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On-site monitoring of occupational exposure to volatile organic compounds by a portable comprehensive 2-dimensional gas chromatography device†

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A fully automated portable comprehensive 2-dimensional (2-D) gas chromatography (GC) device was utilized for the first time for the field analysis of occupational volatile organic compounds (VOCs) at the Spray and Finishing Shop of the University of Michigan. The instrument contains a full set of micro-preconcentrator/injectors, commercial columns, micro-Deans switches, micro-thermal injectors, micro-photoionization detectors, data acquisition cards, and power supplies, as well as computer control and user interface. The indoor air was sampled and analyzed before, during, and after spraying the five most frequently used paints. The 2-D analysis yields enhanced peak capacity and shortened analysis time as compared to those achieved by portable GC instruments reported to date. In addition, the portable system is able to perform on-site analysis of VOCs, providing the results every 5 to 15 min, which would allow for enhanced acquisition of information regarding workers' safety and health risks from airborne VOCs. The performance of the portable 2-D GC device was validated by comparing the quantitative results of various type of paints using traditional occupational VOCs monitoring techniques in accordance with Occupational Safety and Health Administration Method ORG-07.

1. Introduction

Because most people spend 80–90% of their time indoors and the concentrations of volatile organic compounds (VOCs) in indoor air can be up to ten times higher than outside, VOCs in indoor air have been extensively investigated in the last few decades.[1–3] Furthermore, people routinely working with chemicals in their workplaces (*e.g.*, the petroleum industry, manufacturing plants, the vehicle repair industry, and the paint industry) are at an even higher risk of exposure, as they are more frequently exposed to a wider array of VOCs at higher concentrations than those present in other indoor or outdoor environments.[4–9] VOCs that are commonly encountered in the workplace include acetone, benzene, butyl acetate, ethanol, *n*-hexane, and toluene, among others.[5,6] In particular, these compounds can exert various forms of acute health effects (*e.g.*, eye, nose, and throat irritation, headaches, nausea, and

dizziness) along with chronic health effects (*e.g.*, cancer and organ damage), depending upon the particular compound and its exposure time and concentration.[10–12]

To help ensure safe conditions for workers, the US Occupational Safety and Health Administration (OSHA) has established regulatory limits on many toxic compounds that are termed 8 hours Permissible Exposure Limits (PELs).[13] Alternative occupational exposure limits and recommendations (see Table S1†) are used by other agencies, including Recommended Exposure Limits (RELs) from the National Institute for Occupational Safety and Health (NIOSH), and Threshold Limit Values (TLVs) and Biological Exposure Indices (BEIs) from the American Conference of Governmental Industrial Hygienists (ACGIH).[13–15] Both NIOSH and ACGIH also recommend Short-Term Exposure Limits (STELs) appropriate for 15 min exposure periods during a work shift.

To identify and evaluate the concentrations of VOCs, indoor air has traditionally been collected using three methods: active, passive, and whole.[1,16–19] In active sampling, the air is drawn through a column by a pump and VOCs are adsorbed selectively onto carbon or porous polymer-based adsorbents (*e.g.*, Carbotrap®, Carboxen®, Carbosieve®, Carbopack™, or Chromosorb®).[19–21] Passive sampling using devices such as Radiello®, Chemcatcher®, ULTRA®, solid-phase micro-extraction (SPME), and charcoal or polymer-based sampler is

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carried out by diffusion without the aid of a pump.[16,22–31] Whole sampling involves using bags (ALTEF, Tedlar, or multi-layer foil) or canisters (stainless steel or Siltek®-treated) to collect a grab sample of air in which VOCs might be present.[32,33] After sampling, off-site determination of VOCs usually follows through the use of bench-top gas chromatography coupled with mass spectrometry (GC-MS) or a flame ionization detector (GC-FID).[1] Unfortunately, this off-site laboratory analysis is time-consuming (often requiring up to one week) and relatively expensive (up to $200 per sample analysis), thus delaying recognition of the immediate health risk associated with over-exposure to VOCs and the administration of interventions.

