

Using Smoothing Algorithms to Reduce Baseline Noise in Chromatography

INTRODUCTION

While most modern data analysis systems are adequate for determining peak areas and heights, proper integration parameters must be used for good quantification. Results will depend on:

- How the systems filter or average short-term noise
- The frequency of data collection
- The computer algorithms used to process the data

Short-term noise (also known as high-frequency noise, > 1 Hz) is of primary interest for most signal-to-noise (S/N) measurements. Short-term noise is caused by a number of factors, including detector noise, pulsations of the pumping system, and electronic noise in the integration system.

Long-term noise (variations in the signal with a frequency between 0.1 and 1 Hz) is often indicative of an external source (e.g., room temperature) or a system problem, and limits the accurate measurement of chromatographic peaks. Long-term noise can be caused by poor on-line mixing, slight variations in the mobile phase over time, temperature variations, bleed of stationary phase, or late-eluting compounds from prior injections.

To detect peaks, baseline noise (the level above which a peak can be detected), and the appropriate peak width must be established. The baseline noise level can be established with reasonable accuracy if enough data points are collected (about 20 points per peak). The peak width helps set the beginning and end of each peak and should be set to detect the narrowest peak expected. If the peak width setting for an expected peak is too narrow, the peak will not be detected. If the setting is too high, then integration may be inaccurate.¹

This Technical Note describes how to use the smoothing algorithms available in PeakNet software to reduce baseline noise. There are three smoothing algorithms available in PeakNet: Moving Average, Olympic, and Savitzky-Golay. Below is a brief description of each algorithm.

Moving Average

The Moving Average algorithm is a simple and basic filtering technique where the average of an input set is used to generate one output value. This algorithm has a tendency to reduce signal amplitude because peak apexes are averaged down with the lower values that surround them. Moving Average is a primitive algorithm, but it can be useful in cases where peaks are relatively broad (more than 30 seconds).

Olympic

The Olympic algorithm is a modified form of the Moving Average algorithm. The high and low values of a data set are discarded, and the rest of the values are averaged. This algorithm is very effective at screening out spikes (high-frequency noise), but it can still reduce amplitude like the Moving Average algorithm.

Savitzky-Golay

The Savitzky-Golay algorithm was originally developed for spectroscopy, but works well for other data sets. This algorithm averages the points in a data set, but first multiplies each point by a weighting factor. The factors, which are derived from second- and third-degree polynomials, give the most emphasis to the center point of the data set, and progressively less emphasis to the points further out. Distortion of peak apexes is minimized with this algorithm.



CONDITIONS

Conditions for Figures 1A–1D

Analytical Column: IonPac® AS9-HC
Guard Column: IonPac AG9-HC
Eluent: 9.0 mM Sodium carbonate
Eluent Flow Rate: 1.0 mL/min
Inj. Volume: 25 µL
Detection: Suppressed conductivity, ASRS®-II, AutoSuppression® external water mode

Conditions for Figures 2A–2D

Analytical Column: IonPac AS14
Guard Column: IonPac AG14
Eluent: 3.5 mM Sodium carbonate, 1.0 mM Sodium bicarbonate
Eluent Flow Rate: 1.2 mL/min
Inj. Volume: 25 µL
Detection: Suppressed conductivity, ASRS-II (4 mm), AutoSuppression external water mode

Seven Anion

Standard: Fluoride (100 ppb), chloride (200 ppb), nitrite (300 ppb), bromide (500 ppb), nitrate (500 ppb), phosphate (800 ppb), and sulfate (600 ppb)

Conditions for Figures 3A–3D

Analytical Column: IonPac AS11
Guard Column: IonPac AG11
Eluent: 50 mM Nitric acid
Eluent Flow Rate: 1.5 mL/min
Inj. Volume: 100 µL
Detection: PAD, Ag electrode
Collection Rate: 1 Hz

EQUIPMENT

Dionex DX-500 Ion Chromatography system consisting of:
GP40 Gradient Pump
CD20 or ED40 Detector
AS40 or AS3500 Autosampler

LC20 Chromatography Enclosure with a rear-loading valve

PeakNet Chromatography Workstation, v. 4.3

RESULTS AND DISCUSSION

PeakNet software has three independent smoothing algorithms: Savitzky-Golay, Moving Average, and Olympic. Using these algorithms to reduce baseline noise can increase the S/N ratio and lower detection limits.

