Identification and Discrimination of Herbicide Residues Using a Conducting Polymer Electronic nose

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***Abstract*— The identification of herbicide residues on crop foliage is necessary to make crop-management decisions for weed pest control and to monitor pesticide residue levels on food crops. Electronic-nose (e-nose) methods were tested as a cheaper, alternative means of discriminating between herbicide residue types (compared with conventional chromatography methods), by detection of headspace volatiles released from inert surfaces. Detection methods were developed for a conducting polymer (CP)-type electronic nose device, the Aromascan A32S, to identify and discriminate among eight herbicide types from five different herbicide organic chemical classes including: chlorophenoxy acids, cyclohexenones, dinitroanilines, organoarsenics, and phosphonoglycines. A herbicide-specific aroma signature library was developed from known herbicide residues. The A32S e-nose effectively distinguished between eight different herbicide residues, correctly identifying them at frequencies ranging from 81-98%. The distribution of aroma class components, based on artificial neural net (ANN) training and analysis, indicated the percentage membership of aroma classes shared by herbicide types. Principal component analysis (PCA) provided indications of the relatedness of herbicide types based on sensor array response patterns (aroma profiles) of individual herbicides. PCA generated precise statistical values (quality factors of significance) as numerical indications of chemical relatedness between herbicides based on pairwise comparisons of headspace volatiles from individual herbicide types. The potential applications, advantages and disadvantages of e-nose methods (compared to current chromatographic methods) for the detection and identification of herbicide residues on crop surfaces in agronomic fields are discussed.**

Keywords- artifician olfaction; electronic aroma detection; e-nose; pesticide residue detection; volatile organic compounds.

I. INTRODUCTION

The presence of pesticide residues on food crops is a major health concern especially on fresh fruits and leafy vegetables. Environmental regulations specify pesticide residue levels that are allowed on food products in commercial markets. Consequently, there is a strong need to determine pre-harvest and postharvest pesticide residue levels on the surfaces of plant products using rapid chemical-detection methods to effectively monitor and enforce pesticide residue regulatory requirements for plant products prior to fresh food introductions into commercial markets.

Electronic chemical-detection methods are well suited for rapid detections of pesticide residue levels needed for making pesticide-management decisions and for monitoring pesticide levels on food crops and produce [1]. Portable electronic-nose (e-nose) devices are useful for these applications due to rapid detections, high reproducibility, accurate determinations, and high sensitivity to volatile organic compounds (VOCs), such as commercial pesticides. E-nose sensors produce unique electronic signature patterns in response to VOCs released from chemical sources [2]-[4]. Electronic noses, unlike other analytical instruments, are capable of identifying VOCs without having to identify individual chemical compounds present in volatile mixtures [5]-[7]. Many different types of e-nose sensors have been developed including optical sensors [8], metal oxides [9] [10], semi-conducting polymers [11]-[13], and conducting polymers [14]-[16] for different applications. The broad agricultural and food industries have utilized electronic aroma detection (EAD) technologies to evaluate food quality and freshness [17]-[21], detect industrial wastes [22][23], diagnose plant diseases [24], and many other applications [25][26], including the detection of environmentally hazardous agricultural chemicals [27]-[29].

The Aromascan A32S e-nose, selected for efficacy testing in this pilot study, currently is commercially available only for specialized applications following a recent instrument redesign after the current study was completed. This instrument contains 32 conducting polymer (CP) sensors in the sensor array that respond to changes in electrical resistance (ER) when pesticide molecules adsorb to the surface of each sensor. The resulting combined-sensor output from the sensor array generates a unique aroma signature pattern that is specific to the gaseous volatile organic compounds (VOCs) present in the headspace above the sample analyte. Alternative e-nose technologies, such as carbon nanofiber (CN) and metal oxide semiconductor (MOS) types, also operate by measuring ER, but other e-nose types such as quartz crystal microbalance (QCM) and surface acoustic wave (SAW) operate by measuring mass changes or frequency shifts associated with gas-analyte adsorption to sensors [30].

