Short communication

Unsuitability of using the DNPH-coated solid sorbent cartridge for determination of airborne unsaturated carbonyls

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ABSTRACT

Measurements of aldehydes and ketones are typically conducted by derivatization using sorbent cartridges coated with 2,4-dinitrophenylhydrazine (DNPH). The collected samples are eluted with acetonitrile and analyzed by high-pressure liquid chromatography coupled with an ultra-violet detector (HPLC/UV). This paper intends to examine artifacts about its suitability in identification of unsaturated carbonyls. Kinetic tests for acrolein, crotonaldehyde, methacrolein and methyl vinyl ketone (MVK) showed formations of carbonyl-DNP-hydrazone during sampling, which could further react with DNPH, resulting in undesired UV absorption products [e.g., carbonyl-DNP-hydrazone-DNPH (dimer) and 2 (carbonyl-DNP-hydrazone)-DNPH (trimer)]. The dimerization and trimerization occurred for acrolein and MVK whereas only dimerization for crotonaldehyde and methacrolein. The polymerization products undoubtedly affect the integrity of the chromatogram, leading to misidentification and inaccurate quantification. Whether precautions taken during sampling and/or sample treatment could avoid or minimize this artifact has not been thoughtfully investigated. More often, such artifacts are usually overlooked by scientists when the data are reported.

1. Introduction

The standard method for determination of airborne carbonyls (aldehydes and ketones) is to collect air onto 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbent cartridge, followed by solvent elution of the cartridge and liquid injection of the eluent into a high-pressure liquid chromatography (HPLC) system for analysis (U.S. EPA, 1999). Many drawbacks have been identified in this analytical method. Airborne oxidants [e.g., nitrogen oxide (NO), nitrogen dioxide (NO_2), and ozone (O_3)] can react with DNPH to form side products (artifacts) that can interfere with the detection of carbonyls (Sirju and Shepson, 1995; Grosjean et al., 1996; van Leeuwen et al., 2004). The artifacts have been observed to affect the determination of unsaturated carbonyls, but this effect has not been thoroughly documented. A few studies use the word "decomposition" to describe degradation of the unsaturated carbonyl-DNP-hydrazone, or so-called DNPH-carbonyl derivative,

observed in solution and cartridge samples (e.g., Huynh and Vu-Duc, 2002). However, this description is not fully informative because the double-bond-containing carbonyls eventually react further with DNPH to form larger molecules that can cause negative or positive artifact in their quantifications (Schulte-Ladbeck et al., 2003).

Acrolein (C_3), crotonaldehyde (C_4), methacrolein (C_4) and methyl vinyl ketone (MVK) (C_4) are well-known airborne unsaturated carbonyls. Methacrolein and MVK are identified as oxidation products of isoprene, and their ratio acts as an indicator of OH-oxidation as the primary isoprene degradation process occurring during the daytime (Trapp et al., 2001). More recent research focuses on quantification of these unsaturated compounds using the DNPH/HPLC method (e.g., Chen et al., 2007; Xie et al., 2008; Zhang et al., 2010). However, the methodological artifacts are not considered. The possible issues in the determination of unsaturated carbonyls using the DNPH/HPLC method are discussed in this paper.

2. Methodology

Carbonyls including acrolein, crotonaldehyde, methacrolein and MVK (Aldrich, Milwaukee, WI) and their certified carbonyl-DNP-hydrazones (Supelco, Bellefonte, PA) were diluted with acetone-

