analysis of such mixtures, chemical methods, ultraviolet absorption, and polarographic analysis were considered.

Preliminary experiments on the last, using the technique of Laitinen and Wawzonek (1) were not promising and this approach was not studied further.

It was found possible, however, to analyze such mixtures by a chemical method and also by means of ultraviolet absorption. Both procedures were readily adaptable to control use and have been successfully applied to the analysis of a large number of samples.

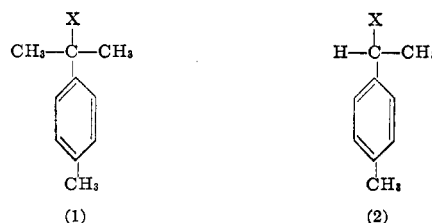
In order to test these methods it was first necessary to obtain pure samples of the various styrenes and p -cymene. The α,p -dimethylstyrene and p -methylstyrene were synthesized and purified in this laboratory. A good grade of commercial styrene was vacuum-distilled several times before use. The p -cymene was distilled through a 40-plate column packed with 0.23-cm. ($3/16$ -inch) stainless steel helices at 100-mm. pressure and a reflux ratio of approximately 60/1, a middle cut being collected and used in this work.

The constants of these compounds are given in Table I. The bromine numbers were run by a modification of the method of Uhrig and Levin (9).

The refractive index results are in good agreement with the International Critical Tables values, the temperature being considered. The samples of the various styrenes were always freshly vacuum-distilled before being used.

CHEMICAL METHOD

The chemical method of analysis depends upon the following reaction. If the addition of HX to α,p -dimethylstyrene and p -methylstyrene follows Markownikoff's rule, where X is either Br or Cl, the following compounds will be formed:



The halogen in (1), formed from α,p -dimethylstyrene, is attached to a tertiary carbon atom, while that in (2), formed from p -methylstyrene, is attached to a secondary carbon atom. The tertiary halogen in (1) is much more readily hydrolyzed than the secondary in (2), and this fact offers a means of analytically determining α,p -dimethylstyrene in the presence of p -methylstyrene and styrene. There is no reaction of HX with p -cymene.

It has been reported that hydrogen bromide adds rapidly to styrene (2, 10), and that the secondary bromide formed by nor-

Table I. Constants of Materials Used in Testing Methods

Compound	Formula	n_D^{20} ^a	n_D (I.C.T.)	Bromine No. Observed	Theory
p -Cymene	$p\text{-CH}_3, \text{C}_6\text{H}_4, \text{CH}(\text{CH}_3)_2$	1.4913	1.4947 (15° C.)	<1	0
Styrene	$\text{C}_6\text{H}_5, \text{CH}:\text{CH}_2$	1.5467	1.5467 (20° C.) ^a	151	154
p -Methylstyrene	$p\text{-CH}_3, \text{C}_6\text{H}_4, \text{CH}:\text{CH}_2$	1.5421	1.5447 (16.4° C.)	137	135
α,p -Dimethylstyrene	$p\text{-CH}_3, \text{C}_6\text{H}_4, \text{C}(\text{CH}_3)_2:\text{CH}_2$	1.5356	1.5344 (18.7° C.)	117	121

^a Value of Moore, Burk, and Lankelma (7).

Table II. Determination of α,p -Dimethylstyrene in Known Mixtures

Other Materials Present	(Using method involving addition of HBr) Weight of α,p -Dimethylstyrene		Recovery %
	Present Gram	Recovered Gram	
None	0.2731	0.2545	93.3
None	0.2131	0.1977	92.8
0.2080 gram <i>p</i> -methylstyrene	0.2408	0.2215	91.9
None	0.2693	0.2477	92.0
None	0.2414	0.2245	94.0
0.1 ml. of benzene, 0.2 ml. of styrene, 0.2 ml. of <i>p</i> -methylstyrene, 0.5 ml. of <i>p</i> -cymene	0.4147	0.3942	95.2
	0.2613	0.2522	96.7
25.6% <i>p</i> -methylstyrene and 48.8% <i>p</i> -cymene	0.0854	0.0796	94.2
	0.1006	0.0926	92.0

mal addition may be hydrolyzed under relatively mild conditions, indicating that the conditions of hydrolysis of the tertiary halide must be chosen so as to avoid interference from the secondary halides present. Based on these facts, the following methods have been developed, involving the addition of HX, removal of excess, followed by hydrolysis, and estimation of the tertiary halide formed from α,p -dimethylstyrene under conditions where there is no appreciable hydrolysis of the secondary halide formed from *p*-methylstyrene and styrene.

