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Intelligent Signal Processing for Detection System Optimization

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A wavelet-neural network signal processing method has demonstrated approximately tenfold improvement in the detection limit of various nitrogen and phosphorus compounds over traditional signal-processing methods in analyzing the output of a thermionic detector attached to the output of a gas chromatograph. A blind test was conducted to validate the lower detection limit. All fourteen of the compound spikes were detected when above the estimated threshold, including all three within a factor of two above. In addition, two of six were detected at levels 1/2 the concentration of the nominal threshold. We would have had another two correct hits if we had allowed human intervention to examine the processed data. One apparent false positive in five nulls was traced to a solvent impurity, whose presence was identified by running a solvent aliquot evaporated to 1% residual volume, while the other four nulls were properly classified. We view this signal processing method as broadly applicable in analytical chemistry, and we advocate that advanced signal processing methods be applied as directly as possible to the raw detector output so that less discriminating preprocessing and post-processing does not throw away valuable signal.

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Progress in analytical chemistry over the years has enabled increasingly lower detection limits. Much of this has been due to advances in electronics, better materials, and better microfabrication capabilities. One area that does not appear to have been fully exploited yet is advanced signal processing, which can be a key component of any sensing system. If not done well, the preprocessing inherent in any instrument design can throw out valuable information, and subsequent use of advanced signal processing methods, no matter how capable, will not be able to recover signal lost by improper pre-processing. A very significant advantage in utilizing advanced signal processing is that as more capable algorithm is available, upgrading system performance can be very simple since it entails no hardware component changes and no expensive system to replace.

It is useful at the outset to contrast the objective of our work to other signal interpretation activities. Chemometrics[1] ordinarily looks at methods of separating a signal into its constituent parts, be it determining the relative fractions of spectral mixtures, as in principal component analysis, or resolving overlapping spectral or chromatographic peaks, although two review articles[2,3] did report of few papers on denoising. Instead, the focus here is to separate the signal from noise coming from instrumentation and/or the detector so that it is more amenable to interpretation by chemometrics or other methods. One can conceive of hybrid systems in which the integration of separation from noise and separation into components maximizes system performance.

Combination of signal processing methods has the potential to extract information more completely than by using a single method. Different non-redundant methods have different strengths and weaknesses, and these combinations can take advantage of these different characteristics. Biological systems, such as vision, often use such combinations.[4]

We have developed an intelligent signal processing method that can be a central aspect of optimized system design and extraction. It is based on an adaptive combination of wavelet filtering and neural network processing. Because our system came from biological inspiration, we call our system BISP, which stands for biological inspired signal processing. It is currently implemented with a graphical user interface to enable various users to access these advanced techniques. In the long term, this type of method could be built into a signal-processing chip (ASIC, full-custom, or DSP) for real time processing, especially when handling the enormous amount of data that some 2-D or 3-D high-resolution sensors collect.

In this work, we show that it is possible to reliably extract gas chromatographic (GC) peaks at signal-to-noise levels substantially less than one. This method has demonstrated almost tenfold improvement over more conventional methods based on running averages and a low-pass analog filter. We view this as prototypical of what might be possible for a wide range of analytical detection devices.

MATHEMATICAL METHODS

The entire signal extraction process can be summarized by the following sequence of operations: (a) remove background or other long-scale-length variations through spline-fitting, (b) wavelet decomposition and/or denoising of each of the wavelet components, (c) a separate neural network for signal extraction working in the wavelet domain for each unprocessed or processed wavelet component, (d) combining the outputs of all the neural networks, and finally (e) inverse wavelet transform to return a clean signal in the time domain.

Wavelets are a kind of transform that break data into coefficients in both time and frequency, thus getting around a major difficulty of the Fourier transform, which is the loss of all

time information after doing the transform. Many sorts of data have important features that are localized in time, etc., like spectra, gas-chromatography readouts, etc., and applying a wavelet transform will preserve this time localization. Preserving exact peak locations while denoising is a very important constraint on signal processing in equipment like gas chromatography.

