JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

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Detection of Pesticides and Dioxins in Tissue Fats and Rendering Oils Using Laser-Induced Breakdown Spectroscopy (LIBS)

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ABSTRACT: In laser-induced breakdown spectroscopy (LIBS), a series of powerful laser pulses are directed at a surface to form microplasmas from which light is collected and spectrally analyzed to identify the surface material. In most cases, no sample preparation is needed, and results can be automated and made available within seconds to minutes. Advances in LIBS spectral data analysis using multivariate regression techniques have led to the ability to detect organic chemicals in complex matrices such as foods. Here, the use of LIBS to differentiate samples contaminated with aldrin, 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin, chlorpyrifos, and dieldrin in the complex matrices of tissue fats and rendering oils is described. The pesticide concentrations in the samples ranged from 0.005 to 0.1 μg/g. All samples were successfully differentiated from each other and from control samples. Sample concentrations could also be differentiated for all of the pesticides and the dioxin included in this study. The results presented here provide first proof-of-principle data for the ability to create LIBS-based instrumentation for the rapid analysis of pesticide and dioxin contamination in tissue fat and rendered oils.

KEYWORDS: *pesticides, dioxins, LIBS, multivariate regression, tissue fats, rendering oils*

INTRODUCTION

Dioxins are persistent environmental pollutants that accumulate in the food chain, mainly in the fatty tissue of animals.[1] They belong to a group of dangerous chemicals known as persistent organic pollutants and are of concern because of their high toxicity.[2] Prevention or reduction of human exposure is best accomplished by strict control of industrial processes to reduce formation of dioxins and by careful screening of materials coming into the food manufacturing process.[1] Both aldrin and dieldrin are organochlorine pesticides, with dieldrin being a byproduct of aldrin.[3] Dieldrin has been used in the past to control locusts and mosquitoes, as a wood preservative, and for termite control. Aldrin quickly breaks down to dieldrin both in the body and in the environment. Dieldrin is bioaccumlative, it does not break down easily in the environment, and it becomes more concentrated as it moves up the food chain to humans and wildlife. Due to concerns about potential damage to the environment and human health, all uses of aldrin and dieldrin have been banned in the United States. Dieldrin can still be found in the environment, however, and screening for both pesticides in materials coming into the food supply is very important.[3] Chlorpyrifos is a broad-spectrum chlorinated organophosphate (OP) insecticide, acaricide, and nematicide. Chlorpyrifos is used on agricultural food and feed crops, cattle ear tags, golf course turf, and vehicles, in on-structural wood treatments including processed woods, and in industrial plants. The mode of action of chlorpyrifos is similar for both target and nontarget organisms. It kills insects upon contact by affecting the normal function of the nervous system by inhibiting the breakdown of acetylcholine (Ach).[4] All four of these chemicals, 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HPCDD), aldrin, dieldrin, and chlorpyrifos are difficult to detect in poultry adipose fat and rendered oils because these samples require laborious sample preparation and matrix interferences may complicate analysis.

In laser-induced breakdown spectroscopy (LIBS), a laser spark is focused onto a sample to vaporize and excite microgram to nanogram amounts of material and generate a microplasma, or laser spark. Light from the spark is collected (typically with a fiber optic) and passed through a spectrometer to produce a spectrum that is recorded. The spectrum represents a combination of spectral signals from the bulk sample, surface material, and the atmosphere surrounding the sample. Because the microplasma is formed by focused light, typically no sample preparation is required. LIBS is an analysis technique that has been in use since the early 1960s and is an outgrowth of atomic emission spectroscopy ca. 1860 in which samples were placed in a flame for analysis and the colors observed were used for analysis.[5] Observation that a continuous spectrum was produced by the laser plasma was first made in 1962, and discussion of analysis using a laser was first published in 1963.[6] Since then, characteristics of the laser spark have been well studied, and LIBS has progressed from being a novelty to being a proven analysis technology. LIBS analysis has been applied across a broad range of applications that include, but are not limited to, industrial processing; environmental monitoring; coal analysis; sorting of metals and plastics; cultural heritage studies; detection of toxic metals in liquids; explosive, biological, and chemical detection; rock and soil analysis; aerosol, water, and soil analysis; and detection of trace elements in fresh vegetables and food powders.[6−9] There is even a LIBS instrument operating on the surface of Mars (ChemCam 2012). Most of the above-mentioned applications rely on analysis of

Special Issue: Florida Pesticide Residue Workshop 2012

Received: October 26, 2012
Revised: January 10, 2013
Accepted: January 18, 2013
Published: January 18, 2013

Table 1. Pesticide and Dioxin Samples Diluted in Hexane, Applied to Glass Slides, and Dried Prior to LIBS Analysis

slide	sample in hexane	concentration (μg/g)
1	hexane	NA
2	blank slide	NA
3	aldrin	0.103
4	aldrin	0.052
5	aldrin	0.031
6	aldrin	0.010
7	aldrin	0.005
8	dieldrin	0.104
9	dieldrin	0.052
10	dieldrin	0.031
11	dieldrin	0.010
12	dieldrin	0.005
13	chlorpyrifos	0.101
14	chlorpyrifos	0.050
15	chlorpyrifos	0.030
16	chlorpyrifos	0.010
17	chlorpyrifos	0.005
18	HPCDD	0.100
19	HPCDD	0.050
20	HPCDD	0.030
21	HPCDD	0.010
22	HPCDD	0.005

elemental emission lines observed in the LIBS spectra. More recently, advanced chemometric[10] or other analysis techniques have been applied to LIBS spectra for both classification and identification of various materials in addition to traditional elemental analysis.

The use of LIBS to differentiate pesticide-contaminated samples was first demonstrated by Kim et al.[11] Using pellets made from powdered spinach and rice flour, the ability to differentiate samples contaminated with parathion was demonstrated. Parathion is a chemical used in the farming of fruits, wheat, and vegetables but is banned in several countries because of its toxicity. In this first study, extensive sample preparation was applied to create the pellets used for LIBS data collection, and multivariate regression analysis (PLS-DA) was applied to specific multiple emission lines to achieve sample differentiation.