The objectives of this study were to 1) determine the capability and effectiveness of the Aromascan A32S e-nose to discriminate between eight different herbicide residue types in vitro based on analysis of headspace volatiles, 2)

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assess the potential usefulness of these methods for making crop-management decisions involving detections of herbicide types on crop foliage for pest-control applications, and 3) a minor objective to determine whether principal component analysis (PCA) of herbicide e-nose aroma patterns (from the sensor array) can provide indications of chemical relatedness between herbicide types based on aroma characteristics and interactions with the sensor array. Six herbicide chemical classes were tested with representatives of each class including organoarsenics (cacodylic acid and MSMA), dinitroanilines (pendimethalin and trifluralin), a phosphoglycine (glyphosate), a cyclo-hexenone derivative (sethoxydim), a chlorophenoxy acid (2,4-D), and a chlorinated pyridine oxamic acid (triclopyr).

This paper is composed of an introduction to pesticide residue detection on crops in Section 1, followed by e-nose experimental methods used in Section 2, describing the specific materials and methods used in associated with e-nose run and analytical procedures, followed by results in Section 3 that provide details of experimental research results and findings for CP e-nose analyses of herbicide residues, including sensor outputs, aroma map, and QF analysis of PCA data. Discussion and conclusions (Section 4) are based on e-nose experimental results, summarizing significant findings and efficacy compared with conventional chromatographic methods of pesticide residue identification.

II. MATERIALS AND METHODS

A. Herbicide residue samples collected for analysis

Eight herbicides, having different chemical (pesticide) classes and modes of actions, were selected for this study. The herbicides analyzed via conductive polymer analysis (CPA) using an electronic-nose (e-nose), a type of electronic aroma detection (EAD) technology [24], included cacodylic acid (CA), dichlorophenoxy acetic acid (2,4-D), glyphosate (GL), pendimethalin (PM), sethoxydim (SE), monosodium acid methane arsonate (MA), triclopyr (TC), and trifluralin (TF). All herbicides were obtained in formulations that were commercially available from manufacturers, rather than from technical grade preparations to facilitate practical efficacy testing of formulations actually used in weed-control applications for agronomic crop production.

B. Sample preparation and prerun procedures

Small aliquots (10 µl) of each herbicide were analyzed separately at a standard concentration of 20 ppm by placing them into 14.8 cm3 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. The sensitivity of CP e-noses range from 0.1 to 100 ppm [30]. 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 and purged with moisture-conditioned reference air for 2 min prior to building headspace. The sampling bottle was sealed and volatiles from each herbicide analyte were allowed to build headspace and equilibrate for 30 min prior to each run. Prerun tests were performed as needed to determine sample air relative humidity compared with that of reference air. Reference air was set at 4% relative humidity at 25 °C. The sampling bottle cap and exhaust port were opened between runs to purge the previous sample with conditioned reference air. A reference library (recognition file) for pesticide types was constructed using artificial neural net training by defining aroma classes using reference databases of known pesticides. This recognition file was used to identify unknown samples.