A Fourier transform works by finding a set of coefficients of different-frequency sine waves, which, when added together, will produce the original data. Since these sine waves stretch over the entire time of the transform, the loss of time data is readily understandable. By comparison, a wavelet transform works by finding a set of coefficients of wavelet functions which, when added together, will produce the original data. These wavelet functions are actually a single localized function that has been shifted and stretched in time by various amounts to provide a set of basis functions to synthesize the signal. The shifting captures time information, while the stretching captures frequency information (the frequency is the reciprocal of the amount of stretch). These compact localized basis functions of the wavelet approach enable the wavelet transform to maintain simultaneous time and space (or frequency) information, a very important difference from the Fourier Transform.

Such fitting seems like a difficult task. But there is a convenient shortcut algorithm for doing the fitting in the discrete case. One applies a pair of wavelet filters to the original data, and keeps every second point of both, thus retaining the original number of data points. These filters may be described as smooth (finds the average) and rough (finds the details). The smooth part is approximately a local average of the data, while the rough part contains the local details.

This operation can be repeated on the resulting smooth part, resulting in a new smooth part and a rough part corresponding to a length scale twice as large as the original's. Continuing this repeat produces a sequence of rough parts for length scales increasing as 1, 2, 4, 8, … (powers of

2), with a smooth part at the highest length scale. The length scales correspond to frequencies 1, 1/2, 1/4, 1/8, … as one goes up the sequence, and the indexes of data points in a part corresponds to time, with neighboring data points being separated in time by 1, 2, 4, 8, … as one goes up the sequence.

This operation can be undone with a similar sort of filtering, which is especially convenient if one wishes to proceed with further processing of the data in its untransformed form. And with appropriate selection of filters, the forward and inverse filters can be made identical. Such "orthogonal" filters include the Daubechies and Coifman filter families.

Our wavelet preprocessing, or more precisely, discrete wavelet transform (DWT) serves three different purposes. First, it provides a means to segment the data that allows progressive processing that can save time. The specific method used for this work is a 4-level decimated Daubechies-2 wavelet transform,[5,6] which has a shape similar to the Gaussian with exponential tail characteristic of GC peaks. Second, signals most often occur within the smoother scales, which were decimated repeatedly by the DWT process. Consequently, such decomposition allows us to automatically achieve data reduction if using such smoother components proves to be sufficient, as it is in this case here. A 16-fold data reduction was accomplished in this work. Third, the smoothness of the lower scales allows neural networks to perform better in those wavelet component domains. In other words, the transform provides a way to "transfigure" the data into a domain that favors neural network processing.

The function of the neural network[7,8] is to extract relevant features that it learns from the training process. The training tunes the neural network to recognize certain common features that would occur in the targeted signals. A unique feature of our neural network processing is that data is processed in the wavelet domain to take advantage of both smoothness of the signals and the

data reduction in the smoother scales. Secondly, by using or allowing more than one neural network, we have devised a divide-and-conquer technique. Separate neural networks may handle separate decomposed wavelet signals representing different scales. Together, we have a progressive system that allows us to trade off computational complexity with accuracy. Furthermore, because of the adaptiveness of neural networks, we do not have to precisely tune the wavelet preprocessing for absolute optimal denoising. The two systems overlap and thus yield a more flexible or "forgiving" signal processing.

The specific approach we use is a projection neural network. Artificial neural networks mimic their biological counterparts by using networks of interconnected neurons through appropriate synaptic connections to perform simple but effective parallel computations. A neuron can be a simple "fire or not-fire" processing element or more effectively a computation unit that sums all its inputs modified by the corresponding synaptic strengths as defined by the synaptic values; then further modified by a non-linear transfer function. A projection neural network projects the original input vectors into a space with one higher dimension before feeding the projected vectors into the neural network. A modified Logicon projection system is used for this preprocessing, which enables the hidden unit's decision boundaries to take on a much greater variety of shapes, such as an ellipse, compared to straight lines in the case of backpropagation.[9] This leads to more efficient use of neurons—we typically need only 6 or 9 neurons, which allows fast and efficient generalization. Because of the four orders of magnitude change in the dynamic range of the input data, we used four different neural networks to handle the different ranges and these four neural networks use either 6 or 9 neurons. The projection is described mathematically by

$$I'_k = S\frac{(I_k / R)}{1+\sum_m (I_m /(2R))^2} \quad (1a)$$

and

$$I'_{extra} = S\frac{1-\sum_m (I_m /(2R))^2}{1+\sum_m (I_m /(2R))^2} \quad (1b)$$

where I'_k is the projected input based on I_k; I'_{extra} is the extra projected input to raise the dimension by one; R is the projection radius; and S is the projection size.

