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Colorimetric Environmental Sensor: Aerosol versus Vapor Targets

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14. ABSTRACT

This report describes work focused on a component of an effort intended to develop wireless sensor networks for real-time monitoring of airborne targets across a broad area. The performance of the sensor devices will depend heavily on the selection of appropriate indicator elements in design of the arrays. This document summarizes results for aqueous screening of meso-tetra (4-aminophenyl) porphyrin (N4TPP) and metalloporphyrin (XN4TPP) variants of this structure.

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EXECUTIVE SUMMARY

In October 2012, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort intended to develop wireless sensor networks for real-time monitoring of airborne targets across a broad area. The goal was to apply the spectrophotometric characteristics of porphyrins and metalloporphyrins in a colorimetric array for detection and discrimination of changes in the chemical composition of environmental air samples. Prior reporting on the device has focused on exposure to targets as vapors; however, aerosolized targets are also of interest for the application. The current document summarizes results for use of the prototype sensor device in a glove enclosure. Responses to exposures of equivalent concentrations of targets introduced as either vapor or liquid are reported and discussed.

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COLORIMETRIC ENVIRONMENTAL SENSOR: AEROSOL VERSUS VAPOR TARGETS

INTRODUCTION

In October 2012, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort (69-6594) intended to develop wireless sensor networks for real-time monitoring of airborne targets across a broad area. The goal was to apply the spectrophotometric characteristics of porphyrins and metalloporphyrins in a colorimetric array for detection and discrimination of changes in the chemical composition of environmental air samples. The effort encompasses hardware, software, and firmware development as well as development of algorithms for identification of event occurrence and discrimination of targets.[1-5] Prior reporting on the device has focused on exposure to targets as vapors; however, aerosolized targets are also of interest for this application. The current document summarizes results for screening of meso-tetra(4-sulfonatophenyl) porphyrin (S_4TPP) and metalloporphyrin (XS_4TPP) variants of this structure (Figure 1) using the prototype sensor device in a glove enclosure. Reponses to exposures of equivalent concentrations of targets introduced as either vapor or liquid are reported and discussed.

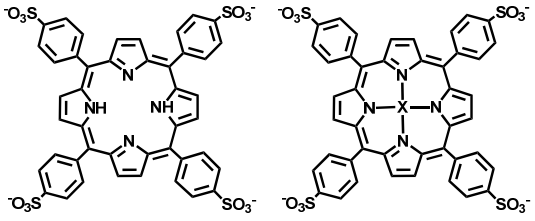

Fig. 1 — Molecular structures of meso-tetra(4-sulfonatophenyl) porphyrin (S_4TPP) and the metalloporphyrin (XS_4TPP) variants of this structure.

The targets utilized in the evaluation of these indicator materials are acetone, ethanol, methanol, and isopropanol. These targets were selected for prototype development because they present a low degree of hazard allowing for their use in a range of environments and scenarios while providing the potential for evaluation of the full sensor package. The screening approach uses paper supported porphyrins which are exposed to varying concentrations of the targets as vapors and aerosols. The changes in reflectance upon exposure are monitored and data is analyzed by both manual and automated approaches.

METHODS

Meso-tetra(4-sulfonatophenyl) porphyrin (S_4TPP) was obtained from Frontier Scientific (Logan, UT). Metalloporphyrin variants of S_4TPP were prepared by reflux.[1-3] The porphyrin (20 mg) was dissolved in 2 mL water with sodium hydroxide (sufficient only to dissolve the porphyrin full). The metal salt was added to this solution in a 3:1 molar ratio with the porphyrin. The total volume was brought to 100 mL with deionized water and refluxed overnight. The volume of the resulting solution was reduced to 20 mL through rotary evaporation. Prepared metal salt solutions were stored in the dark at room temperature. The metal salts used here were: yttrium (III) chloride, zinc chloride, copper (II) chloride, silver chloride, and thallium (III) chloride.

Paper supported porphyrin indicators were prepared using a dip and dry technique.[2, 3] For a 5 x 33 cm swatch, 0.4 mM porphyrin in water (total volume 6 mL) was used. The paper support (WypAll X60) was pulled through this solution and allowed to dry slightly before being pulled through the solution again.

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This was repeated until all porphyrin solution had been deposited (typically three cycles). Samples were then dried at 100°C before storing in the dark in sealed plastic bags.

The original prototype reflectance instrument developed by NRL utilized low cost, commercially available color sensing breakout boards from Parallax, Inc. (model TCS3200-DB, Rocklin, CA), providing a color light-to-frequency integrated circuit from AMS (model TCS3200, Plano, TX), a pair of white LEDs, and an adjustable lens.[1] The device output consists of a stream of digital pulses proportional to the intensity of the color being measured. A custom printed circuit board (PCB) interfaces with and controls six of the commercial color sensors. Communications between the instrument and the computer are via USB; power is supplied through a DC barrel jack. A LabWindows developed software-based graphical user interface (GUI) communicates with the PCB firmware through simple ASCII commands. The prototype sensor device used here is a slightly modified version of the previously reported NRL device (v2.08) [1-4, 6] (Figure 2). Airflow through the sample tube at 2.7 CFM is provided by two small 5 VDC fans (Orion Fans, model #OD2510-05HB), one mounted at each end.

The conditions established for use of the device under this effort were 400 ms integration with a 30 s sampling interval. These conditions are based on optimal performance when used with the prototype device. The detection algorithm used to identify the occurrence of events has been described previously.[3, 4] A detailed description with implementation approaches is provided in a recent NRL report.[6] The algorithm first populates background windows with the time duration required dependent on sampling increment (total number of points, rather than a time interval). With data collected at the 30 s increment used here, it is necessary to have 120 points for a stable initial condition (Background); 20 additional points fill the detection windows (Active and Snap). The 120 point Background window is intended to provide a smooth, slowly changing slope. This should capture any device drift over time as well as any changes resulting from diurnal and environmental changes. The Active window (20 points) provides a faster changing slope that will respond to chemical presence, while the shorter Snap window (10 points) is used to capture large, rapid changes. Comparing the Active and Snap windows to the slowly changing Background window provides the discrimination needed for identification of an event. Here, the conditions for ending positive event identification were changed based on recent evaluations.[5] The global cooldown was changed from 60 min (120 points) to 5 min (10 points), and the buffering period for the global event was changed from 5 min (10 points) to 1 min (2 points).

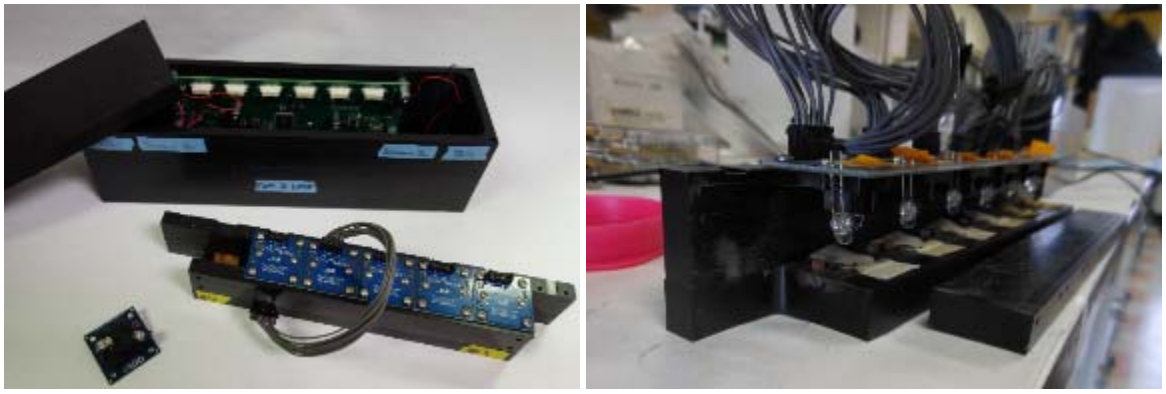

Fig. 2 — The prototype device includes six color sensing breakout boards, a custom control board, fans, and indicator supports with custom housing. The device used for these evaluations required external power and was controlled by a laptop computer.

For these measurements, each of the prototypes devices utilized one copy of each of the six indicator materials, S_4TPP, seat #1; AgS_4TPP, seat #2; ZnS_4TPP, seat #3; CuS_4TPP, seat #4; YS_4TPP, seat #5; TlS_4TPP, seat #6. Several of the prototypes were used simultaneously. These prototypes with mounted indicator materials were placed in a glove chamber (65 L; Techni-Dome, Bel-Art,Wayne, NJ, USA), and the volume was purged with humidified air for establishment of baseline measurements. Exposures were accomplished by adding a fixed volume of target to the continuous air stream to produce varied concentrations of the targets, acetone, ethanol, methanol, and isopropanol. Alternatively, an aerosol generator (Paasche H-Set Airbrush) was used to introduce aerosolized targets. Identical volumes were used in both cases. Full data sets are provided in the Appendices.

RESULTS

A series of paper supported meso-tetra(4-sulfonatophenyl) porphyrin (S_4TPP) variants were prepared for use with the prototype devices, incorporating six unique indicators as the six elements in the array. Four devices were exposed to repeated vapor target exposures over a period of more than 140 h (Appendix A). Figure 1 presents representative data for responses to methanol. Data was processed using the algorithm described previously. Figure 4 provides the calculated slopes (20 point windows) for the data in Figure 3. As shown, changes in slope are distinct for each of the exposures. For exposures 2 and 3, return to baseline triggers the device as well. In prior implementation, the cooldown window would have covered these time durations, preventing additional indication.

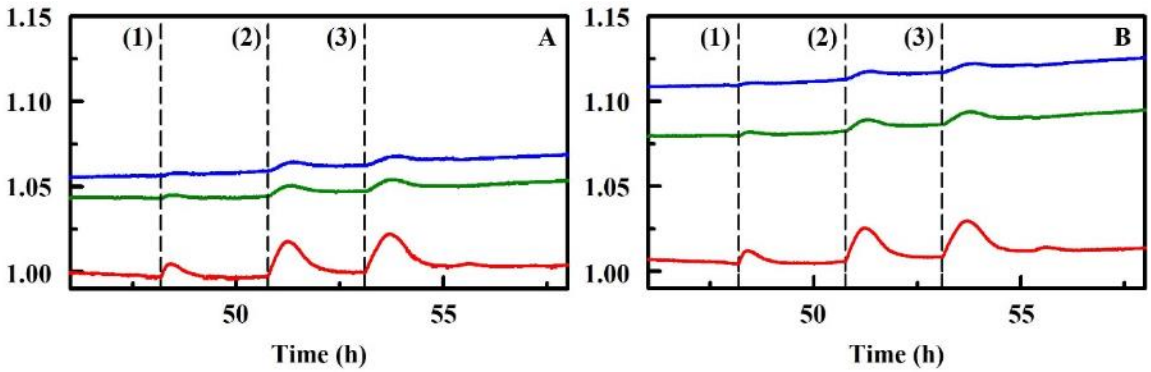

Fig. 3 —Normalized reflectance for the S_4TPP (seat #1; A) and AgS_4TPP (seat #2; B) paper supported indicators during exposure to 230 (1), 760 (2), and 1140 (3) ppb methanol. Data normalized to first 120 points. Dashed lines indicate initiation of exposure to vapor targets.