The goal of this work is to evaluate the use of LIBS to detect organic contaminants in complex food matrices such as tissue fats and rendering oils. The contaminants used were HPCDD and the pesticides aldrin, dieldrin, and chlorpyrifos. In our work, a simpler analysis approach, requiring essentially no sample preparation, is used to differentiate pesticide- and dioxin-contaminated fat tissue and rendered oil samples from uncontaminated samples with 100% accuracy.

MATERIAL AND METHODS

To differentiate pesticide- and dioxin-contaminated fat tissue and rendered oil samples from uncontaminated samples with 100% accuracy, an analysis method published previously by the authors to differentiate pathogens and viruses[12,13] using chemometric models combined in a predictive flow[14] is employed. By applying this method of analysis, it is possible to differentiate the unprepared pesticide-contaminated samples to much lower contamination levels than previously published.

It should be noted that multivariate analysis (either using the full spectrum or a subset of the spectrum as is the case when multiple emission lines are identified and used) of LIBS spectra does not demonstrate absolute detection of the detection target as the LIBS spectrum observed is always the combined signals arising from the

Table 2. Pesticide and Dioxin Samples Diluted in Tissue Fat and Rendered Oil and Applied to Filter Paper Just Prior to LIBS Analysis

sample in hexane	concentration in tissue fat (μg/g)	concentration in rendered oil (μg/g)
hexane	NA	NA
aldrin	0.120	0.095
aldrin	0.052	0.055
aldrin	0.029	0.024
aldrin	0.010	0.017
aldrin	0.006	0.009
dieldrin	0.063	0.103
dieldrin	0.040	0.054
dieldrin	0.021	0.040
dieldrin	0.010	0.007
dieldrin	0.005	0.007
chlorpyrifos	0.072	0.120
chlorpyrifos	0.044	0.101
chlorpyrifos	0.0.027	0.072
chlorpyrifos	0.009	0.049
chlorpyrifos	0.004	0.050
HPCDD	0.090	0.981
HPCDD	0.045	0.433
HPCDD	0.054	0.291
HPCDD	0.018	0.101
HPCDD	0.011	0.060

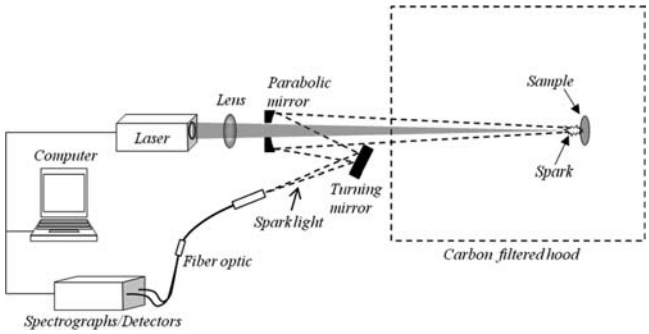

Figure 1. Experimental setup used to collect LIBS spectra. The samples were located inside a carbon-filtered hood. LIBS emission was collected along the path of the laser light to remove parallax.

experimental sampling conditions (laser energy, lens-to-sample distance, mass of material ablated and excited, etc.), characteristics of the sample being interrogated, and the atmosphere surrounding the sample. What is demonstrated is the ability to differentially identify samples from within a predefined set of samples (contaminant + matrix) for defined experimental sampling conditions. Such analysis is useful for developing LIBS instruments for specific applications in which sampling conditions can be fixed and in which the samples to be differentiated can be characterized and the natural sample variability captured in the detection algorithm. In terms of this study, the specific algorithms created are applicable only to the same equipment configuration that was used to collect the data used to build the algorithm and only to detection in the matrices of hexane, tissue fats, and rendered oils. However, the detection algorithm development methodology for a different equipment configuration would be the same.

The samples used in this study were prepared by Diversified Laboratories and included one dioxin (1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin from Accustandard) and three pesticides (all from Chemservice): aldrin, dieldrin, and chlorpyrifos. The samples were mixed with rendered tissue fat from poultry and rendered oils. The samples were spiked at five target concentration levels: 0.10, 0.05, 0.03, 0.01, and 0.005 μg/g. Sample concentrations were verified independently