C. Instrument configuration and run parameters

Electronic-nose analyses of herbicides were conducted with an Aromascan A32S (Osmetech Inc., Wobum, MA) intrinsically conducting polymer (ICP) e-nose instrument with 32 sensors in the sensor array consisting of polypyrrole, polyanaline, and polythiophene sensor types with 15 volts across sensor paths. Eight sensors, (including sensors 11, 12, 21-24, 31 and 32) that did not respond or did not contribute to the discrimination of pesticide volatiles, were turned off. 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 polymer used in the sensor matrix coating, the type of proprietary 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 analyses indicating relative analyte sensitivities for individual sensors in the array to various analyte types (representative of different chemical classes) were reported previously [24]. The block temperature of the sensor array was maintained at 30 °C. Reference air was preconditioned by passing it sequentially through a carbon filter, silica gel beads, inline filter, and Hepa filter to remove organic compounds, moisture, solid particulates, and microbes, respectively (to prevent interference of these factors), prior to humidity control and introduction into the sampling bottle. The flow rate of sampled reference air was maintained at 702 cm3 min-1 with a calibrated ADM 3000 flow meter (Agilent Technologies, Wilmington, DE). Sensor surfaces were purged between runs using a 2% isopropanol wash. The instrument was interfaced with a personal computer via an RS232 cable and controlled with Aromascan Version 3.51 software. The instrument plumbing (reference air flow route through the instrument) was altered for static sampling of the headspace by allowing air flow, maintained at 605 cm^3 min-1 flow rate, to release out of the external vent port of the instrument during analytical runs, closing the exhaust port on the sampling bottle so that headspace volatiles were taken by vacuum suction from a homogeneous static air mass within the sampling bottle to minimize headspace-dilution effects.

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

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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 e-nose aroma reference library was constructed from the eight herbicides included in this study. Database files were linked to specific aroma classes defining each herbicide type. All databases were constructed from sensor output data collected during a 20 s interval, 85-105 s into the run cycle, immediately prior to closing of the reference air valve at the end of each run. The recognition network options (neural net training parameters) used for each training session were: 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. A typical neural net training required 2–35 min, depending on database size, 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 to compare individual database files for similarity matches to each specific aroma class by test-assigned aroma class distributions among related aroma 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. [24].

F. Principal component analysis

Detailed pairwise comparisons of herbicide types (aroma classes) were determined using principal component analysis (PCA) algorithms provided by the Aromascan 3.51 software. Three-dimensional PCA was used to distinguish between herbicide headspace volatiles. PCA mapping parameters were: iterations = 30, units in Eigen values (%), and use of normalized input data. PCA generated a quality factor (statistical significance value) for each aroma comparison. The relatedness (distance between data clusters) of mapped aroma profiles between herbicide types provided indications of similarity in aroma elements and chemical characteristics as well as interactions with the sensor array.

III. RESULTS

A. Identification of herbicide analytes

The Aromascan A32S electronic nose provided consistent correct identifications for all eight herbicide residue types analyzed based on differences in sensor-array responses to headspace volatiles (Table 1). Individual sensor responses to each herbicide varied widely within the 3 to 8 percent sensor-intensity range (% change in sensor response relative to base resistance) with good precision as indicated by low standard deviations (SD) of mean normalized values. Sensors 25, 26, and 30 had no responses to some herbicides. In particular, sensor 26 could not detect any of the herbicides, whereas sensors 25 and 30 were unable to detect four herbicides including sethoxydim, monosodium acid methane arsonate , triclopyr and trifluralin.

