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碘量法测定丙烯环氧化产物中双氧水 质量分数的研究

STUDY ON IODOMETRIC DETERMINATION OF H₂O₂ MASS FRACTION IN PROPYLENE EPOXIDE

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摘要: 模拟 H₂O₂ 氧化丙烯的环氧化产物, 利用正交实验方法得到了测定 H₂O₂ 质量分数的最佳滴定条件。结果表明, 滴定时被测样品质量对测定结果的影响很显著, KI 和 H₂SO₄ 溶液的加入量的影响显著。当被测丙烯环氧化产物中 H₂O₂ 的质量分数为 0.5%~3.3% 时, 其最小的滴定样品质量 m 由式 $m = 0.17/x$ (x 代表被测环氧化产物中 H₂O₂ 的质量分数) 估计, 且在滴定过程中 KI 和 H₂SO₄ 溶液的加入量分别在 3~8 ml 和 2~7 ml 范围时, 测定结果与真实值相吻合。在丙烯环氧化产物中 H₂O₂ 质量分数相对较低 (<0.5%) 时, 应控制 KI 和 H₂SO₄ 溶液的加入量不能超过 8 ml 和 7 ml, 而在 H₂O₂ 质量分数相对较高 (>3.3%) 时, 应控制 KI 和 H₂SO₄ 溶液的加入量不能低于 3 ml 和 2 ml。该规律在后来的实验中得到了验证。

关键词: 碘量法; H₂O₂; 正交实验设计; 方差分析

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Abstract: The orthogonal design was employed to research the optimized titration conditions for a simulated solution of propylene epoxides. It is concluded that the amount of sample gave the most significant influence to the titration result, while the amounts of both KI and H₂SO₄ solutions only provided significant influences. The mass fraction (x) of H₂O₂ measured by titration in propylene epoxide solution was well consistent with its true value if x was in the range of 0.5% - 3.3%, and the minimal amount (m) of the solution being titrated was estimated by $m = 0.17/x$ and the amounts of KI and H₂SO₄ solutions used in titration were between 3 - 8 ml and 2 - 7 ml respectively. It is shown that titration results of the solution with different H₂O₂ contents were always well consistent with their true value under these conditions. The maximum amounts of KI and H₂SO₄ solutions used in titration were not more than 8 ml and 7 ml respectively at the relative low mass fraction (<0.5%) of H₂O₂ in propylene epoxide solution, and the minimum amounts of them are not less than 3 ml and 2 ml respectively at the relative high mass fraction (>3.3%) of H₂O₂, which is then verified by further experiments.

Key words: iodometric titration; H₂O₂; orthogonal array design; variance analysis

Since Taramasso^[1] synthesized titanium silicalite-1 (TS-1) with the MFI structure in 1983 for the

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first time, this material has received much attention^[2-5]. It can be used to prepare an extremely effective catalyst for the epoxidation of unhindered alkenes by dilute solution of H₂O₂ in methanol with high selectivity under mild conditions^[6,7]. This process is considered as the most potential industrial technology to produce propylene oxide economically.

In a commercial plant, TS-1 is a very effective catalyst during propylene epoxidation by H₂O₂, therefore, the H₂O₂ content in the system should be reduced to a quite low level and is the important value in evaluation of catalyst behaviors and operating parameter influences. The H₂O₂ content in H₂O₂ aqueous solution was often measured by the standard KMnO₄ titration method, but the result was not accurate, because KMnO₄ in the solution containing H⁺ can oxidize the stabilizing agents commonly added to H₂O₂ solution, giving a positive deviation for H₂O₂ content. An iodometric titration method can provide satisfactory results for this system with the advantage of preventing from the interference of these stabilizing agents. Although iodometric titration method has been accepted by many researchers^[8,9] and widely used for this propylene oxide production process, little has been reported about the influences exerted by titration parameters on the precision of the measured H₂O₂ content. In this paper, an orthogonal design method will be introduced to solve this problem and the optimum conditions will be given by variance analysis.

1 Experimental

1.1 Principle of iodometric titration

At first, H₂O₂ thoroughly reacts with I⁻ ions, which are then oxidized to I₂ under the action of the ammonium molybdate catalyst.



Then the standard solution of Na₂S₂O₃ is added drop by drop and reacts with I₂ to produce I⁻ ions again as shown by Eq. (2).