Data is projected according to these equations, and vector quantization is performed to obtain an initial weight vector for each hidden neuron. The projection creates a new input dataset one dimension higher than the original dataset because of the I'_{extra}. The projected input data are initially assigned randomly to the hidden units, and quantization is done by iteration using the Linde-Buzo-Gray algorithm.[10] This new dataset is then fed into a feed-forward neural network for training. Many different training algorithms can be used including conventional gradient descent, quasi-Newton, and conjugate gradient methods.[11]

EXPERIMENTAL SECTION

The target analytes used in this study were chosen from a set of surrogate compounds proposed for use in instrument characterization for detection of chemical weapons, and included organophosphates and nitrogen containing materials. Compounds used were trimethylphosphate (TMP), 99+%; tributylphosphate (TBP), 99+%; 1-fluoro-4-nitrobenzene (FNB), 99%; 5-chloro-

2-methylaniline (CMA), 97% (Aldrich, Inc.) Two organophosphate insecticides were included: Malathion (Mal, [(dimethoxyphosphino-thioyl)thio]butanedioic acid diethyl ester), 98.2% was obtained from Chem Service, Inc. (West Chester, PA) and Amiton (Am, S-[2-(diethylamino)ethyl]phosphoro-thioic acid O,O-diethylester), 98%, was obtained from the Edgewood Aresenal. Compounds were suspended in dichloromethane (Mallinckrodt SpectrAR®, 99.5% min.); dilutions were prepared using volumetric ware and gastight analytical syringes, and sealed in septum-capped vials for use; septa were replaced at the end of each day to prevent solvent loss. All materials were used without further purification.

Compounds were separated on an HP/Agilent 5890 equipped with a capillary column (DB-5, 10m x 0.100 mm, 0.10µ film, J&W Scientific). The carrier was helium, with a column head pressure of 50 psi, for a flow rate of approximately 0.5 $ml \cdot min^{-1}$. Liquid injections (1.0 µl throughout) were made with the split-splitless injector held at 250 C, operated in the splitless mode with a 2 mm, silanized, straight-bore injection sleeve (Supelco, Inc.) and a purge "off" time of 30 sec following injections. Optimum precision was achieved using a hot needle technique (Grob, 2001), with a preinjection heating period of five seconds. Split vent and septum purge flows were maintained at 10.0 and 1.0 $ml \cdot min^{-1}$, respectively. The column oven was programmed: 40 °C, 20 sec hold, 50 $°C \cdot min^{-1}$ to 200 °C, then 30 $°C \cdot min^{-1}$ to 270 °C, with a 1 min final hold. All target compounds were eluted within six minutes (Figure 1).

Compound elution times were confirmed with detection by an HP/Agilent 5970 mass selective detector, and comparison of spectra with NIST libraries, prior to attaching the column to a thermionic detector (Detector Engineering & Technology, Inc., Walnut Creek, CA), equipped with TID-2 detector beads, operated in the N-P mode with air/H_2 makeup gas (50.0 and 2.4 $ml \cdot min^{-1}$, respectively), and held at 300 °C. Beads were exchanged when baseline depression

following the solvent peak became significant; generally this was within five to seven days of installation. We observed that even though the thermionic detector maintained good sensitivity, there was subtle drift in response. To minimize this effect, particularly during collection of data for "blind" processing with the combined signal processing approach, filtered and unfiltered runs were interleaved for each sample; samples were analyzed in triplicate with unfiltered signal capture, and in duplicate for filtered capture. Similarly, "blind" mixtures and known standard blends were interleaved.

As we intended to evaluate the utility of the combined signal processing approach to enhance sensitivity in medium-resolution, portable analytical equipment, we captured chromatograms with a 12-bit analog to digital PCMCIA card (DAQ-Card 1200, National Instruments, Inc. Austin, TX), using in-house, custom LabVIEW programs for signal acquisition. Signals were designated as either "filtered" (10 Hz low-pass, two-pole R-C filter; sampling at 200 Hz, 50-point software moving average), or "unfiltered" (no R-C filtering, sampling at 1000 Hz, 3-point software moving average). Filtered data were analyzed with a custom LabVIEW chromatogram analyzer, based on peak detection from first derivatives calculated on moving eight point data windows; unfiltered data could not be analyzed with this software, and were processed in parallel with the combined wavelet/neural network system.

