Use B-spline interpolation fitting baseline for low concentration 2, 6-di-tertbutyl p-cresol determination in jet fuels by differential pulse voltammetry

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Abstract. The B-spline interpolation fitting baseline in electrochemical analysis by differential pulse voltammetry was established for determining the lower concentration 2,6-di-tert-butyl p-cresol(BHT) in Jet Fuel that was less than 5.0 mg/L in the condition of the presence of the 6-tert-butyl-2,4-xylenol.The experimental results has shown that the relative errors are less than 2.22%，the sum of standard deviations less than 0.134mg/L, the correlation coefficient more than 0.9851. If the 2,6-ditert-butyl p-cresol concentration is higher than 5.0mg/L, linear fitting baseline method would be more applicable and simpler.

1. Introduction

Taking characteristic peak of a substance as the shoulder peak of another is a common way to analyze overlapping peaks in spectral analysis [1]. For accurately picking up the shoulder peak and determining its height or area, the primary task is to the baseline definition of the overlapped shoulder peak, which directly makes a great impact on the accuracy and precision of the determination [2]. For the obvious shoulder peak, the baseline is determined by the line passing through the starting point and end point of shoulder peak. But if the concentration of the substance concerned is lower, its peak will be seriously overlapped, it is impossible to determine the linear baseline because the starting and end point of the peak could not be acquire daccurately [3].The phenomenon was also found in examining the adaptability of determining 2, 6-di-tert-butyl-p-cresol (BHT) in jet fuel by differential pulse voltammetry in the condition of the presence of the more than one antioxidants [4]. The mixed antioxidant is composed of BHT, 6-tert-butyl-2, 4-xylenol and p-cresol. If the BHT in the mixed antioxidant is as low to 15%~20% and the 24.0 mg/L mixed antioxidants are added in jet fuel, the BHT oxidation peak will be concealed by the oxidation peak of 6-tert-butyl-2,4-xylenol and the baseline cannot be determined. So a new baseline determination method must be established.

2. Basic Principle

2.1. B-spline Interpolation Fitting

B-spline which suggested by Schoenberg in 1946, essentially is a method of segmented curve fitting and is applied in free curve and surface modeling widely for its characteristic of low order smooth[4-6].

$\{(x_i, y_i)\}_{i=1}^n$ is the electrochemical data point range in two-dimensional space and P represented the nodes in x axis , x_i is increasing sequence:

$$P_0 = min\, x_i = x_0 = a, \quad P_{N+1} = max\, x_i = x_n = b \tag{1}$$

The number of internal nodes in $B = [a, b]$ is N, and P_0, P_{N+1} are as the boundary nodes [7]. After defining the sequences of nodes, $B_j^k(x)$ is can be computed by DeBoor-Cox [4], which is k or $k-1$ order B-spline function on x.

$$B_j^k(x) = \begin{cases} B_j^1(x) = \begin{cases} 1, & P_j < x < P_{j+1} \\ 0, & \text{other} \end{cases} \\ B_j^k(x) = \frac{x-P_j}{P_{j+k-1}-P_j} B_j^{k-1}(x) + \frac{P_{j+k}-x}{P_{j+k}-P_{j+1}} B_{j+1}^{k-1}(x) \end{cases} \tag{2}$$

The B-spline curve equation on $\{(x_i, y_i)\}_{i=1}^n$ is written as follow: $y = \sum_{j=-k+1}^N c_j B_j^k(x)$, where $\{c_j\}$ is column vector of control factor.

If $B_j^k(x_i) = t_{i,j}$, $\{(x_i, y_i)\}_{i=1}^n$ could be expressed by the equations (3):

$$Y_n = T_n C_n + E_n \tag{3}$$

Where $Y_n = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}$, $T_n = \begin{bmatrix} t_{1,-k+1} & \cdots & t_{1,N} \\ \vdots & \ddots & \vdots \\ t_{n,-k+1} & \cdots & t_{n,N} \end{bmatrix}$, $C_n = \begin{bmatrix} c_{-k+1} \\ c_{-k+2} \\ \vdots \\ c_{-k+n} \end{bmatrix}$, fitting error $E_n = \begin{bmatrix} e_1 \\ e_2 \\ \vdots \\ e_n \end{bmatrix}$.

Here it's used for determining the baseline of the electrochemical characteristic curve of BHT. The key is to determine the peak width of BHT. The electrochemical characteristic curve of antioxidant mixture described above is shown in figure 1.Where the concentration ratio of three main additives which are BHT, 6-tert-butyl-2, 4-xylenol and 6-tert-butyl-2,4-xylenol is 3:15:2.

