Fungicide Residue Identification and Discrimination
Using a Conducting Polymer Electronic-nose

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Abstract— The identification of fungicide residues on crop foliage is necessary to make periodic pest management decisions. The determination of fungicide residue identities currently is difficult and time consuming using conventional chemical analysis methods such as gas chromatography-mass spectroscopy. Different fungicide types produce unique electronic aroma signature patterns when headspace volatiles are analyzed using a multi-sensor array within an electronic–nose device. The advantage of electronic-nose sensor devices over conventional methods is that fungicides may be rapidly identified even in the presence of complex plant volatile organic compounds derived from crop foliage that may be present in the headspace mixture. New methods were developed for a conducting polymer type electronic nose device, the Aromascan A32S with a 32-sensor array, to accurately identify and discriminate between fungicide residues types in vitro. The A32S electronic nose distinguished between nine of eleven fungicide types, providing correct identification determinations at frequencies ranging from 84-98%. The distribution of aroma class components, defined by the principal aroma elements detected for each fungicide type analyzed, was determined providing some indications of chemical relatedness between different fungicide aroma classes. The A32S electronic-nose device was capable of providing effective identification and discrimination determinations of most fungicide residue types tested in vitro and has strong potential feasibility for making e-nose fungicide residue determinations on plant (crop) surfaces in the field.

Keywords- electronic aroma detection; e-nose technologies; volatile organic compounds; fungicide identification

I. INTRODUCTION

The detection and identification of pesticides and other chemical residues on agricultural and landscape plants currently requires time-consuming and expensive chemical analyses [1-4]. This problem has led to delays for crop and land managers who must make frequent crop-management and pest-control decisions involving pesticides applications. Pesticide residues on food crops also are a significant health concern, particularly on vegetables and fruits, which broadly impacts environmental regulatory decisions regarding the safety and legal-sale of food products in commercial markets. The inadequacies of current analytical methods for determining the identities and concentrations of pre-harvest and postharvest crop pesticide residues on the surfaces of food products has produced a strong need for new rapid chemical-detection methods to effectively identify pesticide residues on plants in crop fields and in postharvest storage facilities prior to plant-product introductions into commercial food markets. Thus, a portable electronic analytical gas-sensing device capable of quickly identifying agricultural pesticides on crop surfaces to avoid the high cost of conventional chemical analyses would have high utility.

Electronic-nose (e-nose) devices are designed to produce digital electronic aroma signature patterns (EASPs) derived from sensor-array responses to volatile organic compounds (VOCs) released from chemical sources [5-7]. Unlike other analytical instruments, e-nose devices have the capability of identifying organic samples from the VOCs they release without having to identify individual chemical compounds present in volatile mixtures [8-10]. A variety of different e-nose sensors have been developed including optical sensors [11], metal oxides [12, 13], semi-conductive polymers [14-16], and conductive polymers [17-19] for different applications. The broad agricultural and food industries have utilized electronic aroma detection (EAD) technologies to evaluate food quality and product aromas [20-21], food storage life and freshness [22-24], detect industrial wastes [25-26], diagnose plant diseases [27], and for many other agricultural applications [28-29], including the detection of hazardous agricultural chemicals in the environment [30-32].

The purposes of this study were to 1) determine if an electronic-nose (e-nose) device, the conductive polymer (CP)-type Aromascan A32S e-nose, has the capability of identifying different fungicide residue types in vitro, 2) evaluate the effectiveness (accuracy) of fungicide determinations, and 3) assess whether e-nose aroma data outputs provide some indications of chemical-relatedness between fungicide types from different chemical classes. The fungicide chemical classes tested include polychlorinated aromatic (chlorothalonil), piperazine (triforine), phenylamide (metalaxyl), organochlorine (PCNB), five triazoles (propiconazole, myclobutanil, triadimefon, difenoconazole, and tebuconazole), strobilurin (azoxystrobin), and dicarboximide (iprodione).