RESULTS AND DISCUSSION

Figure 2 shows the kind of signal recovery that can be attained using the combined wavelet-neural network method. Repeated measurements recover the signal from two nitrogen compounds having a signal-to-noise of ~0.16, where the noise is the full peak to valley width. Even though the peaks are only twice as large as the bit

resolution of the A/D converter**,** they are recovered cleanly, suggesting that the detection limit is considerably lower. When used separately, neural networks performed better than wavelets, but neither performed as well as the combination.

An obvious question is how well this method compares to other methods. Much of the noise is high frequency, so a simple multiple-point running average can improve the signal-to-noise ratio several fold, although peak broadening is produced by this approach and thus may affect the exact peak positions. Even more noise reduction can be achieved with more sophisticated filtering. A comparison of signal recovery using Butterworth/matched filtering and the wavelet-neural network method is shown in Figure 3. Although the four peaks were resolved by the Butterworth/matched filters combination, the doublets of the two peaks at ~5000 and ~12500 were not resolved by it, even though they were made visible using BISP. In addition, the poor noise floor from the Butterworth/matched filters will lead to false peak detection.

A test matrix was constructed to determine the factor of improvement in detection sensitivity and the reliability of detection using the wavelet-neural network signal processing algorithms. The first part of the test matrix consisted of seven calibration solutions having a 200-500 fold range in concentration each. The lowest concentration turned out to be lower than the detection limit ultimately achieved by BISP based on our current height threshold for detection, and one intermediate-concentration solution was rejected from regression as statistical outlier, likely a result of detector drift. The second part consisted of 5 blind samples having various concentrations of the calibrated compounds, with some nulls, and a couple spikes of a blind compound (Amiton) near its suspected detection limit. The complete comparison process is shown for one sample near the detection limit in Figure 4.

A typical calibration curve is shown in Figure 5 to illustrate two points. At high concentrations, variations in injection and detector performance limit the precision of the peak areas to a range of 2-3. Near the detection limit, the integrated peak area varies by more like a factor of ten. Detection limits for the wavelet-neural network method, based on current threshold setting for peak identification, were approximately 1 pg for Malathion and the two alkyl phosphates, 10 pg for chloro-methylanaline, and 50 pg for fluoro-nitrobenzene. The detection limit for the conventional data processing was approximately 10 times higher for all compounds when compared at the same level of human intervention—automatic peak detection using mathematical criteria. Peaks are visible at 2-3 times lower concentration, but they are not reliably above false peaks due to noise. Even lower detection limits for BISP are possible by lowering the threshold setting; however more sensitive detection will result in more false detections. Based on data from our calibration sets, BISP has 3.5 false peaks versus over 200 false peaks using conventional processing; as a result, BISP can be made much more sensitive before its false detection level matches that of conventional processing.

The results of the blind test are given in Table 1, which includes the formulated and measured concentrations. The ratio of measured-to-formulated concentrations vary similarly to the calibration data in Figure 5. All spikes greater than the nominal detection threshold were detected, albeit sometimes with a relatively large error consistent with the large deviation in the calibration area near the threshold. In one null case, a small peak was reported. Subsequent inspection showed that this was due to a solvent impurity, which introduces the double blind aspect of the test.

During the calibration process, up to ten small “extraneous” peaks not associated with the known spiked compounds were observed frequently, but not always, in the gas chromatograms.

The obvious explanation is that these might be impurities in the solutions that are not above signal to noise using conventional methods but were extracted using BISP. This was verified by evaporating a portion of solvent to 1% residual volume and injecting the concentrate into the gas chromatograph. About half the "extraneous" peaks were present in the solvent concentrate. Because the levels are so low, it is possibly that many of the others were picked up during processing, so the false positive rate, though difficult to estimate quantitatively, is very low.

One additional aspect of the blind test was the addition of Amiton at the 0.5 and 1.5 pg levels, respectively, in two of the solutions. The 0.5 pg spike was detected in three of three injections and reported as an unknown hit. The 1.5 pg was detected in two of three injections, so was not reported as a reliable hit because we typically set the criteria for detection as 4 out of 6 detected peaks. These variations in detection are consistent with the considerable variation in area near the detection limit.