TABLE I. SENSOR OUTPUT RESPONSE PATTERNS FROM THE A32S E-NOSE SENSOR ARRAY DERIVED FROM EIGHT HERBICIDE RESIDUE TYPES

E-nose	**Herbicide residue sensor responses[a]**							
Sensor	**CA**	**2,4-D**	**GL**	**PM**	**SE**	**MS**	**TC**	**TF**
1	4.76	4.22	5.16	5.05	3.54	4.75	6.87	3.97
2	4.31	3.87	4.70	4.60	3.15	4.32	6.20	3.59
3	4.92	4.49	5.35	5.21	3.74	5.02	7.08	4.22
4	2.34	2.46	2.53	2.84	2.96	2.60	3.57	4.27
5	2.34	2.39	2.53	2.86	2.93	2.59	3.56	4.21
6	2.34	2.45	2.53	2.84	2.98	2.61	3.58	4.30
7	5.19	5.34	5.31	4.88	4.83	5.83	6.84	4.64
8	5.25	5.12	5.40	5.11	4.74	5.61	6.65	4.33
9	4.47	4.83	4.42	4.07	4.75	4.79	5.33	3.86
10	3.84	4.60	3.80	3.38	5.39	5.04	5.19	4.30
13	3.54	3.66	3.43	3.37	4.67	3.89	3.77	4.67
14	3.30	3.26	3.23	3.15	4.21	3.44	3.79	4.38
15	3.61	3.98	3.57	3.33	4.65	4.14	4.27	4.52
16	3.36	3.49	3.34	3.28	4.50	3.65	3.80	4.64
17	4.59	4.49	4.06	4.36	5.65	5.27	0.42	5.15
18	4.74	4.57	4.30	4.58	5.70	5.30	0.88	5.17
19	4.45	4.32	4.08	4.37	5.31	5.09	0.94	4.91
20	3.49	4.21	2.53	3.50	6.55	3.71	-2.51	5.40
25	5.38	5.16	5.63	5.78	NR	NR	NR	NR
26	NR	NR	NR	NR	NR	NR	NR	NR
27	6.45	6.71	6.75	5.85	6.82	8.11	8.47	6.98
28	6.38	6.21	6.58	6.01	6.63	7.49	8.27	6.60
29	6.21	5.78	6.47	6.50	6.31	6.76	8.00	5.91
30	4.76	4.40	4.32	5.08	NR	NR	NR	NR

a. Values are mean sensor response intensities; herbicide type abbreviations: cacodylic acid (CA), dichlorophenoxy acetic acid (2,4-D), glyphosate (GL), pendimethalin (PM), sethoxydim (SE), monosodium acid methane arsonate (MA), triclopyr (TC), and trifluralin (TF).

Normalized output values from individual sensors were significantly different between herbicides types at the P < 0.001 level of significance. The resulting electronic aroma signature patterns (EASPs) or aroma profiles for individual herbicides, composed of the collective outputs of all the sensors in the sensor array, were different and unique for each herbicide type. The high level of significant differences between sensor outputs for all of the sensors (in each aroma profile) provided a highly unique electronic signature to identify and discriminate herbicide residue types on inert

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surfaces (in vitro) without the presence of plant volatiles when on crop surfaces of the same plant species.

The instrument correctly identified individual herbicide residues at frequencies ranging from 81-98% among all herbicide residue types tested. None of the herbicides from any of the six chemical classes was incorrectly identified. Also, no herbicide from the five chemical classes was unsuccessfully identified or classified as unknown due to variations in aroma signature patterns. All of the herbicides were clearly assigned an aroma profile with a majority aroma class present in the reference library. None of the herbicides determinations were found to be incorrect or ambiguous, defined as determinations that resulted in a herbicide residue type being assigned to a different majority aroma class from separate analyses of sample replications.

B. Discrimination between herbicide residues

The discrimination of herbicide residue types was further evaluated by determining the aroma class distributions of principal components of VOCs in headspace volatiles of the herbicide types (Table 2). Aroma class distributions indicate percentage components in common between herbicides residue types.

The occurrence of secondary aroma elements within the aroma class distribution provided some indications of chemical relatedness between herbicides. Cacodylic acid residues had a relatively large proportion of secondary aroma elements in common with pendimethalin (16.6%) and sethoxydim (11.5%). Similarly, glyphosate shared secondary elements of 12.5% with MSMA, while pendimethalin shared secondary elements of 11.9% with trifluralin. The proportion of secondary aroma elements attributed to aroma classes besides the principal aroma elements ranged from <1% for MSMA to highs of >16% for cacodylic acid.