dx.doi.org/10.1021/jf304589s | J. Agric. Food Chem. 2013, 61, 2348−2357

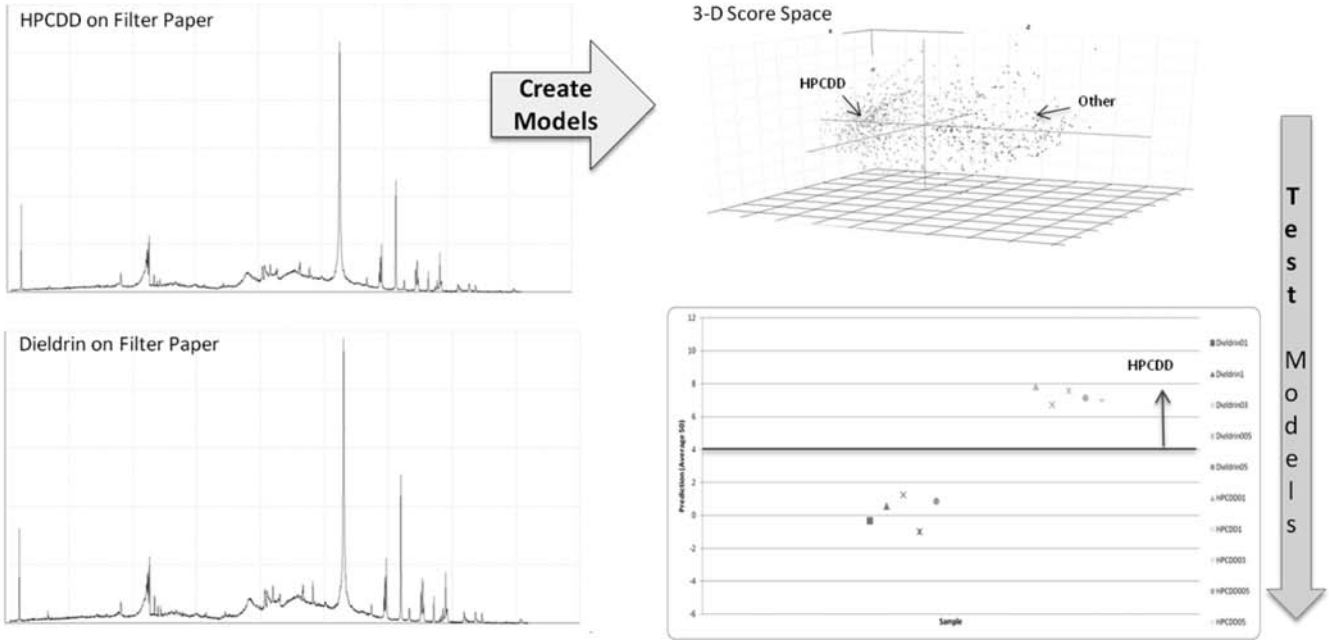

Figure 2. Illustration of the process used to create the differential models used to build a detection algorithm. Example spectra are shown on the left. On the right are (top) the three-dimensional score space plot for the resulting model and (bottom) the prediction values obtained for spectra reserved for testing the model.

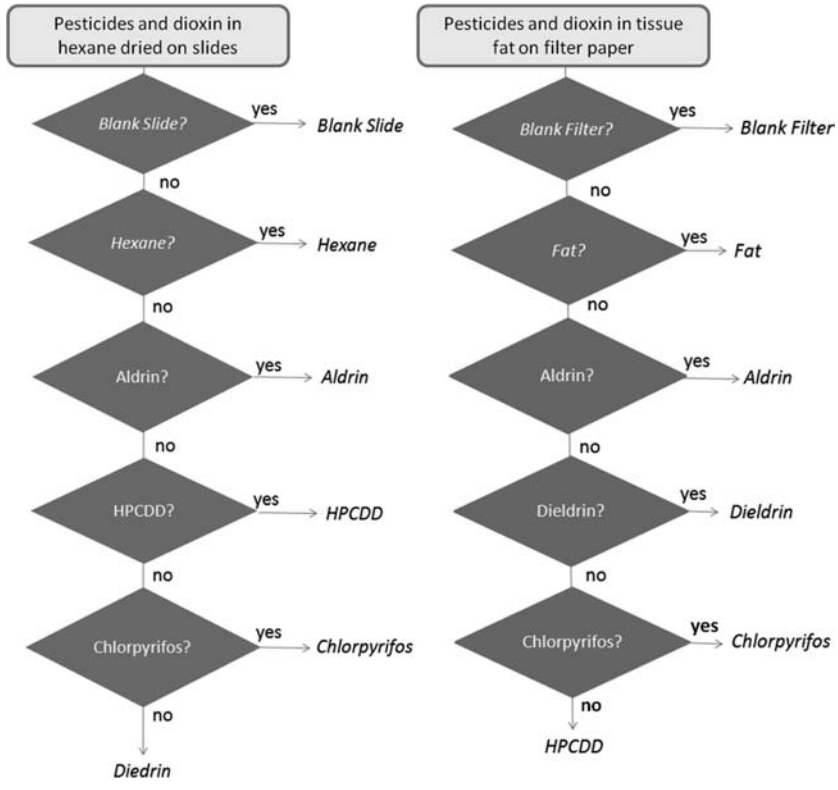

Figure 3. Algorithm flows for the differentiation of pesticides and dioxin in hexane dried on slides (left) and in tissue fat applied to filter paper (not dried).

using an Agilent 6890N GC-μECD equipped with an autosampler (Gentech Scientific, Arcade, NY, USA). The columns used were Restek Rtx-CLPesticides and Rtx-CLPesticides2, which consist of a proprietary Crossbond phase, and each column has a different film thickness (0.5 vs 0.42 μm). Operating temperatures (°C) were as follows: column oven, 140; detectors, 330; injection port, 250 (see Tables 1 and 2 for measured sample concentrations from the GC-μECD measurements). To within the error of measurement, the concentration of the samples matched the target concentrations, and all discussion will use these values. The tissue fat and rendered oil samples were prepared in serial dilutions using hexane (pesticide quality or equivalent) as the dilution solvent as follows: Approximately 1.0 g of each sample was weighed into a 1 dram

