DECONVOLUTION OF OVERLAPPED CHROMATOGRAPHIC PEAKS AND ITS APPLICATION FOR COMPLEX MIXTURES COMPONENTS QUANTITATION

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Introduction

The number of the components that must be detected simultaneously by GC constantly increases but constant increase of the analysis time is not possible. Therefore some peaks on the chromatogram are not fully resolved even when modern capillary columns are used. Then precision of the quantitative determination of the components become dependent on the method of deconvolution of the overlapped peaks.

The most of chromatographic data processing system divide overlapped chromatographic peaks by use of the perpendicular drop method [1], although an error in such case is reported to be more than 50% for symmetrical peaks with areas ratio 1:1, and more than 200% in case of peaks asymmetry and non-equal peak areas [2].

For the chromatograms registered using single-channel detector two main approaches exists for deconvolution of the overlapped peaks: (a) the methods based on Fourier deconvolution and (b) the methods based on the approximation of the overlapped peaks with the superposition of a mathematic functions. The essence of the methods based on Fourier deconvolution is to multiply Fourier

transform of the original signal by a weighting function, which decays more slowly, and then to transform the multiplied signal back to the time domain. However, sometimes it is not easy to choose the appropriate apodization or smoothing functions. Furthermore, the sidelobes, especially the positive sidelobes, will cause extra component peaks [3].

The essence of the methods based on the approximation of the chromatogram with a mathematical function is to represent a chromatogram as a superposition of functions, where one of function represent the baseline and other the peaks. The deconvolution consists in the establishing of the parameters in those functions. Because of the superposition function is nonlinear in respect to parameters it is necessary to use iteration methods for its determination.

The deconvolution of the overlapped peaks by using the approximation method embodied, for example, in PeakFit software [4] representing specialized software for deconvolution of the overlapped peaks. However, our investigation has shown that the using of PeakFit for real complex chromatograms is not possible because of its time-expension, and that the used minimization algorithm in some cases was divergence.

In this connection actual is the development of fast deconvolution methods for the chromatographic peaks. Thus the aim of this research is the investigation of possibility of the developing of high-

performance software for mathematical deconvolution of the overlapped chromatographic peaks.

Experimental

The processing of the generated chromatograms was accomplished on the computer with Intel Celeron 366 MHz processor and RAM 128 Mb. For generation, processing and deconvolution of the overlapped peaks we used hand-made software developed on C++ for MS Windows 95/98/ME/NT/2000/XP.

Result and discussion

Hooke-Jeeves algorithm being one of the most effective minimization algorithms of the first order was chosen as iteration method. The advantage of this algorithm is the possibility of minimization of the function depending on relatively great number of the parameters. The using of original Hooke-Jeeves method has shown that it possesses slow convergence in task under consideration. First of all, a slow convergence is due to the fact that the first approximation may be far from minimum. It gives rise to the step length is reduced greatly in first iterations, but the possibility to increase the step length is absent in the original algorithm. We have modified Hooke-Jeeves algorithm for increasing step length and prediction of minimization direction that give rise to reduction minimization time in several times on task in question.

The program created was tested on generated model chromatograms with different resolution. The chromatograms of 3 peaks are presented in Fig. 1. The peaks parameters are given in the Table 1 (chromatograms are generated with zero baseline drift). The comparison results of the integration of this chromatograms using the perpendicular drop method and proposed program based on approximation of the overlapped peaks with superposition of the functions are given in the Table 2. As it is seen from the table the determination of peak areas using perpendicular drop method may give rise to an error more then 40%. However, for the same chromatograms approximation method give rise to the error less than 0.1%. The processing for every chromatogram took about 10 seconds.

The chromatogram of 10 overlapped peaks is presented in Fig. 2. The comparison results of the integration of this chromatogram using the perpendicular drop method and proposed program are given in the Table 3. The chromatogram was generated with drifting baseline and high noise level condition (the noise level was 1% from height of the greatest peak, and 10% from height of the smallest peak). The width of the greatest peak was more then width of the smallest peak in 10 times. It should be stressed that although such order of the peak heights and the range of the peaks widths doesn't occur in real chromatograms, generated chromatogram were generated so complex artificially. As it is seen from Table 3, the determination of peak areas using perpendicular drop method may give rise to an error more then 100%. However, in the same time in the case of

considerable noise and ascending baseline the error was less than 3%. When our program was used the processing for every chromatogram took about 3 minutes.

Conclusion

The program for fast and precise mathematical deconvolution of the overlapped chromatographic peaks of complex mixtures components under drifting baseline and high noise level conditions was proposed. It was shown that high integration accuracy pf peak area was achievable using this program.