All noise measurements are performed in the “Optimize” mode by expanding the flat region of the baseline (without peaks) and selecting a one-minute segment. The “Auto Threshold” option measures the peak-to-peak noise of this segment. Larger time segments should not be measured because the noise measurement may include baseline drift.

Figure 1A shows a chromatogram obtained by analyzing 4–40 ppm concentrations of an anion standard on an IonPac AS9-HC column. Figure 1B shows the low frequency noise in this chromatogram. Each smoothing algorithm was applied separately using a range of iteration numbers and points. Peak heights and area counts of fluoride, chloride, and sulfate were monitored in relation to noise reduction. Fluoride and chloride have narrow peaks and sulfate has a wide peak. Wider peaks are defined by more data points, so they will be less affected by smoothing than narrow peaks.

Initial unfiltered noise was 4.8 nS. The data in Table 1 show that none of the smoothing algorithms reduce this low-frequency noise (source unknown) without the concurrent reduction of the fluoride peak height. For example, Figure 1C shows the results of 50 iterations of the Moving Average algorithm using 17 points. Simultaneously lowering both signal and noise did not produce any gain in the detection limit. However, the detection limit for sulfate was lowered as a result of smoothing (noise was greatly reduced, but area count and peak height remained close to their initial values). This demonstrates that for low-frequency noise, smoothing can improve detection limits for wide peaks, but has little effect on narrow peaks. For this chromatogram, the Moving Average algorithm (50 iterations at 17 points) yielded the best noise reduction with the least impact on sulfate peak height and area. Figure 1D shows the noise of the smoothed chromatogram in 1C.

