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Solvent Sublation of Hexachlorobutadiene and 2,4,6-Trichlorophenol

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Abstract

Hexachlorobutadiene and 2,4,6-trichlorophenol were removed from aqueous solutions into paraffin oil by solvent sublation. Over 99% of hexachlorobutadiene was removed from a solution containing 100 ppb hexachlorobutadiene initially in 10 min. The rate of removal of hexachlorobutadiene by air stripping is somewhat slower than that by solvent sublation. The effects of added salt and ethanol on solvent sublation and air stripping of hexachlorobutadiene were studied. About 64% of 2,4,6-trichlorophenol were removed by solvent sublation from a solution containing 50 ppm 2,4,6-trichlorophenol initially at pH 1.84 for a 1-h run. The rate of removal of 2,4,6-trichlorophenol can be improved by adding the cationic surfactant, hexadecyltrimethylammonium bromide (HTA). As high as 95% of 2,4,6-trichlorophenol was removed in 1 h if 10 ppm HTA was added to the solution before solvent sublation runs.

INTRODUCTION

Solvent sublation, a surface chemical separation method originated by Sebba (*1*), has shown promise for the removal of certain types of organic compounds from aqueous systems. In the solvent sublation procedure a surface-active (or volatile) solute is transported from the aqueous phase to an overlying layer of nonvolatile organic liquid on the air-water interfaces (or in the interior) of bubbles rising through the solvent sublation column.

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Lemlich's book on adsorptive bubble separation includes a review on solvent sublation by Karger (*2*). Wilson et al. included material on this subject in a more general review (*3*) and two recent books (*4*, *5*).

Reports of particular interest to us are the extensive works of Wilson's group on solvent sublation of alkyl phthalates, volatile chlorinated organics, dichlorobenzenes, nitriphenols, polynuclear aromatics, and chlorinated pesticides (*3–11*). Grieves et al. (*12*) studied the removal of phenol by solvent extraction, solvent sublation, and foam fractionation. Caragay, Karger, and Lee separated methyl orange from rhodamine B with a cationic surfactant at a pH at which the methyl orange was anionic while the rhodamine B was zwitterionic (*13*, *14*). Karger, Pinfold, and Palmer carried out a detailed study of the solvent sublation of a methyl orange–hexadecyltrimethylammonium ion pair (*15*). Womack, Lichter, and Wilson (*6*) reported on the solvent sublation of two dye–surfactant ion complexes, methylene blue–tetradecyl sulfate and methyl orange–hexadecyltrimethylammonium. We recently reported on the solvent sublation of diphenyl (*16*), a cationic dye, magneta, with sodium lauryl sulfate (*17*), and an anionic dye, C.I. Direct Red 1, with hexadecyltrimethylammonium bromide (*18*).

In this paper we report that hexachlorobutadiene and 2,4,6-trichlorophenol can be removed from aqueous solutions by solvent sublation. Both of these chlorinated organics are serious pollutants.

EXPERIMENTAL

The solvent sublation system used consisted of a glass column 60 cm in length with an inside diameter of 3.5 cm. The bottom of the column was closed with a rubber stopper with holes for a gas sparger and a stopcock to take samples and to drain the column. The gas sparger was a commercially available gas dispersion tube. A lipped side arm near the top of the column served as a foam outlet (for the runs with the addition of surfactant).

Compressed air was generated from an air pump. The air flow rate was adjusted with a Hoke needle valve with micrometer control and measured with a soap film flowmeter. The air was purified by passing it through glass wool to remove particulates, through Ascarite to remove carbon dioxide, and through distilled water for controlled rehumidification.

Merck reagent-grade hexachlorobutadiene and 2,4,6-trichlorophenol were used for sample preparation. Reagent-grade sodium lauryl sulfate

(NLS, Wako Pure Chemical Industry, Japan) and hexadecyltrimethylammonium bromide (HTA, Aldrich, 95%) were used for solvent sublation of 2,4,6-trichlorophenol.