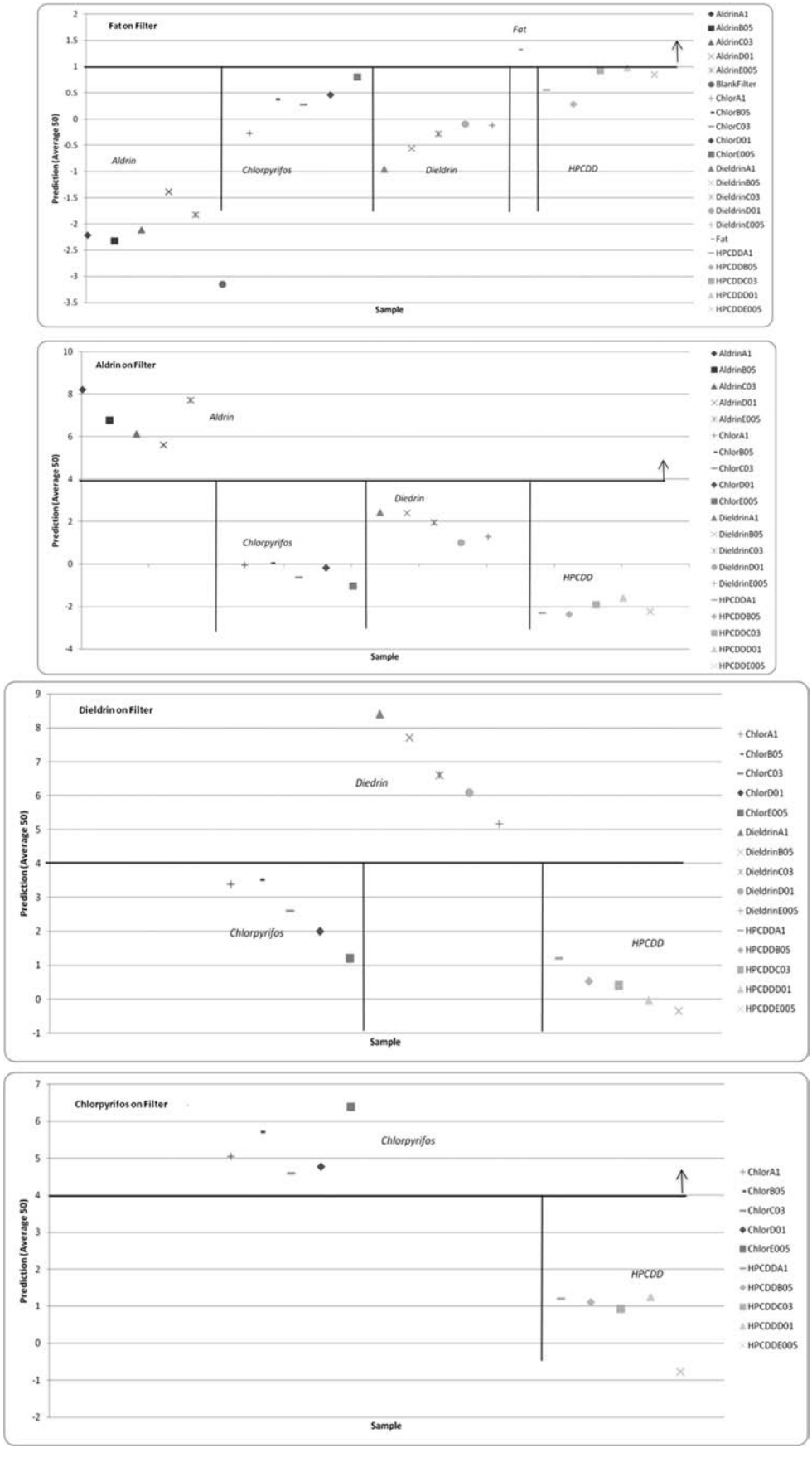

Figure 4. Plots of the prediction values obtained for the models used to differentiate the pesticides and dioxin in tissue fat. Sample name appended with a "1" = 0.1 μg/g sample; a "05" = 0.05 μg/g sample; a "03" = 0.03 μg/g sample; a "01" = 0.01 μg/g sample; and a "005" = 0.005 μg/g sample.

dx.doi.org/10.1021/jf304589s | J. Agric. Food Chem. 2013, 61, 2348−2357

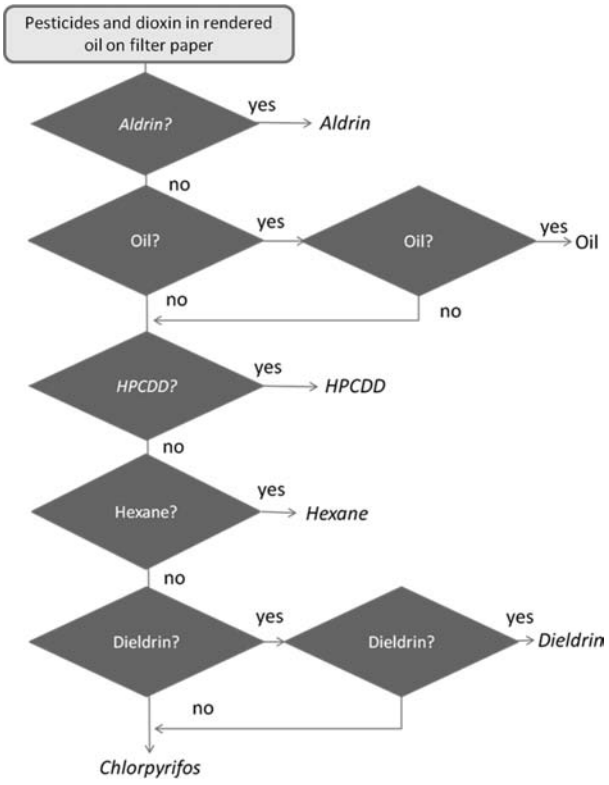

Figure 5. Algorithm flow for the differentiation of the pesticides and dioxin in rendered oil. Rendered oils from two different sources were included in the analysis.

vial using a Mettler analytical balance (Mettler Toledo, Columbus, OH, USA). The appropriate amount of standard solution was added, and the weight was brought to 2.00 g with the oil. Afterward, the samples were vortexed for 15 s and placed in vials to be shipped for LIBS analysis. The samples were applied to Whatman filter paper just prior to LIBS interrogation. A sample set of the same dilutions in hexane and dried on slides was also prepared as a first step in this investigation for pesticide and dioxin detection in a simple matrix. Dilutions of hexane (with no pesticide and dioxin) in tissue fat and rendered oils were also prepared and included as control samples to demonstrate that differentiation of the pesticide or dioxin could be separated from the differentiation of the dilution matrix.

The experimental setup used for LIBS data collection is illustrated in Figure 1. Laser pulses (1064 nm, 20 mJ/pulse, 10 Hz) from a Q-switched Nd:YAG laser (model CFR 400, Big Sky Laser, Bozeman, MT, USA) were focused onto a sample mounted either horizontally (for pesticide in hexane samples dried on slides) or vertically (for pesticide in tissue fat or rendered oil applied to filters). Plasma light was collected using an off-axis parabolic mirror and fiber optic and then routed to a spectrometer (model AvaSpec-2048-2-USB2 dual channel fiber optic spectrometer, Avantes, Broomfield, CO, USA). A hole in the parabolic mirror permitted the optical path of the laser pulses and light collection to be collinear, eliminating parallax. The sample was positioned inside a carbon-filtered hood and moved by a motorized translation stage during data collection such that a fresh spot was presented to each spark. Each recorded spectrum represented the accumulation of 10 spectra (camera acquisition parameters: 1 μs delay, 1.1 ms window). A total of 100 spectra were collected from each sample for analysis. This study included three separate data collections: (1) pesticides in hexane dried on glass slides to demonstrate proof-of-principle for the differentiation of pesticide and dioxin samples in a relatively simple matrix; (2) pesticides and dioxin samples in a more complex matrix of tissue fat applied to filter paper (no drying); and (3) pesticides and dioxin samples in the very complex matrix of rendered oils applied to filter paper (no drying). Spectra collected from each of these data collections were analyzed separately to see if a detection algorithm could be created to differentiate both sample type and sample concentration.