We believe that this is the first reported work using a combination of wavelet and artificial neural network technologies to extract trace peaks found in chromatography. Other researchers have applied neural network technology in this area, but most of the twenty-three citations we found are not relevant to the work reported here. There are two citations for using both wavelet transforms and artificial neural networks on chromatography, but the objective was classification, not trace signal extraction, and the mathematical details are significantly different.

Voisin[12] and Hernandez-Borges[13] reported processing the spectra by neural networks to identify bacteria based on certain identifiers such as the concentration of n-alkanes or fatty acids as measured by gas chromatography. Fatemi[14] and Jalali-Heravi[15] reported using ANN's to learn from certain chemical parameters such as molecular weights and energy levels of the highest occupied molecular orbitals, to predict retention indices or retention time, whereas Bell[16] and

Cai[17] reported using the spectra as inputs to the neural network for chemical classification such as level of toxicity or active substructures. Our work is more fundamental. We report here using neural networks to recognize components of the spectra— either part of a peak or the entire peak. We use a moving window to keep the size within reasonable limits, whereas previous reported work[12,13,16,17] use the full spectrum. Each pass through our neural network yields a single point on the spectrum, whereas the outputs of others' neural networks yield different classifications. As a result, our work dovetails with these reported works, because if the spectra can be made clean and noise-free then classification can be done relatively easily.

The two references using both wavelet and neural network on chromatography are used liquid chromatography. Collantes[18] reported using wavelets and neural networks on HPLC data for the classification of L-tryptophan from six different manufacturers. Similar to the work here, they used wavelet preprocessing, but the details are very different. They used a wavelet package, a combination of wavelets and an oscillating function, whereas we use pure wavelets. The use of the Haar function does not have a clear justification, since the stepwise function of Haar function makes it ill suited for extracting smooth data, which is our goal. However, for the purpose of classification into the six different manufacturers, details may not be needed, and Haar wavelets do offer computation simplicity. Probably for the same reason, they only retained some of the most important but not all wavelet coefficients as inputs to the neural network. However, these coefficients alone were not sufficient, so they were supplemented with their corresponding positional information. They used relatively straightforward backpropagation neural networks for the purpose of classification, and achieved good results. Much like the works cited in the previous paragraph, this work is mostly restricted to doing classification.

Schirm[19] reported using a combination of wavelet processing and neural network for quality assurance of pentosan polysulfate based on fingerprint electropherograms. They reported using Coiflet wavelets, which has higher computational demand than Haars orDachechies-2 wavelets, to preprocess the electrophoresis data. They found using a combination of mid-level transforms yield the best results for baseline and noise considerations whereas we simply use the smoothest level and have shown that it retains all vital information for our peak reconstruction. The approach to wavelet preprocessing probably depends on the data to be processed as well as the purpose of such preprocessing. Schirm's group is to provide wavelet processed data as inputs to the neural network for the purpose of classification whereas we are trying to use our neural network to extract trace peaks. Collantes, Schirm, and our work reported here indicate that the types and the details of preprocessing are important considerations for effective signal processing design especially under resources constraints. Schirm reported using simple backpropagation neural network, which performs the classification well. Our experience with backpropagation is that it is inadequate in pulling out trace signals. Both Schirm and we share the same assessment that a complete optimization of all neural network parameters would be extremely time-consuming.

CONCLUSIONS

Advanced signal processing methods, as exemplified by the wavelet-neural network approach shown here, have the potential to extract signals at a minimum of ten times lower signal to noise than standard filtering and averaging techniques. Although we have not done an exhaustive comparison of all conceivable methods, the wavelet-neural network approach is better than any we have tried. The detection limit turned out to be lower than the bit resolution of the

data acquisition equipment. Consequently, we were not able to truly determine the absolute sensitivity achievable with our BISP approach — it could be more than a factor of ten better than a conventional approach.