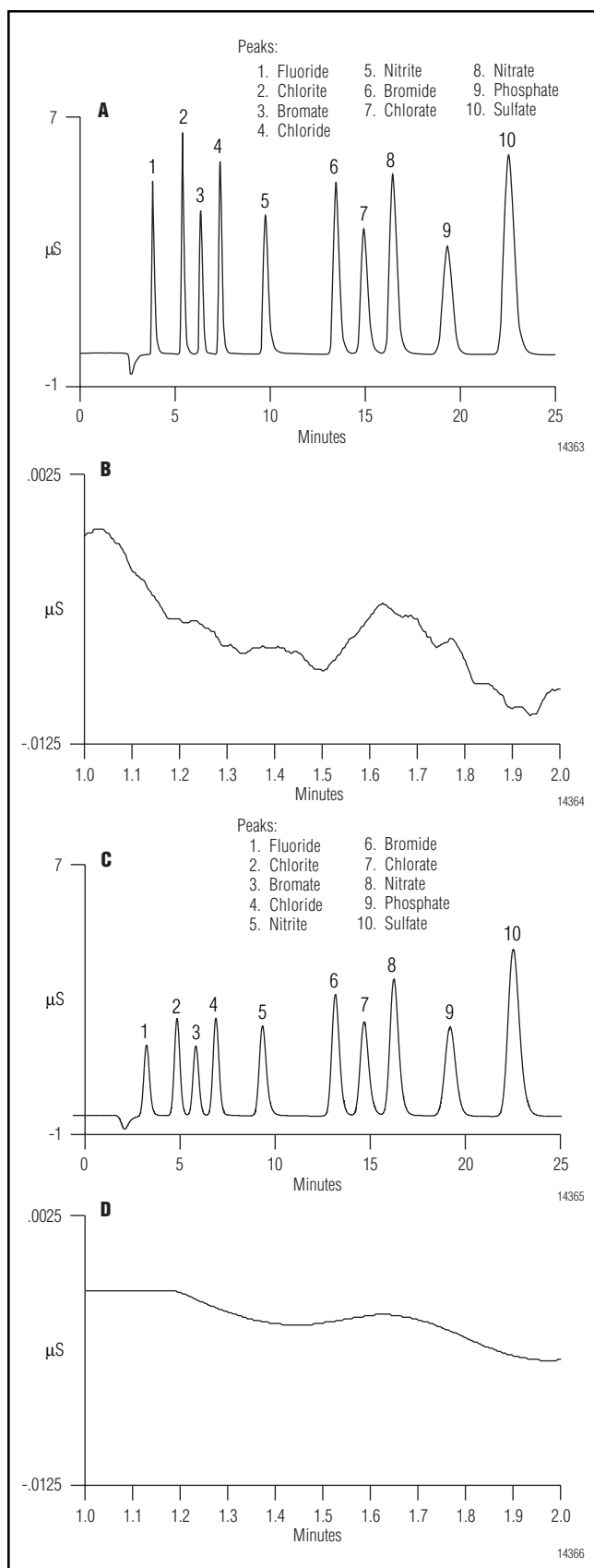


Figure 1 A. Seven anion and oxyhalide standard, B. Seven anion and oxyhalide standard—noise, C. Seven anion and oxyhalide standard—smoothed, D. Seven anion and oxyhalide standard—smoothed noise. For smoothing, 50 iterations of a 17 point Moving Average Algorithm were used.

When analyzing low analyte concentrations, peak smoothing is especially important. In Figure 2A, a seven anion standard was analyzed on an IonPac AS14 column. The noise in this chromatogram was already low (see Figure 2B), but the data in Table 2 show that each of the smoothing algorithms can be successfully applied to reduce the initial unfiltered high-frequency noise and improves S/N. The Savitzky-Golay algorithm (20 iterations at 25 points) reduced this noise without a significant impact on the chloride and nitrite peak heights. Figure 2C shows the effect of this smoothing on the chromatogram in Figure 2A. Figure 2D shows how this smoothing reduced the noise.

When smoothing data collected at lower frequencies (1 Hz), start with a lower number of points than when smoothing data collected at higher frequencies (5 Hz). This concept is demonstrated in Figure 3. Figure 3A shows the chromatogram of 10 ppb iodide analyzed on an IonPac AS11 column with electrochemical detection. Figure 3B shows the noise of the chromatogram in Figure 3A. Data were collected at 1 Hz. This collection rate can be viewed as a smoothing operation, because the rate is slower than high-frequency noise. Additionally there are portions of time in pulsed amperometry when signal is not collected. Table 3 shows that the additional application of smoothing algorithms resulted in a drastic reduction of iodide peak heights and complete disappearance in the case of multiple iterations of the Moving Average and Olympic algorithms.

The Moving Average algorithm (5 points, 1 iteration) is optimal for noise reduction with the least impact on iodide peak height (Table 3). Peak area may increase due to peak broadening. When smoothing is performed on analytes present at very low (trace) concentrations, it is important to verify the start and end of each peak to ensure accurate results. Figure 3C shows the effect of smoothing on the chromatogram in Figure 3A. Figure 3D shows how this smoothing reduced the noise.

In all of the above examples (Tables 1, 2, and 3), the reduction in peak height was not immediately followed by a reduction in area count. To find the appropriate smoothing procedure, the number of points and iterations of each algorithm and their effect on the chromatogram should be investigated.

Table 1 Smoothing results for the chromatogram in Figure 1A
(The data collection rate was 5 Hz)