The volume of the sample solution used for a run was 200 mL. The sample solutions contained 100 ppb hexachlorobutadiene or 50 ppm 2,4,6-trichlorophenol initially. The solution was poured into the column, paraffin oil was added (30 mL for the runs with hexachlorobutadiene and 20 mL for the runs with 2,4,6-trichlorophenol) immediately, and the timer started. Five milliliters of solution was taken each time for analysis. Five milliliters of *n*-hexane (Merck reagent grade) was used to extract hexachlorobutadiene or 2,4,6-trichlorophenol into the organic solvent. The standard solutions were prepared by dissolving hexachlorobutadiene or 2,4,6-trichlorophenol in hexane. The concentrations of hexachlorobutadiene were measured with a Shimadzu GC-9AM Gas Chromatograph with a C-R 3A integrater and an electron capture detector. A 2-m OV-17 packed column was used. The column temperature, injection temperature, and detector temperature were set at 110, 220, and 250°C, respectively. The 2,4,6-trichlorophenol concentrations were measured with a Jasco 505 UV/Vis Spectrophotometer at 295 nm.

Some of the data of solvent sublation were plotted as $\log_{10} C(t)/C_0$ versus time in minutes to display any deviations from first-order kinetics, which would yield linear plots. All solvent sublation runs were performed at room temperature.

The pH of the solution was measured with a Radiometer pHM83 Autocal pH meter.

RESULTS AND DISCUSSION

Solvent Sublation and Air Stripping of Hexachlorobutadiene

The effect of air flow rate on solvent sublation of hexachlorobutadiene is shown in Table. 1. The separation was very effective. Over 99% of hexachlorobutadiene was removed in 10 min. The rate of removal increases with increasing air flow rate, as expected. Hexachlorobutadiene is very volatile; its vapor pressure at 20°C is 0.5 mbar (*19*). It can also be removed from aqueous solution by air stripping (without an organic layer on the top of the separation column). The rate of removal of hexachlorobutadiene by air stripping and by solvent sublation are compared in Table 2. The rate of removal of hexachlorobutadiene by solvent subla-

TABLE 1
Effect of Air Flow Rate on Solvent Sublation of Hexachlorobutadiene

	% Removal	
Flow rate (mL/min)	5 min	10 min
100	91.4	99.0
120	91.9	99.0
160	94.9	99.2
180	96.3	99.4

TABLE 2
Hexachlorobutadiene Removal by Solvent Sublation and Air Stripping[a]

	% Removal[b]			
Method	3 min	6 min	9 min	15 min
Solvent sublation	73.8 ± 1.0	92.2 ± 0.4	97.9 ± 1.0	99.3 ± 0.5
Air stripping	56.4 ± 5.2	82.6 ± 2.8	94.3 ± 1.9	98.7 ± 0.5

[a] Air flow rate = 80 mL/min.
[b] Average value and standard deviation of duplicate runs.

tion is somewhat higher than that by air stripping. The improvement in separation by solvent sublation is presumably due to the adsorption of surface-active hexachlorobutadiene on the surface of the bubbles. The surface-adsorbed hexachlorobutadiene and the hexachlorobutadiene in the vapor phase inside the bubble are carried into the organic layer on the top of the separation column during solvent sublation. Only the hexachlorobutadiene vapor inside the air bubble is removed by air stripping.

The effects of added salts ($NaNO_3$) on the solvent sublation of hexachlorobutadiene are shown in Table 3. We see that the presence of salt increases the rate of separation somewhat. Presumably this is due to the same mechanism that causes the widely used "salting out" effect in which organics are made less soluble in aqueous phases by the addition of salts. These tie up water molecules in ion hydration shells, thereby decreasing the amount of water available for solubilizing the organic. Similar effects were observed in the solvent sublation of other organic substance (*7*, *10*, *11*, *18*).

TABLE 3
Effect of $NaNO_3$ on Solvent Sublation of Hexachlorobutadiene[a]

	% Removal[b]			
$NaNO_3$ (*M*)	3 min	6 min	9 min	15 min
0	73.8 ± 1.0	92.2 ± 0.4	97.9 ± 1.0	99.3 ± 0.5
0.01	73.9 ± 4.5	93.0 ± 0.4	98.2 ± 0.3	99.6 ± 0.2
0.05	76.5 ± 1.9	94.2 ± 0.3	97.7 ± 1.1	99.3 ± 0.1
0.1	78.5 ± 0.7	94.1 ± 0.1	97.8 ± 1.0	99.6 ± 0.1
0.5	85.9 ± 0.6	97.8 ± 0.1	99.6 ± 0.0	>99.9
1.0	88.7 ± 0.6	98.6 ± 0.1	99.8 ± 0.1	>99.9