The method of analysis used in this study was to build mathematical models to differentiate samples or groups of samples included in the analysis and then use these models in a predictive flow that relies on sequential screening.[14] The differentiation models are based on single-variable partial least-squares regression combined with principal component analysis. This technique is commonly referred to as PLS and is especially useful when trying to predict a set of dependent variables from a very large set of independent variables. In PLS analysis it is assumed that all of the measured variance is useful variance to be explained. The latent variables are estimated as exact linear combinations of the observed measures to create an exact definition of component scores. Through an iterative estimation technique, a general model is developed that encompasses canonical correlation, redundancy analysis, multiple regression, multivariate analysis of variance, and principal components. The iterative algorithm consists

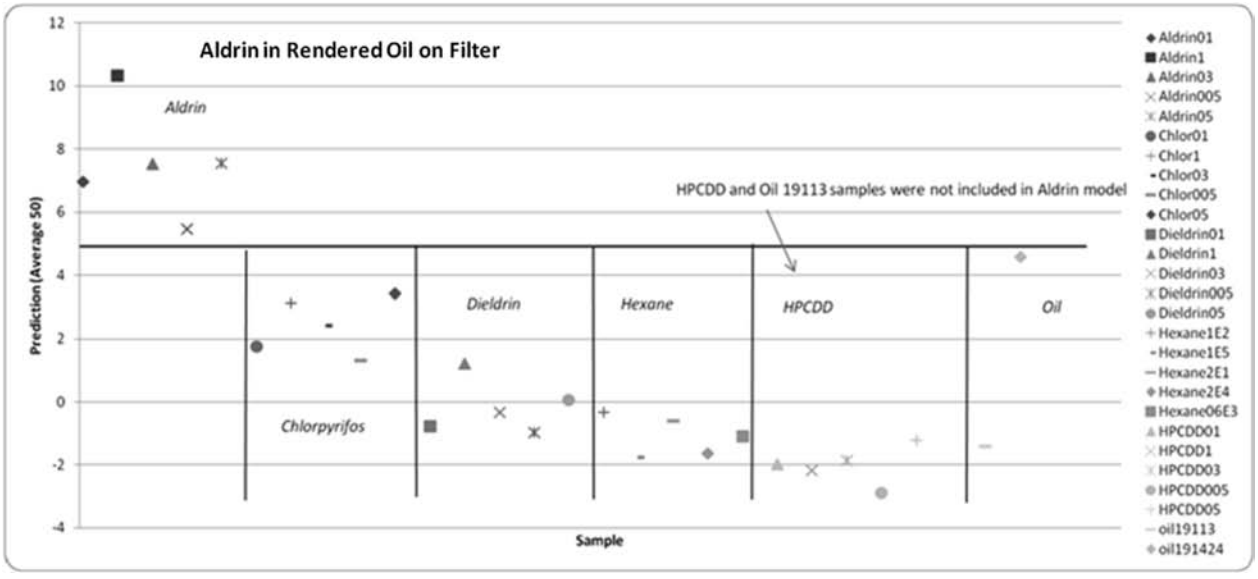

Figure 6. Differentiation model created for the detection of aldrin in rendered oil did not include the dioxin and the second oil in the modeling and is still able to differentiate the aldrin sample from the HPCDD sample in the second oil. Sample name appended with a "1" = 0.1 μg/g sample; a "05" = 0.05 μg/g sample; a "03" = 0.03 μg/g sample; a "01" = 0.01 μg/g sample; and a "005" = 0.005 μg/g sample.