Sample name/# of iterations	# of Points	Noise measurement range (min)	Noise n(S)	Peak height			S/N ratio (height)			Area count			Algorithm
				F	Cl	SO ₄	F	Cl	SO ₄	F	Cl	SO ₄	
Anions and oxyhalides				F	Cl	SO ₄	F	Cl	SO ₄	F	Cl	SO ₄	
0	0	1-2	4.8	51521	56267	59200	10734	11722	12333	474363	668257	2267501	Savitzky-Golay
1	17	1-2	4.8	51489	56244	59168	10727	11718	12327	482548	667957	2260794	Savitzky-Golay
20	17	1-2	4.4	50574	55947	59190	11494	12715	13452	484216	667635	2258734	Savitzky-Golay
50	17	1-2	4.5	49324	55577	59162	10961	12350	13147	482476	668493	2255375	Savitzky-Golay
1	25	1-2	4.7	51341	56183	59179	10924	11954	12591	483905	667963	2260968	Savitzky-Golay
20	25	1-2	4.4	48527	55192	59181	11029	12544	13450	516531	673937	2258713	Savitzky-Golay
50	25	1-2	4.4	45721	55119	59130	10391	12527	13439	513247	685265	2258713	Savitzky-Golay
0	0	1-2	4.8	51521	56267	59200	10734	11722	12333	474363	668257	2267501	Moving Average
1	5	1-2	4.8	51282	56139	59189	10684	11696	12331	482547	667933	2267343	Moving Average
20	5	1-2	4.6	47446	53899	58994	10314	11717	12825	483035	667202	2265190	Moving Average
50	5	1-2	4.5	42771	51850	58646	9505	11522	13032	473437	666281	2261764	Moving Average
1	17	1-2	4.5	48891	54788	59067	10865	12175	13126	482345	667742	2260820	Moving Average
20	17	1-2	3.1	31030	40589	56735	10010	13093	18302	486909	678234	2266612	Moving Average
50	17	1-2	1.6	22727	30961	53481	14204	19351	33426	478541	669399	2261807	Moving Average
0	0	1-2	4.8	51521	56267	59200	10734	11722	12333	474363	668257	2267501	Olympic
1	5	1-2	4.8	51367	56218	59190	10701	11712	12331	481584	667940	2267343	Olympic
20	5	1-2	4.6	49810	55383	59113	10828	12040	12851	482733	667376	2265125	Olympic
50	5	1-2	4.6	47598	54141	58982	10347	11770	12822	472594	666483	2261622	Olympic
1	17	1-2	4.5	49131	55033	59079	10918	12230	13129	481874	667506	2260804	Olympic
20	17	1-2	3.2	32663	42518	57191	10207	13287	17872	478599	675726	2266328	Olympic
50	17	1-2	2.0	24328	33229	54508	12164	16615	27254	467921	667775	2261464	Olympic

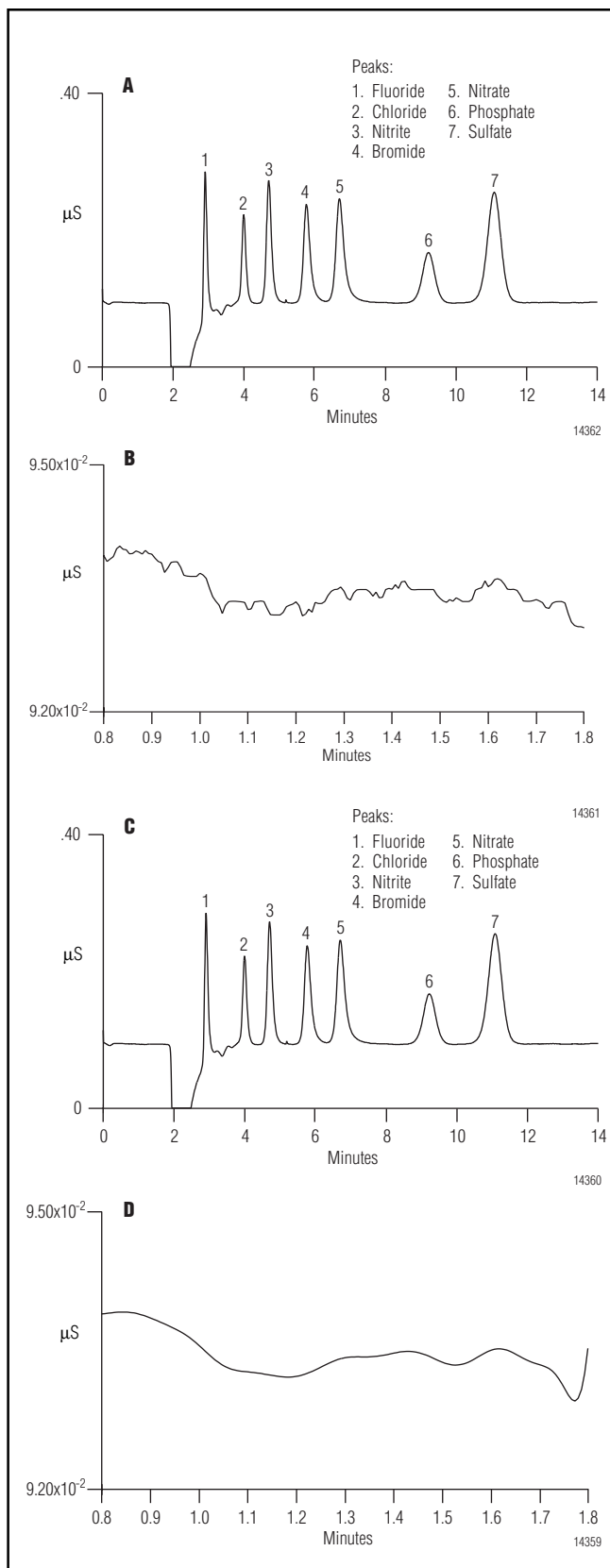


Figure 2 A. Seven anion standard, B. Seven anion standard—noise, C. Seven anion standard—smoothed, D. Seven anion standard—smoothed noise. For smoothing, 20 iterations of a 25 point Savitsky-Golay algorithm were used.