free acetonitrile (HPLC/GC grade, Aldrich). For solid sorbent-phase kinetic tests, each sample was prepared by spiking 4 μg of an unsaturated carbonyl onto a Sep-Pak DNPH-silica cartridge (55–105 μm particle size, 125 Å pore size, Waters Corporation, Milford, MA). The carbonyl consumed 0.05–0.06% of the total amount of DNPH (1 mg per cartridge). All spiked cartridges were stored at 4 ± 1 °C, standard for storage of air-collected cartridges. Each cartridge was eluted with 2.0 mL of acetonitrile to a volumetric flask and immediately analyzed by injecting 20 μL of the eluent to an PE Series 2000 HPLC system (PerkinElmer, Norwalk, CT) equipped with an ultra-violet (UV) detector. The kinetic time was counted from time of storage to time of injection into the HPLC system. For liquid-phase kinetic tests, the acidic DNPH solution was obtained by elution of 2 mL of acetonitrile from a blank DNPH-coated cartridge. The kinetic time was counted from the time of acrolein being added into the acidic DNPH solution to time of injection onto the HPLC system. The liquid-phase kinetic solutions were stored at room temperature (~22 °C). A 4.6 × 250 mm Spheri-5 ODS 5 μm C-18 reversed-phase column (PerkinElmer) was used for separation. The mobile phase consisted of two solvent mixtures: mixture A, 6:3:1 (v/v) of water/acetonitrile/tetrahydro-furan; mixture B, 4:6 (v/v) of water/acetonitrile. The gradient program was 80% A/20% B for 1 min, followed by a linear gradient to 50% A/50%B for 8 min, and then 100% B for the next 10 min. The flow rate was 2.0 mL min^{-1} throughout the run. The absorbance at 360 nm was used for identification of the carbonyls. The chromatographic peaks were identified by an LC/mass spectrometry (MS) system (Series 6100, Agilent Technologies, Santa Clara, CA) for electrospray ionization (ESI) analysis.

3. Results and discussion

Acrolein–DNP-hydrazone ([M + H]$^+$ = 237) is the product from the reaction between acrolein and DNPH. However, no acrolein–DNP-hydrazone was seen in the DNPH-coated cartridge, which was spiked with acrolein and kept at 4 °C for 6 h [Fig. 1b(i)]. Two isomer peaks of acrolein–DNP-hydrazone-DNPH ([M + H]$^+$ = 435), named dimers, were formed in significant quantities. Continuous polymerization occurred in the cartridges over the next 42 h. Isomer peaks of 2(acrolein–DNP-hydrazone)-DNPH ([M + H]$^+$ = 671), named trimers, were found while the abundance of the dimers decreased [Fig. 1b(ii)]. These results are consistent with and supported by Schulte-Ladbeck et al. (2003), where the same dimerization and trimerization products were detected in the acidic DNPH solutions for the impinger and eluents from the DNPH-coated cartridges. Schulte-Ladbeck et al. (2003) found the chemical structures of these products were confirmed by the MS and nuclear magnetic resonance (NMR) spectroscopy. The dimerization and trimerization can neither be terminated nor fully regulated in solutions and cartridges without changing the original concentrations, though Wang et al. (2009) reported that the acidity and the ratio of DNPH to carbonyl influence the amounts of dimers or trimers formed. It is reasonably assumed that the trimers, whose abundances increased as a function time, are more stable products than dimers, whose abundances decreased. The reaction reached equilibrium in the cartridges at 4 °C after seven storage days, when no further significant changes in the peak abundances were found (Fig. 2). Unfortunately, the coexistence of the dimers and trimers in the kinetic samples indicates no single end-product can be formed for quantification. No significant changes in the formation rates of dimers and trimers were observed after adding an additional 4 mg of acidified DNPH (five times that found in a DNPH-coated cartridge) into the eluents from the kinetic samples. No other polymers or by-products were detected.

Kinetic study was also done by spiking certified acrolein–DNP-hydrazone onto the DNPH-coated cartridges. The formation of dimers and trimers was also seen in the chromatogram, and their rates were compared with those in which an equal molar amount of acrolein was added onto the cartridge (Fig. 2). The dimers and trimers were also formed in the acrolein–DNP-hydrazone spiked cartridges, confirming the dimerization and trimerization are not initialized from an intermediate product in the nucleophilic addition reaction during acrolein reacted with DNPH. However, the detailed mechanism for dimer and trimer formation is still uncertain, so the kinetics cannot be well explained. The reaction kinetics in the liquid-phase were demonstrated at room temperature by injecting an equal amount of acrolein into the acidic DNPH solution, resulting in comparatively slower dimerization and trimerization rates were observed (Fig. 2). These results indicate the silica-gel solid sorbent plays an important role in the polymerizations.

Crotonaldehyde forms crotonaldehyde–DNP-hydrazone ([M + H]$^+$ = 251), which also undergoes dimerization in the DNPH-coated cartridges at 4 °C (Fig. 1c). After 14 days in storage, only trace amounts (2%) of crotonaldehyde–DNP-hydrazone remained and crotonaldehyde–DNP-hydrazone-DNPH ([M + H]$^+$ = 449, identified as its corresponding dimer) was dominant. However, no other chromatographic peak (e.g., its corresponding trimer) was found during the kinetic test period. These results are consistent with Schulte-Ladbeck et al. (2003). The chemical configuration of the dimer may inhibit further addition to other compounds.