This paper is composed of an experimental section describing the materials and methods used in associated with e-nose procedures, followed by results of research findings for CPA e-nose chemical analyses of fungicides residues, and a discussion and conclusions section, based on research

results, to summarize the significance of findings and new discoveries resulting from this research.

II.   MATERIALS AND METHODS

A.   Collection and storage of fungicide samples

Eleven technical grade fungicides with the following specified common names and formulations, obtained from various pesticide manufacturers, including chlorothalonil (Bravo), triforine (Funginex), metalaxyl (Apron), pentachloronitrobenzene abbreviated as PCNB (Terrachlor), propiconazole (Tilt), azoxystrobin (Quadris), iprodione (Rovral), myclobutanil (Systhane), triadimefon (Bayleton), difenoconazole (Dividend), and tebuconazole (folicur) were utilized in this study. The fungicide azoxystrobin is unique among the eleven fungicides in that it is composed of a mycotoxin secondary metabolite (primarily strobilurin A), produced by mushrooms of the agricaceous fungi *Oudemansiella mucida* and *Strobilurus tenacellus*, common in Czechoslovakian forests.

B.   Sample preparation and prerun procedures

Small aliquots (10 µl) of each fungicide type were analyzed separately by placing them into 14.8 ml uncapped glass vials inserted into a 500 ml Pyrex glass sampling bottle no. 1395 (Corning Inc., Corning, NY) fitted with reference air, sampling, and exhaust ports on a polypropylene bottle cap. Reference air entered the sampling bottle through a 3 mm polypropylene tube extending to just above the bottom of the sampling bottle. The sampling bottle was held in the sampling chamber at a constant air temperature of 25 C. The sampling bottle was purged with moisture-conditioned reference air for 2 min prior to building headspace. The sampling bottle was sealed and volatiles from each fungicide analyte were allowed to build headspace and equilibrate for 30 min prior to each run. Reference air was maintained at 4% RH at 25 C. Prerun tests were performed as needed to determine sample air relative humidity compared with that of reference air. A reference library (recognition file) for fungicide types was constructed using neural net training by defining aroma classes using reference databases of known fungicides. This recognition file then was used to identify unknown samples.

C.   Instrument configuration and run parameters

All analyses were conducted with an Aromascan A32S (Osmetech, Inc.,Wobum,MA) CP e-nose instrument with 32 sensor capacity in the sensor array and 15 V across sensor paths. The response sensitivities of individual sensors, measured as percent changes in electrical resistance response across sensor paths relative to base resistance (%ΔR/Rbase), varied with the type of plastic polymer used in the sensor matrix coating, the type of ring substitutions used to modify its conductive properties, and the type of metal ions used to dope the matrix to improve and modulate sensor response. Detailed results of analyses that provided prior characterization and calibration of the sensor array were reported previously [27]. The block temperature of the sensor array was maintained at a constant 30 C. Reference air was preconditioned by passing room air sequentially through a carbon filter, silica gel beads, inline filter, and Hepa filter to remove organic compounds, moisture, particulates, and microbes, respectively, prior to humidity control and introduction into the sampling bottle. The flow rate (suction) of sample air at the sampling port was maintained at -702 ml/min using a calibrated ADM 3000 flow meter (Agilent Technologies, Wilmington, DE). Sensor surfaces were purged between runs using a 2% isopropanol wash solution. The instrument was interfaced with a personal computer via an RS232 cable and controlled with Aromascan Version 3.51 software. The instrument plumbing was altered from conventional architecture and specifically configured for static sampling of the headspace by allowing air flow, maintained at 605 ml/min flow rate, coming out of the external vent port of the instrument during analytical runs, and closing the exhaust port on the sampling bottle so that headspace volatiles were taken from a homogeneous static air mass within the sampling bottle.

D.   Data acquisition parameters and run schedules

Data from the sensor array were collected at 1 s intervals using a 0.2 detection threshold (y-units), a 15–20 y-max graph scale, and with a pattern average of five data samples taken per run during data acquisition. A uniform run schedule was used consisting of reference air 20 s, sampling time 90 s, and wash 20 s, followed by 90 s of reference air for a total run time of 220 s. A 2 min reference air purge was completed between runs after each sample was removed from the sampling bottle.