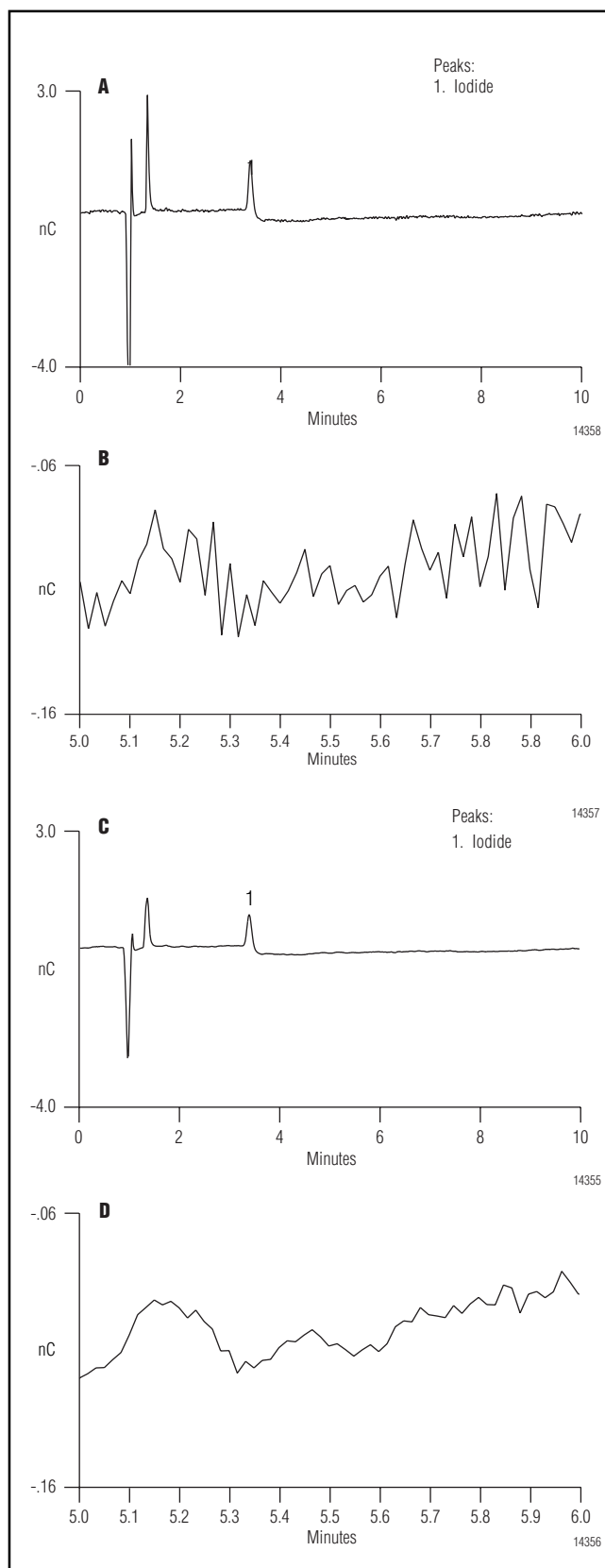


Figure 3 A. 10 ppb iodide standard, B. 10 ppb iodide standard—noise, C. 10 ppb iodide standard—smoothed, D. 10 ppb iodide standard—smoothed noise. For smoothing, 1 iteration of a 5 point Moving Average algorithm was used.

