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Authors

Hunsaker, Haylee C

Robertson, Nicholas E

Poulin, Brett A

et al.

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Article

Validation of a Spectroscopic Quantification Method for Total Carbonyls and Small Organic Acids in Aerosols Relevant to Indoor and Outdoor Environments

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Haylee C. Hunsaker, Nicholas E. Robertson, Brett A. Poulin, and Tran B. Nguyen*

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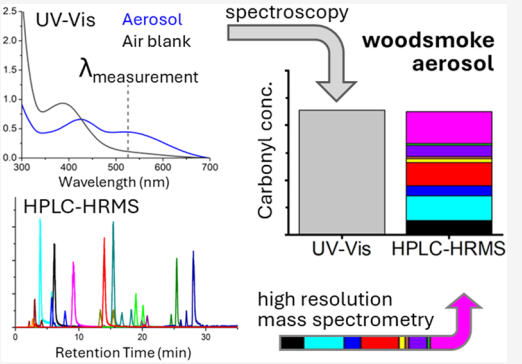
ABSTRACT: Carbonyls and small organic acids are ubiquitous in indoor and outdoor atmospheres; carbonyls also have significant health implications. In this study, we validate a rapid, simple, and cost-effective method for carbonyl and small organic acids quantification by ultraviolet−visible (UV−vis) spectroscopy detection after derivatizing the C═O moiety with 2,4-dinitrophenylhydrazine (DNPH). The spectroscopic method is benchmarked against accurate mass speciation by using high-performance liquid chromatography coupled to high-resolution mass spectrometry (HPLC-HRMS). Complex natural mixtures relevant to indoor and outdoor air quality were examined: electronic (e-) cigarette aerosols from nicotine and cannabinoid sources, woodsmoke aerosols, and secondary organic aerosols from limonene ozonolysis. The spectroscopy method measured the UV−vis absorption of quinoidal ions, formed from DNPH hydrazones in alkaline solution, at 530 nm (A_{530}). A significant correlation was established between the two methods across a range of aerosol mass and chemical compositions tested, resulting in a recommended calibration factor (CF) of ~5.16−5.34 × 10^{-5} (M cm), where $C_{carbonyls}$ (M) = A_{530} × CF (M cm) × path length^{-1} (cm^{-1}). The calibration factors, determined via two approaches—(1) by measuring the effective molar absorptivity of quinoidal ions produced from eight carbonyl-DNPH and acid-DNPH calibration standards, and (2) empirically from the correlation data without assumptions, were in good agreement with one another. The simple UV−vis spectroscopic method was a robust total carbonyl quantification method for multiple aerosol systems of environmental interest, which has utility in functional group apportionment, teaching laboratories, student projects, and preliminary screenings of carbonyl-related toxicity prior to more-detailed analyses.



KEYWORDS: *aldehyde, ketone, carbonyls, UV−vis spectroscopy, high resolution mass spectrometry, functional group apportionment, indoor air quality*

1. INTRODUCTION

Airborne carbonyl compounds, aldehydes (RCHO) and ketones (RC(O)R′), are a significant class of volatile and semivolatile organic compounds (VOCs and SVOCs) with widespread environmental and health implications.[1−5] Inhalation of certain carbonyls like formaldehyde, acetaldehyde, and acrolein are known to produce harmful toxicological effects, including inflammation, carcinogenicity, and respiratory health risks.[6−9] Carbonyls are ubiquitous in the indoor and outdoor atmosphere: they can be emitted directly (e.g., aerosols emitted from fires,[10,11] gases volatilized from indoor surfaces[12,13]) or formed secondarily through the oxidation of hydrocarbons.[4,14−16] Carbonyls are also emitted during the heated aerosolization process in electronic (e-) cigarettes, or vaping, devices—mechanistically via the heat-induced dehydration or radical-initiated oxidation of solvents,flavoring compounds, and other additives.[17−21] Once emitted or formed, further oxidation of carbonyls in the atmosphere can propagate radicals and produce a complex mixture of products, which significantly impact air quality.[22−25]