The method should be generally applicable to a variety of chemical analysis equipment. The current method, with proper calibration, works on any one-dimensional array, so spectra as well as chromatograms are treatable. Extensions to two-dimensional data (e.g., spectra versus time, as in GC/MS) are possible. The method really only accomplishes signal recovery, not signal interpretation, so it is different from the standard objectives of chemometrics. However, without signal recovery, chemometrics will not be able to achieve its objectives. As a result, the two methods are not redundant but complementary to each other. The enhanced signal recovery might be especially important in small portable devices, which seek to minimize power consumption at the expense of detection capability. For instruments that operate in the signal-averaging mode, it is important to remember that a tenfold difference in signal-to-noise detection limit translates into a hundredfold difference in signal acquisition time, because the signal-to-noise ratio increases as $t^{1/2}$.

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Table 1. Comparison of formulated and reported concentrations for the blind test.

Compound (approx. detection limit)		1	2	3	4	5
Trimethyl phosphate	injected	1.6	None	53	260	0.5
(1 pg)	*reported*	*2.2*	*n.d.**	*66*	*193*	*n.d.*
Tributyl phosphate	injected	1.6	268	0.5	54	none
(1 pg)	*reported*	*3.4*	*500*	*1.5*	*23*	*n.d.*
Malathion	injected	1.5	51	0.5	102	none
(1 pg)	*reported*	*7.7*	*58*	*2.6*	*47*	*(0.6)***
Chloro-methylaniline	injected	53	none	265	1060	5.3
(10 pg)	*reported*	*92*	*n.d.*	*415*	*417*	*d.*
Fluoro-nitrobenzene	injected	11.8	590	5900	5.9	none
(50 pg)	*reported*	*d.*	*750*	*9415*	*n.d.*	*n.d.*

*n.d. = not detected

**actually due to a solvent impurity peak

***d. = detected based on manual examination

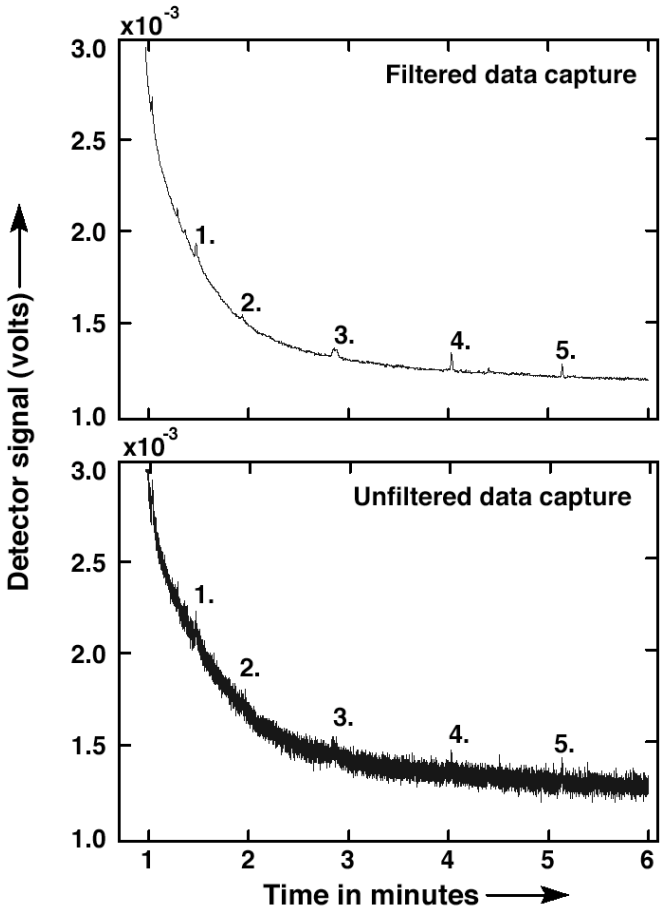

Figure 1. Sections from representative filtered (upper) and unfiltered (below) chromatograms. Peaks are: 1. TMP (5.3 pg), 2. FNB (59 pg), 3. CMA (53 pg), 4. TBP (5.3 pg) and 5. (Mal (5.1 pg). Amiton was not included in this run, but eluted just after TBP.