[a] Air flow rate = 80 mL/min.
[b] Average value and standard deviation of duplicate runs

The effect of added ethanol (representative of a polar organic solute) on the rate of solvent sublation of hexachlorobutadiene is shown in Table 4. The rate of separation increases with increasing ethanol concentration (from 0 to 0.25% ethanol). This is presumably due to the decrease of the air bubble size (we observed that the air bubble decreased significantly with the addition of ethanol into the solution) by the added ethanol, which reduces the surface tension of the solution. Smaller bubbles are more efficient at solvent sublation than are larger bubbles; they rise more slowly, so have a longer contact time with the solution, and they have a larger surface-to-volume ratio than larger bubbles. The larger the surface area generated, the greater is the number of sites available for adsorption and

TABLE 4
Effect of Ethanol on Solvent Sublation of Hexachlorobutadiene[a]

	% Removal[b]			
Ethanol (%)	3 min	6 min	9 min	15 min
0	73.8 ± 1.0	92.2 ± 0.4	97.9 ± 1.0	99.3 ± 0.5
0.025	78.9 ± 1.3	94.9 ± 0.2	98.6 ± 0.2	99.7 ± 0.0
0.25	83.4 ± 4.5	96.9 ± 0.9	99.5 ± 0.5	>99.9
1.0	83.6 ± 0.8	96.0 ± 0.3	98.1 ± 0.1	98.5 ± 0.0
5.0	77.0 ± 0.9	92.9 ± 0.6	97.1 ± 0.7	97.5 ± 1.1

[a] Air flow rate = 80 mL/min.
[b] Average value and standard deviation of duplicate runs.

consequently the faster the rate of separation. The decrease in bubble size with decreasing surface tension of the solution may be explained using the Young-Laplace equation (*20*); assuming the same presssure inside the air bubbles which are freshly generated from the surface of the gas sparger, the radius of the air bubble decreases with decreasing surface tension of the solution. Excessive amount of ethanol (e.g., 5% ethanol), however, had a deleterious effect on the rate of removal, presumably due to the attractive forces between hexachlorobutadiene and ethanol molecules, which would increase the solubility of hexachlorobutadiene in the aqueous solution.

The effects of added salt and ethanol on hexachlorobutadiene removal by air stripping are similar to that by solvent sublation, as shown in Tables 5 and 6.

TABLE 5

Effect of $NaNO_3$ on Air Stripping of Hexachlorobutadiene[a]

	% Removal[b]			
$NaNO_3$ (*M*)	3 min	6 min	9 min	15 min
0	56.4 ± 5.2	82.6 ± 2.8	94.3 ± 1.9	98.7 ± 0.4
0.01	76.8 ± 4.0	92.7 ± 0.1	97.5 ± 0.3	99.3 ± 0.1
0.05	76.4 ± 2.3	92.6 ± 1.0	97.3 ± 0.6	99.4 ± 0.3
0.5	86.9 ± 0.4	97.4 ± 0.2	99.5 ± 0.0	>99.9
1.0	88.8 ± 2.1	98.3 ± 0.4	99.7 ± 0.1	99.9 ± 0.1

[a] Air flow rate = 80 mL/min.

[b] Average value and standard deviation of duplicate runs.

TABLE 6

Effect of Ethanol on Air Stripping of Hexachlorobutadiene[a]

	% Removal[b]			
Ethanol (%)	3 min	6 min	9 min	15 min
0	56.4 ± 5.2	82.6 ± 2.8	94.3 ± 1.9	98.7 ± 0.4
0.25	61.5 ± 6.5	90.2 ± 0.4	96.6 ± 0.3	99.5 ± 0.1
1.0	66.3 ± 1.6	89.4 ± 1.5	96.4 ± 1.2	99.7 ± 0.1
5.0	63.9 ± 2.1	89.5 ± 6.1	93.9 ± 1.8	99.0 ± 0.6

[a] Air flow rate = 80 mL/min.

[b] Average value and standard deviation of duplicate runs.