The BHT peak width is determined by the following method. Combining $\{(x_i, y_i)\}_{i=1}^n$ and $R_{j,x_i} = \Delta \frac{d_{y_i}}{d_{x_i}}$, the sequence is obtained:

$$R_{j,x_i} = \{R_{j,0} = \Delta_a \frac{d_{y_i}}{d_{x_i}}, R_{j,N+1} = \Delta_b \frac{d_{y_i}}{d_{x_i}} / j \in Z^*\} \tag{4}$$

Where R_{j,x_i} can determine the peak width, j is the sequence of $R_{j,x_i} = 0$. According to figure 1 and figure 2, the BHT peak width node could be determined by the following criteria:

$$\left[x_{R_{1,x_i}=0}, x_{maxR_{j,x_i}}\right], \text{ where } x_i \in \left[x_{R_{1,x_i}=0}, x_{R_{2,x_i}=0}\right]$$

2.2. Signal processing algorithm

(1)Input the original data, the smooth curve by Savitzky-Golay smooth in figure 1 is indicated in red. Here using the 27 points Savitzky-Golay filter will offer a better fit, because it can retain the more information as much as possible.

(2)Determine the peak width of BHT by 1st derivative curve of smooth curve and the blue line area, $\left[x_{R_{1,x_i}=0}, x_{maxR_{j,x_i}}\right]$ is the peak width, shown in feigure 2.

(3) Fit the curve of 6-tert-butyl-2, 4-xylenol based on B-spline interpolation method, then taking it as the baseline of BHT, shown in figure 3.

(4) Fit with GuassAmp after subtracting baseline, obtain the peak height of the oxidation peak, shown in figure 4.

(5) Construct a standard addition calibration plot and calculate BHT concentration in jet fuel.

Here the standard addition curve is calculated by following equation: $i_p(\times 10^{-7}A) = kc + b$, c as the BHT standard addition concentration c(mg/L) and $i_p(\times 10^{-7}A)$ as the oxidation peak height.

The BHT concentration in jet fuels is calculated by equation (5):

$$c_0 = \frac{b}{k} \times \frac{V}{V_0}.$$

(5)

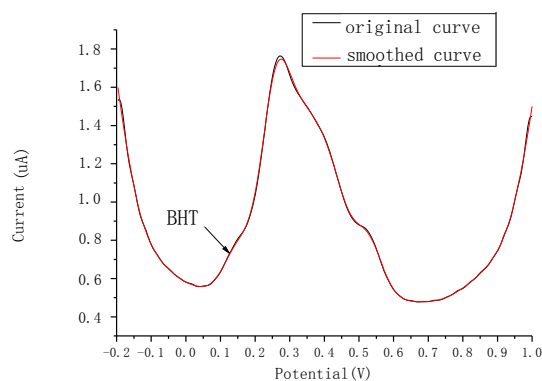Here c_0(mg/L) is the BHT concentration in sample, V is volume of volumetric flask,V_0 is sampling volume.

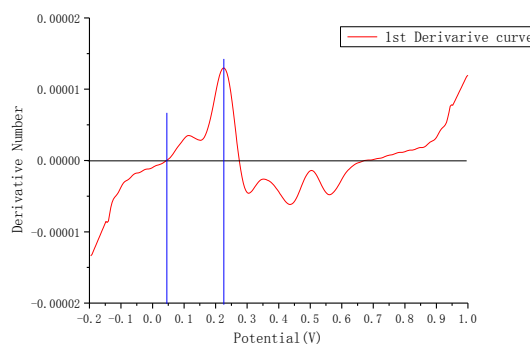

Figure. 1 The characteristic electrochemical curve.
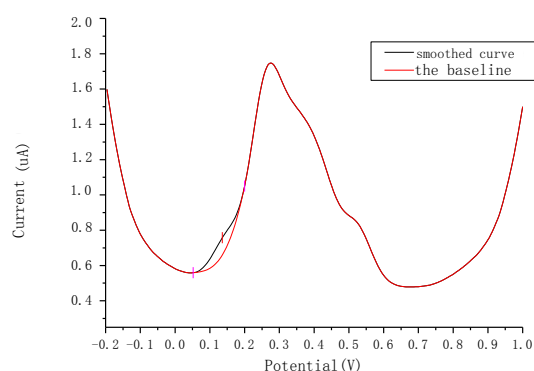

Figure. 2 The BHT peak width.