Accurate quantification of carbonyls is crucial for understanding indoor and outdoor air composition as well as the associated health risks. Chemical derivatization of the C═O group on the carbonyl with 2,4-dinitrophenylhydrazine (DNPH) to form an imine has long been used for this purpose (Scheme 1).[26] Generally, a DNPH-impregnated silica cartridge[27] or impingers containing acidic ethanolic DNPH solutions[28] are used to collect aerosols.[29] Small organic acids

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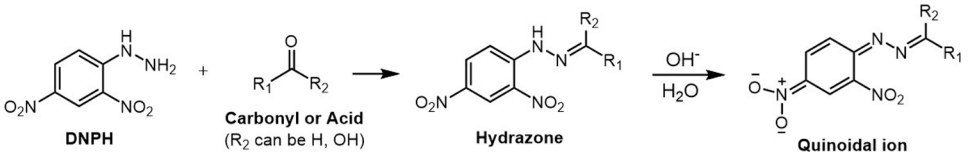
Scheme 1. Reaction of Carbonyls or Small Organic Acids with 2,4-Dinitrophenylhydrazine (DNPH) to Form a Hydrazone[a]



[a]The hydrazone can be converted to a wine-colored quinoidal ion with hydroxide ion.

(e.g., formic acid, acetic acid) have also been demonstrated to quantitatively react with DNPH in a similar manner.[17,30] These small organic acids are also abundant in nature and represent an important part of atmospheric composition.[31−33] For the purpose of this paper, we lump the small organic acids and carbonyls together (hereinafter they will be referred to collectively as "carbonyls" for brevity), although we acknowledge the terminology is inexact.

The resultant DNPH-carbonyl hydrazones are measured primarily via hyphenated chromatography techniques, including liquid chromatography−mass spectrometry (LC-MS, with many variations including tandem MS), LC with ultraviolet detection (LC-UV), or gas chromatography with mass spectrometry detection (GC-MS).[17,34−43] Among these analytical techniques, high-performance liquid chromatography coupled to high-resolution mass spectrometry (HPLC-HRMS) can be considered a gold standard due to its ability to combine isomeric separation using chromatographic retention times with exact mass determinations of individual hydrazone molecular formulas at a high level of mass accuracy (>30,000 $m/\Delta m$).[17,38,44,45] This level of speciated detail for carbonyls is especially useful for toxicological assessments, as different carbonyls exhibit highly variable levels of toxicity. However, there are also drawbacks to hyphenated mass spectrometry analyses. These instrument systems can be costly to purchase, operate, and maintain, as well as require specialized knowledge and training for operation and data analysis.[46−48] Furthermore, they require regular calibrations to maintain quantification precision; the purchase of analytical grade standards and the performance of regular calibrations can be costly and time-consuming. Chromatography runs can also be lengthy, which limits the higher throughput analysis.

Alternatively, the DNPH hydrazone can be converted to a chromaphoric quinoidal ion (Scheme 1) for spectroscopic ultraviolet−visible (UV−vis) analysis in alkaline conditions.[49−52] The spectroscopic method is fast, simple, robust, and does not suffer from calibration instability; however, the spectroscopic approach forfeits chemical specificity. Thus, this method has been generally used with single carbonyl compounds for calibration purposes. Aimanant and Ziemann (2013)[53] applied the spectroscopic method to determine the carbonyl content of an environmental complex mixture: α-pinene ozonolysis secondary organic aerosols (SOA). This demonstrates the potential usefulness of this method for functional group apportionment. However, the calibration factor (CF) in that study[53] was not yet validated by molecular techniques and it is not clear if the same calibration factor is valid for other carbonyl-containing complex mixtures. This work develops a single effective absorption coefficient to quantify carbonyls in environmental mixtures with the UV−vis spectroscopic technique and validates the spectroscopic technique using accurate mass HPLC-HRMS for a diverse range of carbonyls and aerosol complex mixtures, including e-cigarette aerosols, combustion aerosols, and SOA. We demonstrate the ability of the spectroscopic method to be broadly applied.

