Detection of citraconic anhydride with gas chromatography

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Abstract: The content of citraconic anhydride is analyzed by a gas chromatography in this study. Using HP6890A gas chromatography with hydrogen flame ionization detector, SE-54 capillary column (50 m × 0.53 mm × 1.00 μm) as the stationary phase and *cis*-butenedioic anhydride as internal standard, a practical temperature programmed method for determination of citraconic anhydride content is built up. The GC recovery and repeatability indicate that this method is accurate and precise for determination of content of citraconic anhydride in mixed liquid.

Key words: gas chromatography; hydrogen flame detector; internal standard method; citraconic anhydride; *cis*-butenedioic anhydride

1 experiments

1.1 equipments

HP6890A Gas Chromatograph, Hydrogen flame ionization detector(FID), ZB-2020 Chromatography data processing workstation, One ten-thousandth Analytical Balances.

1.2 chemiclas

Citraconic anhydride purity 98%min, Maleic anhydride:Analytical purity, Ethyl acetate :Analytical purity, o-Xylene :Analytical purity, N,N-Dimethylformamide :Analytical purity.

1.3 Chromatographic conditions

SE-54 Column: 50m *0.53mm*1.00μm; Vaporization chamber temperature: 255℃; Detector temperature: 270℃; Column temperature: program temperature, initial temperature 70℃, hold 2min, temperature gradient 20℃/min, final temperature 250℃, hold 2min; carrier gas: nitrogen; column pressure: 65kPa; 0.5 μL injection needle; injection method: manual injection.

1.4 Steps

Under the above chromatographic conditions, qualitative analysis was performed by the retention time of each substance. Inject the citraconic acid anhydride sample 0.1μL, gas chromatography shown in Figure 1:
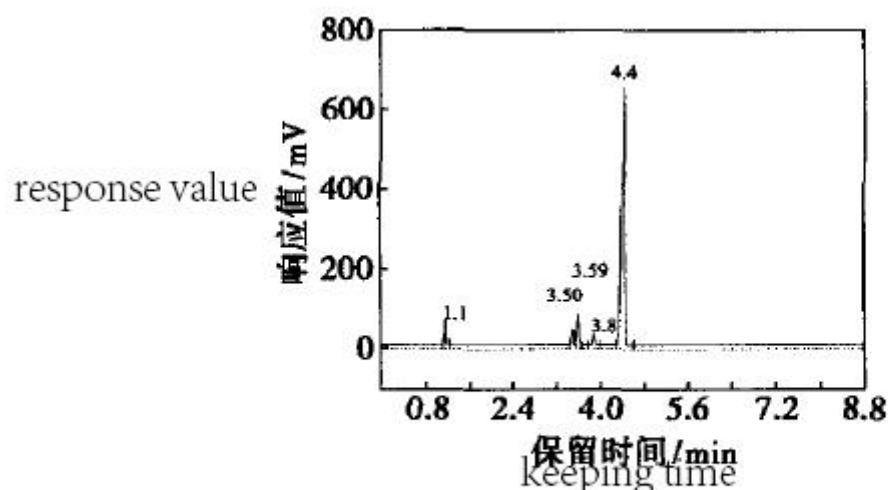

图 1　柠康酸酐样品谱图
citranoic anhydride sample Spectrogram

As can be seen from Figure 1, each group of peak separation effect is good, peak-symmetrical, and after repeated measurements, good reproducibility, easy operation and speed.

2 Experimental results and analysis

2.1 Qualitative analysis

Inject analytical purity Citraconic anhydride, Maleic anhydride(soluded in Ethyl acetate), Ethyl acetate, o-Xylene, N,N-Dimethylformamide, each 0.1μL, According to their respective retention time, the samples

were qualitatively analyzed. The retention time of each sample is shown in the figure below:

表1 各分析纯样品的保留时间

name 名称	keeping time 保留时间/min	name 名称	keeping time 保留时间/min
乙酸乙酯 ethyl acetate	1.981	二甲苯 Maleic anhydride	5.024
N,N-二甲基甲酰胺 DMF	3.530	柠康酸酐 Citraconic anhydride	5.487
顺丁烯二酸酐 Maleic anhydride	4.389		

2.2 Quantitative analysis

2.2.1 Determination of the calibration curve

Because the response values of different substances on the detector are different, the data measured according to the area normalization method will be biased. Consider using the internal standard method to draw the relative calibration factor standard curve. According to the selection principle of the internal standard, maleic anhydride is only one methyl group less than citraconic anhydride in structure, and can be selected as an internal standard. Ethyl acetate is used as the internal standard solvent.

The content of citraconic acid anhydride was in the range of 0%-90% without the detection of internal standard substance. If 2g sample is assumed to be selected, then the points of the standard curve are selected as 10%, 20%, 30%, 40%, 50%. , 60%, 70%, 80% and 90%. Relative correction factor calculation formula:

$$f = (A_s/A_i) \times (m_i/m_s) \qquad (1)$$

In the formula, A_i is citraconic acid anhydride area, A_s is maleic anhydride area, m_s is Maleic anhydride quality, m_i is citraconic acid anhydride quality.