To date, most research has been focused on enhancing and advancing bench-top analysis; only a few groups have published studies employing portable systems for rapid on-site analysis. Pawliszyn *et al.* reported on the use of a SPME device with a commercially available portable GC equipped with in-series detectors: photoionization detector (PID), FID, and dry elec-trolytic conductivity detector (DELCD) for indoor air moni-toring.[34] They also reported using membrane extraction with a sorbent interface (MESI) with a Chrompack micro-GC system that exhibited improved sensitivity.[35] Recently, the same group developed a carbon mesh supported thin film microextraction (TFME) device coupled with GC-toroidal ion trap mass spec-trometry (GC-TMS) providing a detection limit down to the level of hundreds of ppt.[36]

While these systems have achieved enhanced sensitivity, they have focused mainly on the development of sampling methods rather than actual indoor air analysis, thus only a few chemicals (*i.e.*, benzene, toluene, ethylbenzene, and xylene) were detected. Kim *et al.* reported a microfabricated GC (μGC) system equipped with an array of four chemiresistor micro-sensors for the field measurement of indoor trichloroethylene (TCE).[37,38] Short- and long-term on-site analyses of TCE with sub-ppb sensitivity were demonstrated. While portable and automated, the system has only been used for TCE monitoring rather than analysis of a broader range of VOCs. Very recently, Jian *et al.* investigated the on-site, real-time and continuous analysis of VOCs inside a semiconductor cleanroom using a micro-GC device coupled with a photo-ionization detector (μGC-PID).[39] Six compounds (acetone, isopropanol, *n*-hexane, toluene, *m*-xylene, and anisole) were identified by their system, which were subsequently verified by standard canister/GC-MS analyses. However, in most actual workplaces, the air may contain many more complex VOC compositions, which may impose a significant challenge on the current portable system due to their relatively low peak capacities. Consequently, a versatile portable GC system, which has a large peak capacity and is able to perform sensitive and on-site analysis of a broad range of VOCs, is highly desirable.

We recently reported on a fully automated portable 1 × 4-channel comprehensive 2-dimensional (2-D) GC device (60 cm × 50 cm × 10 cm and <5 kg. See Fig. 1(a)).[40] As illustrated in Fig. 1(b), the entire device consists of a micro-preconcentrator/injector (μPI), commercial column, micro-Deans switch (μDS), micro-Thermal injector (μTI), and μPID, as well as solenoid valve, pump, helium cartridge, power supply, and Labview™-
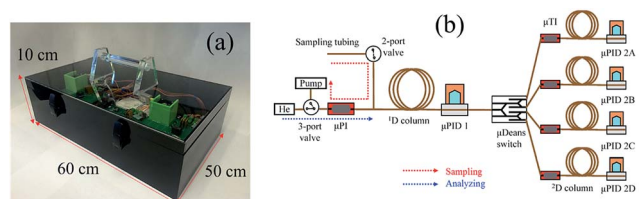

Fig. 1 (a) Picture and internal layout (b) of the portable 2-D GC device.
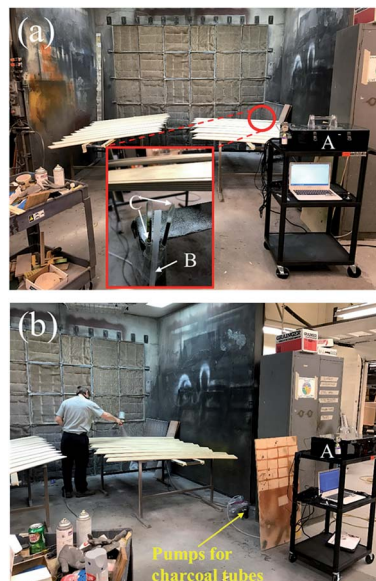

Fig. 2 Picture of the device (marked as "A") as placed at the Spray and Finishing Shop of the University of Michigan (a) before and (b) during spraying. The inset in (a) shows the details of the sampling tubing (marked as "B") used in the portable 2-D GC device and the two charcoal tubes (marked as "C") used for standard GC-MS analysis.

based user interface and operation control. Laboratory measurements demonstrated the 2-D separation of 50 analytes in 14 min with a peak capacity of 430–530 and peak production of 40–80 min^{-1}, both of which are much larger than those provided by the portable GC described previously.[40] In this article, we demonstrate for the first time the field analysis of indoor VOCs using this portable 2-D GC device at the Spray and Finishing Shop of the University of Michigan (see Fig. 2(a) and (b)) and benchmarked against the standard OSHA Method ORG-07. We show that our portable 2-D GC is able to quantitatively analyze various types of VOCs in paints in real time with the results comparable to those obtained using standard OSHA measurement and analytical methods.