1.2 Titration procedure

A calibrated H₂O₂ solution measured up to mg (to 0.1 mg) is dropped in the iodine flask containing V₁ ml of H₂O. V₂ ml of 2 mol/l H₂SO₄ solution, V₃ ml of 10% KI solution and *n* drops of 30 g/l ammonium molybdate solution are then added orderly. The mixed solution is titrated with a standard Na₂S₂O₃ solution of 0.1000 mol/l until yellow color of the mixed solution appears. Then added V₄ ml of starch solution before the mixed solution was continuous titrated with the standard Na₂S₂O₃ solution to be colorless. Na₂S₂O₃ volume (*V*) totally used in titration is recorded.

The mass fraction of H₂O₂ is calculated as follows:

$$x = \frac{34.016 \times C \times V}{2 \times m \times 1000} \times 100 \quad (3)$$

where *x* is the mass fraction of H₂O₂ in products solution, %; *C* is the concentration of standard Na₂S₂O₃ solution, mol/l; *V* is the titration volume of standard Na₂S₂O₃ solution, ml; *m* is the mass of H₂O₂ solution, g.

If KI solution is added before H₂SO₄, bubbles will be observed in the solution because of H₂O₂ decomposition under the catalytic action of I⁻, resulting in that the mass fraction (*x*) of H₂O₂ titrated and calculated by Eq. (3) is obviously lower than the mass fraction (*x*) of H₂O₂ calculated by Eq. (4), as shown in Table 1.

$$x = \frac{m \times c}{m_i} \times 100 \quad (4)$$

where m is the mass of H_2O_2 solution, g; c is the mass fraction of aqueous H_2O_2 solution, %; m_i is the mass sum of all propylene epoxide products in simulated sample, g.

1.3 Error analysis

The composition of the simulated sample for propylene epoxide production from propylene catalyzed by TS-1 catalyst is listed in Table 2.

Table 1 The mass fractions of H_2O_2 titrated (x) and calculated (x) by Eq. (4) %

Sample	x	x
1	3.8367	3.4737
2	3.2063	2.9773
3	2.2528	1.3388

Table 2 Solution composition simulating propylene epoxide production

Substance	w/ %
Methanol	84.7862
H_2O	11.3060
Propylene oxide	3.0662
1-Methoxy-2-propanol	0.2982
H_2O_2	0.5434

The precision of m and C is 0.0001 g and 0.0003 mol/l respectively, and the reading error of the acidimetric tube is 0.02 ml, that is, $m = 0.0001$ g, $C = 0.0003$ mol/l and $V = 0.02$ ml. When m is 0.1, 0.3 and 0.5 g respectively, the theoretical volume V_T of titration calculated by Eq. (3) according to x and the measurement error, including V/V_T , C/C and m/m , and also the maximum absolute measurement deviation $x(\text{max})$ calculated by $V_T \times (V/V_T + C/C + m/m)$ are all shown in Table 3.

Table 3 Maximum absolute measurement deviation $x(\text{max})$ and measurement error in the titration

m/g	V_T/ml	$x/\%$	/ %			$x(\text{max})/\%$
			V/V_T	C/C	m/m	
0.1	0.33	0.5434	6.1	0.3	0.1	0.0355
0.3	0.98	0.5434	2.0	0.3	0.0	0.0129
0.5	1.63	0.5434	1.2	0.3	0.0	0.0084

The simulated samples of about 0.5 g were titrated under various amounts of KI and H_2SO_4 and results of the mass fractions of H_2O_2 in samples were 0.5693 %, 0.5537 %, 0.5393 % and 0.5542 % respectively. The maximum deviation of titration $x(\text{max})$ is 0.0300 % which was significantly larger than 0.0084 %. So the optimum titration conditions should be obtained through orthogonal array design.

1.4 Orthogonal array design

In the orthogonal array design of iodometric determination of H_2O_2 concentration in propylene epoxide, six design variables as listed in Table 4 were involved. A, B, C denotes the amounts of H_2O , H_2SO_4 and KI respectively, D denotes mass of H_2O_2 solution, while E and F denotes the amounts of ammonium molybdate solution and starch solution. In addition, each design variable has three levels. Considering errors involved by the operator, the orthogonal array of $L_{27}(3^{13})$ was selected, where the interactions among the design variables were disregarded.

