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PROBABILISTIC-STATISTICAL METHODS FOR DETERMINING THE ADSORPTION PEAK DESCRIBED BY THE GAUSS FUNCTION

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Abstract

The paper reports probability-statistical methods of determination of adsorption peak described by the Gaussian function. The following are presented: diagram of peak determination on excess adsorption functions pertinent to some advance given threshold values; the particularities of the determination of the end peak. As a result, after finding of the extremum peak in accordance with methods on determination of the start point and the end point we obtain the inaccuracy G, three thresholds are set, i.e., 2G, 3G and 4G, respectively. If and when signal about presence of the end does not enter before moment 4G, that curve value in this moment is taken for the end peak. At arrival of the signal, corresponding to end peak for time less than 2σ, *device gives the signal on PC that he calculated the area on subroutine, taking into account merged spades (peaks). At the time of arrivals of the signal before importance of time* 3σ *curve value is taken for the end at moment* 3σ. *In interval between* 3σ *and* 4σ *moments of the arrival the end is taken for true end. If and when signal about presence of end peak does not enter before moment* 4σ *, that curve value in this moment is taken for the end peak. Greater accuracy of the determination end peak is obtained due to this introduction that accordingly enlarges accuracy of the processing to whole information range. Thus, we obtain greater accuracy of the determination of the end peak that accordingly enlarges accuracy of information handling at determination of adsorption peak described by Gaussian function.*

Key words: *adsorption peaks, area peak, Gausses curve, integration, the start and the end points of peak.*

Determining the peak during processing means identifying points that deviate from the baseline. In automatic processing, the peak detection operation, which usually also includes the operations of setting the integration limits and determining the passage of the adsorption function through the maximum, is performed by the peak selector. The method of peak detection by determining the degree of exceeding the adsorption function of some predefined threshold values is most easily implemented [1,2,3]. In this case, the initial and final parts of the peak are lost (hatched in Fig.1).

In this case, for the detection condition and the start error, we can write:

$$y \geq y_r\,; \tag{1}$$

$$\delta_{3n} = 0{,}5 - \Phi\sqrt{\left(2\ln\frac{h}{y_r}\right)}; \tag{2}$$

where y_r is the threshold value. It is known that it does not depend on the peak and practically on the asymmetry of the peak, determined only by the ratio y_r/h.

If condition (2) is realized by a digital selector, the marginal error at starting point will have the following form:

$$\delta_{3n} = 0{,}5 - \Phi\sqrt{\left(2\ln\frac{h}{y_r} - \frac{\Delta t}{\delta}\right)}; \tag{3}$$

Where is the inquiry interval.