E.   Construction of reference libraries and validation

An aroma signature reference library was constructed from known fungicide residue types included in this study. All database files were linked to specific (designated) aroma classes defining each sample type or category. The following recognition network options (neural net training parameters) were used for each training session: training threshold = 0.60, recognition threshold = 0.60, number of elements allowed in error = 5, learning rate = 0.10, momentum = 0.60, error goal = 0.010 (P = 0.01), hidden nodes = 5, maximum iterations (epochs) = 10,000, using normalized input data, not actual intensity data. Some parameters were modified for improvement of recognition accuracy. A typical training required 2–35 min, depending on the size of the database applied, using an IBM-compatible personal computer with a minimum of 64 mb of RAM and 350 MHz run speed. Neural net trainings were validated by examining training results that compare individual database files for compatibility or by similarity matches to each specific odor classes by test-assigned odor class distributions among related odor classes included in each library. The specific detailed analytical methods used for identification of unknowns, data processing, and statistical determinations followed the procedures and specifications indicated by Wilson et al. [27].

F.   Principal component analysis

Detailed comparisons of relatedness of odor classes (fungicide types) were determined using principal

component analysis (PCA) algorithms provided by Aromascan Version 3.51 software. Three-dimensional PCA was used to distinguish between headspace volatiles released from eleven fungicide residue types in vitro. The mapping parameters for three-dimensional PCA were: iterations = 30, units in Eigen values (%), and with normalized input data.

III. RESULTS

A. Identification of fungicide residue types

The A32S CP e-nose effectively identified nine of the eleven fungicide types tested based on differences in the aroma profiles of headspace volatiles derived from technical grade fungicide samples. Correct identifications of unknown fungicides residues were determined at rates ranging from range 84-98% for all fungicide types except for azoxystrobin and iprodione. Aroma discrimination software could not assign these two fungicide residue types to a principal aroma classification, among all of the aroma profiles present in the aroma reference library, because a large proportional majority of aroma components within the headspace volatiles from these fungicides did not fall into a single aroma class. The aroma components of both fungicide residues were predominantly distributed evenly among the two aroma classes of these two residue types. Thus, ambiguous identity determinations resulted for azoxystrobin and iprodione because a large percentage of aroma components were assigned to primarily two different aroma classes.

B. Discrimination between fungicide types

The aroma profiles of each fungicide type were further evaluated by neural net training validation during the process of creating a diagnostic pesticide library for the selected fungicides. Analysis of data from the sensor array for each aroma class (defined by the principal components present in aroma profiles from each fungicide type) provided a precise breakdown of the aroma class distribution of principal aroma components present in volatiles among the eleven fungicide types (Table I). The aroma class distribution indicated (on percentage bases) the proportion of aroma components, present in the headspace volatiles from each fungicide type, that were in common with principal aroma elements of volatiles from other fungicide types present in the reference library. The amount (percentage) of overlap among principal aroma elements from volatiles of each fungicide type provided an indication of relatedness between the chemical classes or chemical nature of volatiles released from individual fungicide residue types. Nine of the eleven fungicide types were identified correctly with a majority proportion of the aroma profile that was assigned to the principal aroma element characteristic of each fungicide type. The range of aroma class distributions attributed to the principal aroma class characteristic of each fungicide type ranged from 86.3% in difenoconazole to 98.4% in triadimefon. Unusually low proportions of the aroma class distribution profiles of azoxystrobin (57.8%) and iprodione (45.0%) were attributed to their respective principal aroma component. Consequently, these two fungicides residue

types were determined as unknown aroma profiles and could not be identified. The proportion of secondary aroma elements attributed to aroma classes (besides the principal aroma element) ranged from 10.3-53.5% for azoxystrobin with three minor aroma elements, and 5.0-41.0% for iprodione with four minor aroma elements.