HYDROGEN BROMIDE METHOD. A sample weighing approximately 0.5 to 1.0 gram is accurately weighed out into a 125-ml. Erlenmeyer flask containing 25 ml. of carbon tetrachloride. Gaseous hydrogen bromide, generated by dropping bromine onto naphthalene and purified by passing through several towers of naphthalene and finally one containing Drierite, is bubbled through the sample for 30 minutes at a rate of 3 to 4 bubbles per second. At the end of this time the addition tube is washed down with 10 ml. of carbon tetrachloride and a brisk stream of nitrogen is passed through the solution for 30 minutes to remove unreacted hydrogen bromide. The flask is then removed and chilled in an ice-salt bath for 10 minutes. Thirty milliliters of

previously chilled 90% alcohol are then added, the flask is swirled for a few seconds, two drops of methyl red indicator are added, and the cold solution is rapidly titrated with standard 0.1*N* alcoholic potassium hydroxide to a bright yellow end point lasting for 10 seconds. Table II gives the results obtained by this method on known samples.

HYDROGEN CHLORIDE METHOD. The procedure is the same as that used in the hydrogen bromide method with the following changes:

Benzene instead of carbon tetrachloride is used as the solvent. Forty milliliters of 80% alcohol are used to effect hydrolysis of the tertiary halide.

The titration is performed at room temperature and the sample titrated with 0.1*N* alcoholic potassium hydroxide to a 30-second bright yellow end point. Hydrogen chloride was generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid. The evolved gas was passed through a tower filled with concentrated sulfuric acid before being passed into the solution being analyzed.

Table III gives the results obtained by this method on known samples. The end points are considerably sharper than those given by the hydrogen bromide method.

Table III. Determination of α,p -Dimethylstyrene in Known Mixtures

Substances Present	(Using method involving addition of HCl) Weight of α,p -Dimethylstyrene		Recovery %
	Present Gram	Recovered Gram	
<i>p</i> -Cymene	None	None	...
Styrene	None	None	...
<i>p</i> -Methylstyrene	None	None	...
α,p -Dimethylstyrene	0.2936	0.2740	93.5
	0.4739	0.4508	95.3
	0.4116	0.3903	94.7
	0.3077	0.2940	95.5 ^a
	0.5693	0.5415	95.3 ^a
α,p -Dimethylstyrene plus 0.5 ml. each of <i>p</i> -cymene, styrene, and <i>p</i> -methylstyrene	0.4015	0.3855	96.0
	0.4052	0.3902	96.2

^a HCl gas added for 1 hour instead of 30 minutes as in all other cases.

Table IV. Analyses by Hydrogen Bromide and Hydrogen Chloride Methods

Sample	α,p -Dimethylstyrene	
	HBr method %	HCl method %
A	19.6, 20.2	19.8, 20.6
B	29.2, 29.5	28.2, 29.3
C	20.2, 19.9	20.2, 19.8
D	20.5, 20.4	20.6, 20.6
E	22.6, 22.0	22.6, 23.3
F	10.6, 10.7	9.5, 9.5
G	32.8, 32.6	32.2, 32.0
H	32.9, 32.6	31.8, 32.5

DISCUSSION OF RESULTS

An examination of Tables II and III shows that somewhat low recoveries (about 95%) of α,p -dimethylstyrene are obtained in every case. Therefore, to correct for this a factor of 1.05 is used in calculating the results. This low recovery of α,p -dimethylstyrene is not raised by a longer time of addition of the hydrogen halide. It may be due to the fact that a small fraction of the addition takes place contrary to Markownikoff's rule. A consideration of the results obtained by use of these methods in the analysis of over fifty samples of known and unknown composition indicates that the precision of the methods is approximately $\pm 3\%$ of the α,p -dimethylstyrene present.

Table IV shows the agreement between the hydrogen bromide and hydrogen chloride methods in the analysis of eight different samples of unknown composition.