Table 1 summarizes the results for algorithm analysis of the data sets. Each set consists of 13 exposures. Vapor exposures for the four devices produced specificity of 0.998 with sensitivity 0.673 based on standard ROC analysis approaches. Under this analysis, specificity is calculated as the ratio of the total number of true negatives to the sum of the true negatives and the false positives. Sensitivity is calculated as the ratio of the true positives to the sum of the true positives and the false negatives. Results here are similar to those noted for the devices under laboratory conditions previously. Sensitivity here is lower than in recent reports because the target concentrations have been deliberately selected to push the capabilities of the array being used.

Analysis of the aerosol exposure data sets produced specificity 1.00 and sensitivity 0.846. As shown in Table 2, the increased sensitivity is a result of greater sensitivity across the entirety of the array. In the vapor responses, YS_4TPP did not respond to any of the targets. Aerosol exposures produced a concentration

dependent response across all of the targets by this indicator (Figure 5). The difference in the shape of the response (compare to Figure 3) is a result of the concentration profile differences for these types of exposures. For aerosol, the concentration within the enclosure increases rapidly to the peak and rapidly dissipates. In the vapor exposures, the concentration increases more gradually before reaching the peak and beginning to dissipate. Because the algorithm is based on changes in slope, the more rapid change in reflectance upon target exposure is reflected in an effective greater sensitivity. As shown in Figure 6, there are changes for this indicator in response to vapor exposures. They are simply smaller or less rapid than those of the aerosol exposure and, therefore, do not produce a positive response.

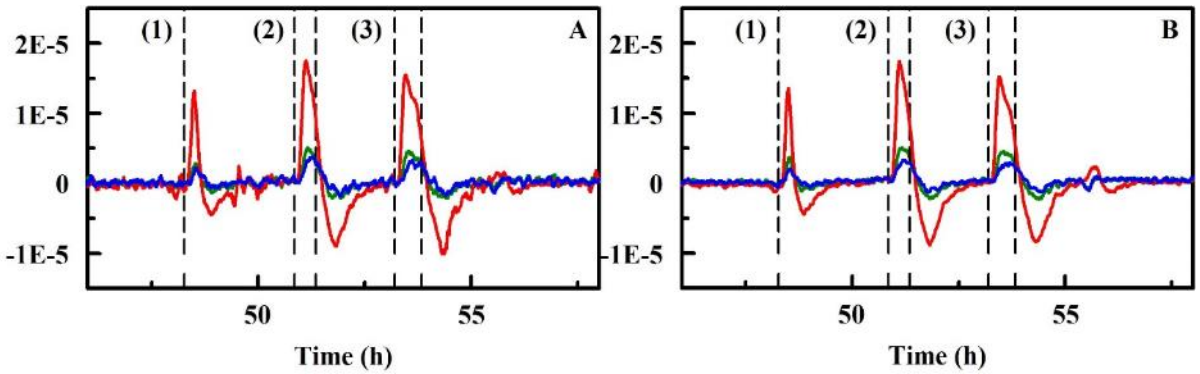

Fig. 4 —Slopes from data in Figure 3 calculated using 20 point sliding window. Based on reflectance for the S_4TPP (seat #1; A) and AgS_4TPP (seat #2; B) paper supported indicators during exposure to 230 (1), 760 (2), and 1140 (3) ppb methanol. Dashed lines indicate identification of events by the algorithm.

Table 1 – Summary of Algorithm Responses. Total exposures are 52 for vapor and 39 for aerosol.

Device#	True Positives	False Positives	False Negatives	True Negatives	Specificity	Sensitivity
Vapor Exposures, 13 exposures per device						
Overall	35	2	17	1057	1.00	0.67
1	8	0	5	277	1.00	0.62
2	9	0	4	238	1.00	0.69
3	9	0	4	277	1.00	0.69
4	9	2	4	265	0.99	0.69
Aerosol Exposures, 13 exposures per device						
Overall	33	1	6	2019	1.00	0.85
1	11	0	2	671	1.00	0.85
3	11	0	2	678	1.00	0.85
4	11	1	2	670	1.00	0.85

Table 2 – Response Summary by Indicator. Total exposures at each concentration are four for vapor and three for aerosol with the exception of 790 ppb acetone for which there are eight and six exposures, respectively.

Target	Conc (ppb)	S_4TPP	AgS_4TPP	ZnS_4TPP	CuS_4TPP	YS_4TPP	TlS_4TPP
Vapor Exposures							
Acetone	160	0	0	0	0	0	0
	530	1	2	1	1	0	1
	790	3	6	3	2	0	2
Ethanol	160	2	4	3	0	0	3
	530	2	4	3	0	0	3
	790	2	4	3	0	0	3
Methanol	230	2	4	0	0	0	3
	760	2	4	1	0	0	3
	1140	2	3	1	0	0	3
Isopropanol	120	0	0	0	0	0	0
	400	0	0	0	0	0	0
	600	0	0	1	0	0	0
Aerosol Exposures							
Acetone	160	0	0	0	0	0	0
	530	1	0	0	2	1	2
	790	4	2	2	4	3	4
Ethanol	160	2	2	2	0	0	2
	530	3	3	3	2	3	3
	790	3	3	2	1	3	3
Methanol	230	3	2	1	0	0	2
	760	3	3	2	1	2	3
	1140	3	3	3	1	3	3
Isopropanol	120	0	0	1	0	1	1
	400	3	0	2	2	2	2
	600	1	3	2	1	3	2

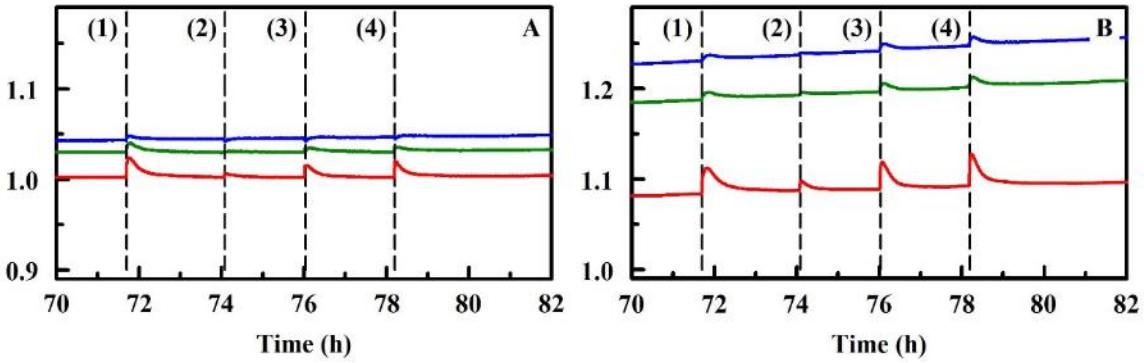

Fig. 5 —Normalized reflectance for the YS_4TPP (seat #5; A) and TlS_4TPP (seat #6; B) paper supported indicators during exposure to 790 ppb ethanol (1), 230 (2), 760 (3), and 1140 (4) ppb methanol. Data normalized to first 120 points. Dashed lines indicate initiation of exposure to aerosol targets.

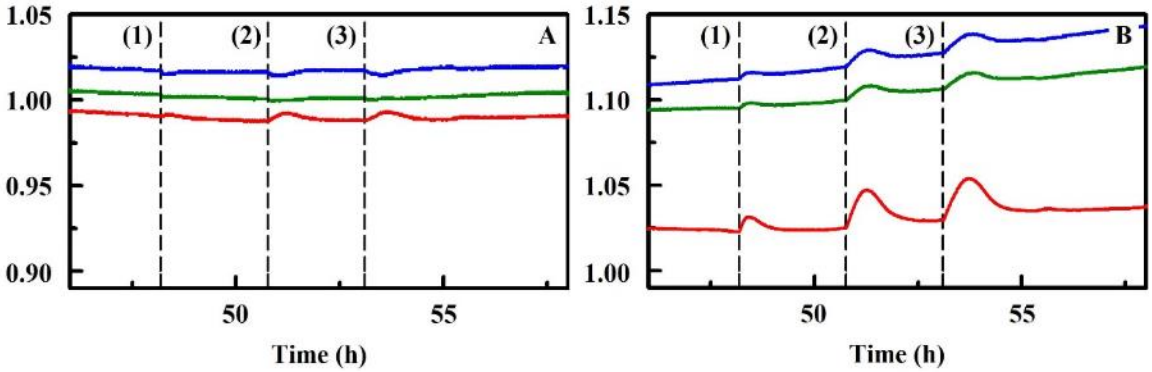

Fig. 6 —Normalized reflectance for the YS_4TPP (seat #5; A) and TlS_4TPP (seat #6; B) paper supported indicators during exposure to 230 (1), 760 (2), and 1140 (3) ppb methanol. Data normalized to first 120 points. Dashed lines indicate initiation of exposure to vapor targets.

CONCLUSIONS

The study presented here is intended to demonstrate the utility of the prototype reflectance device in detection of aerosol targets. Determining the presence of these targets presents no problem for either the prototype device or the current algorithm. The difference in sensitivity may present issues in development of target identification algorithms. Currently under development, identification algorithms will utilize the differing response across all of the array elements, or the fingerprint response, in order to provide discrimination and identification of targets. The striking differences in sensitivity noted for these array elements may require evaluation of both vapor and aerosol variants as appropriate to ensure proper discrimination of aerosol as well as vapor threats. The ongoing effort continues to screen additional indicators and targets as well as to address development of the target identification algorithms. The overall goal is to design an array of indicators that provides the potential for discrimination of targets based on the relative response of the individual elements.

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Appendix A

REFLECTANCE DATA AND ALGORITHM PROCESSING: VAPOR

Figure A-1. Device #1. Normalized reflectance for the paper supported indicators: S_4TPP, seat #1; AgS_4TPP, seat #2; ZnS_4TPP, seat #3; CuS_4TPP, seat #4; YS_4TPP, seat #5; TlS_4TPP, seat #6. Data normalized to first 120 points. Dashed lines indicate exposure to vapor targets (left to right), 160, 530, 790 ppb acetone; 160, 530, 790 ppb ethanol; 230, 760, 1140 ppb methanol; 400, 600 ppb isopropanol; 790 ppb acetone; 120 ppb isopropanol.