2. Experimental

2.1. Description of the Spray and Finishing Shop

Fig. 3(a) shows the floor layout of the Spray and Finishing Shop (Shop) (22.8 m × 16 m × 4 m). Specifically, the Shop has three open booths (1, 2, and 3) that are usually used for the work (spraying, painting, staining, or drying), one preparation room
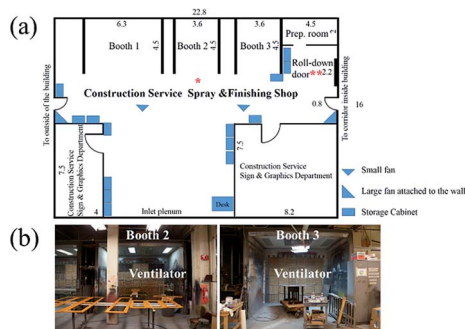
Fig. 3 (a) Floor layout of the Spray and Finishing Shop (in units of meters). The indoor air outside booth 2 (marked as "*") was sampled after spraying paint 3, Magnamax C148 14 Satin-35. The indoor air was sampled at the location marked as "**" during spraying paint 4 and 5, Magavar 1M.4304 Satin and Kem Kromik Universal Metal Primer B50NZ6. (b) Pictures of booth 2 and 3 used in our work.

(mixing or shaking the materials), and two offices. Each booth has a ventilator system inside attached to the wall as shown in Fig. 3(b) and is operated by an on/off switch. Two large and two small fans facing toward the booths are frequently used, and a fresh-air inlet plenum is positioned on the wall directly across from booths 1 and 2. There are three doors including a roll-down door and one hinged door that are connected to the outside of the building, and the other hinged door that is connected to a corridor inside the building; all outside-access doors are usually closed (depending on the season). Other doors to the preparation room and offices are usually open. There are 14 metal cabinets storing various paints, stains, and sealers in the shop and one working desk in the back for the technician.

2.2. Materials

Table S2† shows the five paints most frequently used at the shop that were analyzed, including sealers, top-coats, and primer. The PELs, RELs, and TLVs of chemicals in the paints are listed in Table S1.† Anasorb® Coconut Shell Charcoal tubes were obtained from Bureau Veritas (Novi, MI) and Aircheck 52 sample pumps were purchased from SKC Inc. (Eighty Four, PA).

2.3. Experimental setup

A detailed description and specification of the portable 1×4-channel comprehensive 2-D GC device can be found in ref. 40. Briefly, as illustrated in Fig. 1(b) the system consists of a ^{1}D module and four ^{2}D modules. The ^{1}D module includes μPI loaded with Carbopack™ B (60–80 mesh), one 10 m long Rtx-5MS column (250 μm i.d., 0.25 μm coating thickness), and μPID 1A. Each of the four ^{2}D modules includes a μTI loaded with Carbopack™ B, a 3 m long Rtx-200 (250 μm i.d., 0.25 μm coating thickness), and a μPID (2A–2D). The analyte from the ^{1}D module is transferred to the ^{2}D modules via a μDS subsystem controlled by two three-port solenoid valves. The entire system is controlled by a home-made LabView™ program for automation. For the current work, a length of polytetrafluoroethylene (PTFE) tubing

(1 m long and 0.64 cm i.d.) was attached to the inlet of the μPI for air sampling.

2.4. Portable 2-D GC operation

During the measurement, the portable 2-D GC device, secured to a rolling cart, was placed near the booth where the worker was spraying (see Fig. 2(a) and (b)). The PTFE sampling tubing (see the inlet of Fig. 2(a)) was connected to the device and placed in front of the ventilator to draw the air. As shown in Fig. 2(b), during spraying, workers used a spray gun to coat the woods or metals with the paint or sealant, and they wore a vapor respirator while the ventilator was operating (the ventilator is usually turned off immediately after spraying). The relevant operation procedures and parameters of the portable 2-D GC are described as follows.

(1) The indoor air at the shop was drawn at a flow rate of 25 mL min^{-1} by a diaphragm pump into the μPI and adsorbed by Carbopack™ B. After sampling, the μPI was heated up to 270 °C in 0.6 s and then kept at 250 °C for 10 s for complete thermal desorption.