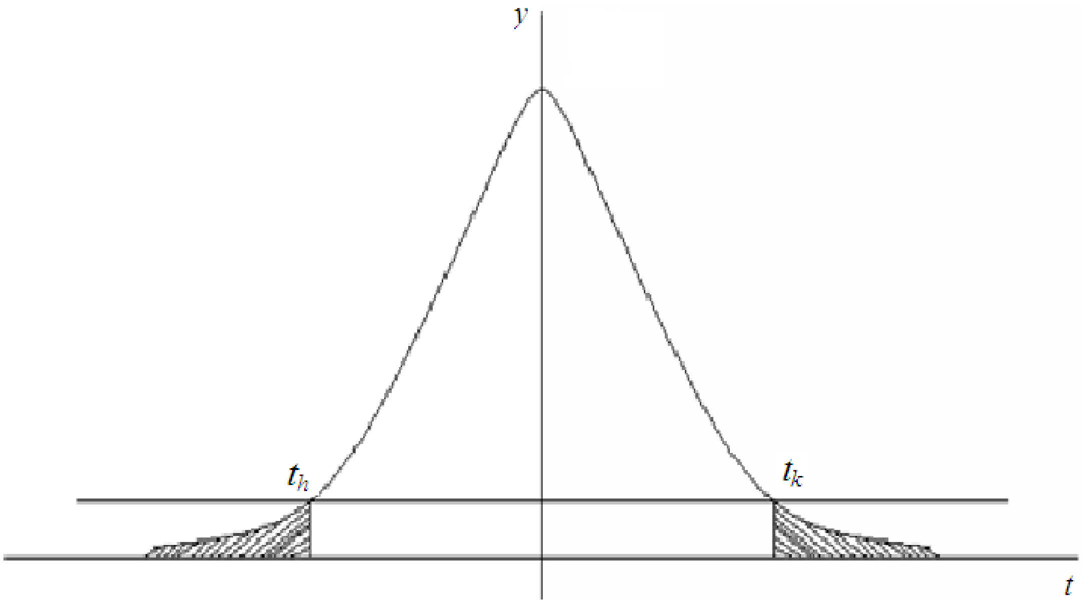

Fig. 1. The diagram for determining the peak by implementing the technique of measuring the degree of excess of the adsorption function of some predefined threshold values

Increasing the ratio (inquiry rate) decreases δ_{3n} , when $\delta/\Delta t \to \infty$ analog selection is implemented.

Peak detection with respect to the derivative is performed when the value of the derivative of the detector signal exceeds the sensitivity threshold of the selector. The resulting error in launch point:

$$\delta_{3n} = 0{,}5 - \Phi(x_r); \tag{4}$$

where x_r is the abscissa of peak detection, determined from the equation:

$$x_r f(x_r) = \frac{s\delta}{h}. \tag{5}$$

Thus, in this case δ_{3n} it depends on the parameter $s\delta/h$, increasing with its increase.

If the derivative is calculated by the incremental analog selector, then the effect of time quantization must be considered,

$$\delta_{3n} = 0{,}5 - \Phi\left(x_r - \frac{\Delta t}{\delta}\right); \tag{6}$$

where x_r is determined by the expression:

$$f(x) - f\left(x_r + \frac{\Delta t}{\delta}\right) = \frac{S'}{h}; \qquad (7)$$

In this case, the absolute value δ_{3n} has a minimum at $\delta/\Delta t$ =3 - 5. With a decrease $\delta/\Delta t$, the probability of occurrence and the value of an additional error from time quantization increases, and with an increase $\delta/\Delta t$ (decrease Δt), the error δ_{3n} increases due to a later determination of the peak.

In the case of a digital selector for the first difference, it is necessary to take into account the additional quantization by level. Assuming a a quantum value equals 1, we herewith obtain:

$$\delta_{3n} = 0{,}5 - \Phi\left(\frac{k^*\Delta t + \varepsilon}{\delta}\right); \qquad (8)$$

where k^* is determined from the equation:

$$Ent\left[hf(k^*\Delta t + \varepsilon)\right] - Ent\{hf\left[(k^* + 1)\Delta t + \varepsilon\right]\} = S^I;$$

Here Ent (A) is the integer part of the number A, K = 1,2,3, ..., K*;

ε - shift of the moment the function crosses the quantization scale in level relative to the beginning of the current interval Δt; $0 \le \varepsilon \le \Delta t$.

During the entire adsorption process, the baseline during the entire analysis changes in correlation with the applicable signal. In this case, the method with preliminary setting of threshold values leads to significant errors; therefore, it is more expedient to use the peak detection method for changing the derivative of the processed signal.

When the automatic device operates in real time, it is used to predict a change in the base signal during the passage of the peak, i.e. the baseline is extrapolated throughout the analysis (or the next peak). Usually in this case, the value of the base signal is kept constant in the device memory until the next measurement.

Compensation of the baseline drift in devices that do not have memory sections is possible only when the slope of the baseline is known in advance, in devices with existent memory it is possible to construct extrapolation polynomials or calculate the average slope *m* of the baseline in the sections until the peak is determined and this slope is maintained during occurrence of the peak [5,6]:

$$m = \frac{q\sum_{i=1}^{q-1} t_i y_i - \sum_{i=1}^{q-1} t_i \sum_{i=1}^{q-1} y_i}{q\sum_{i=1}^{q-1} t_i^2 - \left(\sum_{i=1}^{q-1} t_i\right)^2}; \qquad (9)$$

where q – is the number of averaging points when measuring the baseline.

A device operating on this principle corrects the baseline before determining the start of the peak. This is possible only with good peak separation, since with closely spaced peaks it is not possible to fix a sufficient number of points to determine a change in the slope of the baseline [7,8]. In addition, the baseline drift in most cases is random and often the behavior of the baseline before determining the start of the peak may differ from the behavior of the baseline during the passage of the peak.