Solvent Sublation of 2,4,6-Trichlorophenol

The effect of air flow rate on the solvent sublation of 2,4,6-trichlorophenol is shown in Fig. 1. The rate of removal also increases with increasing air flow rate. The runs followed first-order kinetics approximately. We found 41% removal of 2,4,6-trichlorophenol in 30 min when the air flow rate was 100 mL/min (the pH of the solution was 5.42). The effect of pH on separation is shown in Fig. 2. Less than 5% of 2,4,6-trichlorophenol was removed in 1 h at pH 9.25. The poor separation efficiency from the alkaline solution is presumably due to the dissociation of the phenolic hydrogen such that the charged species is no longer surface-active. The amounts of 2,4,6-trichlorophenol removed from the solutions at pH 5.42 and 1.84 after aeration for 1 h were 58 and 64%, respectively.

It was found that additions of 0.2 or 0.4 *M* $NaNO_3$ into the solution have no significant effect on the separation efficiency of 2,4,6-trichlorophenol by solvent sublation. This is probably due to the fact that the salting out effect is not significant for this polar molecule.

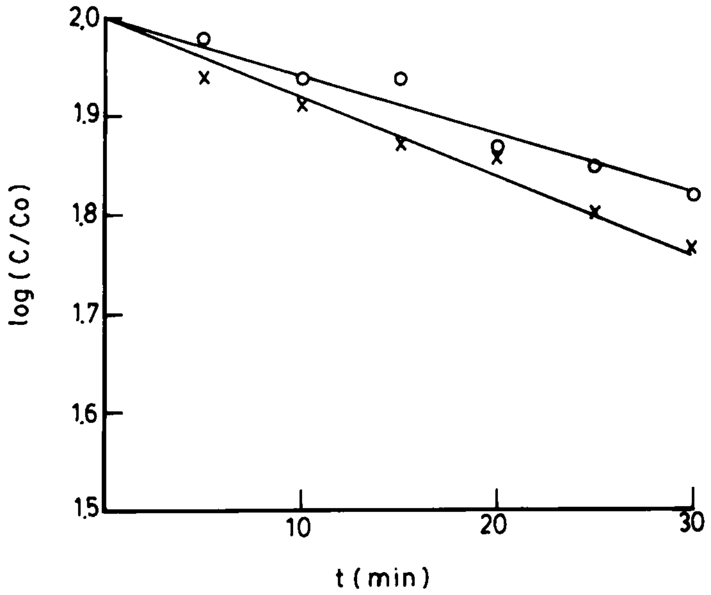

FIG. 1. Effect of air flow rate on solvent sublation of 2,4,6-trichlorophenol: (O) 80 mL/min, (X) 100 mL/min.

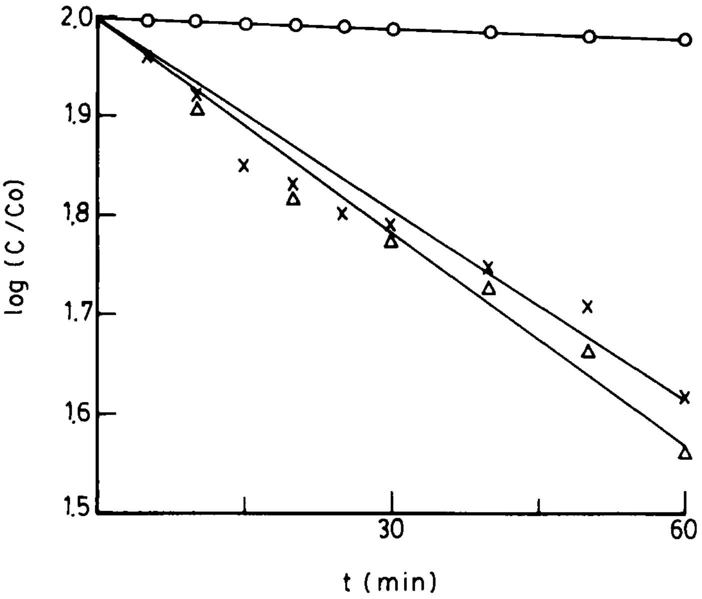

FIG. 2. Effect of pH on solvent sublation of 2,4,6-trichlorophenol: (O) 9.25, (X) 5.42, (Δ) 1.84.