(2) The analytes underwent separation through the 10 m long Rtx-5MS column, and then were detected by μPID 1. During the separation, the column was heated and maintained at 30 °C for 1 min, and then ramped at a rate of 3 °C min^{-1} to 120 °C and kept at 120 °C for 4 min. μPID 1 was kept at room temperature (25 °C). The flow rate was 2 mL min^{-1}.

(3) We used a modulation period of 8 s. The 1st 8 s long slice of the eluent from the ^{1}D column was routed by the μDS and trapped by the μTI in one of the ^{2}D modules (for example, channel A in ^{2}D) kept at room temperature (25 °C). Then the μTI was heated to 270 °C in 0.6 s and kept at 250 °C for 5 s to inject the trapped analytes. The 2nd, 3rd, 4th, and 5th 8 s long slices of the ^{1}D eluent were alternately sent to channel B, C, D, and A in ^{2}D, respectively.

(4) The analytes underwent ^{2}D separation through one of the 3 m long Rtx-200 columns (kept at 40 °C during the entire operation) and then were detected by μPID 2 (kept at room temperature, 25 °C). During the separation, the helium flow rate was 2 mL min^{-1} for each ^{2}D column. The maximal separation time for each ^{2}D column was 32 s (4 times the modulation period).

(5) A 2-D chromatogram contour was constructed by using the data from μPIDs at the end of each column. Details of the construction are discussed in ref. 40.

2.5. OSHA Method ORG-07 and GC-MS measurement

For validation, we utilized the OSHA Method ORG-07 for air sampling and analysis.[41] SKC, Inc. Aircheck 52 sample pumps (Eighty Four, PA) were used to collect measurements for validation purposes using Anasorb® Coconut Shell Charcoal (CSC) tubes that were provided by the analyzing laboratory, Bureau Veritas (Novi, MI). We attached two Anasorb® CSC tubes with both ends severed immediately adjacent to the portable 2-D GC sampling tube (see the inset of Fig. 2(a)). The Aircheck 52 sample pump drew air through the CSC tubes via a 6 m long Tygon® tubing at a rate of approximately 100 mL min^{-1}. Note that a 6 m

long tubing was used to increase the distance between the pump and sampling media so that the pump itself would not be contaminated. Sample caps were applied to both ends of each CSC tube immediately following sampling and samples were transported to the lab in a chilled cooler (10 °C). The pumps and Tygon® tube assemblies were calibrated with a Mesa Labs Bio Defender 520 M DryCal (Butler, NJ) before and after each use, and all samples calibrated within ±10% of 100 mL min^{-1}. Daily blanks were obtained by breaking both ends of a CSC tube in the same location where sample tubes were fractured and immediately capping both ends. The blank tubes were then transported alongside sample tubes and analyzed using the same methods, equipment, and solutions within the laboratory. Blank values were subtracted from the samples taken that day if the results exceeded detectable levels. Bureau Veritas performed all VOC analyses according to OSHA Method ORG-07 for organic vapors using GC-FID (and further analyzed by GC-MS for peak identification).

3.   Results and discussion

3.1.   On-site indoor air analysis using portable 2-D GC (paint 1)

First, we analyzed indoor air while a worker was spraying one of the enamel paints, electrostatic semi-gloss enamel clear base V260-88 (paint 1 in Table S2†) at booth 2. The total measurement took only about 8 min, including sampling (5 min) and analyzing (3 min). Of the eight ingredients listed in Table S2,† four chemicals (*m*-xylene, *o*-xylene, *t*-butyl acetate, and ethylbenzene) were detected and well-separated, along with toluene (a commonly used solvent for paint[42]), as shown in the 2-D contour plot in Fig. 4(a). The VOC associated with each peak was identified by its retention times in the 2-D chromatogram using the reference library constructed with individual pure sample.