The agreement between the results obtained by the two methods is seen to be good. Since the hydrogen chloride method is somewhat easier to use and the end point is sharper, it is recommended for use.

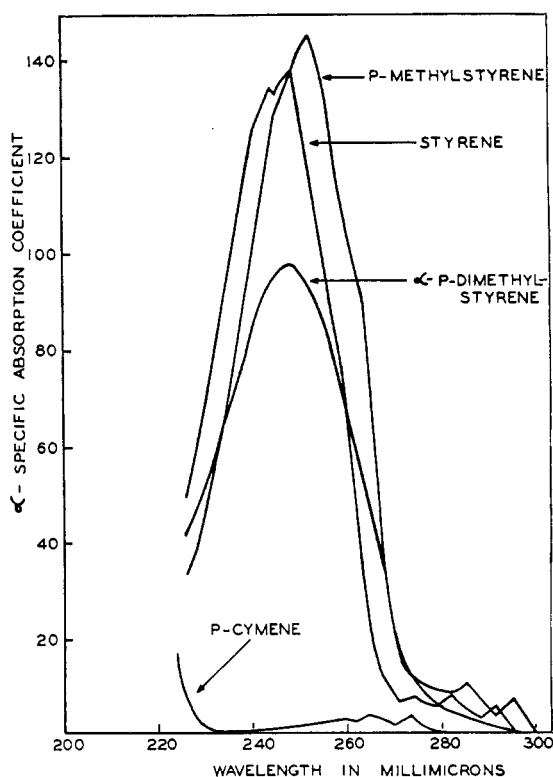


Figure 1. Ultraviolet Absorption Curves
For α,p -dimethylstyrene, *p*-methylstyrene, styrene, and *p*-cymene in ethanol solutions

ULTRAVIOLET ABSORPTION METHOD

The spectrophotometric method has been successfully applied to the quantitative determination of compounds having characteristic absorption bands in the ultraviolet region of the spectrum. Good examples of this method used in calculating two, three, and four constituents of a mixture have been reported in the literature (3-6).

In mixtures of pure styrene, α,p -dimethylstyrene, p -methylstyrene, and p -cymene it was found possible to determine the amount of each styrene present within 2% of the known value.

The absorption data were obtained from measurements made with a Beckman quartz spectrophotometer. The solvent was ethanol in all cases. The formulas used in making the calculations use the term specific α :

$$\text{Specific } \alpha = \frac{\log_{10} \frac{I_0}{I}}{cl}$$

where α = absorption coefficient

I_0 = intensity of radiation transmitted by the solvent

I = intensity of radiation transmitted by the solution

c = concentration of solute in grams per 1000 ml.

l = length in centimeters of solution through which the radiation passes

The samples of pure α,p -dimethylstyrene, p -methylstyrene, styrene, and p -cymene used to obtain the specific absorption coefficients of the pure compounds were the same as those used in the development of the chemical method previously described.

The values at different wave lengths are shown in Figure 1. The curve for styrene agrees very closely with previously published data concerning this compound (8).

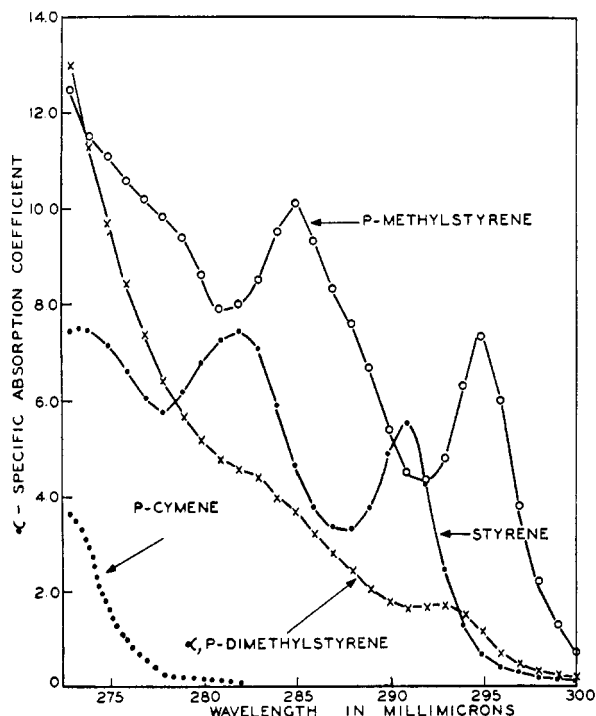


Figure 2. Ultraviolet Absorption Curves
For α,p -dimethylstyrene, p -methylstyrene, styrene and p -cymene in ethanol solutions
(enlarged scale of spectral region 275 to 300 $m\mu$)