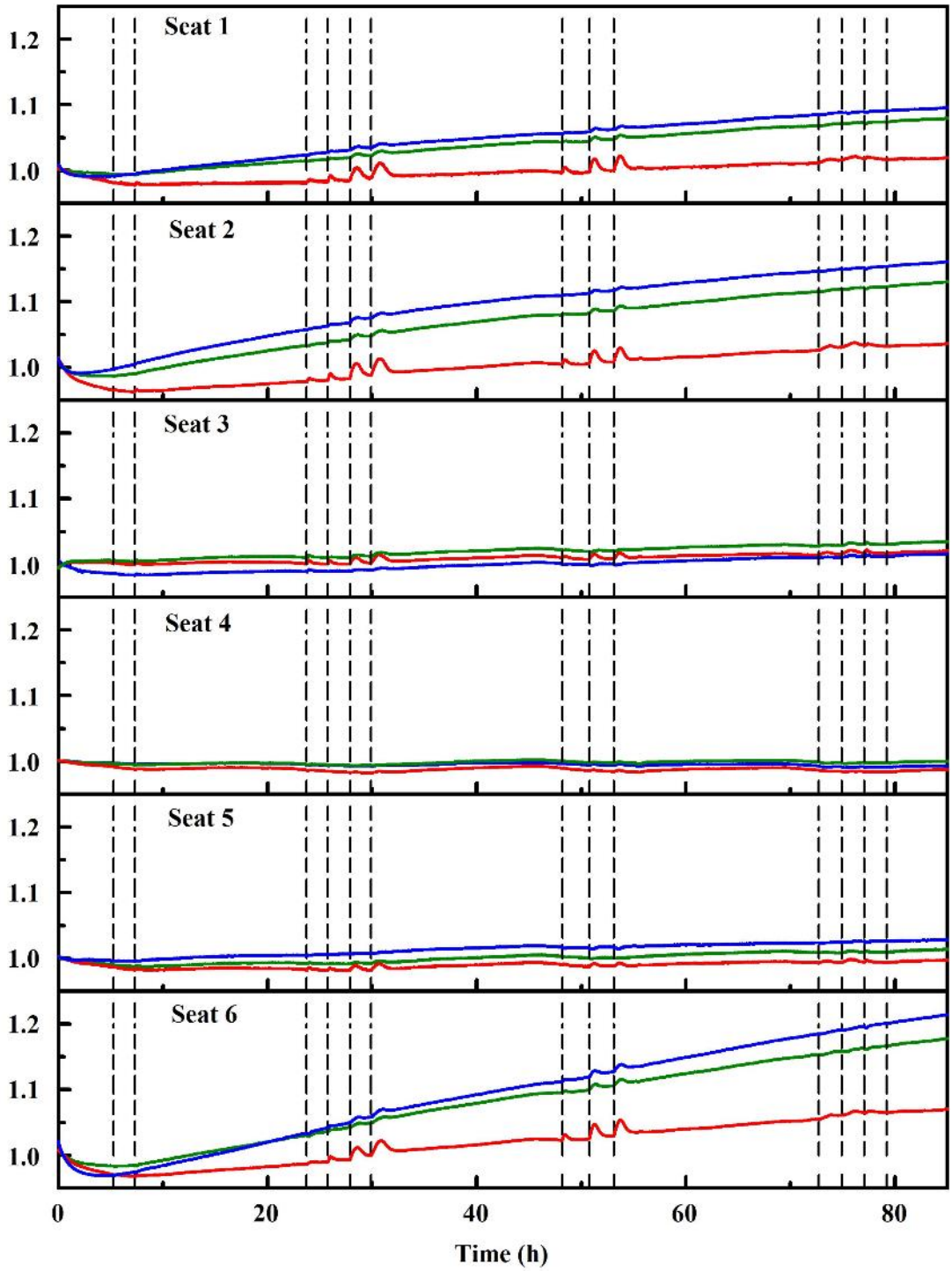


Table A-1. Exposures and Event Indication for Figure A-1 Data.

Type	Concentration (ppb)	Begin		End	Seats
Start		07/10/2018 10:03			
Acetone	160	07/10/18 15:19			
Acetone	530	07/10/18 17:20			
Acetone	790	07/11/18 09:47	07/11/2018 09:54	09:59	2, 3
Ethanol	160	07/11/18 11:48	07/11/2018 11:54	12:03	1, 2, 3, 6
Unknown			07/11/2018 12:13	12:30	1, 2
Ethanol	530	07/11/2018 13:55	07/11/2018 13:59	14:21	1, 2, 3, 6
Unknown			07/11/2018 14:41	15:13	1, 2, 6
Ethanol	790	07/11/2018 15:56	07/11/2018 16:02	16:31	1, 2, 3, 6
Unknown			07/11/2018 16:57	17:27	1, 2, 6
Methanol	230	07/12/2018 10:14	07/12/2018 10:19	10:28	1, 2, 6
Methanol	760	07/12/2018 12:49	07/12/2018 12:54	13:13	1, 2, 6
Unknown			07/12/2018 13:24	13:57	1, 2, 6
Methanol	1140	07/12/2018 15:09	07/12/2018 15:15	15:37	1, 2, 6
Unknown			07/12/2018 15:53	16:25	1, 2, 6
Isopropanol	400	07/13/2018 10:47			
Isopropanol	600	07/13/2018 12:57			
Acetone	790	07/13/2018 15:07	07/13/2018 15:15	15:20	3
Isopropanol	120	07/13/2018 17:16			
End				07/16/2018 10:33	

Yellow indicates an undetected exposure; pink a detected exposure; all green events result from detection of the device return to baseline conditions following an event

Figure A-2. Slope (40 point window) for the data presented in Figure A-1. Dashed lines indicate identification of an event by the algorithm.

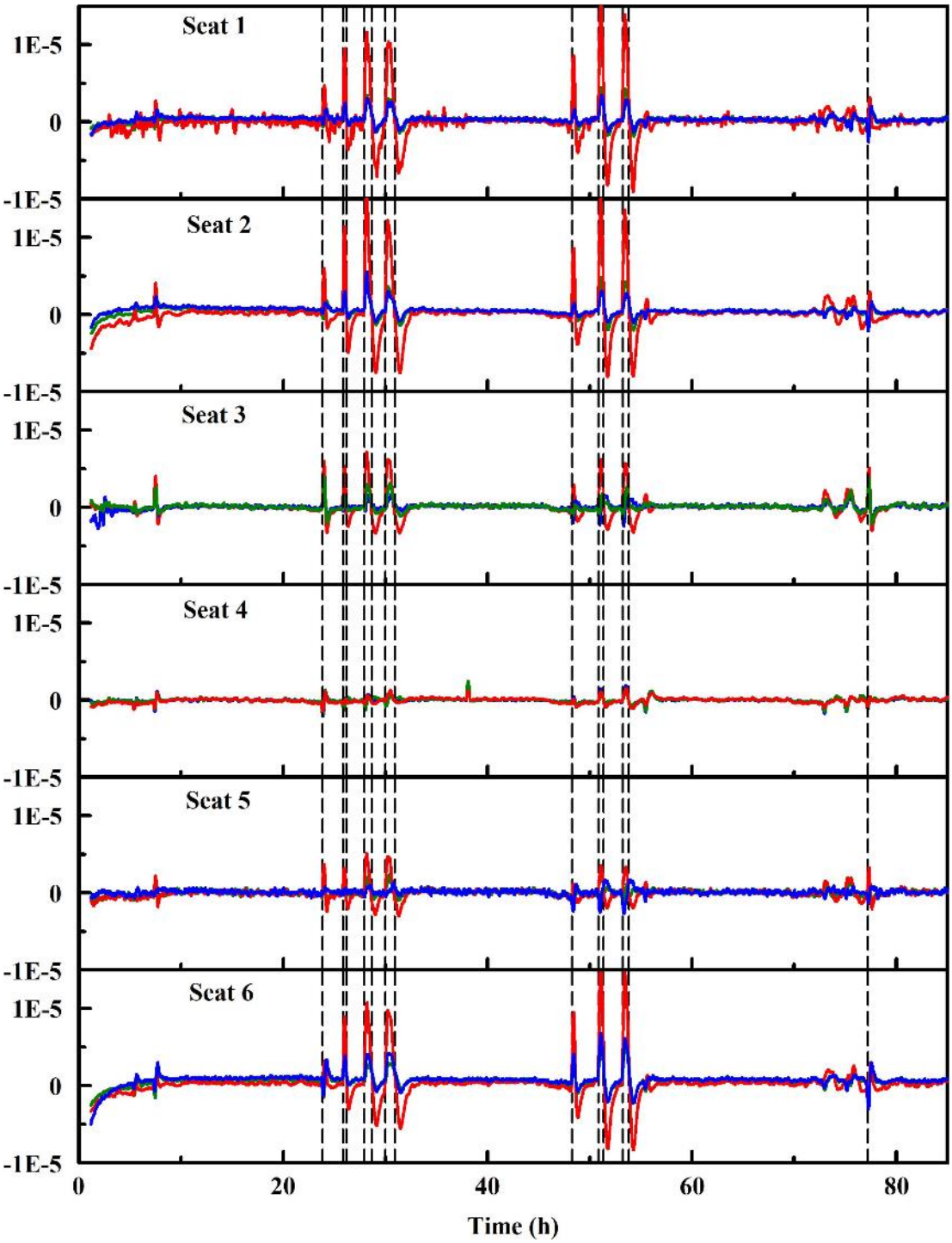


Figure A-3. Device #2. Normalized reflectance for the paper supported indicators: S_4TPP, seat #1; AgS_4TPP, seat #2; ZnS_4TPP, seat #3; CuS_4TPP, seat #4; YS_4TPP, seat #5; TlS_4TPP, seat #6. Data normalized to first 120 points. Dashed lines indicate exposure to vapor targets (left to right), 160, 530, 790 ppb acetone; 160, 530, 790 ppb ethanol; 230, 760, 1140 ppb methanol; 400, 600 ppb isopropanol; 790 ppb acetone; 120 ppb isopropanol.