Methyl ethyl ketoxime, 2-butoxyethanol, and 2-pentanone were not detected, likely due to their low concentrations in the paint. Limestone, kaolin, and short oil alkyd resin were also not detectable, due likely to their low volatilities. OSHA method ORG-07 and GC-MS measurement could detect 14 chemicals (5 above 10 mg m^{-3} and 9 below 10 mg m^{-3}), including cyclohexane, *m*-xylene, *o*-xylene, *t*-butyl acetate, and ethylbenzene, whose concentrations were above 10 mg m^{-3}. The concentrations of other nine chemicals ranged from 0.1 to 1 mg m^{-3}. The ^{1}D chromatogram detected by µPID1 that shows several peaks were not fully separated (two coelutions of VOCs 1 and 2, and VOCs 6, 7 and 8 in ESI Fig. S1†), but they were further separated in ^{2}D, which clearly demonstrated that the portable 2-D GC is capable of analyzing a complex sample in a short period of time (less than 10 min), potentially providing rapid feedback to a worker or industrial hygienist.

To validate the result by the portable 2-D GC device, two air samples were also collected using the two charcoal tubes concomitantly (sampling time: 5 min) and analyzed later by GC-FID and MS by Bureau Veritas. Among nine ingredients, we chose ethylbenzene and *m*-xylene as representative VOCs, because both compounds have good Carbopack™ B adsorptivity and µPID response. To get the mass of ethylbenzene and *m*-xylene detected in Fig. 4(a), the portable GC was calibrated with an injection mass ranging from 1.1 ng to 13.3 µg in Fig. 5. The peak areas in Fig. 5 show excellent linear response with $R^2 >$ 0.99 in the linear regression analysis (forced zero Y-intercept in the linear–linear scale).[43] Table 1 summarizes the concentrations from the portable 2-D GC device and GC-MS, and their difference was calculated as follows:

$$\text{Difference } (\%, \text{ against GC-MS})$$
$$= \frac{\text{conc. } (\text{2-D GC}) - \text{conc. } (\text{GC-MS})}{\text{conc. } (\text{GC-MS})} \times 100 \qquad (1)$$

Despite different total masses and materials used in Carbopack™ B (1.135 mg) and charcoal tubes (150 mg), the two data sets demonstrated a high level of agreement (OSHA standard within 25%),[44] supporting the validity of the portable 2-D GC device for air analysis. For workers' safety, we compared the
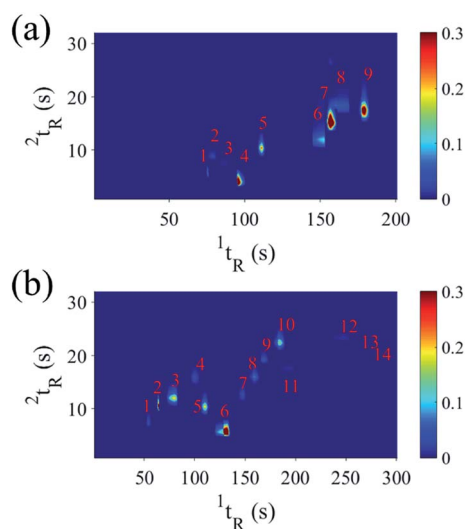

Fig. 4   2-D contour plot of (a) electrostatic semi-gloss enamel clear base V260-88 (paint 1) at booth 2 (sampling time: 5 min) and (b) level sealer C117 029 at booth 3 (sampling time: 10 min) generated with the portable 2-D GC device. See the list of VOCs in Table S3.†
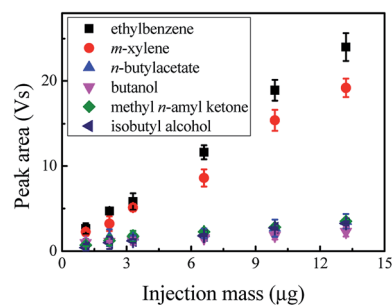

Fig. 5   Calibration of the portable 2-D GC device. The peak area of ^{1}D separation is plotted as a function of injection mass of ethylbenzene, *m*-xylene, *n*-butylacetate, *n*-butanol, methyl *n*-amyl ketone, and isobutyl alcohol on the linear–linear scale. Error bars were obtained with 3 measurements.