The number of minor aroma elements found among the aroma class distributions of the nine identified fungicide residues ranged from two to six. The smallest number of minor elements (two) discovered among the fungicides tested was determined for mycobutanil with aroma class distributions ranging from only 2.0-3.2%. The largest number of minor elements (six) was found for tebuconazole with aroma class distributions ranging from only 1.9-10.4%. The highest proportion of minor elements attributed to a single minor aroma class with identifiable fungicides was determined for propiconazole with 26.4% triforine aroma elements, PCNB with 22.5% propiconazole aroma elements, and chlorothalonil with 17.8% propiconazole aroma class elements.

C. Principal component analysis

An analysis of eleven fungicide residue types using PCA by pairwise comparisons of headspace volatiles in all possible combinations provided indications of possible chemical relatedness between fungicides. The results of relatedness between fungicide volatiles were measured using a statistical algorithm called quality factor (QF) analysis that determines the distance between aroma profiles using Euclidean distance units of measurement. The greater the QF value determined from pairwise comparisons of volatiles, the greater the difference (or distance) between the aroma signature profiles of the two aromas being compared. In terms of statistical determinations, a QF value of 2.0 is roughly equivalent to a statistical difference at $P = 0.10$ level of significance. The aroma relatedness among seven fungicide types from different chemical classes varied considerably based on Euclidean distance as indicated in Table II. QF values ranged from 2.4 to >320, indicating a very wide range of chemical differences between individual fungicide residue types. Among the seven fungicides compared, the QF of 2.4 indicated a significantly different, but relatively close aroma signatures between chlorophalonil and propiconazole. The biggest difference, indicated by a QF of >320, showed a strong difference between the headspace volatiles of PCNB and azoxystrobin. Moderate levels of aroma differences were found between chlorothalonil, triforine, and PCNB, between triforine, PCNB, and propiconazole, and between azoxystrobin and iprodione. Intermediate levels of aroma differences were found between chlorthalonil and iprodione, triforine and metalaxyl, metalaxyl and propiconazole, and between PCNB and iprodione. High levels of aroma differences were found between chlorothalonil, metalaxyl, and azoxystrobin, between triforine, azoxystrobin, and iprodione, and between metalaxyl, PCNB, azoxystrobin, and iprodione.

TABLE I.   DISTRIBUTION OF ELECTRONIC-NOSE AROMA CLASS COMPONENTS AMONG ELEVEN FUNGICIDE TYPES

Fungicide Types	Aroma Class Distribution (%)[a]										
	Fungicide Types (Chemical common name abbreviations)										
	Chlo	Trif	Meta	Pcnb	Prop	Azox	Ipro	Myco	Tria	Dife	Tebu
Chlorothalonil	**90.4**	–	9.7	–	17.8	–	–	–	–	15.8	–
Triforine	–	**92.3**	–	7.2	11.7	16.3	13.2	2.9	–	–	–
Metalaxyl	–	–	**88.8**	–	14.9	8.0	6.4	9.6	11.4	–	–
PCNB	–	10.9	–	**88.1**	22.5	–	–	7.8	–	–	5.6
Propiconazole	–	26.4	7.4	6.5	**86.5**	–	–	–	7.2	14.8	–
Azoxystrobin	–	17.2	–	–	–	**57.8**	53.5	–	10.3	–	–
Iprodione	–	7.5	–	–	–	41.0	**45.0**	–	–	5.5	5.0
Mycobutanil	–	–	2.0	–	–	–	–	**98.4**	–	–	3.2
Triadimefon	–	–	5.3	1.7	–	1.4	–	–	**92.4**	6.5	–
Difenoconazole	–	–	–	3.7	9.3	–	–	–	1.9	**86.3**	5.6
Tebuconazole	3.7	–	–	10.4	–	6.0	9.2	1.9	–	5.9	**91.0**

a. Mean percent aroma class distributions indicated for each fungicide type; read from left to right (by row), not top to bottom. Fungicide abbreviations correspond to fungicide types (column 1).