The specific data is shown in the figure below:

表2 内标法标准曲线测定数据

编号 no.	m(柠康酸酐)/ citraconic anhydrite g	m(马来酸酐)/ maleic anhydride g	m(乙酸乙酯)/ ethyl acetate g	校正 correction 因子 f factor
1	0.2082	0.2083	0.5107	0.9236
2	0.4093	0.2036	0.5016	0.9724
3	0.6051	0.2031	0.5349	0.9736
4	0.8596	0.2028	0.5190	0.9781
5	1.0111	0.2057	0.5067	0.9648
6	1.2141	0.4002	1.0130	0.9593
7	0.7169	0.2026	0.5203	0.9600
8	0.8409	0.2119	0.5224	0.9566
9	0.9251	0.2105	0.5016	0.9638

Based on the above data, except for the lower mass fraction (10%), the response factors for the remaining mass fractions are essentially flat, ie, the mass fraction has little effect on the relative correction factor of citraconic anhydride.

2.2.2 Product Analysis Results

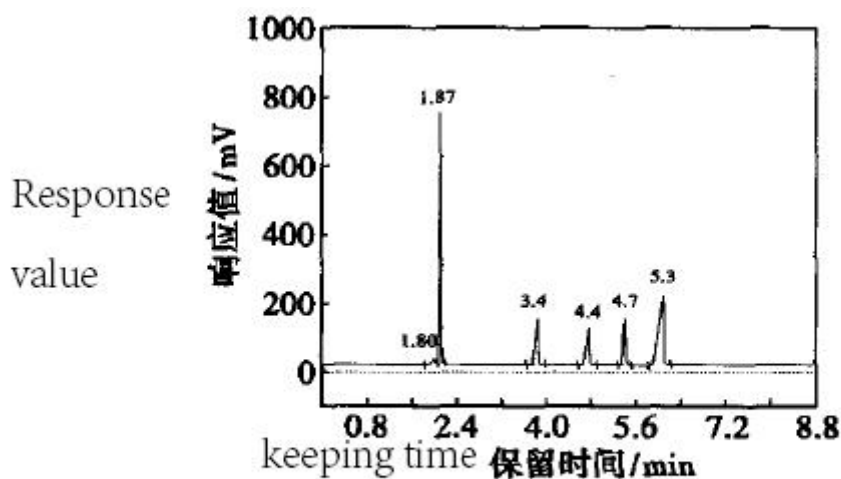The gas chromatogram of reaction sample PK52-6 is shown below:

图2 pk52-6 的气相色谱图

表3　pk52-6 的气相色谱数据

编号	保留时间/min	名称	峰面积	峰面积百分比/%
1	1.803	Acetic acid 乙酸	97694	2.313
2	1.877	Ethyl acetate 乙酸乙酯	1425363	33.75
3	3.422	DMF	539445	12.77
4	4.4758	Maliec anhydride 马来酸酐	431442	10.22
5	4.785	o-Xylene 二甲苯	417284	9.881
6	5.398	Citraconic anhydride 柠康酸酐	1298317	30.74

Citraconic anhydride mass fraction formula:

$$CA\% = f \times (A_i/A_s) \times (m_s/m_t) \times 100\% \qquad (2)$$

In the formula, A_i is citraconic acid anhydride area, A_s is maleic anhydride area, m_s is Maleic anhydride quality, m_t is sample quality. f is correction factor.

According to the above figure, the mass fraction of the reaction product citraconic anhydride is calculated to be 57.99%

2.2.3 Selection of column analysis conditions

Because of the different degrees of detection under different conditions of the separation will be very different. The column temperature is constant at 250℃, and the spectrum of the column temperature from 70℃ to 20℃/min to 250℃ is shown in Fig. 3 and Fig. 4, respectively. It can be seen from Fig. 3 and Fig. 4 that the degree of spectral resolution obtained by program temperature rise is OK, so choose a program to heat up the sample for analysis.
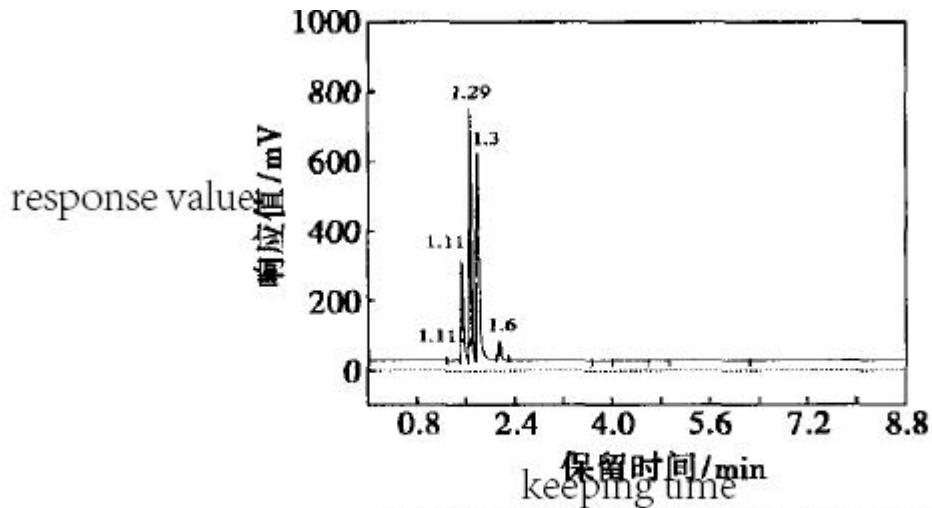
response value 响应值/mV