Table 1 Comparison of the concentration of ethylbenzene, and *m*-xylene from electrostatic semi-gloss enamel clear base V260-88 measured by the portable 2-D GC device and charcoal tube/GC-MS by OSHA ORG-07 method

	2-D GC (mg m^{-3})	Tube 1/GC-MS (mg m^{-3}) Tube 2/GC-MS (mg m^{-3})	Differences against GC-MS (%)
Ethylbenzene	14.6	14.1	3.5
		13.4	8.9
m-Xylene	51.1	64.5	−20.7
		61.1	−16.3

5 min sampling results with the published and recommended 15 min STELs listed in Table S1.† These values were lower than STELs from NIOSH (545 mg m^{-3} and 655 mg m^{-3} for ethylbenzene and *m*-xylene, respectively), and ACGIH (655 mg m^{-3} for *m*-xylene). However, due to the large number of spraying events occurring throughout the day, the average and short-term worker exposure may very well exceed health limits. Therefore, appropriate engineering and administrative controls and continued use of personal protective equipment (PPE) are warranted. This sampling technique was required in order to ensure detectable levels of the various compounds achieved using the OSHA ORG-07 method. Although working hazards and exposure limit comparisons are best determined using breathing zone samples throughout the entirety of a work shift, this type of comparison is not feasible using our portable system, as the tubing connections would be cumbersome and potentially unsafe for workers. However, the benefits associated with obtaining immediate task-based exposure estimates may eventually outweigh the need for 8 hour breathing zone samples.

3.2. Time-dependent on-site indoor air analysis using portable 2-D GC and validation with GC-MS (paint 2)

In this study, we used paint 2 as the model system to test and validate the capability of our portable 2-D GC in time dependent on-site analysis. To examine the indoor air more closely, we sampled air at the same place (booth 3) while the worker was spraying Level sealer C117 029 in the following sequence – the first spraying (at $t = 0$ min), drying (at $t = 20$ min), the second spraying (at $t = 50$ min), drying (at $t = 70$ min), and final spraying (at $t = 130$ min). Before starting the measurement and spraying, we confirmed that there was no interference at booth 3 by analyzing the indoor air three times. First, Fig. 4(b) shows the 2-D contour plot observed during the first 5 min spraying (sampling time: 10 min and ventilator on). Except polyester, butylated melamine formaldehyde polymer, and ethanol, which cannot be trapped, all six ingredients listed in Table S2† were successfully detected and well-separated, and eight more chemicals including three unknowns were additionally detected (note that toluene and xylene were used as a solvent). Although there were coeluted peaks (one from VOCs 7, 8, and 9 and the

other from VOCs 10 and 11) in ^{1}D, they were successfully separated in ^{2}D within 5 min. After 5 min of first spraying, the woodwork pieces dried for 45 min while the ventilator was off. During drying, we collected the indoor air again to observe the concentration changes over time, as shown in Fig. 6 at time 20 min. Similar to the first spraying, the worker did the second 5 min spraying (sampling time: 10 min and ventilator on), drying, and the third 4 min spraying (sampling time: 10 min and ventilator on) with the same woodwork pieces at booth 3. The concentrations are shown in Fig. 6 at time 50, 70, and 130 min, respectively. For comparison, two sets of GC-MS data from the charcoal tubes 1 and 2, and averaged value are also listed in Table S4.†

Overall, the concentrations between the first spraying and drying decreased by 10% and increased 10 times again between the first drying and second spraying. Because of the reduced time on the third spraying, the concentration decreased compared to the first and second spraying, showing that the indoor air quality is highly dependent upon the spray time. The concentrations in Table S4† and Fig. 6 are compared with STELs (from NIOSH and ACGIH) or 3X REL and TLV (If STELs are not provided) in Table S1.†[45] The exposure to all VOCs for each measurement was below STELs from NIOSH and ACGIH. However, even though it is a short period of exposure for our sampling purposes, and our sampling was adjacent to the work pieces and not in the worker's breathing zone, the worker performs these tasks multiple times throughout the workday and engineering and administrative controls supplemented by PPE use are warranted. In addition, we recommend that the ventilator or fans should continue to be operated following spray cessation.
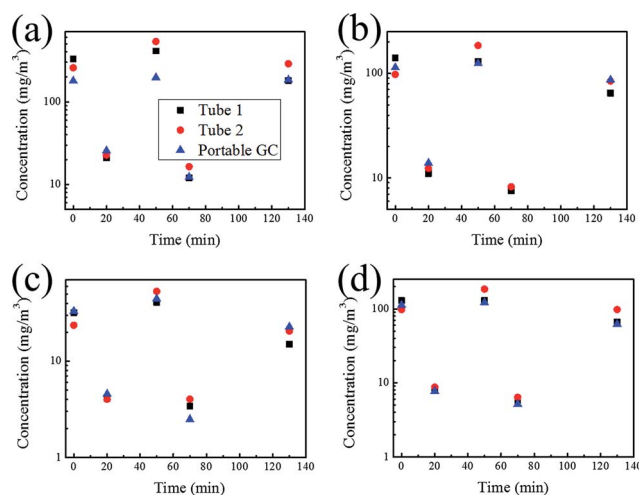