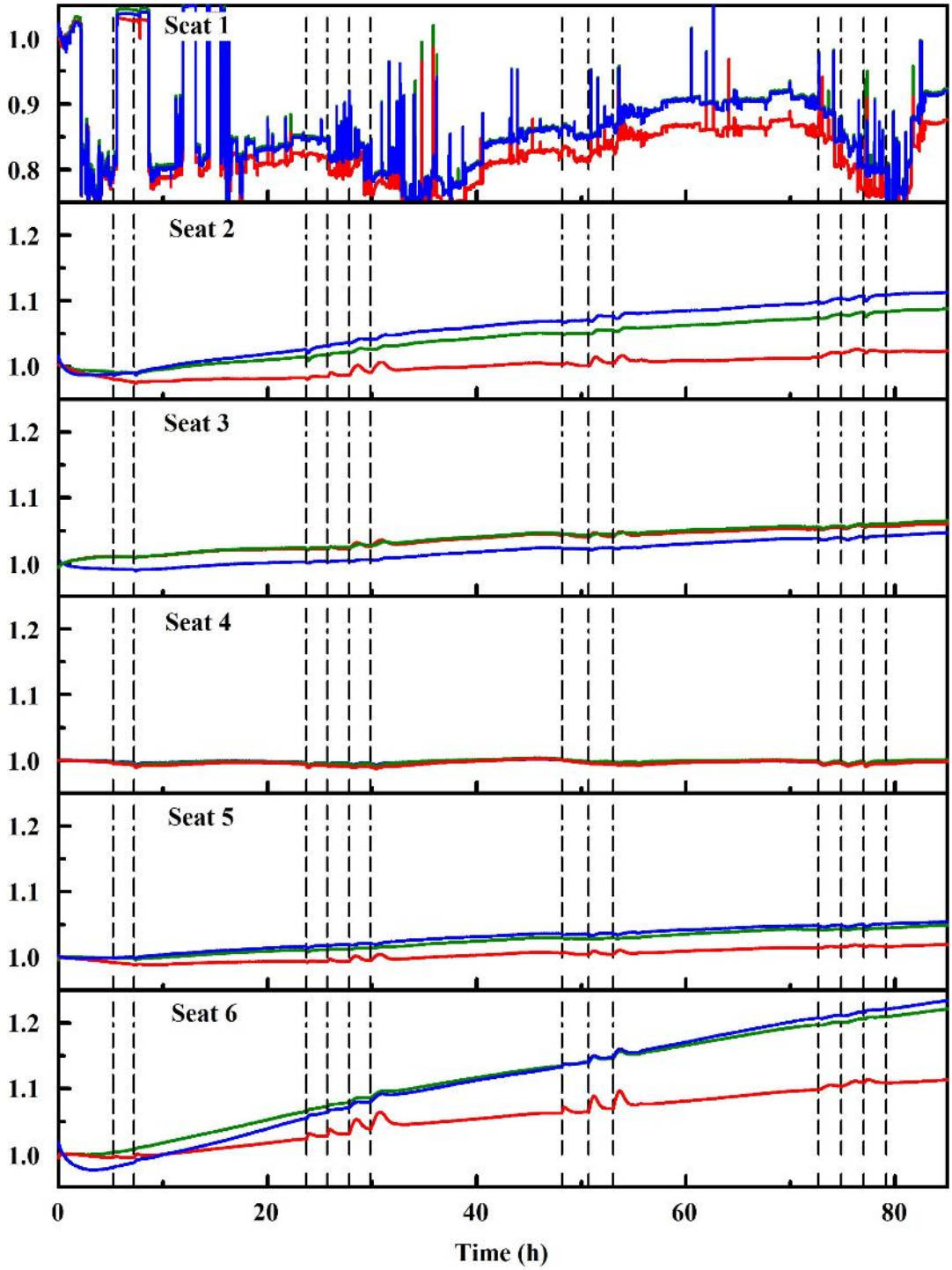


Table A-2. Exposures and Event Indication for Figure A-3 Data. Seat #1 has been excluded from consideration due to apparent device failure.

Type	Concentration (ppb)	Begin		End	Seats
Start		07/10/2018 10:06			
Acetone	160	07/10/18 15:19			
Acetone	530	07/10/18 17:20	07/10/2018 17:25	17:30	2, 4, 6
Acetone	790	07/11/18 09:47	07/11/2018 09:53	10:03	2, 4, 6
Ethanol	160	07/11/18 11:48	07/11/2018 11:54	12:04	2, 6
Ethanol	530	07/11/2018 13:55	07/11/2018 14:00	ongoing	2, 6
Ethanol	790	07/11/2018 15:56	ongoing	17:28	2, 6
Methanol	230	07/12/2018 10:14	07/12/2018 10:20	10:28	6
Methanol	760	07/12/2018 12:49	07/12/2018 12:54	13:58	2, 6
Methanol	1140	07/12/2018 15:09	07/12/2018 15:15	16:27	6
Isopropanol	400	07/13/2018 10:47			
Isopropanol	600	07/13/2018 12:57			
Acetone	790	07/13/2018 15:07	07/13/2018 15:12	15:22	2, 4, 6
Isopropanol	120	07/13/2018 17:16			
End				07/16/2018 10:39	

Yellow indicates an undetected exposure; pink a detected exposure

Figure A-4. Slope (40 point window) for the data presented in Figure A-3. Dashed lines indicate identification of an event by the algorithm.

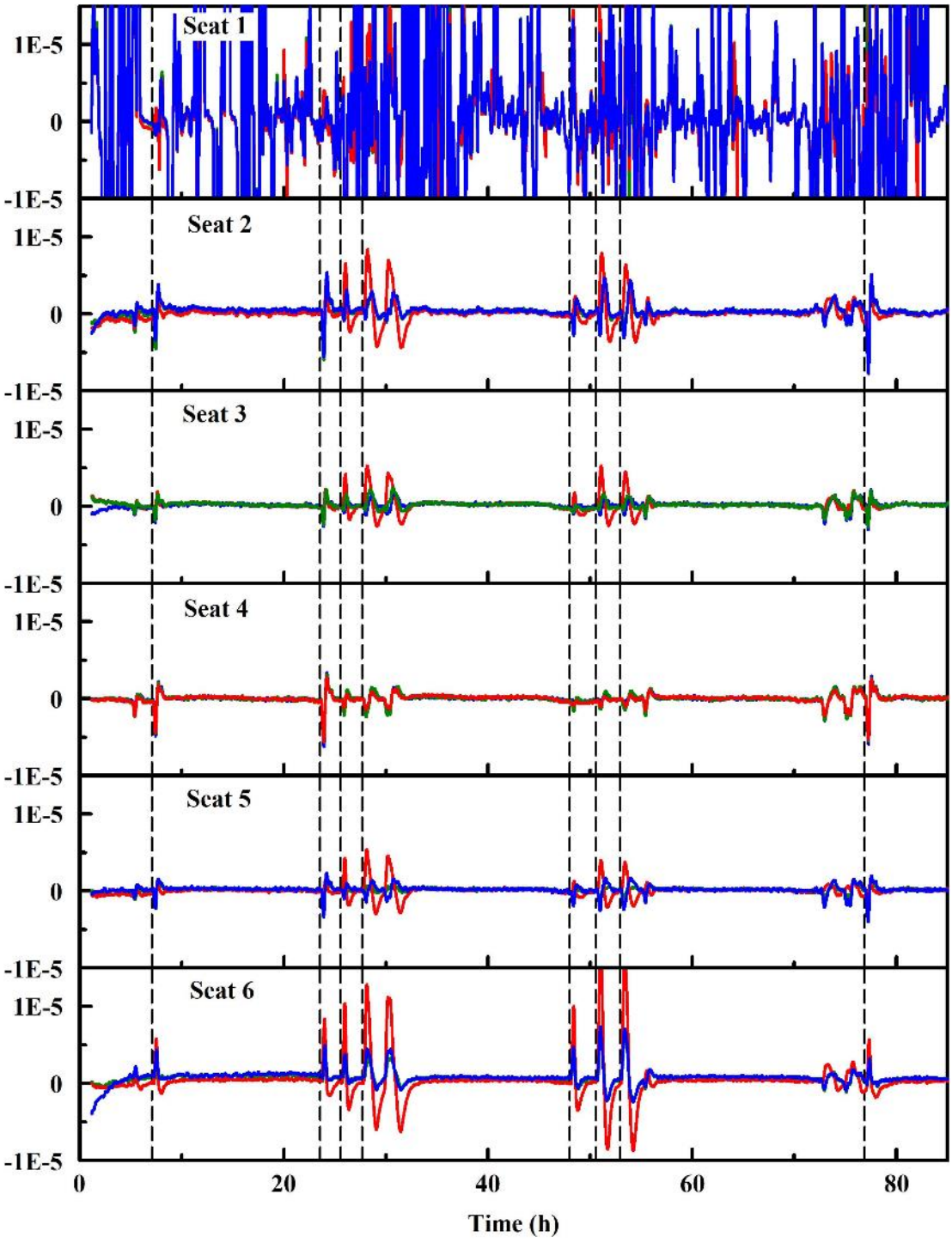


Figure A-5. Device #3. Normalized reflectance for the paper supported indicators: S_4TPP, seat #1; AgS_4TPP, seat #2; ZnS_4TPP, seat #3; CuS_4TPP, seat #4; YS_4TPP, seat #5; TlS_4TPP, seat #6. Data normalized to first 120 points. Dashed lines indicate exposure to vapor targets (left to right), 160, 530, 790 ppb acetone; 160, 530, 790 ppb ethanol; 230, 760, 1140 ppb methanol; 400, 600 ppb isopropanol; 790 ppb acetone; 120 ppb isopropanol.