2. EXPERIMENTAL SECTION

Figure 1A shows the experimental setup for the aerosol collection, which uses an acidic ethanolic DNPH solution

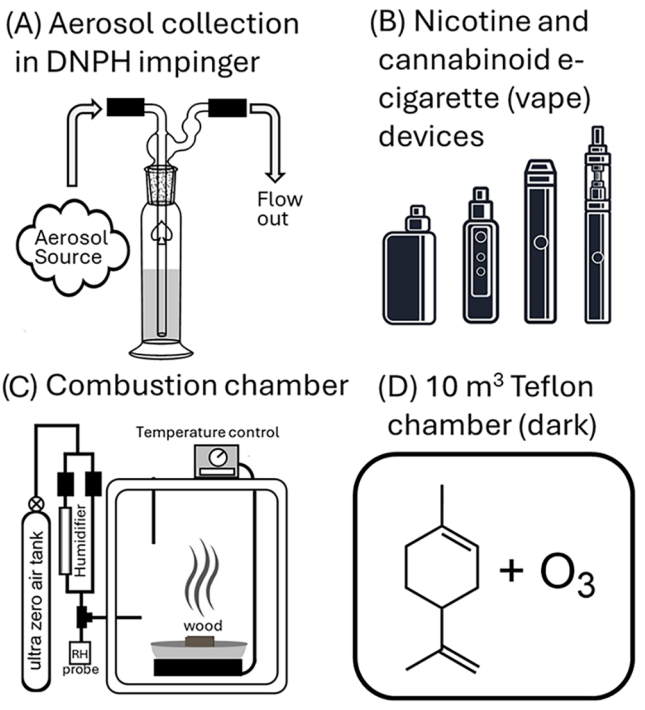


Figure 1. Schematic of (A) acidic DNPH impinger sampling setup for aerosols and the three aerosol source types that were tested for carbonyls in this work: (B) vape aerosols from nicotine and cannabinoid e-cigarettes using various e-liquids and distillates; (C) woodsmoke aerosols produced from a smoldering combustion chamber; and (D) secondary organic aerosols produced from limonene ozonolysis in a Teflon atmospheric chamber.

impinger that has been widely employed for the derivatization of carbonyls and acids to hydrazones,[29,54,55] and for the various aerosol source test systems (Figure 1B−D). Although acidic DNPH impingers are efficient at capturing carbonyls,[56] the sampling and derivatization efficiency is immaterial in this work as we compare quantifications from the same impinger solution between HPLC-HRMS and UV−vis. It is recommended that future applications of this technique validate sampling and derivatization efficiencies for the specific tests systems under study. Aerosols selected for the development of the spectroscopic method for total airborne carbonyls comprise the following systems: "vape" aerosols generated from commercial prefilled and flavored disposable e-cigarettes,

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a fourth-generation refillable e-cigarette using lab-made e-liquid, and a purified cannabinoid distillate in a refillable cannabis vape device (Section 2.1); woodsmoke aerosols generated from a smoldering combustion chamber (Section 2.2); and SOA generated from dry limonene ozonolysis in an atmospheric chamber (Section 2.3). The aerosol systems studied here are relevant for indoor and/or outdoor air quality. Vaping is increasingly popular and is a concern for direct inhalation and secondhand exposure.[57−60] Woodsmoke aerosols released from residential wood burning and forest fires remain important drivers of indoor and outdoor health and air quality worldwide.[61−64] Limonene ozonolysis is a reaction that is relevant to the production of SOA in both outdoor and indoor air.[65−67] Both the gas and particulate phases of the whole aerosol were sampled and analyzed in this work for vape and woodsmoke aerosols, and only the particulate phase was sampled for the SOA. It is assumed that collection onto a particle filter sampled mostly the particulate-phase species. The aerosol sources were chosen to produce carbonyls of diverse size (C_1−C_{10}) and chemical functionality.[68,69]

