Determination of Residual Styrene (Monomer) and Acetophenone in Polymer Latices

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A number of analytical methods for the determination of styrene monomer in solid polymers have been developed.[1-4] These methods are based on the fact that monomeric styrene, with its unsaturated side chain, has an ultraviolet absorption maximum below 260 mμ while polymerized styrene has its absorption maximum above 260 mμ. Since these techniques require solutions of the polymers in a spectroscopic solvent, they cannot be applied to insoluble polymers or emulsion polymer systems. A method of analysis has been developed which takes advantage of the solubility of monomeric styrene in cyclohexane. Acetophenone, a decomposition product of cumene hydroperoxide used to catalyze the system under investigation, was found to interfere, and an appropriate compensation was made for this component.

EXPERIMENTAL

Apparatus

A Beckman Model DK-2 recording spectrophotometer was used. The settings during experiments were: photomultiplier tube in the 20× position with a sensitivity of 12, a time constant of 0.2, a scanning time of 5, and the scale expanded to 1×.

The mechanical shaker used for the extraction produced rapid, vertical shaking with an amplitude of 4 in.

Reagents

Commercial monomeric styrene (Forster Grant) was purified by vacuum distillation. The distillate obtained at 50°C. and 20 mm. Hg was collected in a receiver chilled by an acetone–solid CO_2 mixture and inhibited with 10 ppm *p-tert*-butyl catechol.

The acetophenone was reagent grade, and was distilled *in vacuo* for use as a standard.

The cyclohexane used was a Fisher "spectra-analyzed" reagent.

PROCEDURE

Calibration

The calibration curves were determined for styrene and acetophenone by preparing solution in cyclohexane. The styrene solutions were observed to obey Beer's law in the range 0–7 mg./1., while acetophenone was linear in the range 0–10 mg./1. The absorbances of these solutions were determined at 240 mμ for acetophenone and 250 mμ for styrene. Cyclohexane was used as the reference solvent in all cases.

Extraction of Latex

A 5-ml. portion of the latex was transferred to a weighed 50-ml. Florence flask and the flask reweighed to determine the weight of the sample. Ten milliliters of distilled water was added, together with 25.00 ml. of cyclohexane. The flask was closed securely with a lead foil-covered rubber stopper and then shaken mechanically for a period of 10 min., after which it was left to stand for 15 min. The cyclohexane was separated as a clear top layer.

It was found necessary to make dilutions of the original extract in order to bring the absorbance into a measurable range. Usually a 1:100 or 1:1000 dilution was sufficient for the 0–5% monomer range.

Measurement of Absorbance

Portions of the dilute extract were transferred to 1.0-cm. silica cuvettes for the absorbance measurements. Pure cyclohexane was used in the reference beam. The sample absorbance was recorded at 240 mμ and at 250 mμ. In Table I are listed the absorptivities in l./mg.-cm. for styrene

and acetophenone which were used in the calculations on these components.

TABLE I
Spectral Properties of Components

| Compound | Absorptivities | |
	240 mμ	250 mμ
Styrene	0.132	0.145
Acetophenone	0.109	0.040

The absorptivities were determined from

$$a = A/bc$$

where A is the absorbance of the solution, b is the path length in centimeters, and c is the concentration in milligrams per liter. Using the principle that, on a standard concentration basis, the absorbances of styrene and acetophenone are additive, one may calculate the concentration of these components in the sample by solution of the following equations by the usual method:

$$A_1 = a_{11}c_1b + a_{21}c_2b$$

$$A_2 = a_{12}c_1b + a_{22}c_2b$$

where

A_1, A_2 = absorbances at 240 and 250 mμ, respectively

a_{11}, a_{12} = absorptivities of styrene at 240 and 250 mμ, respectively

a_{21}, a_{22} = absorptivities of acetophenone at 240 and 250 mμ, respectively

c_1 = concentration of acetophenone (mg./l.)

c_2 = concentration of styrene (mg./l.)

b = cell path length (cm.)

DISCUSSION AND RESULTS

This method was developed for determining the unpolymerized styrene in latices of the styrene–butadiene copolymer type. It was suspected that extraction of the emulsion directly removed not only styrene but also other compounds along with it, which might interfere with its analysis. Fortunately, the emulsifiers used (rosin soaps) were not soluble to any extent in cyclohexane; however, a study of the extracts revealed the presence of another compound, acetophenone, which did interfere with the ultraviolet analysis. Known mixtures of styrene and acetophenone were prepared and it was demonstrated that they could be analyzed quantitatively simultaneously.

In order to establish that these compounds could be extracted quantitatively from an emulsion, it was necessary to prepare latices of known composition. To accomplish this goal, production latices were steam-distilled and extracted until repeated extractions with cyclohexane showed no absorbance in the spectral region of measurement. To each of these latices was added different measured quantities of styrene and acetophenone and the mixture was agitated for 16 hr. in a bottle polymerizer. In this manner, it was possible to study the precision and accuracy of this method.

Listed in Table II are the results of a series of thirty samples containing only styrene which were specially prepared and analyzed by this procedure.