The relatedness between aroma profiles of volatiles from the seven fungicide residue types, based on 3-dimensional CPA, was graphed in the form of an aroma map that indicates Euclidean distances among the seven fungicide types (Figure 1). The percentages of the total variance for this analysis, accounting for the variability explained by each orthogonal principal component (PC), are as follows: PC 1 = 61.5%; PC 2 = 25.8%; and PC 3 < 7.4%, representing the x-, y-, and z-axis of the aroma map, respectively. A high proportion (87.3%) of the total variance was explained by the first two principal components (PC 1 and PC 2). Two clusters of data points on the aroma map indicated groups of fungicide residue types that were significantly different, but moderately related based on similar aroma elements. The first data cluster consisted of chlorothalonil, propiconazole, and PCNB that had relatively low pairwise QF values of 2.4, 6.2, and 16.9 for each respective combination tested. The second cluster of data points consisted of azoxystrobin and iprodione with a pairwise QF value of 7.7 indicating a moderate level of chemical relatedness based on aroma elements. The fungicide residues of triforine and metalaxyl were highly separated from the two related data clusters, resulting in pairwise QF values ranging from 30.6 to 316.1 for triforine (relative to the other fungicides) and QF values of 75.6 to 317.1 for comparisons of the other fungicides to metalaxyl. However, the pairwise comparison yielding the largest QF value of >320 was between PCNB and azoxystrobin, indicating very large differences in aroma elements and an extremely low level of chemical relatedness.

The five triazole fungicides also were compared together in a separate PCA analysis to determine the e-nose capability of distinguishing between fungicides within the same chemical class. Comparisons of the triazole fungicide residues generally showed lower pairwise QF values that indicated a greater chemical relatedness between fungicides within the triazole class, based on aroma elements, than between fungicides from different chemical classes. The most chemically-related triazoles were difenoconazole and tebuconazole with a QF of 1.3 showing very similar aroma profiles. Most of the other pairwise comparisons between the triazoles resulted in QF values ranging between 20.3 and 86.4 with intermediate levels of aroma differences, but at high levels of statistical differences (P < 0.001). The triazole pairs that exhibited the greatest differences in aroma profiles were found between triadimefon and tebuconazole (QF=282.5) and between propiconazole and triadimefon (QF>290). High levels of residue discrimination were determined between the triazole fungicides in all cases except between difenoconazole and tebuconazole (P < 0.05).

IV.   DISCUSSION AND CONCLUSION

This study has demonstrated that the CP A32S e-nose has the capability of identifying and discriminating between fungicide residue types (in vitro) from several different chemical classes including: polychlorinated aromatics, piperazines, phenylamides, organochlorines, triazoles, strobilurins, and dicarboximides. Additional work is necessary to determine e-nose detection capabilities with other fungicide classes and the feasibility for fungicide residue detection on crop plants in the field.

Electronic-nose aroma data outputs using PCA provided some indications of chemical-relatedness between fungicide types from different chemical classes. Generally, there were greater differences in aroma profiles between fungicides from different chemical classes than between fungicides in the same chemical class, which implied that the higher the

QF values in pairwise comparisons, the greater the chemical differences between fungicides based on aroma profiles (signature patterns) derived from outputs of the e-nose sensor array. However, high levels of discrimination were not only found between fungicides of different chemical classes, but also between some fungicide pairs within the triazole chemical class. These data suggest that aroma chemical characteristics can reflect big differences in the chemical structure and composition of individual fungicides even within the same chemical class. Thus, the e-nose determined aroma characteristics of fungicides, and probably other pesticides, are not always primarily determined by the functional groups and toxophores present (defining the chemical class), but also are determined by other functional groups that are present in the fungicide chemical structure.