Fig. 6 Comparison of the concentrations of (a) *n*-butyl acetate, (b) *n*-butanol, (c) methyl *n*-amyl ketone, and (d) isobutanol obtained with the portable 2-D GC device (blue triangles) and GC-MS (black rectangles for charcoal tube 1, red circles for charcoal tube 2) during the first spraying, the first drying, the second spraying, the second drying and the third spraying of level sealer C117 029, at 0, 20, 50, 70, and 130 min, respectively. The corresponding detailed comparison can also be found in Table S4.†

The results from the portable 2-D GC are further compared with the GC-MS data with four chemicals, *n*-butyl acetate, methyl *n*-amyl ketone, *n*-butanol and isobutanol as representative VOCs in Fig. 6. Here, we used two data sets from two charcoal tubes (sampling time: 10 min) to validate the portable 2-D GC. Even though there are some variations between tube 1 and tube 2, the percent differences (%) (calculated against GC-MS data) between 2-D GC device and GC-MS show good agreement (OSHA standard within 25% (ref. 44)). However, the concentrations of *n*-butyl acetate at the first (at $t = 0$ min) and second spraying ($t = 50$ min) by the 2-D GC device were far below GC-MS values (29.2 and 53.6%), probably due to the saturation effect resulting from the small total mass of adsorbent and long sampling time (10 min) used in the µPI of our portable 2-D GC device.

3.3. Real-time on-site monitoring of indoor air using portable 2-D GC (paints 3, 4, and 5)

After the validation of the quantitative analysis capability of our portable 2-D GC, in Fig. 7 we employed it in the real-time monitoring of the indoor air while paints 3, 4, and 5 were being used. We tracked the concentration changes of indoor air before and after spraying of Magnamax C148 14 Satin-35 on the woodwork pieces inside and outside the spraying booth to calculate the VOCs concentrations to which a worker or passerby may potentially be exposed. Before spraying, it was confirmed that there were no detectable peaks in the chromatogram obtained by the 2-D GC in booth 3. Right after the 2 min of spraying (regime 1 in Fig. 7(b)), nine peaks were detected, and thereafter the chromatogram was recorded every 15 min as shown in Fig. 7(a)[46] (Regime 2 in Fig. 7(b)). We continued to sample and analyze the indoor air after the woodwork pieces were taken out of the booth at $t = 30$ min (Regime 3 in Fig. 7(b)). The concentration of all analytes for each measurement were below the STELs from NIOSH and

ACGIH (Table S1†). As shown in Fig. 7(b), the concentrations rapidly dropped after spraying, but still some chemicals continued to be detected due to the off-gassing of the painted wood as it dried in the booth. As soon as the woodwork pieces were moved out, the concentrations dropped again and remained approximately stable for an hour. That persistence is likely due to poor circulation of the inside air (ventilator off), and/or paint coating of the walls and structural support holders. After $t = 60$ min, the concentrations of all VOCs were still below the STELs from NIOSH and ACGIH. We also tested the indoor air outside the booth at a 1 m distance marked as "*" in Fig. 3(a) after $t = 90$ min from spraying. The concentration was 1% of the amount detected at $t = 0$ min.