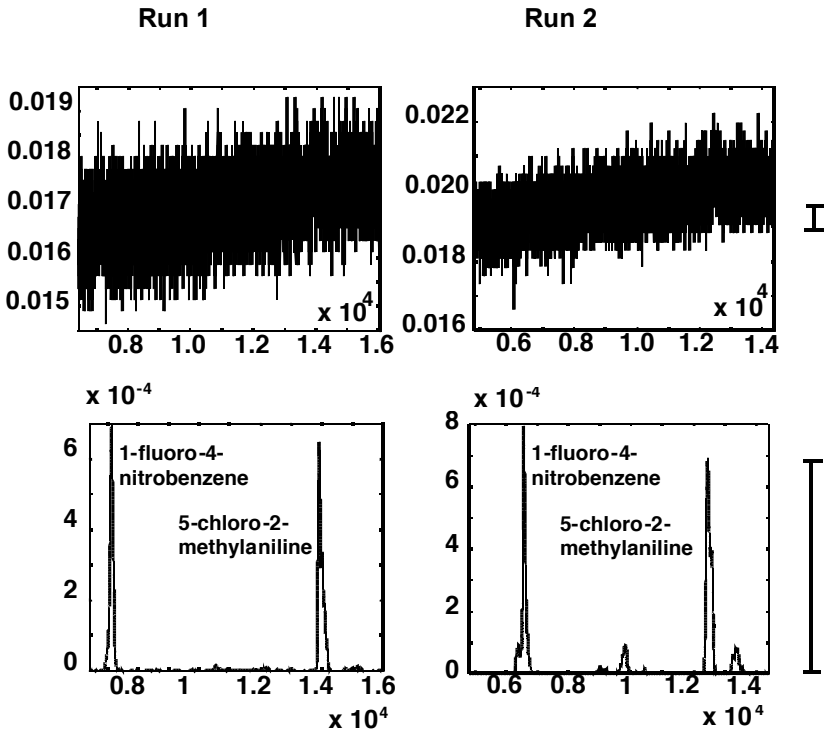

Figure 2. Replicate recoveries fluoronitrobenzene and chloromethylaniline peaks at very low levels in a gas chromatogram (abscissa is point number, not time). The small peaks may or may not be real. The two scale bars for Run 2 show the relative scales for the upper and lower figures.

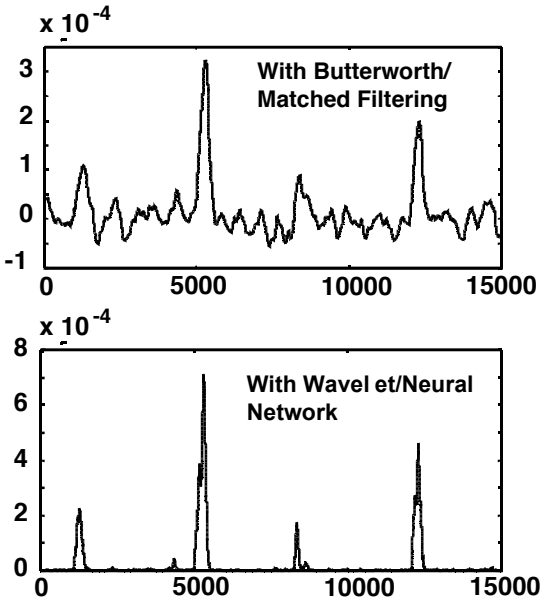

Figure 3. Comparison of recovered gas chromatographic peaks from noisy data (comparable to that in Fig. 1.) using Butterworth/matched filtering and wavelet/neural net filtering.