Acknowledgments

Literature cited

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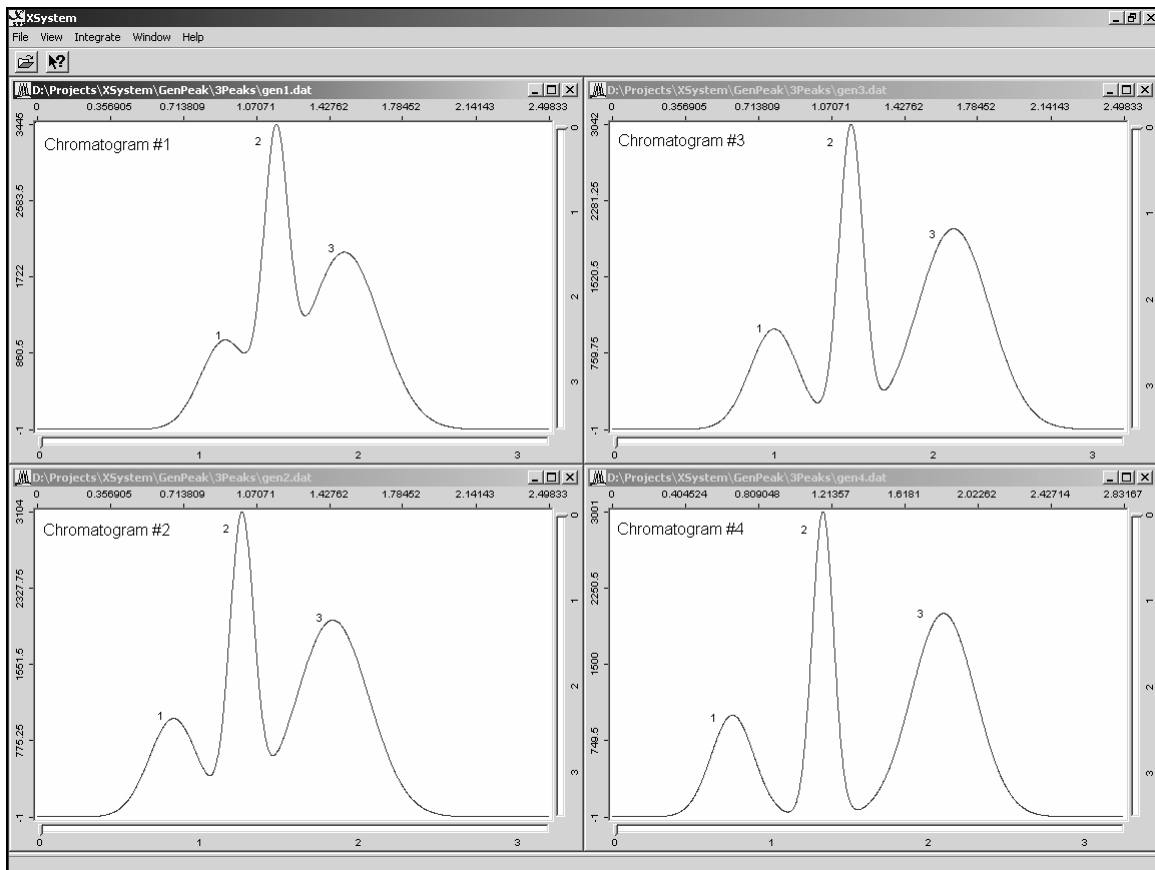4. SPSS Science, Inc. Chicago. Illinois. USA. [http://www.spssscience.com/PeakFit].

Fig. 1. The generated chromatograms of 3 overlapped peaks with the different resolution, the peaks parameters are given in table 1.
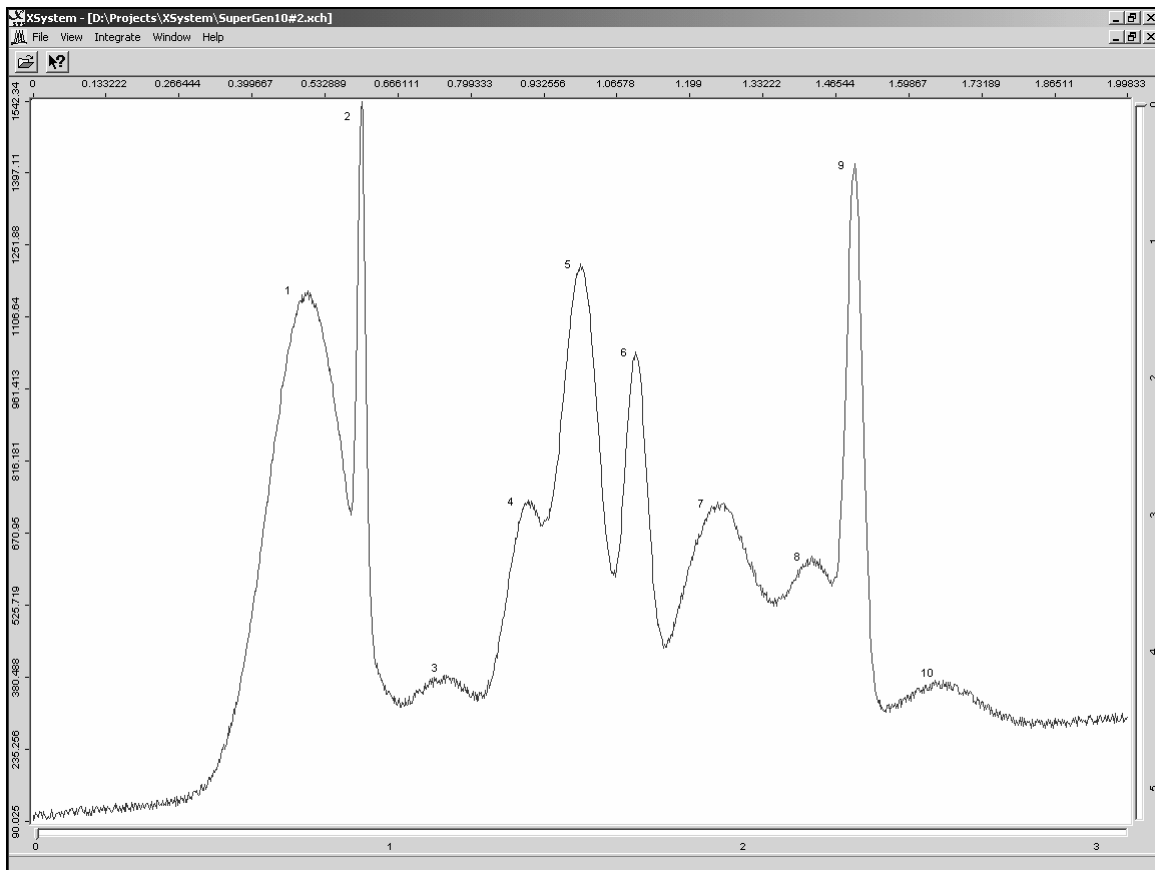
Fig. 2. The generated chromatogram of 10 overlapped peaks, the peaks parameters are given in table 3.