In the solid-phase kinetic samples stored at 4 °C, methacrolein reacts with DNPH to form methacrolein–DNP-hydrazone ([M + H]$^+$ = 251), which further polymerizes to form its dimer methacrolein–DNP-hydrazone-DNPH ([M + H]$^+$ = 449) (Fig. 1d). The kinetic data shows the dimerization rate for methacrolein was the slowest among the unsaturated carbonyls, possibly because of its chemical configuration, contradicting the findings of Possanzini and DiPalo (1995), who suggest it is not possible to dimerize methacrolein–DNP-hydrazone with DNPH as it lacks a hydrogen atom in its double bond on the carbon adjunct to the carbonyl group. Dimerization may not have been observed in Possanzini and DiPalo (1995) as the reaction time was insufficient.

The spiked MVK reacted with DNPH in the kinetic test cartridges at 4 °C. Three isomers of MVK–DNP-hydrazone ([M + H]$^+$ = 251) were initially formed (Grosjean et al., 1996), labeled "m$_1$", "m$_2$" and "m$_3$", in Fig. 1e(i). The isomers have very similar chromatographic behaviors and co-eluted with other C$_4$ carbonyls (e.g., crotonaldehyde–DNP-hydrazone). The isomer ratios of MVK–DNP-hydrazone varied as a function of time. The peak "m$_3$" was initially the largest, but its abundance continuously decreased [Fig. 1e(ii)]. Meanwhile, corresponding dimers [MVK–DNP-hydrazone-DNPH, ([M + H]$^+$ = 449)] and trimers [2(MVK–DNP-hydrazone)-DNPH, ([M + H]$^+$ = 685)] were detected. The intensities of the dimers labeled "d$_1$" and "d$_2$" significantly increased. The kinetic cartridges stored for three days were dominated by the isomer peaks of trimers "t$_1$" and "t$_2$", with a negligible amount of MVK–DNP-hydrazones found [Fig. 1e(iii)].