While the worker wears a respirator during a spraying process, people outside the booths (*e.g.*, in the adjacent offices) may have exposure to VOCs. In order to further demonstrate the capability of our portable 2-D GC, we additionally tested the indoor air outside booths at a 2 m distance from booth 3 and in front of a roll-down door marked as "**" in Fig. 3(a) to estimate VOC concentrations in the Shop as shown in Fig. 8(a).[46] During a 3 h measurement, the worker did one spraying operation at booth 2 and one at booth 3. While the first spraying was in progress at booth 2, the concentration of isobutyl alcohol, *n*-butyl acetate, and one unknown peak slightly increased (regime 1 in Fig. 8(b)), although still below the occupational exposure limits. Once the second spraying started at booth 3 (regime 2 in Fig. 8(b)), VOCs were detected after 10 min in front of the roll-down door. As shown in Fig. 8(b), the concentration of *m*-xylene and ethylbenzene increased significantly (10 and 20 times, respectively). After the drying of woodwork pieces ended, the concentrations of the two analytes were still 2% of the peak concentration detected at $t = 60$ min. As shown in Fig. 8(b), VOCs were detected throughout the shop for an extended period of time
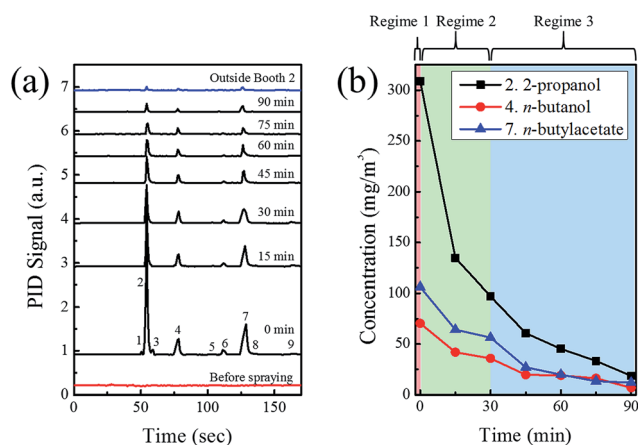

Fig. 7 (a) Time–dependent 1D chromatograms of before, during, and after spraying Magnamax C148 14 Satin–35 (paint 3) at booth 2 (red*) in Fig. 3. (b) Peak areas in (a) plotted *versus* time. Regime 1, 2, and 3 show spraying (2 min), drying with (30 min), and without wood work piece (60 min) sprayed at booth 2. The peak assignment can be found in Table S3.†
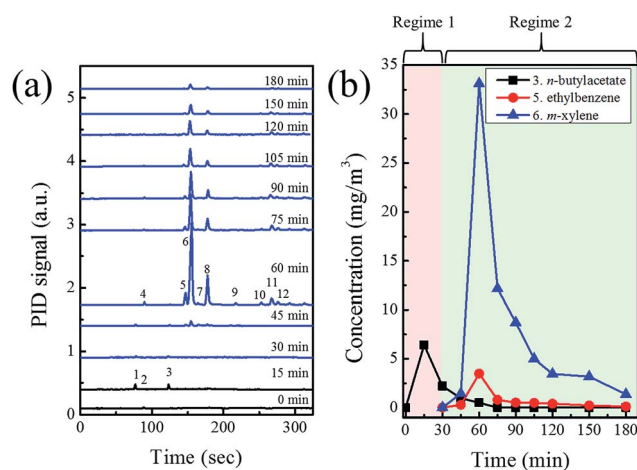

Fig. 8 (a) Time–dependent ^{1}D chromatograms recorded in front of a roll–down door (red**) in Fig. 3. (b) Peak areas in (a) plotted *versus* time. Regime 1 and 2 show Magavar 1M.4304 Satin (paint 4) spraying (booth 2), and Kem Kromik Universal Metal Primer B50NZ6 (paint 5) with (booth 3), respectively. The peak assignment can be found in Table S3.†

(3 h), though the concentrations were still below the occupational exposure limits.

4. Conclusions

We have demonstrated the field analysis of occupational VOCs in real time with a 1 × 4-channel 2-D GC device at the Spray and Finishing Shop, and validated our measurements against traditional assessment methods using OSHA Method ORG-07 for occupational VOC monitoring. Our results show that our portable 2-D GC device can analyze the indoor air quantitatively in 5 to 15 min during work processes. In addition, quantitative comparisons with results obtained with OSHA Method ORG-07 validates the capability of our portable 2-D GC device measurements. Through the rapid on-site detection and analysis of multiple VOCs, managers and workers may better characterize potential VOC exposures and use this information to reduce the likelihood of over-exposures and consequent adverse health outcomes related to chronic and acute chemical exposures in the workplace.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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46 In practice, quantitative 2-D GC anaylsis was performed on paint 3, 4, and 5 by using the portable 2-D GC device at the Paint Shop. However, in Fig. 7 and 8, we wanted to see the concentration change over time by showing the first dimensional chromatograms because the 2-D contour plots show the VOCs changes less distinctly.