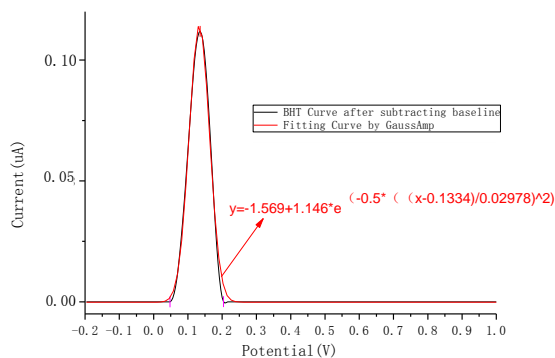**Figure. 3** The baseline difined by b-spline.

Figure. 4 The BHT GuassAmp curve.

3. Experiments

3.1. Materials and instruments

3.1.1. Materials. Absolute ethyl alcohol (AR, Chongqing Chuandong Chemical Co.),KOH (AR, Chongqing Chuandong Chemical Co. Ltd.), n-heptane (AR, Tianjin Kermel Reagent Co.Ltd.), 2,6-di-tertbutylp-cresol(BHT,AR, Chengdu Kelong Chemical plant),p-cresol and 6-tert-butyl-2,4-xylenol (AR, Shanghai Ziyi Reagent Factory),qualitative filter paper, volumetric flasks (100mL,50 mL and10mL),pipets, beakersand weighing bottles (25mm×40mm).

Absolute alcohol saturated with KOH, BHT in n-heptane (500mg/L), p-cresol in n-heptane solution(500mg/L), 6-tert-butyl-2,4-xylenol in n-heptane solution(500mg/L) and Jet fuel containing BHT 8.0mg/L. The seven Jet-fuel samples have been formulated as shown in table 1.

3.1.2. Instruments. Electrochemical station(CHI1230, Shanghai Chenhua instrument company, China) with the composite electrode consisted of glassy carbon work electrode, platinum wire auxiliary electrode and reference electrode. The Absolute ethyl alcohol saturated with KOH was used as supporting electrolyte. The electrochemical characteristic curve of the samples was determined by differential pulse voltammetry.

Instrument conditions: the voltage scan range0.0V to1.0V, the voltage increment 0.005V, the pulse amplitude0.05V, pulse width 0.05s, sampling width 0.01s, silence time 2.0s and sensitivity 1×10^{-5}A/V.

Table 1. Main additives concentration of prepared Jet fuel samples.

Samples	Antioxidant Concentration(mg/L)		
	BHT	6-tert-butyl-2,4-xylenol	p-cresol
A	3.6	20.4	0.0
B	3.6	13.2	7.2
C	5.0	13.2	5.8
D	5.0	18.0	1.0
E	5.0	19.0	0.0
F	10.0	14.0	0.0
G	10.0	13.2	0.8

3.2. Electrochemical analysis

All standard addition solutions were prepared with 10mL volumetric flask at room temperature. The addition concentrations of BHT in samples were 0.0mg/L, 5.0mg/L, 15.0mg/L and 25.0mg/L respectively. The standard addition solutions have been formulated according to the following steps: get the four 10mL volumetric flasks, fill 9.0mL samples in each flask, then add 0.00mL, 0.10mL, 0.30mLand 0.50mL BHT standard addition solution respectively and finally append n-Heptane in each flask to 10mL.

2mL standard addition solution and 2mL supporting electrolyte were added in electrolytic cell respectively. In order to make the solution mixed completely, it is imperative to shake the cell at least10 seconds, and then the composite electrode is inserted in electrolytic cell. The electrochemical analysis was conducted according to the given conditions. Each standard addition solution was measured at least 5 times.

4. Results and discussion

The relative error Δc_0 and the sum of standard deviations were used for expressing accuracy and precision of the method.The correlation coefficient also named Pearson's R is used as criterion of linearity. They could be calculated as following:

$$s= \sum_{c=0}^{c=25} \delta_i, \; \delta_i = \sqrt{\frac{\sum_{c=0}^{c=25}(x_i-\bar{x})^2}{n-1}}(mg/L) \tag{6}$$

$$\Delta c_0 = \frac{c_0-c}{c} \times 100\% \tag{.7}$$

$$R(X,Y) = \frac{Cov(X,Y)}{\sqrt{Var[X]Var[Y]}} \tag{8}$$

Where $Cov(X,Y)$ is the covariance of variable X and Y, $Var[X]$ means the variance about variable X.

The results of sample A to E calculated by B-spline Fitting baseline are shown in table2 and figure 5(a). When the concentration is 10.0mg/L, the results of sample F to G calculated by B-spline Fitting Baseline and Linear Fitting Baseline are shown in table 3 and figure 5(b).