TABLE II. DISTRIBUTION OF ELECTRONIC-NOSE AROMA CLASS COMPONENTS AMONG EIGHT HERBICIDE RESIDUE TYPES

	Aroma class distribution (%)[a]							
	Herbicide residues types							
Herbicide	**CA**	**2,4-D**	**GL**	**PM**	**SE**	**MS**	**TC**	**TF**
CA	**88.5**	9.4	4.2	16.6	11.5	—	—	—
2,4-D	9.6	**92.8**	—	—	2.9	12.5	—	—
GL	4.7	3.4	**87.9**	—	—	5.2	—	—
PM	2.6	—	6.5	**94.4**	2.3	—	—	11.0
SE	7.2	—	—	—	**95.0**	—	—	2.9
MS	—	0.7	2.2	—	6.1	**94.3**	2.8	0.6
TC	2.9	—	2.5	1.5	—	1.4	**98.4**	—
TF	—	3.3	—	5.9	—	4.6	—	**98.7**

a. Values indicate mean percent aroma class distributions indicated for each herbicide type; read from left to right (by row), not top to bottom. Herbicide abbreviations correspond to those given in the materials and methods section (herbicide residue sample types) and in Table I.

The number of principal and secondary aroma elements present in the aroma profiles of individual herbicide residues ranged from three in sethoxydim to six in MSMA, with the majority having four to five total aroma elements in common between herbicide residues. The total percentage of secondary aroma elements in common between herbicide residues contributed to ≤ 25.0% of the aroma class distribution for most herbicide types with cacodylic acid being the exception (41.7%). The lowest total secondary elements in common with other herbicides occurred for trichlopyr (8.3%); while intermediate totals were recorded for sethoxydim (10.1%), MSMA (12.4%), glyphosate (13.3%), trifluralin (13.8%) and higher totals for pendimethalin (22.4%) and 2,4-D (25.0%).

C. Principal component analysis

Analysis of eight herbicide residues using PCA by pairwise comparisons of headspace volatiles (in all possible combinations) provided greater details of possible chemical relatedness and differences between individual herbicide types based on sensor response patterns (aroma profiles). The relatedness among the eight herbicide types varied greatly based on Euclidean distance as indicated in Table 3. The larger the QF value, the greater the significant differences for pairwise herbicide comparisons.

TABLE III. PAIRWISE-COMPARISONS BETWEEN AROMA PROFILES OF EIGHT HERBICIDE RESIDUE TYPES BASED ON 3-DIMENSIONAL PCA

Aroma class	***Aroma class***	***QF value[a]***	***Aroma class***	***Aroma class***	***QF value[a]***
CA	2,4-D	1.4	2,4-D	GL	1.6
	GL	9.5*		PM	1.8
	PM	7.1*		SE	11.5*
	SE	35.6**		MS	69.2***
	MS	95.5***		TC	17.7*
	TC	88.2***		TF	15.0*
	TF	34.4**	GL	PM	11.2*
GL	SE	3.8*	PM	SE	22.0**
	MS	>300****		MS	231.6****
	TC	62.3***		TC	>300****
	TF	15.1**		TF	>300****
MS	TC	15.3**	SE	MS	43.3**
	TF	3.3*		TC	42.2**
TC	TF	31.2**		TF	7.1*

a. Statistical analysis symbols for quality factor (QF) significant difference levels between aroma classes were as follows: * = 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), were as follows: PC 1 = 91.3%; PC 2 = 7.7%.

QF values ranged from 1.4 between cacodylic acid and 2,4-D (indicating close relatedness) to >300 between glyphosate and MSMA, and between pendimethalin and both triclopyr and trifluralin, indicating low relatedness between pairs. The small QF values for 2,4-D compared

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with glyphosate (1.6) and pendimethalin (1.8) indicated close relationships based on aroma characteristics even though these herbicides are from different chemical classes. Cacodylic acid vs. MSMA (both organoarsenics), had a high QF value (95.5) suggesting low relatedness in aroma profiles. The comparison of the two dinitroanilines, pendimethalin and trifluralin, also resulted in a high QF value (>300) despite their chemical relatedness. Significant differences in R-groups may account for aroma profile differences between herbicides in the same chemical class. The relatedness between the aroma profiles of eight herbicide residue types, based on 3-dimensional PCA, was graphed as an aroma map (Figure 1).