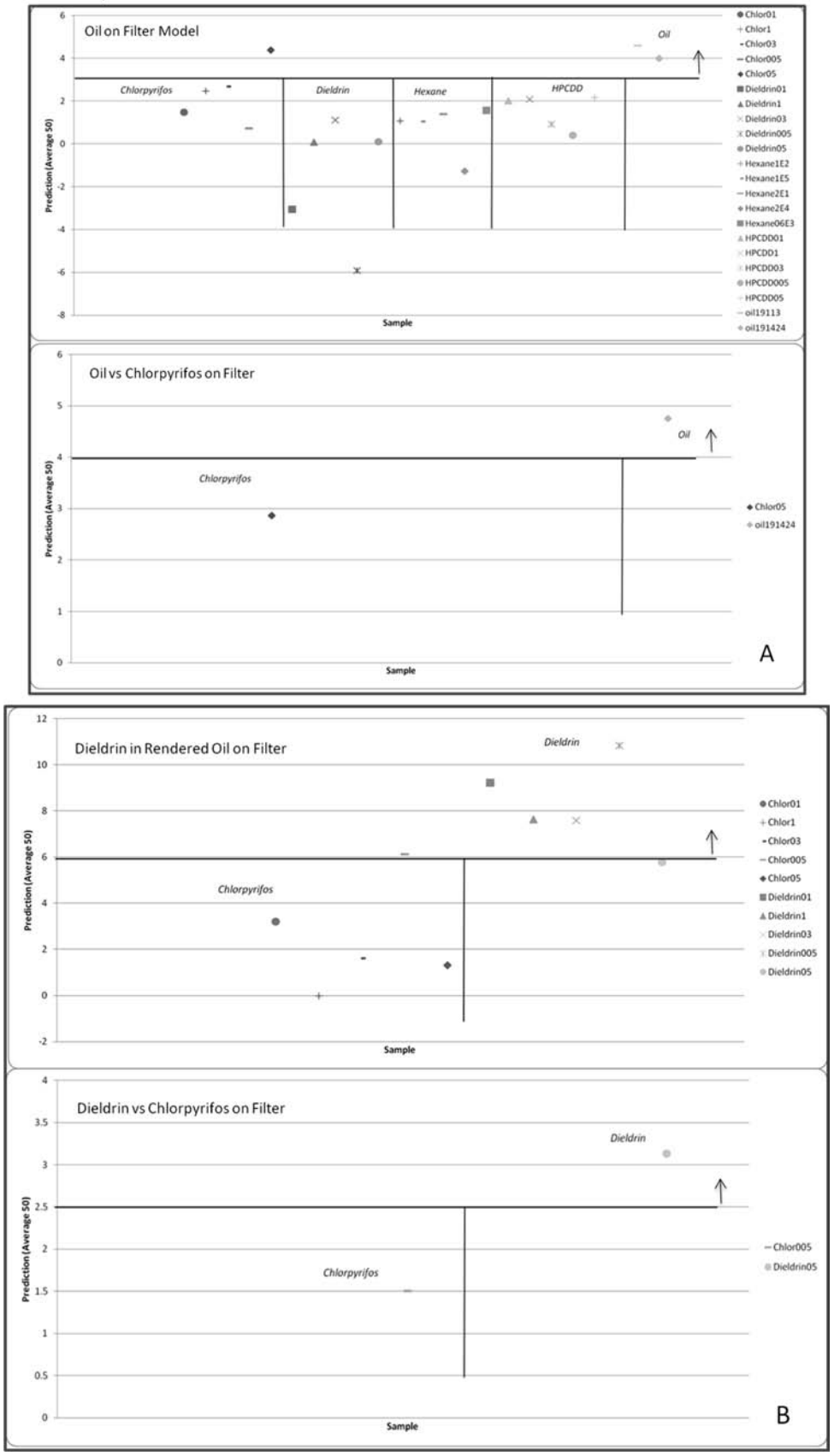

Figure 7. Two models were required to prevent misidentification of chlorpyrifos as a rendered oil (A) and chlorpyrifos sample as dieldrin (B). Sample name appended with a "1" = 0.1 μg/g sample; a "05" = 0.05 μg/g sample; a "03" = 0.03 μg/g sample; a "01" = 0.01 μg/g sample; and a "005" = 0.005 μg/g sample.

dx.doi.org/10.1021/jf304589s | J. Agric. Food Chem. 2013, 61, 2348−2357

of a series of ordinary squares analyses. No distributional form is assumed for the measured variables. PLS1, used in this analysis, is a PLS method in which only one variable is modeled. Once a model has been generated for the sample classes, it can be used on test samples to produce a predictor value (in this case between 0 and 10) to be used to match the input tested sample to one of the sample classes. For this analysis, the dependent variable is the sample and the independent variables associated with the sample are the intensity measurements at each wavelength. Commercially available software (The Unscrambler, Camo Software Inc.) was used for analysis, and spectral normalization (the maximum peak value within each spectrum was equal to 1 following the normalization) was applied to all spectra prior to building models. For the modeling of all samples, the entire observed wavelength range was used as the variable set with the measured intensity treated as the values of the variables. Because the entire spectral range was used, the modeling was done over 4096 variables (spectrometer channels) for each sample (spectrometer channel 1, 232−494 nm, 0.32 nm resolution; spectrometer channel 2, 495−1026 nm, 0.6 nm resolution).

For each group of samples to be differentiated, models were created using 50 of the 100 spectra collected for each sample and then tested using the remaining 50 spectra reserved for the evaluation of model performance. When a spectrum was input into a differentiation model, the model produced a "prediction value" that indicated how well the input sample was matched to the two sample groups used to build the model. Good discrimination models were considered to be those that resulted in a wide enough separation of the prediction values for the two groups that a value in the prediction value gap could be chosen for which input samples with higher prediction values would be considered matched to the sample being discriminated. Samples with prediction values lower than this chosen prediction value would be considered matched to the samples not being discriminated. Figure 2 illustrates this process. As shown in the figure, the best models are those for which there is a wide separation in the prediction values obtained from the model for the two sample groups being differentiated when test spectra are input. To improve the observed separation, prediction values obtained were averaged (typically 50, but less in some cases when fewer spectra were available for testing the model performance). Once a good model (a model that differentiated a sample group from the remaining samples) was created, the model was placed in the algorithm flow, the sample group was removed from the differentiation, and the process was repeated until a model could be created to differentiate another sample group. This process was repeated until all sample groups were identified to create the finalized detection algorithm.

To study the ability to create detection algorithms to differentiate concentration, two approaches were applied. One approach was to build detection algorithms based on differential analysis against concentration within a sample group as described above. The other approach was to apply regression modeling against concentration to create a single model to predict sample concentration as opposed to creating an algorithm using multiple models for sequential differentiation of concentration.

RESULTS AND DISCUSSION

Using the analysis method described above and grouping samples by type regardless of concentration for the modeling, a detection algorithm could be created for the differentiation of the pesticides and dioxin at all concentrations in all matrices studied. Figure 3 shows the algorithm structure for the differentiation of pesticides in hexane dried on slides and for the differentiation in tissue fats applied to filter paper just prior to analysis (not dried). The algorithms created for these two different matrices have similar structure: first the uncontaminated matrix material is differentiated, next is the dilution medium, and third are the samples contaminated with aldrin. At this point, the two algorithms differ in differentiation structure, with HPCDD being the next easiest to differentiate in the hexane samples and dieldrin being the next easiest to differentiate in tissue fats. In both hexane and tissue fat, chlorpyrifos is one of the pesticides hardest to