Table 1. The parameters of generated chromatograms of 3 overlapped peaks form Fig. 1

Peak number	Standard deviation, δ (min)	Height, H^*	Maximum, t_0 (min)			
			Chromatogram #1	Chromatogram #2	Chromatogram #3	Chromatogram #4
1	0.1179	1000	0.9167	0.6667	0.7917	0.6667
2	0.0589	3000	0.1667	1.0000	1.1667	1.1667
3	0.1768	2000	1.5000	1.4417	1.6667	1.8333

Note: * – dimensionless.

Table 2. The comparison results of the integration of the chromatogram (parameters are given in table 1) by perpendicular drop method and the program proposed

| Peak number | Real peak area, A^* | Chromatogram #1 | | | | Chromatogram #3 | | | |
| | | Perpendicular drop method | | Program proposed | | Perpendicular drop method | | Program proposed | |
	A^*	A^*	Δ (%)	A^*	Δ (%)	A^*	Δ (%)	A^*	Δ (%)
1	295.41	238.22	-19.36	295.28	-0.04	285.45	-3.37	295.26	-0.05
2	443.11	621.95	40.36	443.29	0.04	476.00	7.42	443.09	-0.01
3	886.23	767.24	-13.43	885.92	-0.03	863.34	-2.58	886.08	-0.02
Σ	1624.75	1627.40	0.16	1624.50	-0.02	1624.78	0.00	1624.43	-0.02
		Chromatogram #2				Chromatogram #4			
1	295.41	277.09	-6.20	295.27	-0.05	293.13	-0.77	295.26	-0.05
2	443.11	503.59	13.65	443.12	0.00	446.44	0.75	443.05	-0.01
3	886.23	840.39	-5.17	886.01	-0.02	877.90	-0.94	886.03	-0.02
Σ	1624.75	1621.07	-0.23	1624.40	-0.02	1617.47	-0.45	1624.35	-0.02

Notes: * – dimensionless; **A** – peak area; Δ – error of determination of peak area in percents.

Table 3. The comparison results of the integration of the chromatogram of 10 overlapped peaks from Fig. 2 with the perpendicular drop method and the program proposed

Peak number	Maximum, t_0 (min)	Standard deviation, δ (min)	Height, H^*	Resolution between adjacent peaks, R	Real peak area, A^*	Peak area calculated by perpendicular drop, A^*	Error of peak area calculation by perpendicular drop method, Δ (%)	Peak area calculation by proposed program, A^*	Error of peak area calculation by proposed program, Δ (%)
1	0.50	0.07071	1000		177.25	153.01	-13.67	177.35	0.06
2	0.60	0.00707	1000	0.643	17.72	43.00	142.59	17.76	0.18
3	0.75	0.07071	200	0.964	35.45	23.89	-32.60	35.11	-0.96
4	0.90	0.03536	500	0.707	44.31	42.86	-3.27	44.95	1.44
5	1.00	0.03536	1000	0.707	88.62	92.50	4.38	88.15	-0.54
6	1.10	0.02121	750	0.884	39.88	46.81	17.37	40.02	0.35
7	1.25	0.07071	500	0.816	88.62	73.82	-16.71	88.69	0.07
8	1.43	0.05303	350	0.727	46.53	33.83	-27.28	45.99	-1.15
9	1.50	0.01414	1000	0.521	35.45	47.94	35.23	35.89	1.25
10	1.65	0.07071	100	0.884	17.72	9.03	-49.07	18.18	2.55
Σ					591.56	566.69	-4.20	592.08	0.09

Note: * – dimensionless.