TABLE II.   RELATEDNESS OF SEVEN FUNGICIDE RESIDUE TYPES BASED ON 3-DIMENSIONAL PCA OF HEADSPACE VOLATILES

Aroma class	Aroma class	QF value[a]
Chlorothalonil	Triforine	13.7**
	Metalaxyl	125.4***
	PCNB	6.2**
	Propiconazole	2.4*
	Azoxystrobin	109.2***
	Iprodione	59.7**
Triforine	Metalaxyl	30.6**
	PCNB	6.7**
	Propiconazole	9.9**
	Azoxystrobin	109.2***
	Iprodione	316.1****
Metalaxyl	PCNB	178.8***
	Propiconazole	75.6***
	Azoxystrobin	317.1****
	Iprodione	258.9****
PCNB	Propiconazole	16.9**
	Azoxystrobin	> 320.0****
	Iprodione	62.4**
Propiconazole	Azoxystrobin	21.1**
	Iprodione	13.5**
Azoxystrobin	Iprodione	7.7**

a. Quality factor significant difference levels between aroma classes: * = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$; **** = $P < 0.0001$. The percentages of the total variance, accounting for the variability explained by each orthogonal principal component (PC), are as follows: PC 1 = 61.5%; PC 2 = 25.8%; and PC 3 < 7.4%.

The fungicides azoxystrobin and iprodione were the only two fungicide residue types that could not be identified with the A32S e-nose in the current study. In the case of azoxystrobin, this is a very unusual mycotoxin-type biofungicide (a strobilurin) derived from biological sources (agaric fungi) and not a product of petroleum-based chemical synthesis methods used in the manufacture of most fungicides. The complex structure of azoxystrobin may interfere with the effective detection and discrimination of this secondary fungal metabolite by the sensor array. Some chemical compounds, particularly certain pesticides, cause short- or long-term inactivation of specific sensors in the sensor array as a result of the chemical adhesion and interactions of certain pesticides with the surface of individual sensor types. The pesticides causing the most problems are usually those that are highly polarized or have locally-charged components on the pesticide molecule that react strongly to the surface chemistry of specific sensor types. This also may explain the difficulties in detecting iprodione, which is a dicarboximide that is highly polarized due to the presence of chlorines on the phenyl group and nitrogen groups on the imidazole and carboxamide groups.
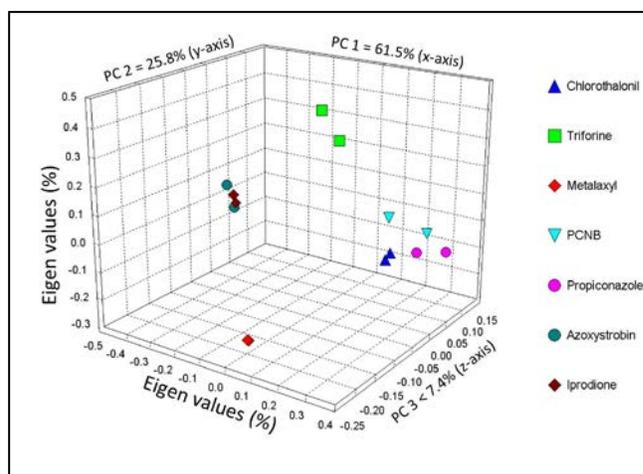

Figure 1.   Aroma map showing the relatedness of volatiles from seven fungicide residue types using conductive polymer analysis (CPA).

The available literature on e-nose detection of pesticides is highly limited [4]. A surface acoustic wave (SAW) e-nose previously was used to detect organophosphate (OP) insecticides in ambient air [33] and on vegetables such as different types of chili samples [34].

The next logical step is to determine the feasibility of the e-nose to detect fungicide residues on plant (crop) surfaces in the field. The addition of plant volatiles to the headspace requires the development of new reference libraries to take into consideration all combinations of crop and fungicide types likely applied to a crop during the growing season. All possible combinations of fungicide residues must be accounted for on each crop type. The theoretical logistics of fungicide identifications on crops are quite feasible given that the discrimination of plant volatiles of different plant species has been well established previously [4, 27, 35].

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