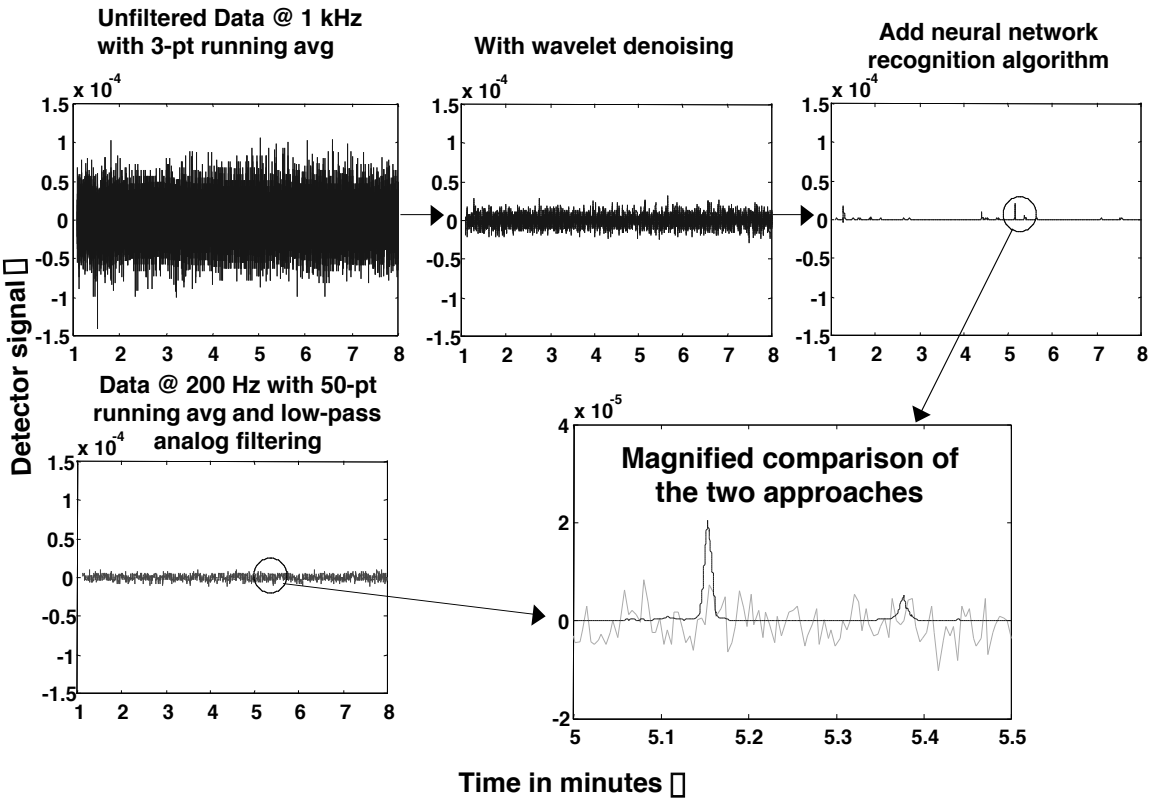

Figure 4. Comparison of the conventional (lower left) and BISP or wavelet-neural network (upper right) methods of data processing. The expanded comparison in the lower right shows clearly the superiority of the advanced signal processing method for extracting low-level signals.

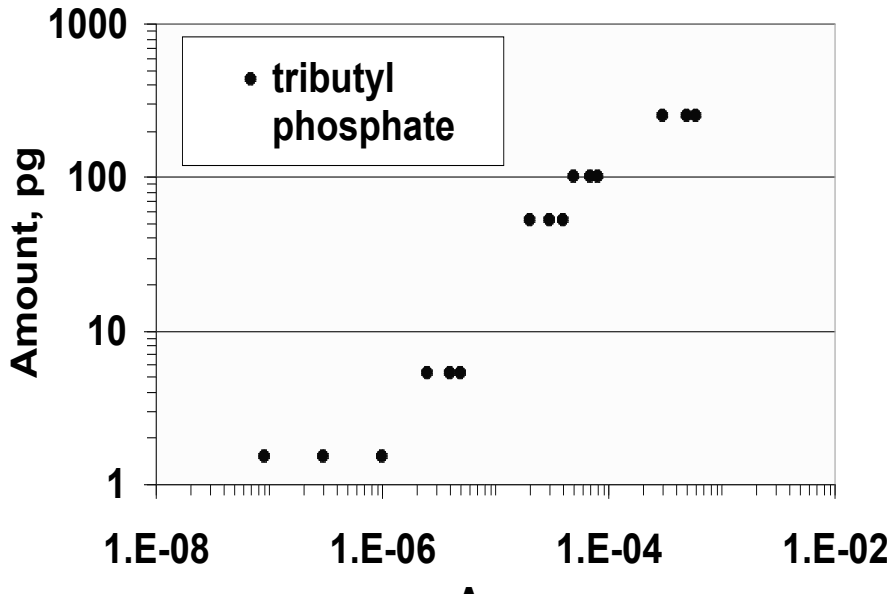

Figure 5. Typical calibration curve for the training of the wavelet-neural network method. This is created in the "application" mode, i.e., the abscissa is a measured area used to calculate the corresponding amount present.