TABLE II
Determinations of Styrene Added to Styrene–Butadiene Latices

| Styrene | | | Corrected styrene content, % |
Added, %	Found, %	Difference	
5.11	5.09	0.02	5.11
4.30	4.28	0.02	4.30
3.47	3.45	0.02	3.48
3.26	3.22	0.04	3.25
1.78	1.63	0.15	1.68
1.78	1.73	0.05	1.77
1.72	1.68	0.04	1.72
1.70	1.55	0.15	1.60
1.70	1.58	0.12	1.63
1.66	1.63	0.03	1.68
0.589	0.465	0.124	0.521
0.574	0.528	0.046	0.583
0.565	0.518	0.047	0.573
0.555	0.530	0.025	0.585
0.553	0.512	0.041	0.567
0.546	0.524	0.022	0.579
0.406	0.320	0.086	0.377
0.395	0.341	0.054	0.398
0.389	0.276	0.113	0.333
0.284	0.215	0.069	0.273
0.276	0.213	0.063	0.271
0.273	0.191	0.082	0.249
0.269	0.179	0.090	0.237
0.260	0.210	0.050	0.268
0.250	0.179	0.071	0.237
0.242	0.154	0.088	0.212
0.233	0.158	0.075	0.216
0.222	0.153	0.069	0.211
0.200	0.145	0.055	0.203
0.187	0.138	0.049	0.196

The data indicate that a quantitative extraction was not obtained. Subsequent experimentation established that there was a distribution of styrene

between the cyclohexane and the aqueous phase, on the order of 0.06% styrene being found in the latter.

In order to test the data, the statistical methods of Mandel and Linning[5] were used to evaluate the uncertainty of the linear calibration curve produced by plotting the "found" against the "added" data. Construction of the joint confidence ellipse made it possible to draw the following conclusions:

(1) A blank is required to correct for the constant error, and the experimentally found value of 0.06% styrene is a valid blank.

(2) The least squares solution also indicates that a relative error exists which can be corrected by dividing the data by the slope value, 1.008.

The fourth column in Table II was obtained after the above factors were used on the styrene analysis. A similar treatment of the acetophenone data showed that a blank value of 0.03% and a slope correction of 1.007 were acceptable.

The effect of the presence of acetophenone was studied by preparing, as previously described, latices containing known quantities of both styrene and acetophenone. In Table III are listed typical results obtained from measurements made by this procedure and solutions of the simultaneous equations.

TABLE III
Analysis of Samples Containing Styrene and Acetophenone

Sample	Styrene, %		Acetophenone, %	
	Added	Found	Added	Found
1	0.586	0.570	2.01	2.04
2	0.894	0.930	0.489	0.395
3	1.17	1.12	2.60	2.62
4	1.37	1.30	1.28	1.29
5	0.896	0.920	0	0.023
6	1.79	1.80	0	0
7	3.52	3.45	0	0.017
8	0	0.018	2.52	2.53
9	0	0.003	3.78	3.74
10	0	0	5.04	5.05

It will be noted that in samples 5–10 either styrene or acetophenone was omitted. This was done to reveal the deviations from the true values resulting from errors in the technique and the equations.

A study of the precision and accuracy of the procedure was made by use of statistical methods. The precision was studied by analyzing a series of

ten replicate samples for both styrene and acetophenone contents. The statistics for small numbers of observations as described by Dean and Dixon[6] were used in determining the 95% confidence intervals and the standard deviations. As a measure of the accuracy of the procedure, a standard error of estimate was determined from the joint confidence ellipse. All the calculated values are listed in Table IV.

TABLE IV
Precision and Accuracy of Test Method

	Styrene, %	Acetophenone, %
95% confidence interval	0.124 ± 0.002	0.021 ± 0.003
Standard deviation	±0.003	±0.008
Standard error of estimate	±0.036	±0.025

From these measurements, it is apparent that a quantitative determination of the monomeric styrene content of an emulsion polymer is feasible within the limits stated. In order to avoid unnecessary interferences, the latices were sampled before additives such as antioxidants were added. The method should be applicable to other styrene emulsion recipes after appropriate checks for interfering substances are made.

The time required by this method, less than 30 min. per determination, makes it suitable for control purposes and for the determination of the residual styrene polymerized following the initial polymerization reaction.

References

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Synopsis

A rapid, quantitative, direct procedure for the determination of monomeric styrene in a styrene-based polymer emulsion has been developed. The method includes the extraction of styrene in cyclohexane and a subsequent measurement of the ultraviolet absorbance of the solution. Determination of, and compensation for interference from, acetophenone is also described. The range of 0–5% monomeric styrene was studied by statistical methods.

Résumé

On a mis au point une technique rapide et quantitative pour la détermination immédiate du styrène monomérique dans une émulsion de polymère à base de styrène. La méthode comprend une extraction au cyclohexane suivie d'une mesure d'absorption dans l'ultra-violet de ce dernier. La compensation pour l'interférence avec l'acétophénone et la détermination de celle-ci est également décrite. Une gamme de 0 à 5 % de styrene a été étudiée par des méthodes statistiques.

Zusammenfassung

Ein rasches quantitatives Verfahren zur direkten Bestimmung von monomerem Styrol in einer Polymeremulsion auf Styrolgrundlage wurde entwickelt. Das Verfahren besteht in einer Cyclohexanextraktion und einer darauffolgenden Messung der Ultraviolettabsorption. Die Kompensation der Einflusses von Acetophenon und seine Bestimmung werden beschrieben. Der Bereich von 0 bis 5% Styrol wurde mit statistischen Methoden untersucht.