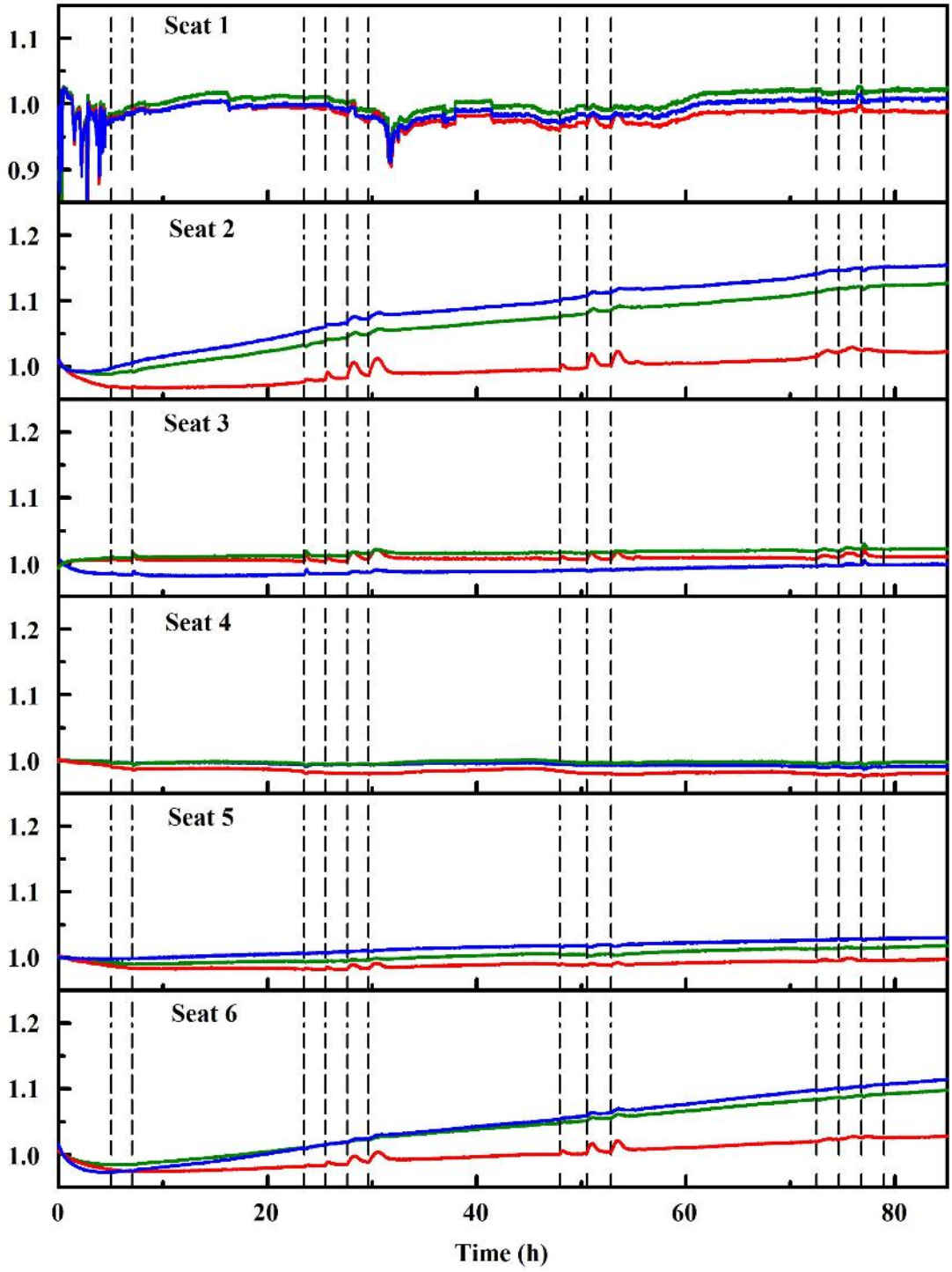


Table A-3. Exposures and Event Indication for Figure A-5 Data. Seat #1 has been excluded from consideration due to apparent device failure.

Type	Concentration (ppb)	Begin		End	Seats
Start		07/10/2018 10:18			
Acetone	160	07/10/18 15:19			
Acetone	530	07/10/18 17:20	7/10/2018 17:25	17:40:50	3
Acetone	790	07/11/18 09:47	7/11/2018 09:53	10:21:00	3
Ethanol	160	07/11/18 11:48	7/11/2018 11:54	12:28:27	2, 3, 6
Ethanol	530	07/11/2018 13:55	7/11/2018 13:59	ongoing	2, 3, 6
Ethanol	790	07/11/2018 15:56	ongoing	17:28:21	2, 3, 6
Methanol	230	07/12/2018 10:14	7/12/2018 10:20	10:27:59	2, 6
Methanol	760	07/12/2018 12:49	7/12/2018 12:54	13:56:55	2, 3, 6
Methanol	1140	07/12/2018 15:09	7/12/2018 15:15	16:25:52	2, 3, 6
Isopropanol	400	07/13/2018 10:47			
Isopropanol	600	07/13/2018 12:57			
Acetone	790	07/13/2018 15:07	7/13/2018 15:13	15:40:53	3
Isopropanol	120	07/13/2018 17:16			
End				07/16/2018 10:43	

Yellow indicates an undetected exposure; pink a detected exposure

Figure A-6. Slope (40 point window) for the data presented in Figure A-5. Dashed lines indicate identification of an event by the algorithm.

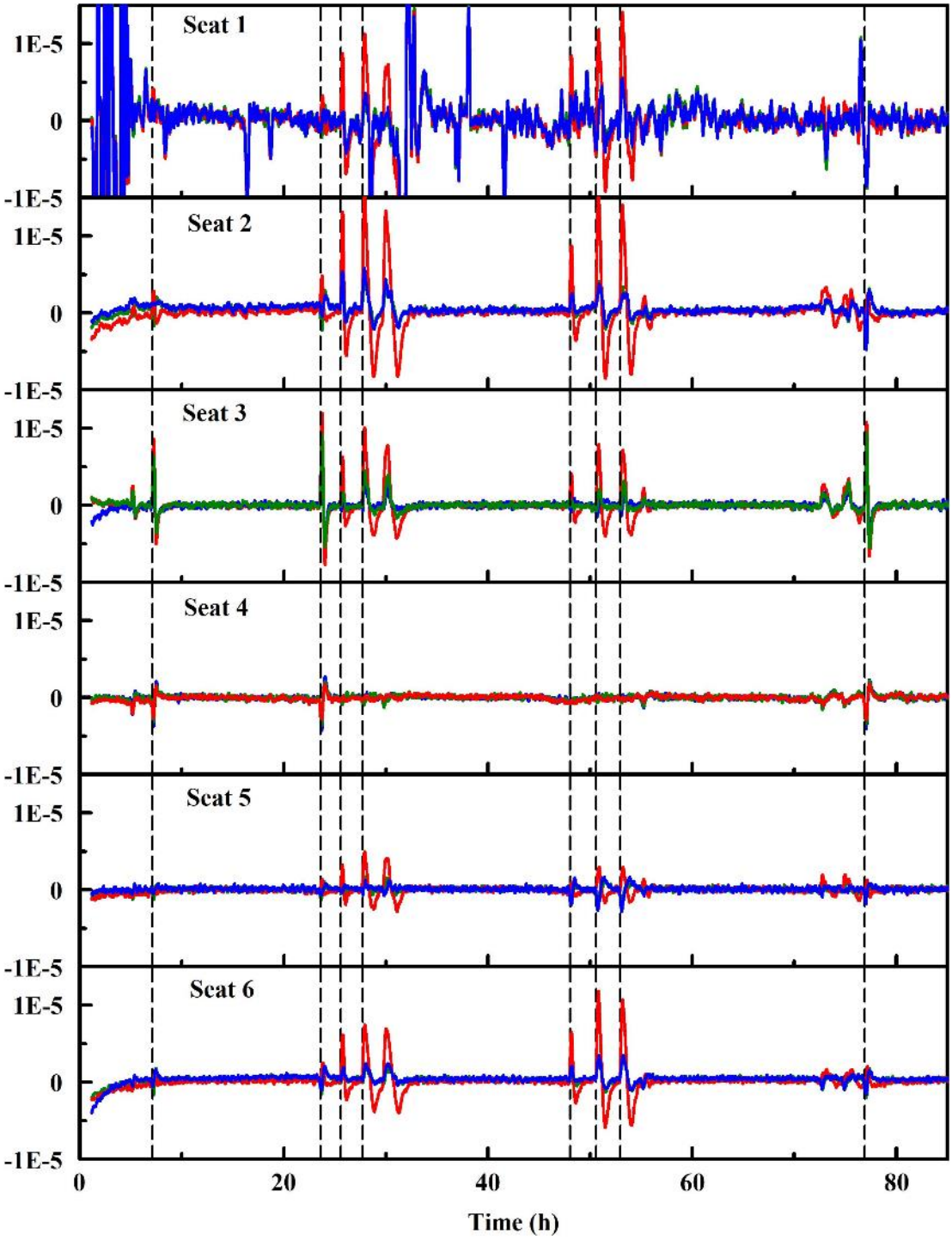


Figure A-7. Device #4. Normalized reflectance for the paper supported indicators: S_4TPP, seat #1; AgS_4TPP, seat #2; ZnS_4TPP, seat #3; CuS_4TPP, seat #4; YS_4TPP, seat #5; TlS_4TPP, seat #6. Data normalized to first 120 points. Dashed lines indicate exposure to vapor targets (left to right), 160, 530, 790 ppb acetone; 160, 530, 790 ppb ethanol; 230, 760, 1140 ppb methanol; 400, 600 ppb isopropanol; 790 ppb acetone; 120 ppb isopropanol.