When the BHT level is 3.6~5.0mg/L, the method of linear fitting baseline cannot achieve any effective information about the peak of BHT. However the method of B-spline fitting baseline could get the datas shown in the table 2 and figure 5(a), the relative errors are less than 2.22%, the sum of standard deviations less than 0.134mg/L and R greater than 0.9851. When the BHT concentration is higher than 5.0mg/L, the two baseline definition methods will have the similar ability shown in the table 3 and figure5 (b). Therefore the b-spline fitting baseline is helpful to gain more test information, no matter in high or low concentration of BHT conditions. And it is more suitable especially in the low concentration. For the linear fitting baseline method, only the concentration is higher than 5.0mg/L, it is more applicable and simpler, because the peak of BHT in the characteristic electrochemical curve is more obvious that the peak height can be obtained.

Table 2. The results of sample A to E with b-spline fitting baseline.

peak height/10^{-7}A sample and times		standard addition concentration/mg/L				BHT concentration/mg/L
		0	5	15	25	
sample A	1	0.1224	0.5269	1.028	1.547	
	2	0.1237	0.5259	1.035	1.551	
	3	0.1271	0.5278	1.041	1.541	
	4	0.1296	0.5252	1.030	1.550	3.68
	5	0.1248	0.5238	1.029	1.548	
average		0.1255	0.5259	1.033	1.547	
precision		s=0.014 , Δc_0 =2.22% , R=0.9963				
sample B	1	0.1389	0.4121	0.8766	1.434	
	2	0.1416	0.4223	0.8175	1.336	
	3	0.1336	0.4105	0.9214	1.369	
	4	0.1372	0.4102	0.8732	1.322	3.52
	5	0.1336	0.4107	0.9023	1.313	
average		0.1370	0.4132	0.8782	1.355	
precision		s=0.097 , Δc_0 = -2.22% , R=0.9994				
sample C	1	0.6941	1.446	2.416	4.221	
	2	0.6756	1.445	2.428	4.332	
	3	0.6675	1.451	2.433	4.232	
	4	0.6691	1.442	2.419	4.444	5.05
	5	0.6828	1.443	2.421	4.344	
average		0.6778	1.445	2.423	4.315	
precision		s=0.113 , Δc_0 = 0.60% , R=0.9903				
sample D	1	0.3960	0.6213	1.203	2.083	
	2	0.3975	0.5988	1.217	2.097	
	3	0.3950	0.5992	1.214	2.094	
	4	0.3910	0.6024	1.211	2.086	5.10
	5	0.3966	0.6136	1.221	2.099	
average		0.3952	0.6071	1.213	2.092	
precision		s=0.026 , Δc_0 = 2.00% , R=0.9915				
sample E	1	0.5372	1.036	1.695	3.162	
	2	0.5198	1.048	1.693	3.163	
	3	0.5284	1.010	1.697	3.162	
	4	0.5360	1.012	1.711	3.169	5.05
	5	0.5297	1.029	1.702	3.159	
average		0.5302	1.027	1.699	3.163	
precision		s=0.034 , Δc_0 = 1.00% , R=0.9851				

Define the limits of quantification (LOD) as the smallest amount of analysis that can be tested with full certainty, then the LOD can be represented with the amount of analysis that average is $\mu_B + 6\delta_B$, here δ_B is standard deviation. The IUPAC defined that the LOD is the amount of analysis that average based on $\mu_B + 3\delta_B$, which is a conditional concept depended on the repeated times and risk of test. The limits of quantification (LOQ) is defined as the minimum concentration of reliable determination and quantification of analyte in a particular degree of confidence. Typically, the LOD for an analysis method is defined as $3\delta_B$ and LOQ is defined as $10\delta_B$.

Here, δB were obtained under the conditions which tested 5 times repeatedly for a particular concentration of antioxidants (3.6~10.0 mg/L) by the antioxidants determination method and analyzed the information to obtain the results by the presented method. The largest standard deviation was

0.303 mg/L from table 3 and table 4, thus the LOD and LOQ should be 0.909mg/L and 3.03mg/L respectively.