Table 4 Factors and their levels in the orthogonal array of $L_{27}(3^{13})$

Level	A	B	C	D	E	F
	$V(\text{H}_2\text{O})/\text{ml}$	$V(\text{H}_2\text{SO}_4)/\text{ml}$	$V(\text{KI})/\text{ml}$	$m(\text{H}_2\text{O}_2 \text{ solution})/\text{g}$	$V(\text{Ammonium molybdate})/\text{Drop}$	$V(\text{Starch})/\text{ml}$
1	10	5	5	0.1	3	1
2	30	10	10	0.3	6	3
3	50	15	15	0.5	9	5

2 Results and discussion

2.1 Variance analysis

Results of each absolute value representation of calculated mass fraction from titration results subtracting true mass fraction were listed in Table 5.

Table 5 Orthogonal array and results

No.	$x^{1)}/\%$	$R_T^{2)}/\%$	No.	$x^{1)}/\%$	$R_T^{2)}/\%$	No.	$x^{1)}/\%$	$R_T^{2)}/\%$
1	0.5256	0.0115	10	0.5413	0.0021	19	0.5256	0.0178
2	0.5547	0.0158	11	0.5537	0.0103	20	0.5547	0.0113
3	0.5338	0.0367	12	0.5393	0.0041	21	0.5338	0.0096
4	0.5404	0.0025	13	0.5790	0.0356	22	0.5404	0.0030
5	0.5542	0.0243	14	0.5982	0.0548	23	0.5542	0.0108
6	0.5296	0.0152	15	0.5925	0.0491	24	0.5296	0.0138
7	0.5773	0.0259	16	0.5313	0.0121	25	0.5773	0.0339
8	0.5792	0.0258	17	0.5572	0.0138	26	0.5792	0.0358
9	0.6059	0.0178	18	0.5478	0.0044	27	0.6059	0.0625

1) Calculated mass fraction of H_2O_2 from titration result ; 2) Absolute value representation of calculated mass fraction subtracting true mass fraction (made up) of H_2O_2

As the sum of square of A and F are so small that near to the blank one , they can be contained in errors and therefore each degree of freedom in these two ranks can be considered to be included in that of errors. The results of variance analysis were listed in Table 6.

Optimum titration conditions for that solution could be expressed with $A_1B_1C_1D_2E_1F_1$, where A_1 , B_1 , C_1 denoted amounts of H_2O , H_2SO_4 and KI , and they were 10ml , 5ml and 5ml. respectively. D_2 denoted the mass of H_2O_2 solution and was 0.3 g , while E_1 , and F_1 denoted amounts of ammonium molybdate solution and starch solution , and they were 3 drops and 1ml respectively.

It is clear that $R_D > R_C > R_B > R_E > R_F > R_A$. This order reveals that sample mass would give the strongest impact to the titration results among factors examined. Meanwhile , it is in decreasing in the order of amounts of KI , H_2SO_4 , ammonium molybdate , starch and H_2O respectively.

Table 6 Variance analysis

Factors	$f^{1)}$	$\bar{T}_1^{2)}$	\bar{T}_2	\bar{T}_3	$R^{3)}$	SS ⁴⁾	MS ⁵⁾	$F^{6)}$
AA	2	0.1755	0.1863	0.1985	0.0230	0.0000		
AB	2	0.1192	0.2091	0.2320	0.1128	0.0008	0.00040	5.538
AC	2	0.1219	0.1907	0.2477	0.1258	0.0009	0.00045	6.23
AD	2	0.3357	0.1110	0.1136	0.2221	0.0037	0.00185	25.615
AE	2	0.1444	0.2027	0.2132	0.0688	0.0003	0.00015	2.077
AF	2	0.1554	0.2016	0.2033	0.0479	0.0002		
Error	18					0.0013	0.00007	
Total	26					0.0070		
$F_{0.01}(2,18) = 8.29$		$F_{0.05}(2,18) = 4.41$			$F_{0.10}(2,18) = 3.01$			

1) The degree of freedom of each factor ; 2) The sum of R_T of all factors at 1st level ; 3) The \bar{T}_i range from minimum to maximum of each factor ; 4) The sum of squares ; 5) The mean of squares ; 6) The factor of significance test

From the variance analysis in Table 6 , it can be seen that F value of the sample mass is higher than $F_{0.01}$ and exert the most significant influence to the titration result. F value of the amount of KI and

H_2SO_4 is higher than $F_{0.05}$ while lower than $F_{0.01}$ so their influences are significant. As for F of other factors are lower than $F_{0.10}$, therefore they are not significant. Effect of factors on redundancy is in line with that of R value.