The styrenes have a strong absorption band in the spectral region 248 to 252 $m\mu$ with less pronounced but yet distinct bands in the region to 300 $m\mu$. For the three styrenes the bands in the region 248 to 252 $m\mu$ are so similar that no attempt was made to use them for quantitative determinations. A larger scale graph of the region 280 to 300 $m\mu$ (Figure 2), shows that at certain

Table V. Per Cent Composition

Mixture	Composition of Mixture of Pure Compounds	Known %	Calculated from Ultraviolet Absorption Data	Error %
			%	
1	α,p -Dimethylstyrene	32	30.8	1.2
	p -Methylstyrene	42	42.4	0.4
	Styrene	26	26.0	0
2	α,p -Dimethylstyrene	5	6.0	1.0
	p -Methylstyrene	5	5.3	0.3
	Styrene	90	88.1	1.9
3	α,p -Dimethylstyrene	5	3.9	1.1
	p -Methylstyrene	90	90.3	0.3
	Styrene	5	5.3	0.3
4	α,p -Dimethylstyrene	25	24.3	0.7
	p -Methylstyrene	26	26.3	0.3
	Styrene	25	25.9	0.9
	p -Cymene	24
5	α,p -Dimethylstyrene	20	21.9	1.9
	p -Methylstyrene	30	29.4	0.6
	Styrene	35	35.8	0.8
	p -Cymene	15

Table VI. Samples of Unknown Composition

Sample	Chemical method %	α,p -Dimethylstyrene	Ultraviolet absorption method %
		%	%
1	23.0, 22.9		21.7, 22.3
2	20.0, 20.2		19.8, 20.3
3	32.5, 32.3		32.8, 32.5
4	27.3, 27.4		27.8, 27.5

wave lengths there are sufficient differences in α of the pure compounds to permit quantitative calculations. It is also evident that p -cymene has its absorption values below 280 $m\mu$ and therefore does not appreciably affect absorption values above 280 $m\mu$, even though present in quantities up to 70 or 80%.

Quantitative determinations on three unknowns require the selection of three suitable wave lengths in order to set up three simultaneous equations. At a given wave length, components a , b , and c present in a solution in percentages of x , y , and z , respectively, will give a total absorption value which can be represented by the equation:

$$\frac{(\alpha_a)x + (\alpha_b)y + (\alpha_c)z}{100} = \alpha \text{ solution}$$

α_a , α_b , α_c represent the specific absorption coefficients for each of the pure compounds at that particular wave length. By setting up three equations at different wave lengths, the percentages (x , y , and z) of each component can be calculated.

Since simultaneous equations with three or more unknowns are customarily solved by the method of determinants, the criterion for the selection of wave lengths is that the determinants in the expressions for the unknown concentrations be as large as possible. Likewise, the individual values of α should be large enough to be measured with accuracy on the spectrophotometer.

In known mixtures of pure compounds, with or without p -cymene, it was found possible to calculate the per cent composition by using the absorption data at wave lengths 285, 291, and 295 $m\mu$ (Table V). Values calculated from the absorption data differ from known values by less than 2%. The presence of p -cymene did not interfere with the calculations. The wave lengths 283, 287, and 291 $m\mu$ were found to give just as accurate values as the previously mentioned wave lengths. It is therefore possible to use two sets of wave lengths to serve as checks on each other.

Four samples of unknown compositions were analyzed for α,p -dimethylstyrene by both the chemical and ultraviolet absorption methods (Table VI).

The agreement between these independent methods is seen to be good.