For example, up to the point of the start of the peak, the slope of the baseline can monotonously increase, and during the occurrence of the peak, it can monotonously decrease, and the peak area is determined with an established error.

The authors also considered a device [9, 10] for embedding the intermediate region between two consecutive vertices of signals generated at the input of a measuring instrument and superimposed on each other. The correction of the baseline of the delayed peak superimposed on the leading one in this device is carried out by means of generating a correction signal, which is taken as the baseline, and the slope of which coincides with the slope in the rear view of the leading signal.

Moreover, the correction signal, subtracted from the original, is being generated in the course of determining the beginning of the peak. After detecting the end of the peak, the excess area of the triangle is subtracted from the peak area bounded by the curve and the line taken as the base. Thus, the correction of the baseline is possible only at peaks that vary greatly in amplitude, which is a prerequisite for the accurate generation of a correction signal, and only if a small peak follows a large one. If the peaks are comparable in amplitude and poorly separated, the correction of the baseline, carried out in this way, leads to substantial errors.

A technique of integrating the output measuring signal is revised in [4] that allows you to select the impulse noise superimposed on the useful signal. Correction of the baseline in this device is as follows. At the moment of determining the beginning of the peak and the beginning of integration, baseline correction is not performed. The result of integration is represented by the area under two peaks (peak N - noise) above a horizontal line passing through a certain point. Then, the peak area is determined by subtracting the triangle from the integrated area.

The above method of baseline correction leads to significant errors if the peak start level is lower than its end, in this case the peak area is defined as the area under the curve bounded below by a line running horizontally through a certain point. Even when adding the integrated area to the area of the triangle, the absolute error will correspond to the area of the triangle.

It should be noted that analyzing the performance of the device for determining the beginning and end of the peak does not provide sufficient accuracy for the correction of the baseline of the adsorption signal. This is due to the random nature of the baseline drift, since it is often not known in advance how the level of the input signal corresponding to the end of the peak will change with respect to the level of its beginning. Ignoring the latter circumstance is, most often, the main source of errors in determining the areas of adsorption peaks.

In the above cases, instead of extrapolation, it is more acceptable to use the interpolation of the base signal by its values before and after the peak. This method of zero correction naturally gives more accurate results. One can consider an option of this method [11,12,13,14]. Let us express the area and the basis signal of the detector between the abscissas of the beginning and end of the peak obtained during integrating, through the areas V and W in the areas τ_v and τ_w before and after the end of the peak with a duration $2\tau_n$:

$$U=\tau_w(l+mt_2)+\tau_v(l-mt_1); \tag{10}$$

where *l*- the midline of the trapezoid U.

Regrouping the terms in expression (10), we obtain:

$$U=2l\tau_n=l(\tau_n+\tau_w)+m(t_2\tau_w-t_1\tau_v). \tag{11}$$

So that the correction does not depend on the slope, we choose τ_v and τ_w or so that the second term would be equal to zero. In this case, we obtain for τ_v and τ_w the following system of equations:

$$\left.\begin{aligned} \tau_v + \tau_w &= 2\tau_n \\ \frac{\tau_v}{\tau_w} &= \frac{t_2}{t_1} \end{aligned}\right\}$$

Experimental studies of the above correction method showed that when the baseline level changes due to drift by 0.25% or more of the whole scale during peak $2\tau_n$, it leads to insignificant errors in identifying a useful peak.

In the above method, the value of the fraction is set, where in the denominator is a unit increment of the input signal per unit time in the numerator. At the moment when the derivative of the useful signal is greater than or equal to the specified value, the device sets a signal about the beginning of the peak. A feature of the predicted method is that when the extreme value of the device for determining the beginning and end of the peak passes, it switches to searching for the end of the peak using the logic below. Derivative selection issues are discussed below.

We turn to the features of determining the end of the peak. To begin with, we note that to determine the peak area with an error of less than 0.5%, it is necessary to cover a peak of 6σ, this can be seen from table 1.

Table. 1.