Co-elution of chromatographic peaks suppresses determination of the unsaturated carbonyls using the DNPH/HPLC method. The 2 (acrolein–DNP-hydrazone)-DNPH (the trimer of acrolein derivative) and glutaraldehyde–DNP-hydrazone peaks have the same retention time when typical C$_{18}$ reversed-phase columns are used for separation (Huynh and Vu-Duc, 2002). Most of the C$_4$ carbonyls, including saturated and unsaturated, and their dimers and trimers have similar chromatographic properties. The problem of peaks overlapping is especially important in these cases. For instance, methacrolein–DNP-hydrazone-DNPH co-elutes with iso-/n-butyr-aldehyde–DNP-hydrazone (saturated C$_4$ carbonyls) and croto-naldehyde–DNP-hydrazone-DNPH (the dimer of crotonaldehyde), and their concentrations therefore would be either over- or
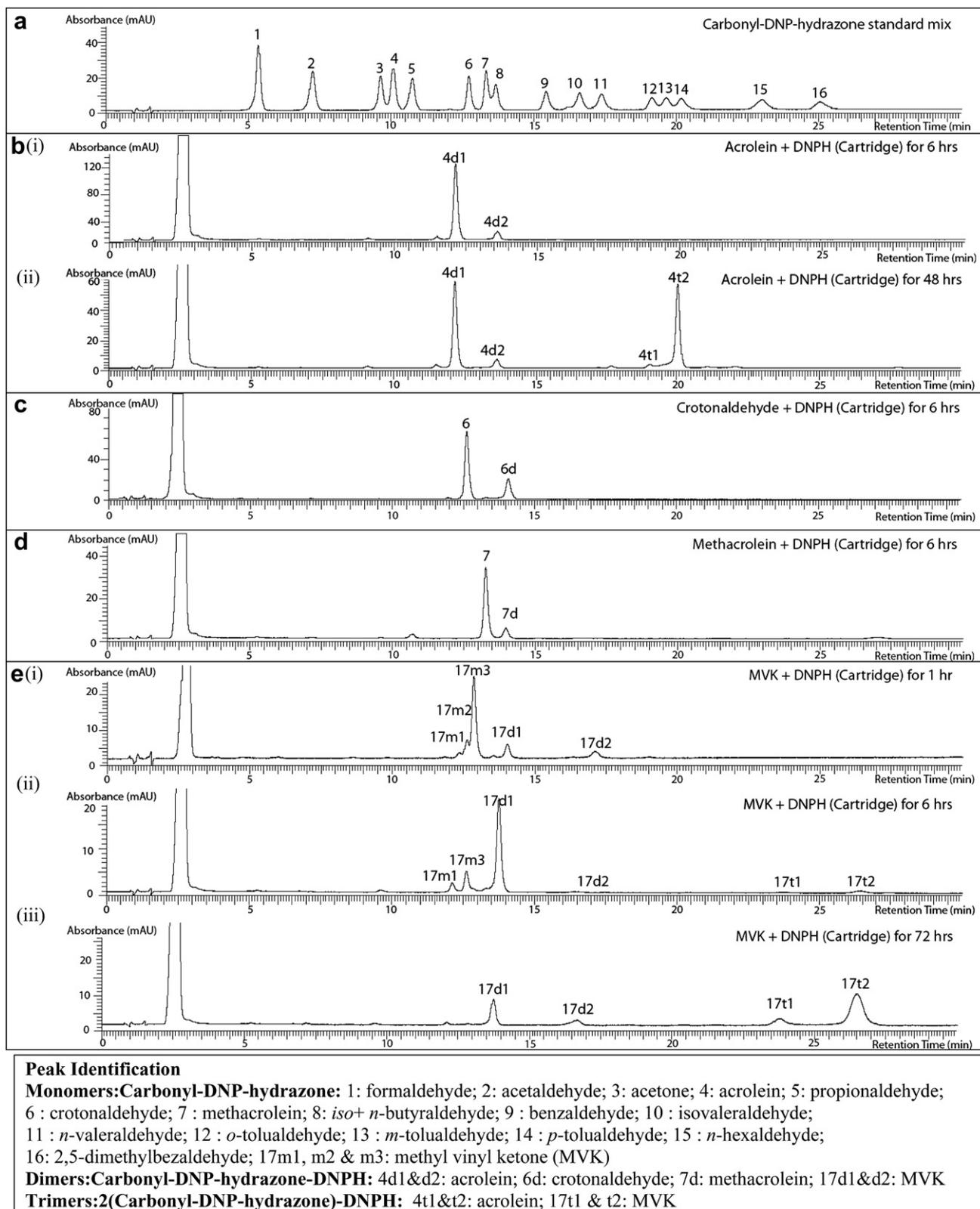
Fig. 1. Chromatograms of carbonyls and DNPH reaction products: a) certified carbonyl-DNP-hydrazones; b) acrolein in the DNPH cartridge for (i) 6 h and (ii) 48 h; c) crotonaldehyde in the DNPH cartridge for 6 h; d) methacrolein in the DNPH cartridge for 6 h; e) methyl vinyl ketone (MVK) in the DNPH cartridge for (i) 1 h, (ii) 6 h and (iii) 72 h.

underestimated if all of corresponding peaks were used in the calculations.