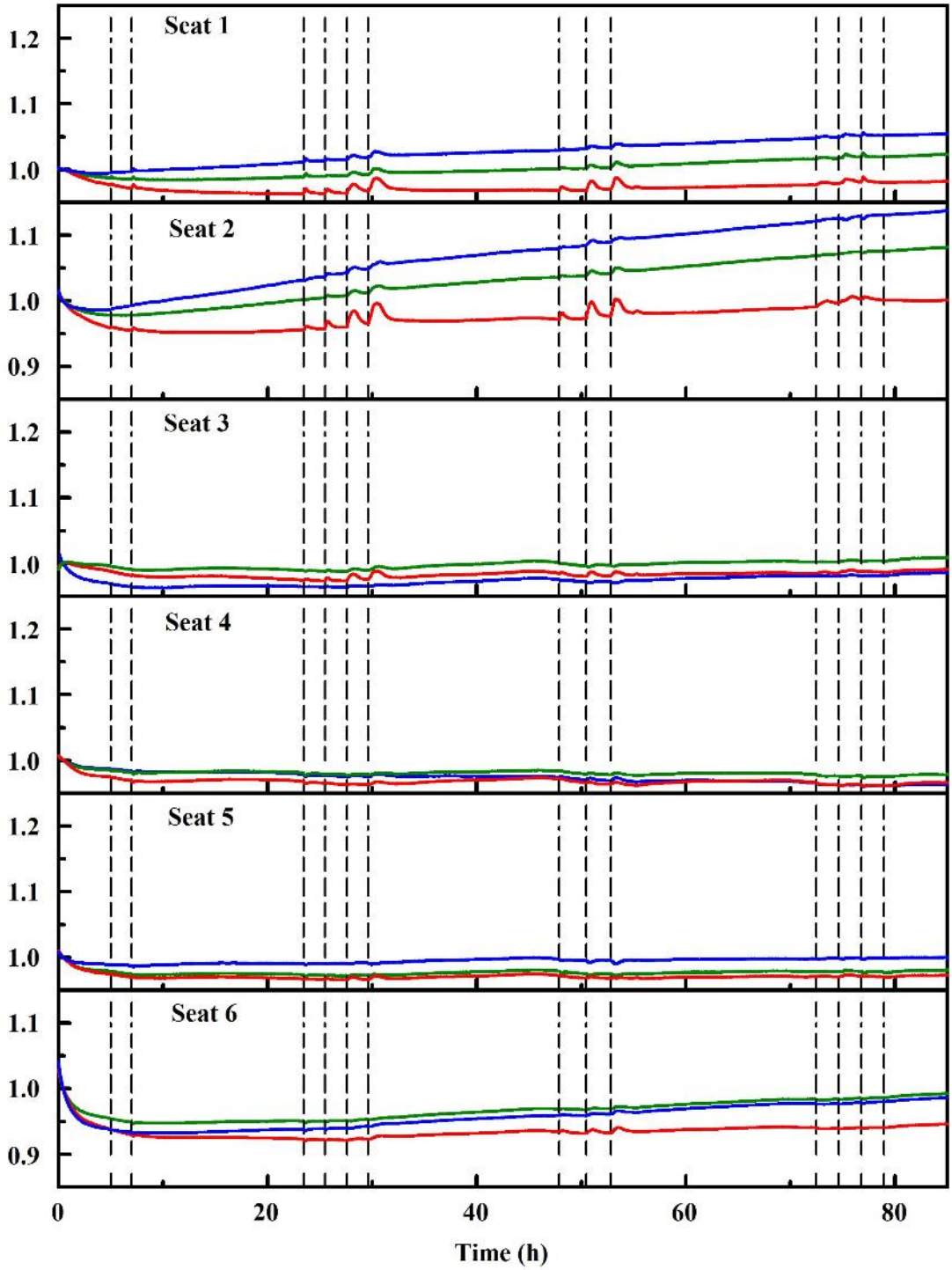
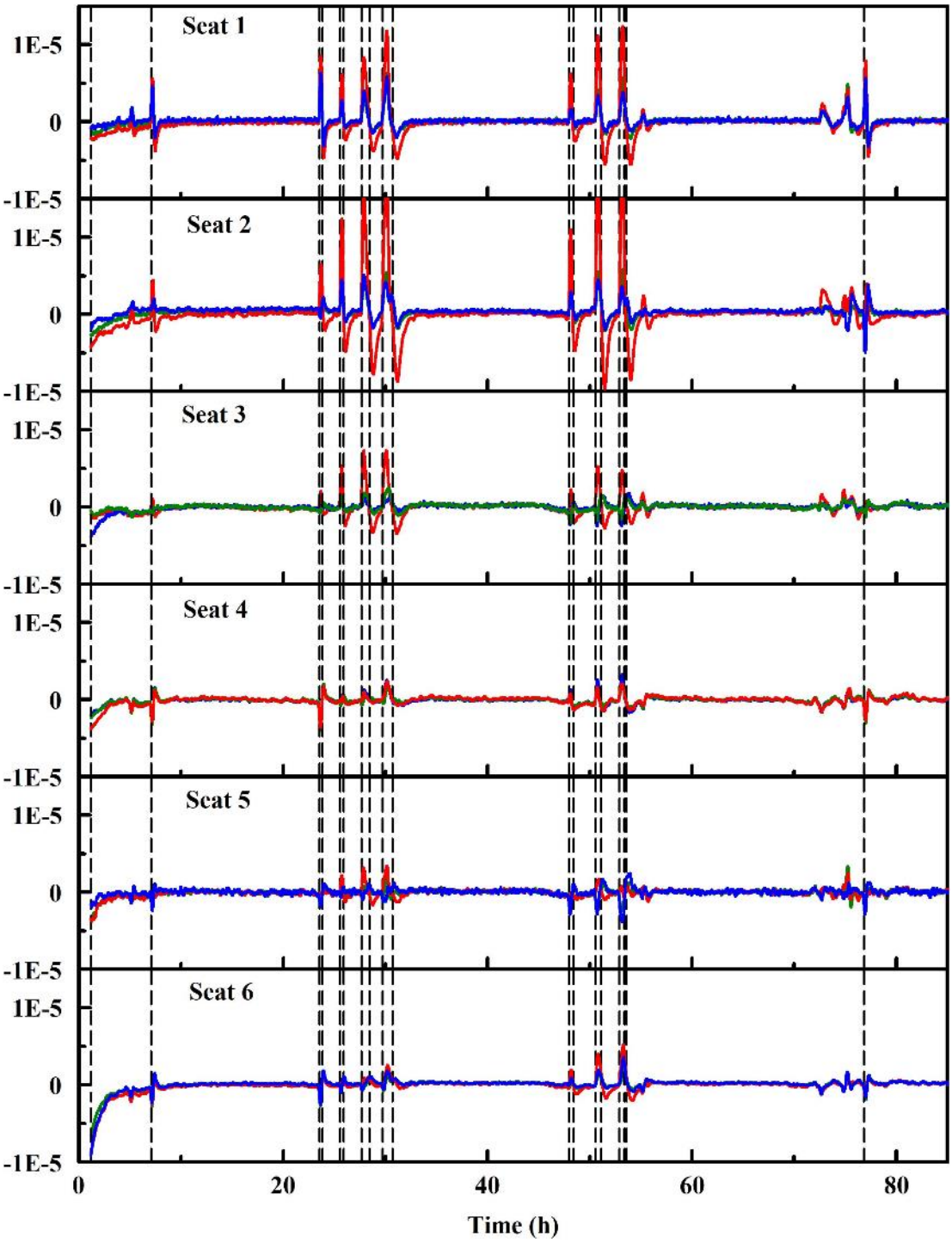


Table A-4. Exposures and Event Indication for Figure A-7 Data.

Type	Concentration (ppb)	Begin		End	Seats
Start		07/10/2018 10:20			
Unknown			7/10/2018 11:29	11:35	6
Acetone	160	07/10/18 15:19			
Acetone	530	07/10/18 17:20	7/10/2018 17:25	17:30	1
Acetone	790	07/11/18 09:47	7/11/2018 09:52	10:00	1
Unknown			7/11/2018 10:10	10:11	1
Ethanol	160	07/11/18 11:48	7/11/2018 11:54	12:04	2
Unknown			7/11/2018 12:16	12:27	2
Ethanol	530	07/11/2018 13:55	7/11/2018 14:00	14:20	2
Unknown			7/11/2018 14:46	15:13	2
Ethanol	790	07/11/2018 15:56	7/11/2018 16:02	16:30	2
Unknown			7/11/2018 17:01	17:30	2
Methanol	230	07/12/2018 10:14	7/12/2018 10:19	10:28	2
Unknown			7/12/2018 10:44	10:52	2
Methanol	760	07/12/2018 12:49	7/12/2018 12:54	13:13	2
Unknown			7/12/2018 13:27	13:58	2
Methanol	1140	07/12/2018 15:09	7/12/2018 15:14	15:36	2
Unknown			7/12/2018 15:43	15:43	2
Unknown			7/12/2018 15:54	16:25	1, 2
Isopropanol	400	07/13/2018 10:47			
Isopropanol	600	07/13/2018 12:57			
Acetone	790	07/13/2018 15:07	7/13/2018 15:11	15:20	1
Isopropanol	120	07/13/2018 17:16			
End				07/16/2018 11:01	

Yellow indicates an undetected exposure; pink a detected exposure; blue a false positive response; all green events result from detection of the device return to baseline conditions following an event

Figure A-8. Slope (40 point window) for the data presented in Figure A-7. Dashed lines indicate identification of an event by the algorithm.



Appendix B

REFLECTANCE DATA AND ALGORITHM PROCESSING: AEROSOL

Figure B-1. Device #1. Normalized reflectance for the paper supported indicators: S_4TPP, seat #1; AgS_4TPP, seat #2; ZnS_4TPP, seat #3; CuS_4TPP, seat #4; YS_4TPP, seat #5; TlS_4TPP, seat #6. Data normalized to first 120 points. Dashed lines indicate exposure to aerosol targets (left to right), 160, 530, 790 ppb acetone; 160, 530, 790 ppb ethanol; 230, 760, 1140 ppb methanol; 120, 400, 600 ppb isopropanol; 790 ppb acetone.

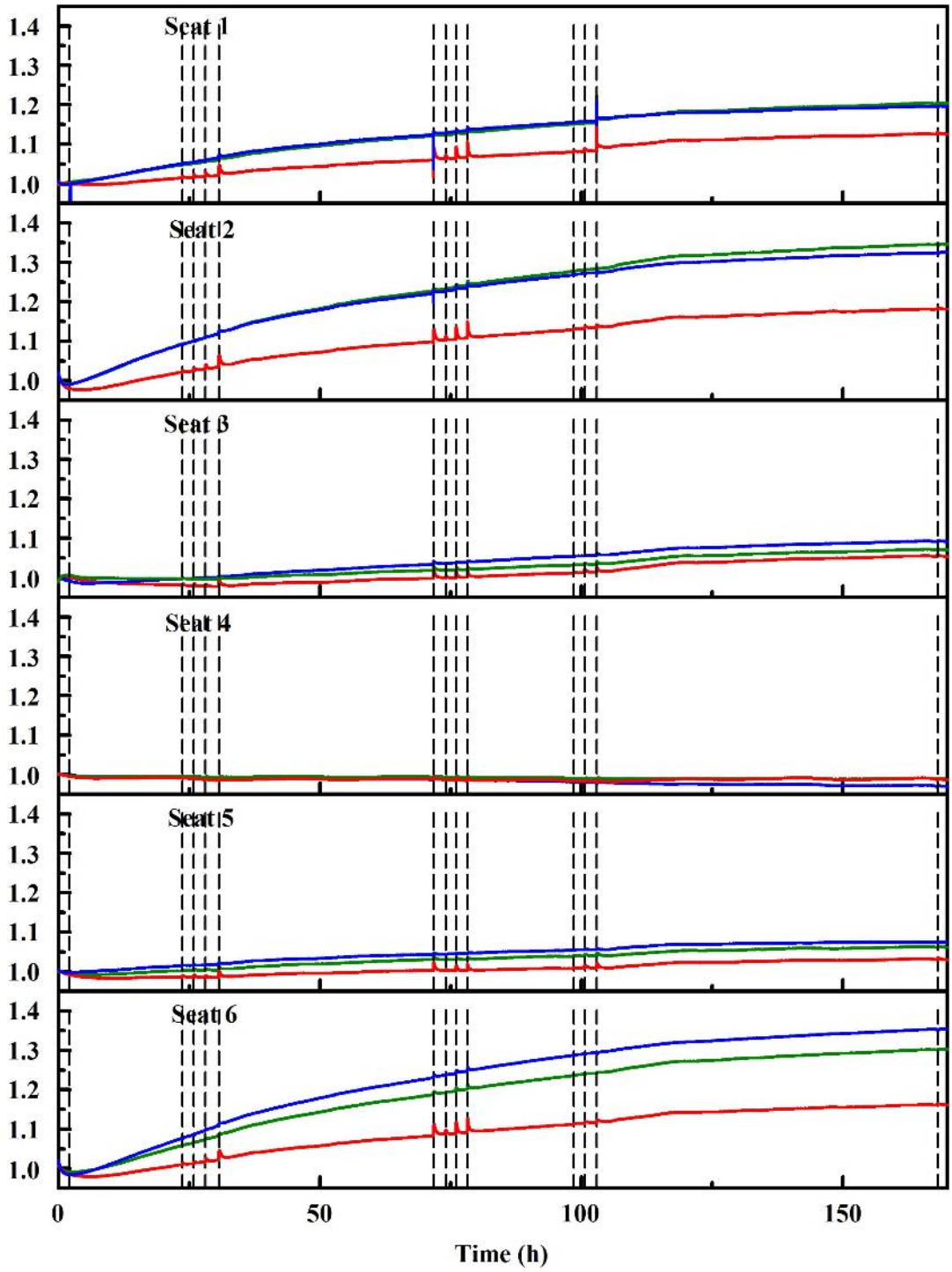


Table B-1. Exposures and Event Indication for Figure B-1 Data.