σ	*h, %*	*S, %*
1σ	0,88	38,3
2σ	0,50	58,3
3σ	0,32	86,6
4σ	0,13	95,6
5σ	0,04	98,8
6σ	0,01	99,7

Therefore, the threshold value is selected based on the derivative at a point corresponding to a peak width of 6δ. From the equation it is clear that with a height equal to 0.01108, the equality:

$$e^{-x^2\sigma^2} = 0{,}01108.$$

Logarithm this expression, we will get the value x_1,

$$x_1 = \frac{\sqrt{4{,}5}}{\sigma}. \tag{12}$$

From here, taking the derivative of function (1) at the point x_1, we obtain the value of the derivative equal to 0.05. This value has the meaning that when a hundred pulses arrive, the ADC (analog-to-digital converter) value will increase or decrease by five values of the least significant digit. That is, when a threshold is set equal to four digits, which corresponds to 15 values of the least significant digit, a period of time equaling to the passage time of 300 clock pulses will be required. These considerations are true when the maximum slope of the output voltage of the analog-digital voltage is equal to the maximum slope of the curve described by the normal distribution function.

In a real signal at the output of the adsorption unit, the peak output process lasts from 0.2 seconds to tens of minutes. Moreover, at the beginning of the output signal at the output of the adsorption unit, the peaks have a minimum duration, and after a lapse of time the peaks begin to expand. Therefore, for a more accurate determination of the beginning and end of the peak, the threshold should not have any definite value. The threshold should vary according to the change in peak width [15,16].

In this case, it is possible either to decrease the threshold with a constant comparison step, at which Y_n is subtracted from the value of Y_{n-1}, or to increase the comparison step with a constant threshold. Whichever of these methods is more preferable will be discussed below.

Taking the value of σ, equal to 1, we determine the value of *K*,

$$K = 1{,}166.$$

We determine the threshold value for the peak of the minimum width, equal to 0.2 seconds, using the coefficient *K*, we also determine the frequency of the clock generator of the analog-to-digital converter in relation to this signal, it will be equal to 34.5 kHz. This is the conversion frequency at which a single increment in the ADC occurs at the inflection point for each clock pulse [17, 18]. We choose a threshold equal to 15, in this case the comparison step will be 8.7 mseconds when the threshold is set to 5 digits, i.e. 31 step comparison will be equal to 17.4. In this case, the number of comparison steps per peak will be 11 [19.20].

With the above number of partitions, the error in determining the beginning and the end may be within $\sigma/2$. Therefore, increasing the threshold to a value of more than 5 digits will lead to significant errors, therefore, we will consider the possibility of changing the threshold for determining the beginning and end of the peak.

As mentioned above, you can change the threshold or step comparison. To begin with, consider the possibility of changing the threshold. In our case, it is 31, it can only be reduced to a value of 2, otherwise the noise isolation property of the device will sharply decrease. And if we divide the maximum threshold into the minimum, we get the corresponding input signal range. In this case, the range is 15. This range for processing adsorption information is clearly insufficient. Therefore, when increasing the width of the peak, it is more expedient to increase the comparison step; it can be increased to a very large value. Therefore, the authors chose a threshold of 15. With this threshold value, in the initial period of the signal at the output of the adsorption unit, the comparison step will be 7-8 ms. After time, this comparison step will increase in direct proportion to the change in time, since σ the value increases in proportion to time.

The increase in σ is not always according to any specific law. Therefore, it is almost impossible to predict in advance the threshold value for determining the beginning and end of the peak. But with this method, the error in determining the beginning and end is significantly reduced. For a more accurate determination of the peak contours depending on the peak width, it is possible to determine with high accuracy the moment of appearance of the end of the peak. To do this, use the following methodology.

Thus, after finding the extremum of the peak in accordance with the methodology for determining the beginning and end of the peak, we obtain a value of σ. Then three thresholds are set, respectively 2σ, 3σ and 4σ. Upon receipt of a signal corresponding to the end of the peak in less than 2σ times, the device issues a signal to the PC so that it calculates the area using a routine that takes into account the merged peaks. At the time the signal arrives up to time 3, the value of the curve at time 3σ is taken as the end. Between 3σ and 4σ, the moment the end arrives is taken as the true end. If the signal of the end of the peak does not arrive before moment 4σ, then the value of the curve at this moment is taken as the end of the peak. Owing to the above approaches, we could achieve greater accuracy in determining the end of the peak, which accordingly increases the accuracy of processing all information as a whole.

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