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

D S Wen¹, H Wen², Y G Shi¹, ⁴, B Su³, Z C Li¹ and G Z Fan¹
¹Department of Training, Army Logistics University of PLA, Chongqing 401311, PRC
²Department of Oil Quality and Technical Supervision, Navy 91458, Hainan 572000, PRC
³Oil Application Group, Beijing Oil Research Institute, Beijing 102310, PRC
⁴E-mail: ygshi@126.com

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-xylene. 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 accurately [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-xylene 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-xylene 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:

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

(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 \(x\).

\[B_j^k(x) = \begin{cases} 1, & P_j < x < P_{j+1} \\ 0, & \text{other} \end{cases} \]

(2)

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

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

\[Y_n = T_n C_n + E_n\]

(3)

Where \(Y_n = \left[\begin{array}{c} y_1 \\ y_2 \\ \vdots \\ y_n\end{array}\right], T_n = \left[\begin{array}{cccc} 1 & \cdots & 1 & \cdots & 1 \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ 1 & \cdots & 1 & \cdots & 1\end{array}\right], C_n = \left[\begin{array}{c} c_{-k+1} \\ c_{-k+2} \\ \vdots \\ c_{-k+n}\end{array}\right], E_n = \left[\begin{array}{c} e_1 \\ e_2 \\ \vdots \\ e_n\end{array}\right].\]

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-xyleneol and 6-tert-butyl-2,4-xyleneol is 3:15:2.

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

\[R_j x_i = \{R_j, 0 = \Delta a \frac{dy_i}{dx_i}, R_{j,N+1} = \Delta b \frac{dy_i}{dx_i} / j \in Z^*\}\]

(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:

\[x_{R_{1,x}} = 0, x_{maxR_{j,x}}\]

where \(x_i \in \left[\begin{array}{c} x_{R_{1,x}} = 0 \cdot x_{maxR_{j,x}} = 0 \end{array}\right]\)

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, \(x_{R_{1,x}} = 0, x_{maxR_{j,x}}\) is the peak width, shown in figure 2.

(3) Fit the curve of 6-tert-butyl-2, 4-xyleneol 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 curve plot and calculate BHT concentration in jet fuel.

Here the standard addition curve is calculated by following equation: \(t_p (\times 10^{-7}A) = kc + b, c\) as the BHT standard addition concentration (mg/L) and \(t_p (\times 10^{-7}A)\) as the oxidation peak height.
The BHT concentration in jet fuels is calculated by equation (5):

\[
c_0 = \frac{A}{V_0} \cdot \frac{V}{V_0}.
\]

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 defined 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-xyleneol (AR, Shanghai Ziyi Reagent Factory), qualitative filter paper, volumetric flasks (100mL,50 mL and10mL), pipets, beakers and 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-xyleneol 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-xyleneol | 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, 0.30mL and 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 $\Delta c_0$ 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:

$$s = \sum_{i=0}^{25} \delta_i, \quad \delta_i = \frac{\sum_{i=0}^{25}(x_i-x)^2}{n-1} (mg/L)$$  \hspace{1cm} (6)

$$\Delta c_0 = \frac{c-\bar{c}}{c} \times 100\%$$  \hspace{1cm} (7)

$$R(X,Y) = \frac{Cov(X,Y)}{\sqrt{Var(X)Var(Y)}}$$  \hspace{1cm} (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 figure 5(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.

| sample and times | peak height/10^`A` | 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                  |
| 5                | 0.1248             | 0.5238                             | 1.029                  | 1.548                  |
| average          | 0.1255             | 0.5259                             | 1.033                  | 1.547                  |
| precision        | s=0.014 , Δc₀ =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                  |
| 5                | 0.1336             | 0.4107                             | 0.9023                 | 1.313                  |
| average          | 0.1370             | 0.4132                             | 0.8782                 | 1.355                  |
| precision        | s=0.097 , Δc₀ =-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                | 0.6828             | 1.443                              | 2.421                  | 4.344                  |
| average          | 0.6778             | 1.445                              | 2.423                  | 4.315                  |
| precision        | s=0.113 , Δc₀ = 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                | 0.3966             | 0.6136                             | 1.221                  | 2.099                  |
| average          | 0.3952             | 0.6071                             | 1.213                  | 2.092                  |
| precision        | s=0.026 , Δc₀ = 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                | 0.5297             | 1.029                              | 1.702                  | 3.159                  |
| average          | 0.5302             | 1.027                              | 1.699                  | 3.163                  |
| precision        | s=0.034 , Δc₀ = 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 μB + 6ΔB, where ΔB is standard deviation. The IUPAC defined that the LOD is the amount of analysis that average based on μB + 3ΔB, 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 3ΔB and LOQ is defined as 10ΔB.

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 | Standard addition concentration/mg/L | BHT concentration/mg/L |
|------------------|-------------------------------------|------------------------|
|                  | 0  | 5  | 15 | 25 |                      |
| Linear fitting   |    |    |    |    | 10.11                 |
| 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               |
|                  | 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, Δc₀ = 1.10%, R = 0.9963 |
| B-spline fitting |    |                                |
| 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               |
|                  | 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, Δc₀ = 2.90%, R = 0.9992 |
| Linear fitting   |    |                                |
| 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               |
|                  | 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, Δc₀ = 8.20%, R = 0.9976 |
| B-spline fitting |    |                                |
| 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               |
|                  | 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, Δc₀ = 9.30%, R = 0.9976 |

**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 Δε₀ /% | standard deviations /mg/L |
|--------|-------------------------------|-----------------------------|----------------------|--------------------------|
| A      | 3.6                           | 3.64 3.64 3.78 3.72 3.64   | 2.22%                | 0.064                    |
| B      | 3.6                           | 3.03 3.68 3.44 3.77 3.52   | -2.22%               | 0.303                    |
| C      | 5.0                           | 5.39 4.98 5.23 4.63 5.02   | 1.00%                | 0.287                    |
| D      | 5.0                           | 5.26 5.03 5.02 5.14 5.10   | 2.00%                | 0.104                    |
| E      | 5.0                           | 5.15 5.07 4.94 5.01 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-xylanol, 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.

Acknowledgments
This work is supported by national standard program 20090226-T-469.

References
[1] Hu Y G, Zhang X X, Zhao Z Y et al 2012 Strategy and implementation of resolve overlapping spectra based on curve fitting. Journal of Chongqing University 76-81
[2] Zhang Lei, Wang Yuming, Wang Yongjun et al. 2009 Recognition Algorithm for the peak of Chromatograph. Computer Application and Software 8 256-258
[3] Shi Yonggang, Liu Shaopu, Li Zicun et al. 2006 The Assay of AntioxidantIn Jet Fuel Based on Differentiating pulse Voltammetry. Petroleum processing and Petrochemicals 7 54-57
[4] Renner G, Weiß V 2004 Exact and approximate computation of B-spline curves on surfaces. Computer-Aided Design 36(4) 351-362
[5] Guo Jianfeng, Zhu Changqing 2000 Spline Least Squares with Two Variables and Its Application in Cartography. Engineering of Surveying and Mapping 9(4) 25
[6] Wang Renhong, Li Chongjun, Zhu Chungang et al. 2008 Computation Geometry.Beijing: Sciencepublishing company(press)
[7] Wang Xin, Fan Xianguang, Xu Yingjie et al 2014 Baseline Correction Method of Raman Spectra Based on B-spline. Spectroscopy and Spectral Analysis 8 2117-21