The effect of NLS addition on the solvent sublation of 2,4,6-trichlorophenol is shown in Fig. 3. The separation efficiency increases with increasing NLS dose (from 0 to 32 ppm). This is presumably due to the decrease of the air bubble size by the added surfactant, which reduces the surface tension of the solution. We found that 77% of 2,4,6-trichlorophenol was removed in 1 h if 32 ppm NLS was also added to the solution before solvent sublation runs.

The rate of removal of 2,4,6-trichlorophenol can be further improved by adding the cationic surfactant HTA. The results are shown in Fig. 4. As high as 95% of 2,4,6-trichlorophenol was removed in 1 h if 10 ppm HTA was added to the solution before solvent sublation runs. The improvement in the rate of separation by the addition of HTA is presumably not only due to the decrease of the air bubble size, but also to the formation of 2,4,6-trichlorophenolate–HTA complexes which are surface-active and can be easily floated.

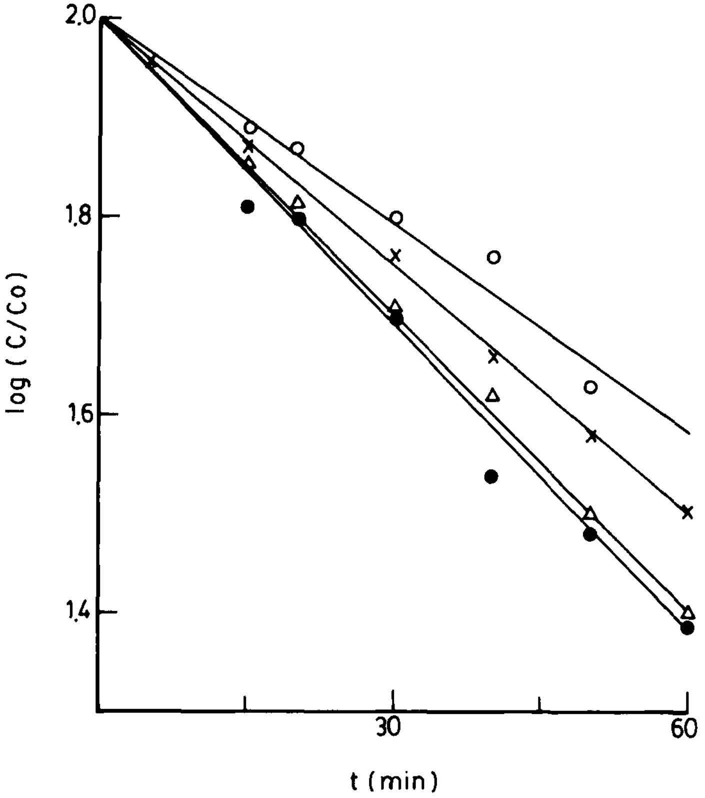

FIG. 3. Effect of NLS addition on solvent sublation of 2,4,6-trichlorophenol: (O) 0 ppm, (×) 12 ppm, (Δ) 20 ppm, (●) 32 ppm.

CONCLUSION

Hexachlorobutadiene and 2,4,6-trichlorophenol can be removed effectively from aqueous solutions into paraffin oil by solvent sublation. Over 99% of hexachlorobutadiene can be removed from a solution containing 100 ppb hexachlorobutadiene in 10 min. The rate of removal of hexachlorobutadiene by air stripping is somewhat slower than that by solvent sublation. The presence of salt or ethanol increases the rate of separation