保留时间/min
keeping time

Spectrogram at constant temperature

图 3　恒温条件下的谱图

response value 响应值/mV
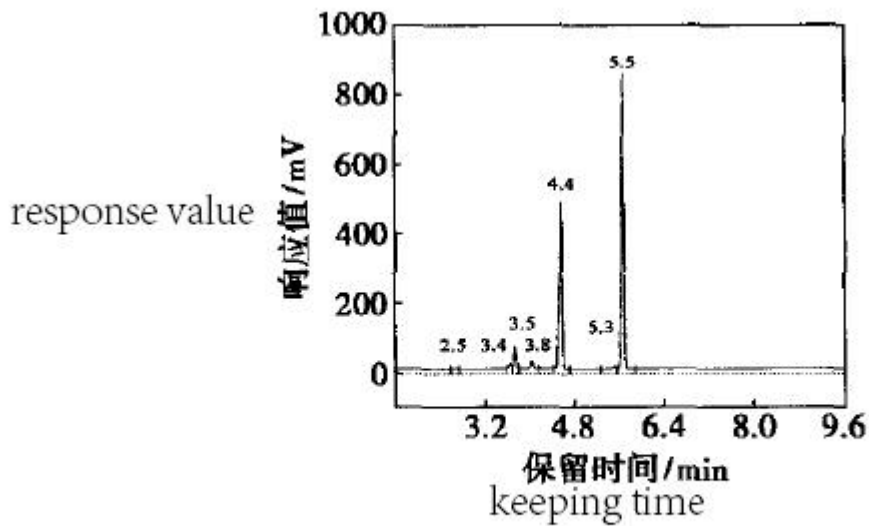
保留时间/min
keeping time

图 4　程序升温条件下的谱图
Spectrograms at elevated temperatures

2.3.4 Measurement of method accuracy and reproducibility

In order to verify the accuracy of the response factor, a standard solution with a mass fraction of 10% to 90% (mass gradient of 10%) was used to determine the mass fraction and calculate the gas chromatographic recovery rate:

$$R = f \times (A_i/A_s) \times (m_s/m_t) \times (1/m_i) \times 100\% \quad (3)$$

In the formula, A_i is citraconic acid anhydride area, A_s is maleic anhydride area, m_s is Maleic anhydride quality, m_i is citraconic acid anhydride quality. f is correction factor.

The recovery data is shown in the figure below：

表4　柠康酸酐回收率
Citric acid anhydride recovery rate

编号 no.	m(柠康 酸酐)/g citraconic anhydride	m(马来 酸酐)/g maliec anhydride	m(邻二 甲苯)/g of Xylene	m(乙酸 乙酯)/g ethyl acetate	回收率 recovery rate R/%
1	0.1148	0.1003	0.8959	0.5048	98.49
2	0.2218	0.1050	0.7990	0.5058	100.10
3	0.3106	0.1022	0.7004	0.5239	98.46
4	0.4107	0.1171	0.6409	0.5016	102.20
5	0.5130	0.1011	0.5079	0.5151	103.20
6	0.7032	0.2012	0.3323	0.5096	98.21
7	0.9032	0.2014	0.1035	0.5061	97.69

As the above table shows, the recovery rate is between 97% and 103%, so the measurement accuracy of the response factor is relatively high.

To verify the reproducibility of the method, the same product (pk52-6) was measured five times as described above. The results are shown in the following table:

表5　柠康酸酐质量分数测定重复性实验数据
Citraconic anhydride mass fraction determination repeatability experimental data

编号 No.	w(柠康酸酐)/ % citraconic anhydride	平均值 average value ($\overline{X}$)	标准差 (S) Standard deviation	相对标准偏差 Relative standard deviation (RSD)/%
1	57.9887			
2	55.7773			
3	56.2323	56.7934	0.8468	1.491
4	56.8862			
5	57.0824			

As can be seen from the above table, the relative standard deviation of the test is 1.491%, and the reproducibility is good.

3 Conclusion

The maleic anhydride was selected as the internal standard. The reaction liquid of citraconic anhydride was analyzed by temperature-elevated gas chromatography using SE-54 capillary column procedure. The results showed that the method had high resolution and good peak shape. After verification, the method was validated. The reproducibility and accuracy of the measurement results are high and can meet the requirements of scientific research production.