The dimers and trimers of unsaturated carbonyls usually have a different absorption maximum than their corresponding carbonyl-DNP-hydrazone. Acrolein dimers and trimers have UV absorption maxima of 351 nm and 349 nm, respectively, compared with 360 nm for acrolein−DNP-hydrazone. The variations in the absorption maxima mean that the monomers, dimers and trimers
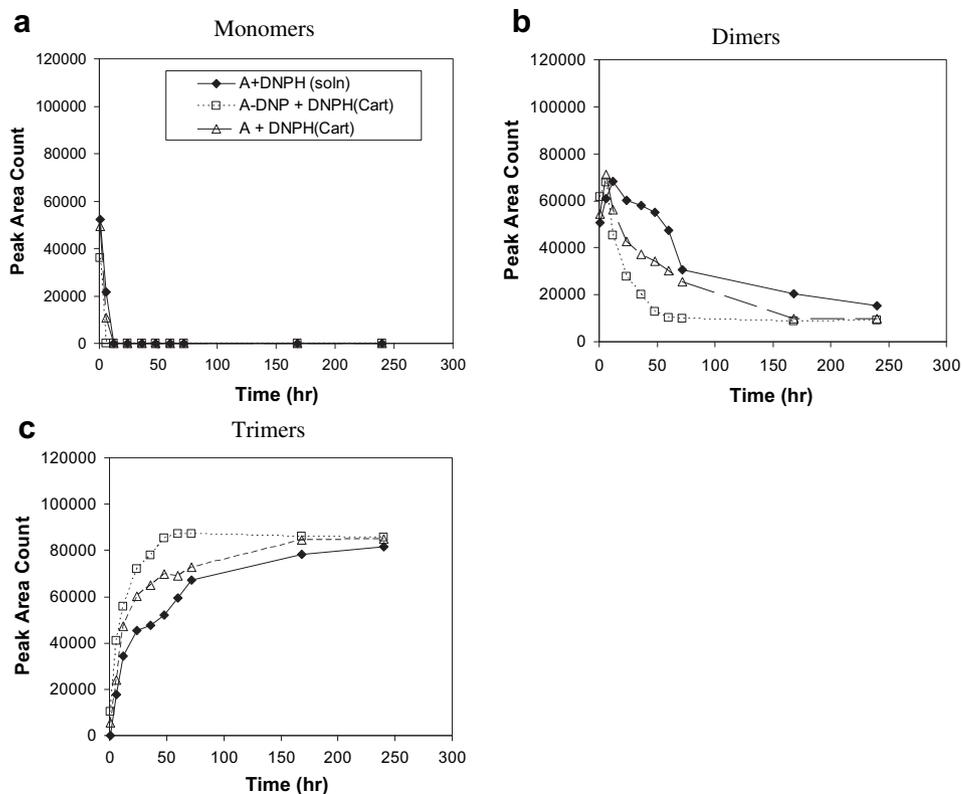
Fig. 2. Reaction kinetics between acrolein and DNPH in the cartridges [A + DNPH(cart)], certified acrolein−DNP-hydrazone with DNPH in the cartridge [A − DNP + DNPH (cart)], and acrolein with DNPH in acidic solution [A + DNPH (soln)], by showing the changing of peak areas of a) monomer (acrolein−DNP-hydrazone), b) dimers (acrolein−DNP-hydrazone-DNPH), and c) trimers [2(acrolein−DNP-hydrazone)-DNPH].

have different response factors for single-wavelength detection (e.g., 360 nm for the general carbonyl monomers). Furthermore, the reaction rates and ratios of polymerization products are uncertain in the air-collected cartridges subject to sample storage durations and other unknown parameters.

No air was passed though the kinetic test cartridges. Chemicals (e.g., oxidants) or meteorological variations (e.g., relative humidity and ambient temperature during sampling) may also affect the dimerization/trimerization in the silica-gel sorbent cartridges that further increases uncertainties in the determination of unsaturated carbonyls.

4. Conclusion

The products formed in the reaction between unsaturated carbonyls and DNPH in the cartridge have been identified. Sequential conversion of carbonyl-DNP-hydrazone (monomer), followed by carbonyl-DNP-hydrazone-DNPH (dimer), and finally 2 (carbonyl-DNP-hydrazone)-DNPH (trimer) is demonstrated in the kinetic study. The dimerization and trimerization products were found for acrolein and MVK whereas only dimerization products were seen for crotonaldehyde and methacrolein. Those products for the C_3 and C_4 unsaturated carbonyls typically have similar chromatographic properties, resulting in peak overlapping were found. The polymerization not only creates uncertainties in their own quantification, but also affects determination of other carbonyls in the samples. The co-elution of chromatographic peaks probably causes over- or underestimation of concentrations. In addition, the absorption maxima of the dimers and trimers are generally different from their corresponding monomers, resulting in variations of response factors under single-wavelength detection, while

detection at multiple wavelengths or using MS is affected by varying formation rates of the dimers and the trimers on cartridges collected from different environments. Based on the results, we thus conclude that the DNPH method is unsuitable for the determination of unsaturated carbonyls. The selection of alternative derivatizing agents or the development of other analytical methods to acquire more accurate data for the unsaturated carbonyls are also recommended (e.g., Ho and Yu, 2002, 2004).

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