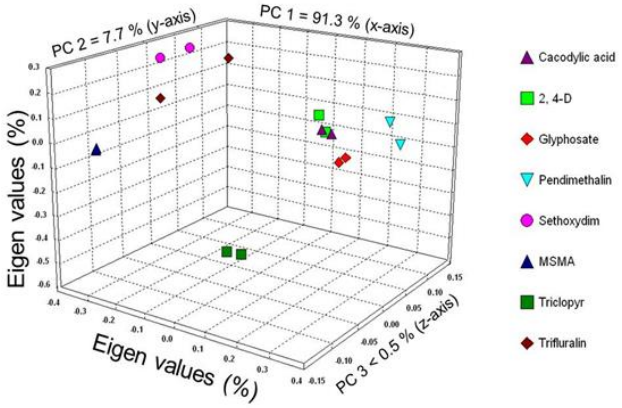

Figure 1. E-nose aroma map showing the chemical relatedness between eight herbicide residue types using Principal Component Analysis (PCA).

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 = 91.3%; PC 2 = 7.7%; and PC 3 < 0.5%, representing the x-, y-, and z-axis of the aroma map, respectively. A high proportion (99.0%) of the variation was explained by the first two principal components (PC 1 and PC 2). Data points of each herbicide type clustered closely on the aroma map with the exception of trifluralin. As expected, data points of 2,4-D were closely clustered with those of cacodylic acid, indicating a very close relationship based on aroma characteristics.

IV. DISCUSSION AND CONCLUSIONS

Electronic-nose devices previously have been used to detect pesticides including fungicides, insecticides, and miticides [1][31]. Déjous et al. [32] used a surface acoustic wave (SAW) e-nose to detect organophosphates in ambient air. Literature on e-nose detection of pesticides residues on fruits, crops, and other plant surfaces is quite limited [33]. E-nose aroma signature libraries developed for detection of pesticides on crop and plant surfaces for field use must necessarily include the specific types of VOCs that are characteristic of those released from the types of plant and parts upon which pesticide residues are being detected. Previous research has demonstrated the capability of e-noses to discriminate between VOCs from different plant species and various tissue types from woody plants [34]-[36], and in the crop environment [37]-[39].

Further research on the e-nose detection of pesticides residues on plant surfaces, following efficacy testing in vitro in the present pilot study, will be required to determine efficacy for field crops and fresh produce subject to Environmental Protection Agency (EPA) pesticide residue regulations. E-nose data of crop pesticide residues are primarily qualitative and only semi-quantitative, a possible limitation for EPA residue testing. The detection limit for CP-type e-nose devices is approximately 0.1 ppm, which is low enough for pesticide residue testing in most countries. Pesticide residue concentrations do not affect aroma signature patterns, but only intensity of sensor responses. Analyses of data indicating unique aroma signature patterns, based on output results from the sensor array of the A32S CP electronic-nose, provided effective discriminations between headspace volatiles from herbicide residues. Discriminations and correct identification of herbicide sample types in vitro were determined at high levels of statistical confidence.

The discrimination of pesticide residues on crop plants is an important function in crop management to assure that the appropriate active ingredient has been applied to a crop for pest control and harvesting operations. Herbicides are used for weed control and as chemical defoliants to facilitate crop harvesting operations. Thus, detection of herbicide residues is necessary to confirm application of appropriate chemicals to achieve desired results for specific crops.

The use of e-nose devices for pesticide residue detection has several advantages over conventional methods such as gas chromatography (GC), liquid chromatography (LC), and mass spectrometry (MS). These expensive chemical analysis methods require laborious and time-consuming sample preparations, solvent extractions, reference standards of each pesticide, and costly analytical equipment. By comparison, electronic-nose methods do not require expensive sample preparations, chemical solvents, or pesticide standards and may potentially consist of relatively cheap instruments such as handheld portable e-nose devices for field use.

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