**Table 2 Smoothing results for the chromatogram in Figure 2A
(The data collection rate was 5 Hz)**

Sample name/# of iterations	# of Points	Noise measurement range (min)	Noise n(S)	Peak height (x 10 ³)		S/N ratio (height)		Area count (x 10 ⁴)		Algorithm
				Cl	NO ₂	Cl	NO ₂	Cl	NO ₂	
Seven anion standard				Cl	NO ₂	Cl	NO ₂	Cl	NO ₂	
0	0	0.5–1.5	0.869	1.266	1.792	1460	2060	1.198	1.931	
1	17	0.5–1.5	0.781	1.264	1.791	1620	2290	1.198	1.934	Savitzky-Golay
20	17	0.5–1.5	0.733	1.294	1.771	1770	2420	1.195	1.899	Savitzky-Golay
50	17	0.5–1.5	0.712	1.265	1.747	1780	2450	1.194	1.895	Savitzky-Golay
1	25	0.5–1.5	0.763	1.314	1.787	1720	2340	1.200	1.932	Savitzky-Golay
20	25	0.5–1.5	0.702	1.233	1.720	1760	2450	1.193	1.893	Savitzky-Golay
50	25	0.5–1.5	0.691	1.163	1.653	1680	2390	1.190	1.887	Savitzky-Golay
0	0	0.5–1.5	0.869	1.266	1.792	1460	2060	1.198	1.931	
1	5	0.5–1.5	0.805	1.261	1.787	1570	2220	1.197	1.981	Moving Average
20	5	0.5–1.5	0.700	1.220	1.692	1740	2420	1.188	1.893	Moving Average
50	5	0.5–1.5	0.662	1.110	1.576	1680	2370	1.182	1.884	Moving Average
1	17	0.5–1.5	0.719	1.255	1.727	1750	2400	1.192	1.895	Moving Average
20	17	0.5–1.5	0.573	0.764	1.186	1330	2070	1.098	1.899	Moving Average
50	17	0.5–1.5	0.484	0.515	0.875	1060	1810	0.922	1.769	Moving Average
0	0	0.5–1.5	0.869	1.266	1.792	1460	2060	1.198	1.931	
1	5	0.5–1.5	0.825	1.264	1.790	153	217	1.198	1.930	Olympic
20	5	0.5–1.5	0.731	1.275	1.754	174	240	1.191	1.932	Olympic
50	5	0.5–1.5	0.699	1.223	1.699	175	243	1.187	1.891	Olympic
1	17	0.5–1.5	0.717	1.259	1.733	176	242	1.191	1.893	Olympic
20	17	0.5–1.5	0.579	0.810	1.250	140	216	1.091	1.898	Olympic
50	17	0.5–1.5	0.519	0.576	0.952	111	183	0.983	1.809	Olympic

Table 3 Smoothing results for the chromatogram in Figure 3A
(The data collection rate was 1 Hz)

Sample name/# of iterations	# of Points	Noise measurement range (min)	Noise (pC)	Peak height	S/N ratio (height)	Area count	Algorithm
0.01 ppm Iodide							
0	0	5-6	54.3	10296	190	52564	Savitzky-Golay
1	17	5-6	27.5	7387	269	70228	Savitzky-Golay
20	17	5-6	12.8	4436	347	80977	Savitzky-Golay
50	17	5-6	10.2	3575	350	81588	Savitzky-Golay
1	25	5-6	20.0	5803	290	80938	Savitzky-Golay
20	25	5-6	8.0	2933	367	73258	Savitzky-Golay
50	25	5-6	4.8	1926	401	53123	Savitzky-Golay
0	0	5-6	54.3	10296	190	52564	Moving Average
1	5	5-6	30.1	8729	290	61580	Moving Average
20	5	5-6	10.4	3762	362	66849	Moving Average
50	5	5-6	5.5	2250	409	53838	Moving Average
1	17	5-6	14.4	3643	253	61593	Moving Average
20	17	5-6	2.4	0	0	0	Moving Average
50	17	5-6	0.6	0	0	0	Moving Average
0	0	5-6	54.3	10296	190	52564	Olympic
1	5	5-6	32.1	8819	275	60156	Olympic
20	5	5-6	16.6	4832	291	58222	Olympic
50	5	5-6	11.6	3419	295	57372	Olympic
1	17	5-6	14.6	3412	234	55469	Olympic
20	17	5-6	2.0	0	0	0	Olympic
50	17	5-6	1.4	0	0	0	Olympic



SUMMARY

This Technical Note describes how PeakNet smoothing algorithms can be used to improve S/N ratio of important analytes.

REFERENCES

1. Snyder, L. R., Kirkland, J. J., and Glajch, J. L.
Practical HPLC Method Development.

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