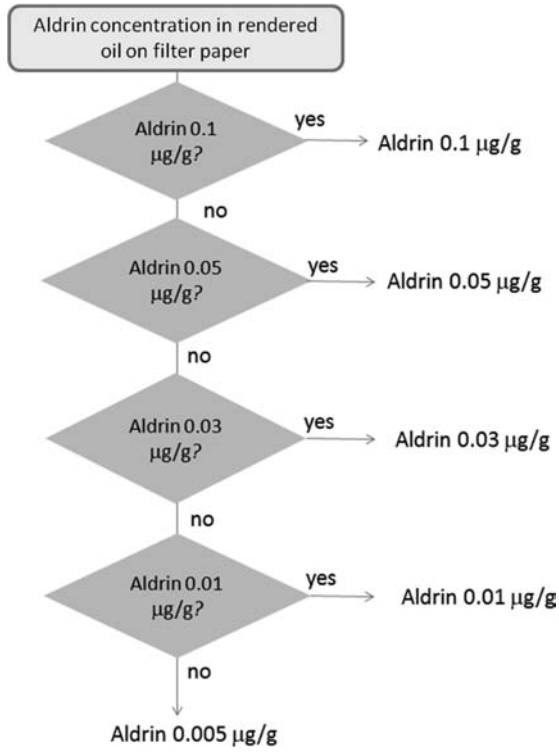

Figure 8. Algorithm flow for the differentiation of the aldrin concentration in rendered oil.

differentiate as can be seen from its positioning in the detection flow. The differentiation performance of the models used in both detection algorithms, as measured by the results obtained when the models were run on the verification spectra, were similar. See Figure 4 for the prediction values obtained for the test spectra when input into the models used to differentiate the pesticides and dioxin in tissue fat. The prediction value used to separate the different samples is indicated by the horizontal black line and arrow.

Differentiation in the rendered oil matrix required a more complicated analysis structure with multiple models needed for two of the differentiation groups (see Figure 5). For this analysis, rendered oils from two different sources were included to further demonstrate detection capability in a matrix for which composition varies and is relatively unknown. The pesticide samples were diluted in rendered oil 1 (oil 191424), and the dioxin sample was diluted in rendered oil 2 (oil 19113). Both uncontaminated oils were differentiated in the flow to verify the detection was due to the presence of the pesticide or dioxin rather than a difference in the rendered oil composition. For detection in rendered oils, aldrin-contaminated samples were the easiest to differentiate, and this differentiation is the first step in the detection algorithm. It should be noted that the aldrin differentiation model was created without including the HPCDD and oil 2 samples in the modeling and is still able to differentiate the aldrin sample from both (see Figure 6). Once the aldrin sample group was removed from the analysis, the process was repeated, and it was found that the next easiest to differentiate sample group was the uncontaminated oil group. However, to successfully differentiate this group, two models were required to successfully identity this group without misidentifying the highest concentration chlorpyrifos sample group as a rendered oil (see Figure 7A). Uncontaminated rendered oils were then removed from the analysis, the process was repeated, and it was

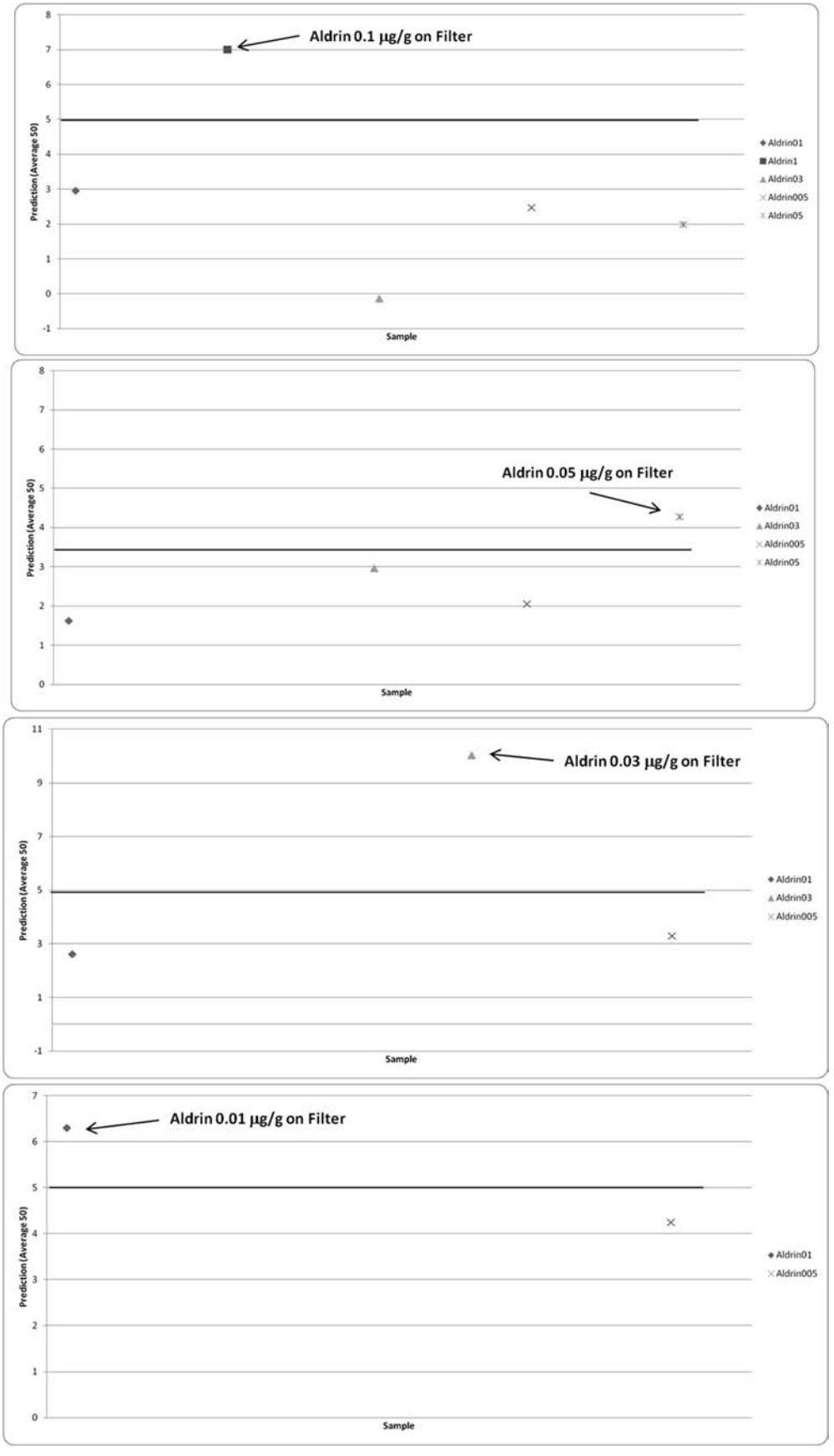

Figure 9. Plots of the prediction values obtained for the models used to differentiate the aldrin concentrations in rendered oil. Sample name appended with a "1" = 0.1 μg/g sample; a "05" = 0.05 μg/g sample; a "03" = 0.03 μg/g sample; a "01" = 0.01 μg/g sample; and a "005" = 0.005 μg/g sample.