Type	Concentration (ppb)	Begin		End	Seats
Start		07/02/2018 09:23			
Acetone	160	07/02/18 11:26			
Acetone	530	07/03/18 09:06	07/03/2018 09:10	09:12	5, 6
Acetone	790	07/03/18 11:17	07/03/2018 11:20	11:24	3, 4, 5, 6
Ethanol	160	07/03/18 13:29	07/03/2018 13:33	13:36	1, 2, 6
Unknown			07/03/2018 13:43	13:55	2
Ethanol	530	07/03/2018 16:03	07/03/2018 16:05	16:50	1, 2, 3, 4, 5, 6
Ethanol	790	07/05/2018 09:05	07/05/2018 09:07	09:54	1, 2, 3, 4, 5, 6
Methanol	230	07/05/2018 11:28	07/05/2018 11:37	11:46	1, 2, 6
Methanol	760	07/05/2018 13:25	07/05/2018 13:27	14:04	1, 2, 3, 4, 5, 6
Methanol	1140	07/05/2018 15:35	07/05/2018 15:37	16:16	1, 2, 3, 4, 5, 6
Isopropanol	120	07/06/18 11:55			
Isopropanol	400	07/06/2018 14:02	07/06/2018 14:04	14:09	3, 5, 6
Isopropanol	600	07/06/2018 16:19	07/06/2018 16:21	16:48	1, 3, 4, 5, 6
Acetone	790	07/09/2018 09:32	070/9/2018 09:34	09:38	2, 5
End				07/09/2018 13:04	

Yellow indicates an undetected exposure; pink a detected exposure; all green events result from detection of the device return to baseline conditions following an event

Figure B-2. Slope (40 point window) for the data presented in Figure B-1. Dashed lines indicate identification of an event by the algorithm.

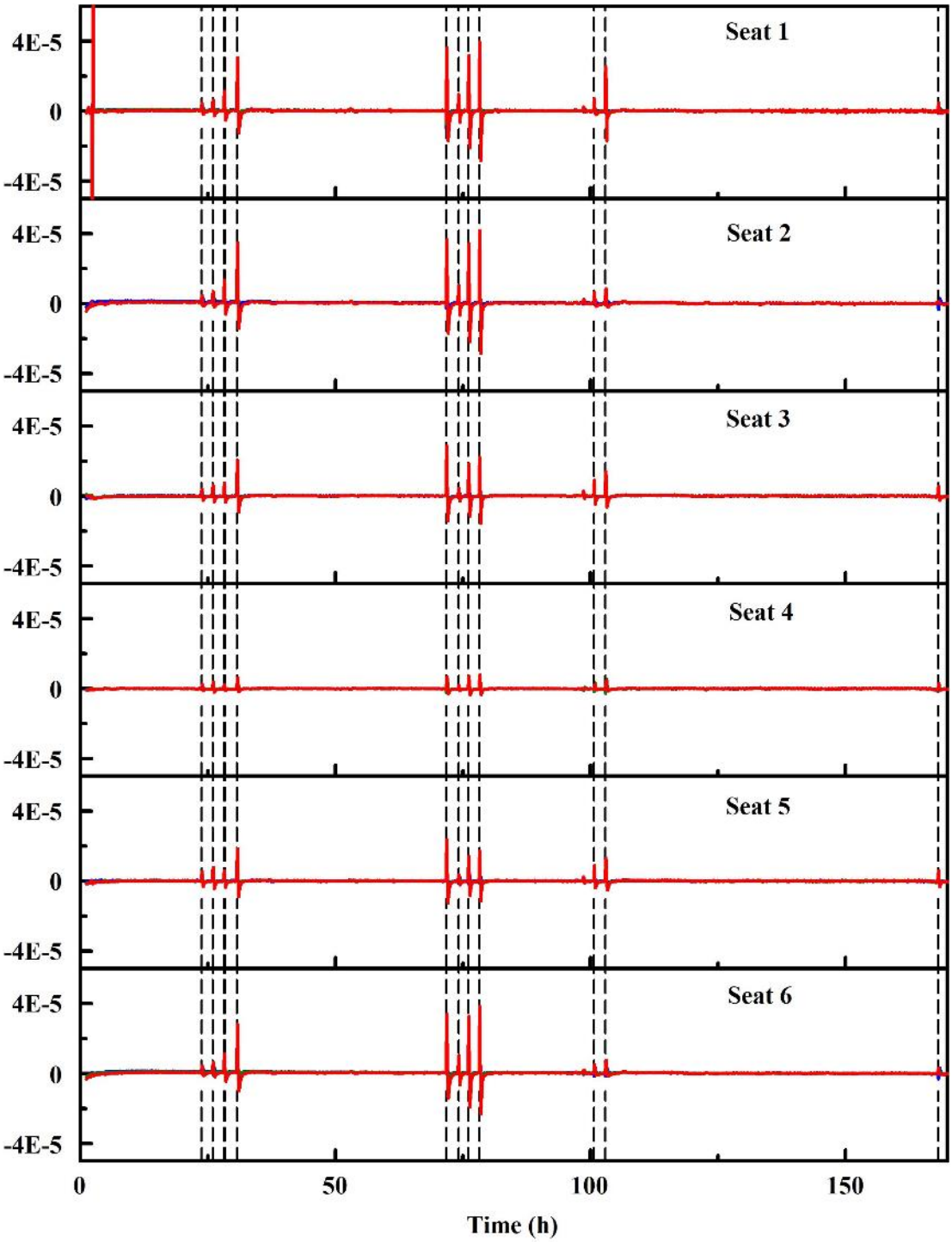


Figure B-3. Device #3. Normalized reflectance for the paper supported indicators: S_4TPP, seat #1; AgS_4TPP, seat #2; ZnS_4TPP, seat #3; CuS_4TPP, seat #4; YS_4TPP, seat #5; TlS_4TPP, seat #6. Data normalized to first 120 points. Dashed lines indicate exposure to aerosol targets (left to right), 160, 530, 790 ppb acetone; 160, 530, 790 ppb ethanol; 230, 760, 1140 ppb methanol; 120, 400, 600 ppb isopropanol; 790 ppb acetone.

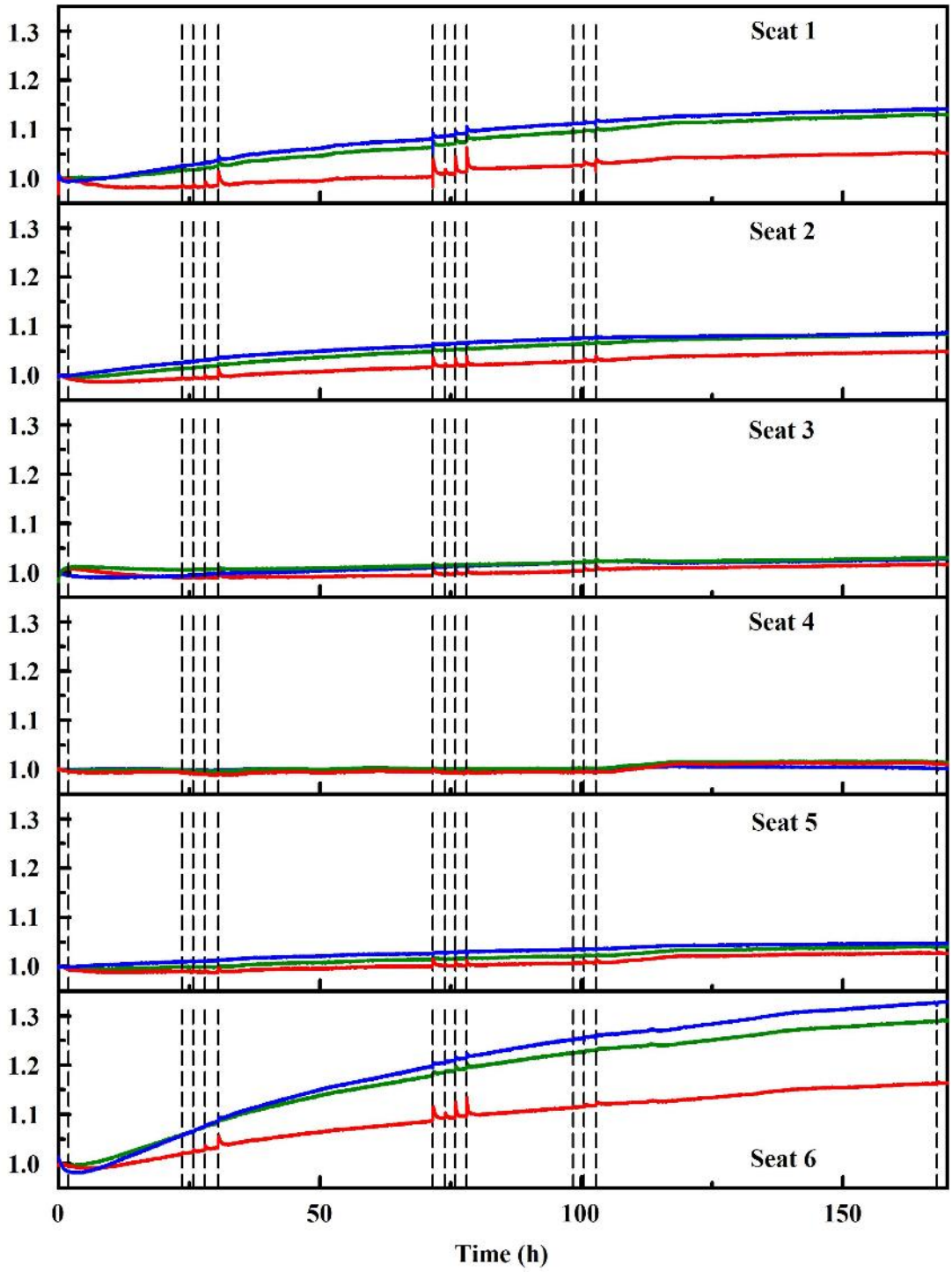


Table B-2. Exposures and Event Indication for Figure B-3 Data.

Type	Concentration (ppb)	Begin		End	Seats
Start		07/02/2018 09:31			
Acetone	160	07/02/18 11:26			
Acetone	530	07/03/18 09:06	07/03/2018 09:11	09:12	4
Acetone	790	07/03/18 11:17	07/03/2018 11:21	11:25	1, 4, 6
Ethanol	160	07/03/18 13:29	07/03/2018 13:33	13:37	1, 3, 6
Ethanol	530	07/03/2018 16:03	07/03/2018 16:06	16:36	1, 2, 3, 5, 6
Ethanol	790	07/05/2018 09:05	07/05/2018 09:08	09:50	1, 2, 3, 5, 6
Methanol	230	07/05/2018 11:28	07/05/2018 11:30	11:46	1, 3, 6
Methanol	760	07/05/2018 13:25	07/05/2018 13:27	13:59	1, 2, 3, 6
Methanol	1140	07/05/2018 15:35	07/05/2018 15:36	16:10	1, 2, 3, 5, 6
Isopropanol	120	07/06/18 11:55			
Isopropanol	400	07/06/2018 14:02	07/06/2018 14:05	14:08	1, 3
Isopropanol	600	07/06/2018 16:19	07/06/2018 16:21	16:35	2, 3, 5, 6
Acetone	790	07/09/2018 09:32	07/09/2018 09:36	09:37	1
End				07/09/2018 13:12	

Yellow indicates an undetected exposure; pink a detected exposure; green a false positive response

Figure B-4. Slope (40 point window) for the data presented in Figure B-3. Dashed lines indicate identification of an event by the algorithm.