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Determination of Soluble Pectin and Pectic Acid by Electrodeposition

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In a new approach to the determination of pectin, solutions of pectin or pectates are deashed by the use of ion-exchange resins. The pectin or pectic acid is electrolytically deposited at a platinum anode in a weighable form. The method requires less of the analyst's time and attention than does the calcium pectate method and, with partially purified solutions, gives results of the same order of accuracy. The method is especially applicable to amounts of pectin ranging between 5 and 50 mg.

INVESTIGATIONS designed to develop new and extended uses for pectin have made desirable an analytical method capable of determining small amounts of pectin. Approximate estimations of pectin can be made by precipitation with 70 to 80 per cent alcohol or 50 per cent acetone (1, 3, 8, 9). Alcohol and acetone of these strengths precipitate gums, some proteins, and calcium and potassium salts of some of the organic acids as well as pectin. However, when dilute solutions are used the results are likely to be low because of incomplete precipitation of the pectin and difficulties in handling small amounts of the precipitate. The alcohol precipitate is difficult to filter and wash thoroughly. This filtration may be improved by precipitation with acidified alcohol, but after several washings enough acid may remain with the pectin to cause charring when the precipitate is dried. Fifty per cent acetone yields a precipitate which is more easily filtered and washed but affords little improvement in accuracy.

The pectic acid method (1) is long and subject to error due to the solubility of the pectic acid. The calcium pectate method of Emmet and Carré (4), although tedious and time-consuming, is probably the most reliable of the methods in use at the present time, but is not readily adaptable to very small amounts of pectin because of the large number of manipulations required. It has been used throughout this investigation for the analysis of stock solutions for comparisons with the proposed method. The proposed method is the result of an attempt to devise an accurate method which requires less of the analyst's time and attention and can be used to determine smaller amounts of pectin than the method of Emmet and Carré.

Since the soluble pectinous materials are negatively charged colloids, it was decided to investigate the possibility of collecting the pectin on the anode of a suitably arranged electrolysis system. Brown (2) unsuccessfully attempted to precipitate pectin electrolytically from aqueous solutions containing large amounts of electrolytes. Griggs and Johnstin (5) observed flocculation of pectin at the anode on electrolysis with 110-volt direct current. The authors have found that pectin can be quantitatively determined by electrodeposition, provided the electrolyte concentration of the solution is low. Ion-exchange resins can be used when it is necessary to remove the electrolytes before electrodeposition.

APPARATUS

A conventional electrolysis apparatus supplied with 220-volt direct current from a rectifier-transformer unit was used. A mercury cathode cell was constructed from a 250-ml. Griffin-type beaker, into the side of which was fused a platinum wire (Figure 1). A mercury-filled side arm was added to provide flexibility in the connection to the negative binding post. Clean mercury completely covering the platinum wire in the vessel served as the cathode. The anode was a disk of 45-mesh platinum gauze 6.25 cm. (2.5 inches) in diameter, edged with 0.075-cm. (0.03-inch) platinum wire to give rigidity and supported by a 15-cm. (6-inch) piece of 0.127-cm. (0.05-inch) platinum wire attached to the center (Figure 1). Similar electrodes are avail-

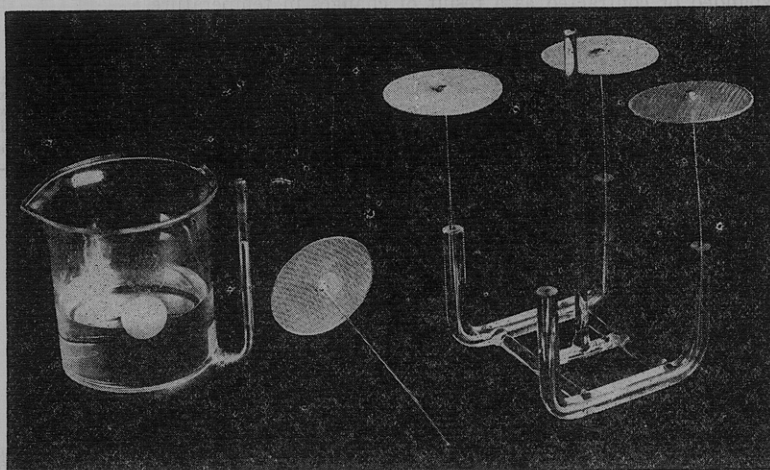


Figure 1. Electrolysis Vessel, Anode and Anodes in Holder