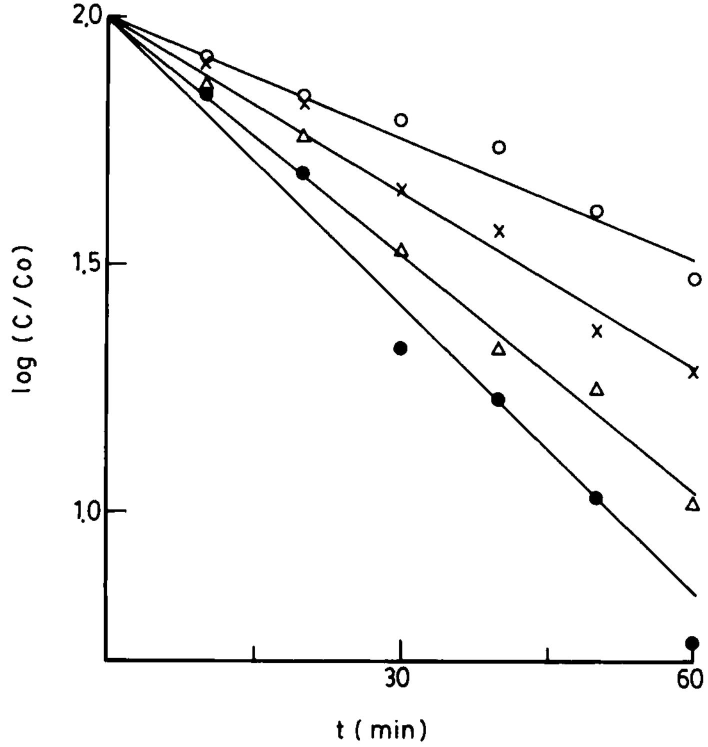

FIG. 4. Effect of HTA addition on solvent sublation of 2,4,6-trichlorophenol: (O) 0 ppm, (×) 2.5 ppm, (Δ) 5.0 ppm, (●) 10.0 ppm.

of hexachlorobutadiene. About 64% of 2,4,6-trichlorophenol was removed by solvent sublation from a solution containing 50 ppm 2,4,6-trichlorophenol at pH 1.84 for a 1-h run. The rate of removal of 2,4,6-trichlorophenol can be improved by adding the cationic surfactant (HTA). As high as 95% of 2,4,6-trichlorophenol was removed in 1 h if 10 ppm HTA was added to the solution before solvent sublation runs.

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REFERENCES

1. F. Sebba, *Ion Flotation*, Elsevier, New York, 1962.
2. B. L. Karger, in *Adsorptive Bubble Separation Techniques* (R. Lemlich, ed.), Academic, New York, 1972, Chap. 8.
3. A. N. Clarke and D. J. Wilson, *Sep. Purif. Methods*, *7*, 55 (1978).
4. D. J. Wilson and D. E. Pearson, *Solvent Sublation of Organic Contaminants for Water Reclamation*, Report RU-83/6, Bureau of Reclamation, U.S. Department of the Interior, 1984.
5. D. J. Wilson and A. N. Clarke, *Developments in Foam Flotation*, Dekker, New York, 1983.
6. J. L. Womack, J. C. Lichter, and D. J. Wilson, *Sep. Sci. Technol.*, *17*, 897 (1982).
7. K. Tamamushi and D. J. Wilson, *Ibid.*, *19*, 1013 (1984–1985).
8. T. Lionel, D. J. Wilson, and D. E. Pearson, *Ibid.*, *16*, 907 (1981).
9. D. J. Wilson and K. T. Valsaraj, *Ibid.*, *17*, 1387 (1983).
10. S.-D. Huang, K. T. Valsaraj, and D. J. Wilson, *Ibid.*, *18*, 941 (1983).
11. K. T. Valsaraj and D. J. Wilson, *Colloids Surf.*, *8*, 203 (1983).
12. R. B. Grieves, W. Charewiez, and S. M. Brien, *Anal. Chim. Acta*, *73*, 293 (1974).
13. A. B. Caragay and B. L. Karger, *Anal. Chem.*, *38*, 652 (1966).
14. B. L. Karger, A. B. Caragay, and S. B. Lee, *Sep. Sci.*, *2*, 39 (1967).
15. B. L. Karger, T. A. Pinfold, and S. E. Palmer, *Ibid.*, *5*, 603 (1970).
16. W.-K. Wang, and S.-D. Huang, *Sep. Sci. Technol.*, *23*, 375 (1988).
17. G.-L. Sheu and S.-D. Huang, *Ibid.*, *22*, 2253 (1987).
18. M.-H. Cheng and S.-D. Huang, *J. Colloid Interface Sci.*, *126*, 346 (1988).
19. *Products for Synthesis*, Manual 85/86, Merck Schuchardt.
20. A. W. Adamson, *Physical Chemistry of Surfaces*, 4th ed., Wiley, New York, 1982.

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