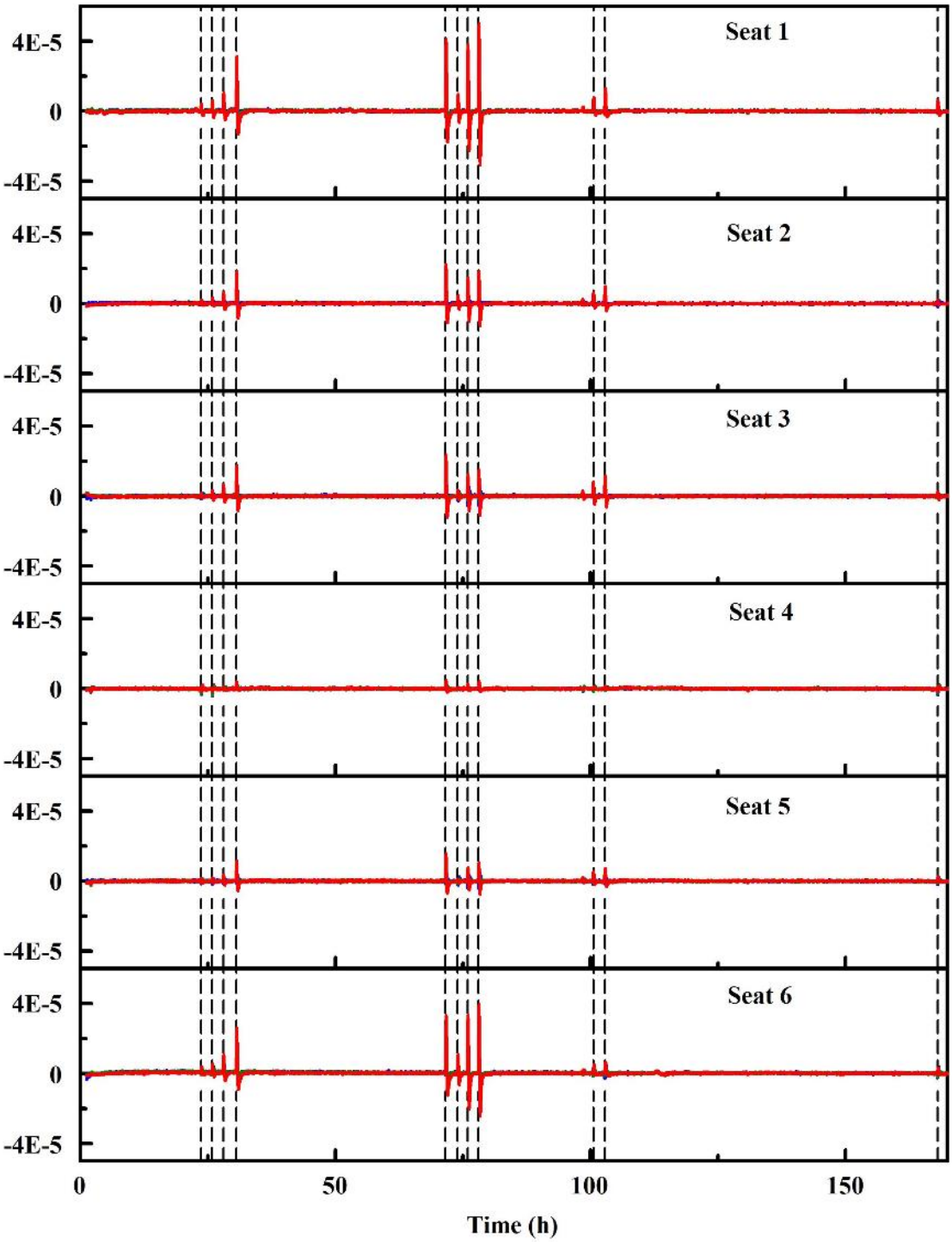


Figure B-5. Device #4. Normalized reflectance for the paper supported indicators: S_4TPP, seat #1; AgS_4TPP, seat #2; ZnS_4TPP, seat #3; CuS_4TPP, seat #4; YS_4TPP, seat #5; TlS_4TPP, seat #6. Data normalized to first 120 points. Dashed lines indicate exposure to aerosol targets (left to right), 160, 530, 790 ppb acetone; 160, 530, 790 ppb ethanol; 230, 760, 1140 ppb methanol; 120, 400, 600 ppb isopropanol; 790 ppb acetone.

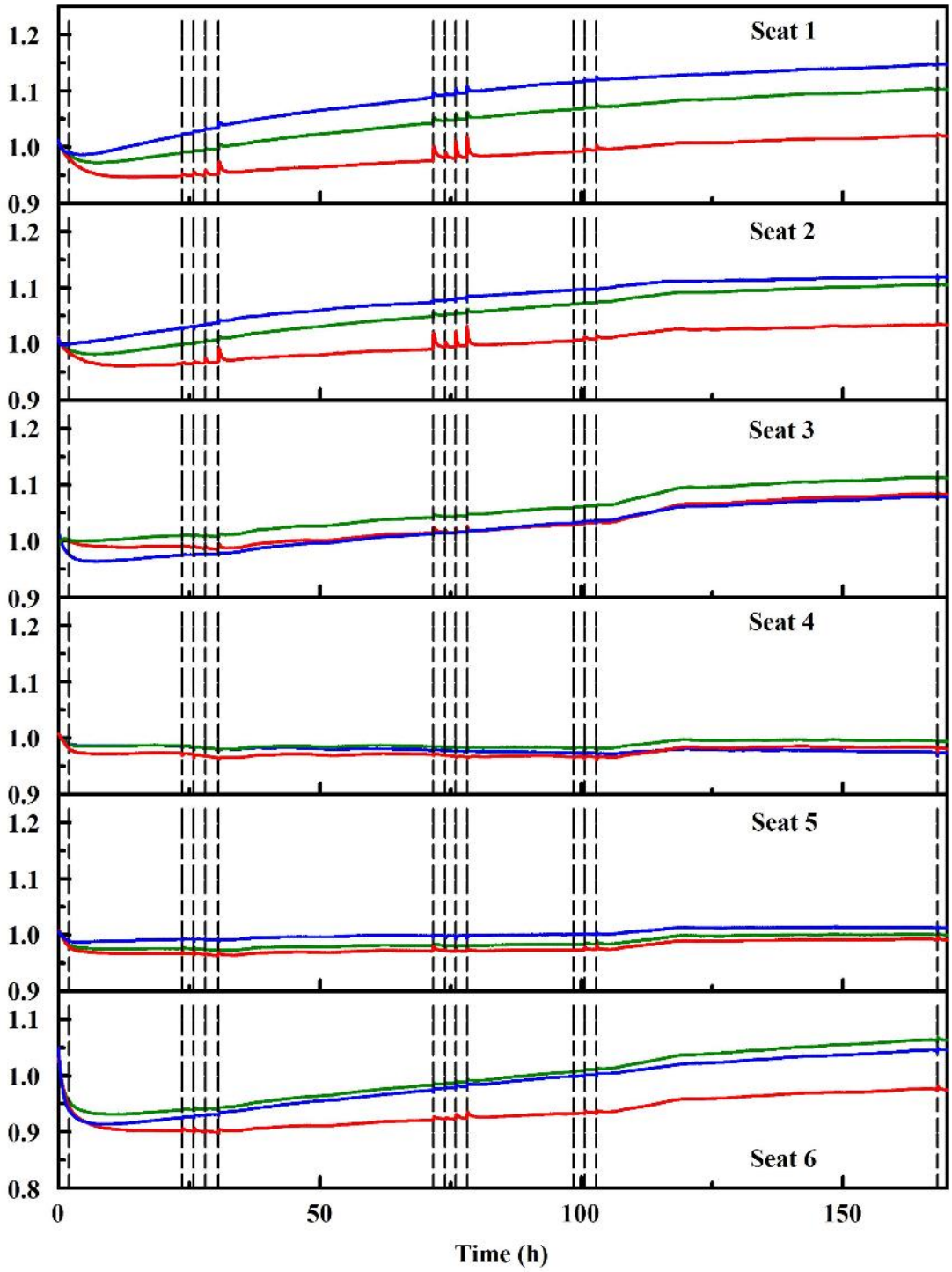


Table B-3. Exposures and Event Indication for Figure B-5 Data.

Type	Concentration (ppb)	Begin		End	Seats
Start		07/02/2018 09:27			
Unknown			07/02/2018 10:36	10:56	6
Acetone	160	07/02/18 11:26			
Acetone	530	07/03/18 09:06	07/03/2018 09:08	09:17	1, 4, 6
Acetone	790	07/03/18 11:17	07/03/2018 11:19	11:30	1, 2, 4, 5, 6
Ethanol	160	07/03/18 13:29	07/03/2018 13:32	13:36	1, 2, 3
Ethanol	530	07/03/2018 16:03	07/03/2018 16:05	16:53	1, 2, 3, 4, 5, 6
Ethanol	790	07/05/2018 09:05	07/05/2018 09:07	09:58	1, 2, 3, 5, 6
Methanol	230	07/05/2018 11:28	07/05/2018 11:30	11:34	1, 2
Unknown			07/05/2018 11:41	11:47	1
Methanol	760	07/05/2018 13:25	07/05/2018 13:27	14:08	1, 2, 5, 6
Methanol	1140	07/05/2018 15:35	07/05/2018 15:37	16:20	1, 2, 3, 5, 6
Isopropanol	120	07/06/18 11:55			
Isopropanol	400	07/06/2018 14:02	07/06/2018 14:04	14:12	1, 4, 5, 6
Isopropanol	600	07/06/2018 16:19	07/06/2018 16:20	16:41	1, 3, 4, 5, 6
Acetone	790	07/09/2018 09:32	07/09/2018 09:34	9:44	1, 2, 3, 4, 5, 6
End				07/09/2018 13:08	

Yellow indicates an undetected exposure; pink a detected exposure; blue a false positive response; all green events result from detection of the device return to baseline conditions following an event

Figure B-6. Slope (40 point window) for the data presented in Figure B-5. Dashed lines indicate identification of an event by the algorithm.