Table 3. The results of sample F to G with B-spline Fitting Baseline and Linear Fitting Baseline.

sample and times (peak height/10^{-7}A)		standard addition concentration/mg/L				BHT concentration/mg/L
		0	5	15	25	
linear fitting baseline	sample F					
	1	1.124	1.456	3.034	4.177	
	2	1.139	1.842	3.110	4.187	
	3	1.147	1.556	3.207	4.122	10.11
	4	1.104	1.664	2.924	4.107	
	5	1.147	1.655	3.327	3.969	
average		1.132	1.635	3.120	4.112	
precision		s=0.404 , $\Delta c_0 = 1.10\%$, R=0.9963				
bspline fitting baseline	sample F					
	1	1.224	1.733	3.225	4.351	
	2	1.229	1.725	3.218	4.359	
	3	1.227	1.745	3.205	4.353	10.29
	4	1.224	1.724	3.231	4.357	
	5	1.227	1.734	3.119	4.352	
average		1.226	1.732	3.120	4.354	
precision		s=0.060 , $\Delta c_0 = 2.90\%$, R=0.9992				
linear fitting baseline	sample G					
	1	0.8022	1.313	2.325	2.987	
	2	0.8061	1.325	2.258	2.988	
	3	0.8094	1.345	2.245	2.997	10.82
	4	0.8089	1.324	2.246	2.998	
	5	0.8052	1.314	2.259	3.075	
average		0.8064	1.324	2.267	3.009	
precision		s=0.086 , $\Delta c_0 = 8.20\%$, R=0.9976				
bspline fitting baseline	sample G					
	1	0.8112	1.313	2.325	2.972	
	2	0.8181	1.325	2.258	2.981	
	3	0.8114	1.345	2.245	2.987	10.93
	4	0.8119	1.324	2.246	2.998	
	5	0.8112	1.314	2.259	3.075	
average		0.8128	1.324	2.267	3.003	
precision		s=0.090 , $\Delta c_0 = 9.30\%$, R=0.9976				

(a) b-spline fitting baseline   (b) b-spline fitting baseline and linear fitting baseline
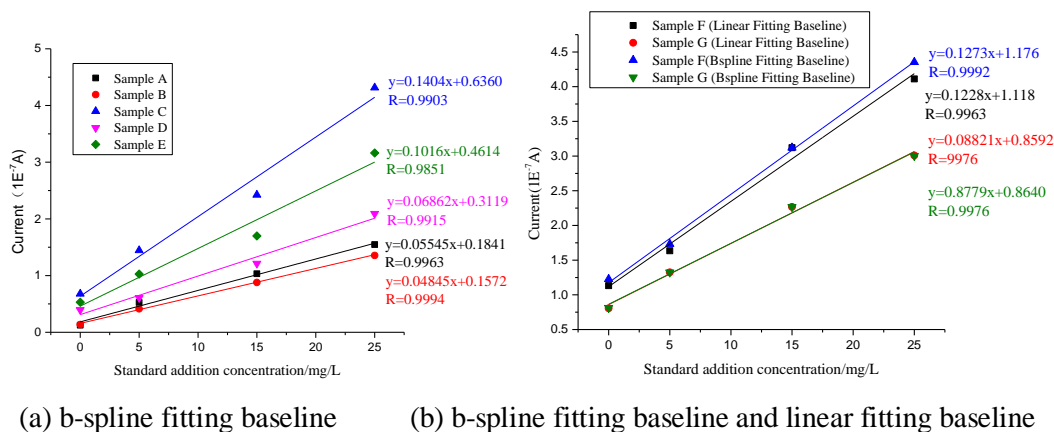
Figure 5. The curve of standard addition concentrations vs peak height.

Table 4. The BHT concentration test results of sample A to G.

sample	BHT actual concentration /mg/L	BHT test concentration /mg/L						relative error Δc_0 /%	standard deviations /mg/L
		1	2	3	4	5	average		
A	3.6	3.64	3.64	3.78	3.72	3.64	3.68	2.22%	0.064
B	3.6	3.03	3.68	3.44	3.7	3.77	3.52	-2.22%	0.303
C	5.0	5.39	4.98	5.23	4.63	5.02	5.05	1.00%	0.287
D	5.0	5.26	5.03	5.02	5.03	5.14	5.10	2.00%	0.104
E	5.0	5.15	5.07	4.94	5.01	5.08	5.05	1.00%	0.079
F	10.0	10.3	10.26	10.37	10.28	10.23	10.29	2.90%	0.053
G	10.0	11.07	11.12	10.88	10.80	10.80	10.93	9.30%	0.152

5. Conclusion

As shown above, the baseline fitting method based on b-spline interpolation was established for determining the low BTH in jet fuel interfered by other antioxidants with electrochemical method. When the BHT concentration was as low as 3.6mg/L-5.0mg/L in the presence of the 6-tert-butyl-2, 4-xylenol, it was difficult to define the baseline of BHT peak. The baseline fitting method based on b-spline interpolation could solve this problem. With the method determining BHT in jet fuel at low concentration(3.6~5.0mg/L), its relative errors are less than 2.22%，the sum of standard deviations less than 0.113mg/L and R more than 0.9851.

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