dx.doi.org/10.1021/jf304589s | J. Agric. Food Chem. 2013, 61, 2348−2357

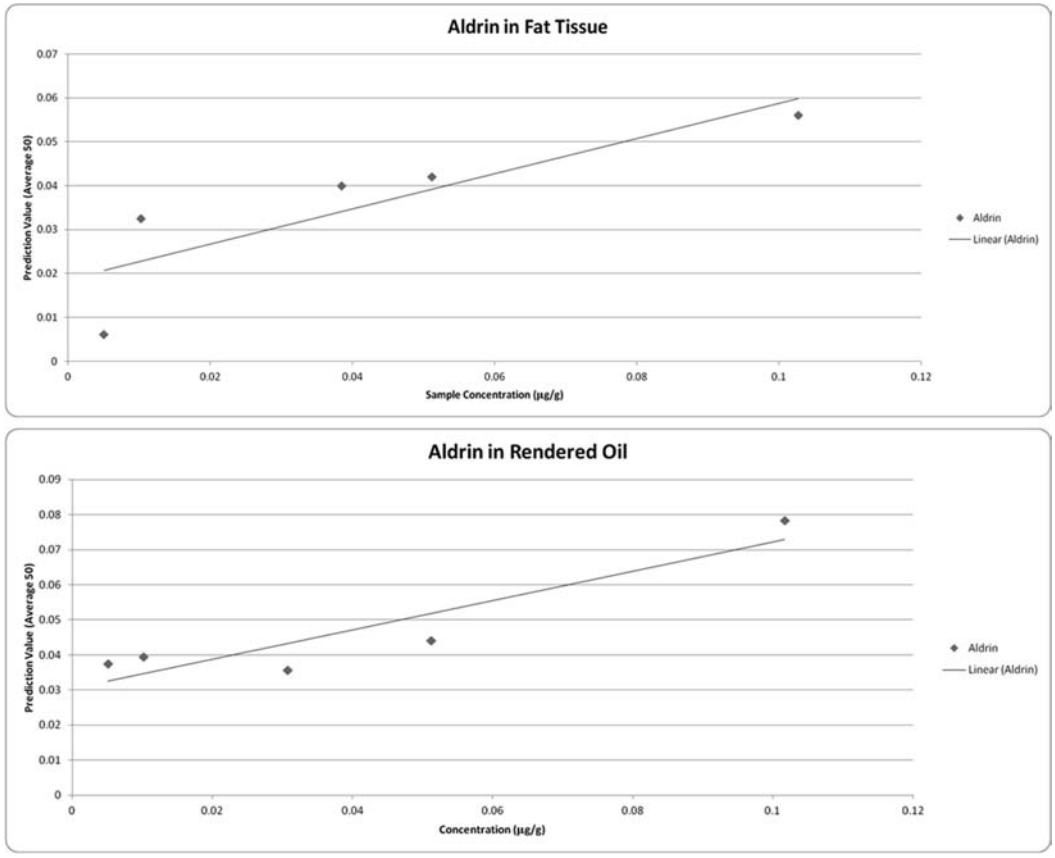

Figure 10. Plots of the prediction values obtained for regression models built used to differentiate the aldrin concentrations in fat tissue (top) and rendered oil (bottom). The line shown is a linear fit in Excel.

found that the next easiest to differentiate groups were the HPCDD sample group followed by the hexane sample group. To differentiate the dieldrin sample group from the chlorpyrifos sample group, two models were also needed to ensure the lowest concentration chlorpyrifos sample was not misidentified as dieldrin (see Figure 7B). As was found in the previous two differentiation algorithms for detection in hexane and tissue fat, the chlorpyrifos sample group is again one of the hardest to differentiate of those studied.

Differentiation of sample concentration using the methods described above was applied to each pesticide and dioxin sample group for all of the matrices studied, and it was found that all samples could be differentiated by concentration for all cases. Figure 8 shows the algorithm flow for differentiating aldrin concentration in rendered oils. Figure 9 shows the results when this algorithm was run on the verification spectra not included in the modeling used to create the detection algorithm. To further investigate the ability to differentiate sample concentration, a regression analysis of prediction value against concentration was performed using the differentiation results for pesticide and dioxin concentrations in fat tissue and rendered oils. In many cases, a strong relationship was found to exist between concentration and the prediction value. Figure 10 shows the results obtained using verification spectra for aldrin in fat tissue and in rendered oil. A good relationship exists for aldrin in rendered oil with an R^2 value of 0.85, whereas the relationship for aldrin in fat tissue is not well-defined. Additional work is needed to verify that a reliable relationship exists between prediction value and concentration and to establish that the prediction value can be used as an indicator for pesticide and dioxin concentration.

The results of this study show that LIBS has demonstrated potential as a diagnostic for the rapid detection of pesticides and dioxins (seconds to minutes) in complex matrices such as tissue fats and rendered oils with practically no sample preparation. Both type and concentration of the pesticide were determined using the new methods of analysis described herein. Detection algorithms are tailored to the application and are developed for a specified set of matrices and targeted species, but the method of detection algorithm development as described is independent of the application and the detection targets.

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Funding

This research was funded by Diversified Laboratories.

Notes

The authors declare no competing financial interest.

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