It is also shown from Table 6, the solution amount gives no influence on titration when that amount of solution is larger than 0.3 g. That is to say, the titration results would give the good consistency with the true value if the error caused by reading error of acidimetric tube is less than 2.0%. The minimal amount of solution can be estimated by $m = 0.17/x$ where x indicates H_2O_2 mass fraction from Eq. (3).

2.2 Influence of different amounts of KI and H_2SO_4

The different simulated solutions were titrated by adding different amount of KI and H_2SO_4 , the titration results and relative errors were listed in Table 7. From Table 7 it can be seen that excess amount of KI and H_2SO_4 gave negative titration response at the relative low mass fraction of H_2O_2 ,

Table 7 Titration results by adding different amounts of KI and H_2SO_4

$x_1^{1)}/\%$	$m_0^{2)}/g$	V_2/ml	V_3/ml	$x/\%$	Relative error/ $\%$
0.5565	0.4334	5	1	0.5572	0.13
0.5565	0.4224	5	3	0.5555	0.18
0.5565	0.4539	5	5	0.5547	0.33
0.5565	0.4813	5	8	0.5587	0.39
0.5565	0.5217	5	10	0.5712	2.65
3.2652	0.1262	5	2	2.5650	21.44
3.2652	0.1255	5	3	3.2753	0.31
3.2652	0.0945	5	5	3.2623	0.09
3.2652	0.1165	5	10	3.2784	0.40
0.5565	0.4539	0.5	5	0.5547	0.33
0.5565	0.3996	2	5	0.5615	0.89
0.5565	0.4140	5	5	0.5585	0.36
0.5565	0.4230	7	5	0.5628	1.13
0.5565	0.3576	8	5	0.5699	2.42
0.5565	0.5007	10	5	0.5712	2.65
3.2652	0.1349	0.5	5	3.1613	3.18
3.2652	0.1207	1	5	3.1643	3.09
3.2652	0.1083	2	5	3.3052	1.23
3.2652	0.0945	5	5	3.2623	0.09
3.2652	0.1153	10	5	3.2977	0.99

1) True value of H_2O_2 mass fraction; 2) Actual mass of the sample being measured

3 Conclusions

In iodometric titration of determining H_2O_2 content it is necessary to add KI solution after H_2SO_4 solution so as to avoid H_2O_2 decomposition catalyzed by I^- , which would bring out incorrect titration results.

From the variance analysis it is concluded that the solution amount gave the most significant influence to the titration results. The titration result was well consistent with the true value if the error caused by reading error of acidimetric tube was less than 2.0%. The minimal amount of solution can be

while insufficient amount of KI and H_2SO_4 gave the same response at the relative high one. It can be concluded that the titration results of the true mass fraction of H_2O_2 between 0.5% to 3.3% would be well consistent with the true value if the amount of KI is between 3 to 8 ml, and the amount of H_2SO_4 is between 2 to 7 ml. The titration results as shown in Table 8 gave a good example in these optimum conditions.

Table 8 Titration results by the optimum conditions

$x_1/\%$	$m_E^{1)}/g$	m_0/g	$x/\%$	Relative error/ $\%$
3.2063	0.053	0.0561	3.2312	0.78
2.2828	0.0755	0.0794	2.304	0.93
1.8979	0.0903	0.0893	1.9182	1.07
1.1683	0.1471	0.1413	1.177	0.74
0.7253	0.2281	0.2266	0.7266	0.18
0.5524	0.3077	0.3109	0.5617	1.68
0.3796	0.4478	0.4455	0.3733	1.66
0.1748	0.9403	0.9437	0.1762	0.80

1) The minimal amount of solution calculated by Eq. (4).

estimated by $m = 0.17/x$, where x indicates the mass fraction of H_2O_2 .

From the variance analysis it also concluded that the amounts of KI and H_2SO_4 only gave significant influences to the titration results. Excess amounts of KI and H_2SO_4 gave negative titration response in the solution with the relative low content of H_2O_2 , while insufficient amounts of KI and H_2SO_4 gave the same response in the solution with the relative high one. The maximum amounts of KI and H_2SO_4 were not more than 8 ml and 7 ml respectively at the relative low mass fraction of H_2O_2 ($< 0.5\%$), and the minimum amounts of them were not less than 3 ml and 2 ml respectively at the relative high one ($> 3.3\%$). The titration results of the true mass fraction between 0.5% to 3.3% would be well consistent with the true value with the amount of KI between 3 ml to 8 ml and the amount of H_2SO_4 between 2 ml to 7 ml.

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