2.1. E-cigarette Aerosol Generation. A fourth-generation Vaporesso XROS 2 pod e-cigarette (Shenzhen Smoore Technology Limited, Shenzhen, China) with a 1.2 Ω coil with a refillable pod cartridge was used with lab-made nicotine salt e-liquid solutions to produce vape aerosols. The entire firsthand aerosol emissions from vape devices were sampled through the DNPH impinger by connecting the mouthpiece of the vape devices (Figure 1B) to the inflow of the impinger (Figure 1A). Nicotine benzoate salt e-liquid was prepared as previously described.[34] Nicotine benzoate e-liquid was prepared at 2% (w/w) by dissolving nicotine and benzoic acid (BA) (>99.5%, Sigma-Aldrich) at a 1:1 molar ratio in 30% propylene glycol (PG) (99%, Sigma-Aldrich) and 70% vegetable glycerin (VG) (>99.5%, Sigma-Aldrich) to mimic the conditions of popular refillable e-liquid formulas.[70−73] All lab-prepared e-liquid solutions were stored in the dark at 2−8 °C prior to use.

For cannabinoid vape experiments, both the purified distillate (>80% cannabinoid) and the e-liquid (purified cannabinoid dissolved in PG/VG) were tested due to the popularity of both modalities of use.[74] A CCELL Palm Pro battery device (CCELL, Shenzhen, China) with a CCELL Kera cartridge was used for all experiments involved in vaping cannabinoid-based distillates, while the Vaporesso XROS (described above) was used for the e-liquid. The CCELL Kera cartridges were chosen due to their reusability and refillable properties. All CCELL devices were activated with an applied voltage of 3.6 V. Δ8-Tetrahydrocannabinol (THC) *O*-acetate distillate (d_8-THCO, Gilded Extracts, San Antonio, TX) is a popular, widely available, and federally legal cannabinoid distillate. The d_8-THCO was purchased and used without modification. A 50 mg/mL CBD e-liquid in PG/VG was prepared as previously described by our group by dissolving CBD isolate (>99%, GVB Biopharma, Las Vegas, NV) in 70% PG and 30% VG (purities 99%, and >99.5% from Sigma-Aldrich), which is comparable to commercially available CBD e-liquids.[35] CBD e-liquid was vaped using a Vaporesso pod with a 0.8 Ω coil.

Currently, flavored disposable vape devices with nonrefillable cartridges are the most popular form of electronic nicotine delivery devices on the market.[75] Three commercially available disposable nicotine e-cigarette devices from three different brands were chosen based on their popularity and availability in local vape shops:[76] Esco Bars Tropical Rainbow Blast (advertised 5% nicotine, Shenzhen Innokin Technology Co., Shenzhen, China), Elf Bar Clear (advertised 5% mg/mL nicotine, iMeracle, Shenzhen, China), and Flum Pebble Straw Mango (advertised 5% mg/mL nicotine, Flumigo Technology Limited, Shenzhen, China).[72,77−79] The commercial devices were used as is, and aerosols were collected identically to the refillable devices.

All e-cigarette devices were activated with a flow of 1.9 L/min controlled by a puffing apparatus that was previously described.[80] A 2-s puff duration was used, correlating to a puff volume of 63.3 mL, which is within the typical range of puffing topography for e-cigarette users.[81] E-cigarette cartridges or tanks that were filled with e-liquid or distillate were weighed before and after the aerosol generation process to quantify the gravimetric mass loss from the tank for a given number of puffs.

2.2. Woodsmoke Aerosol Generation. Woodsmoke aerosols were prepared in a 40 L smoldering combustion chamber (Figure 1C) at a relative humidity of 40% and combustion temperature of ∼330 °C, as previously described.[82] Birch firewood samples obtained from Fairbanks, AK were used as the fuel for combustion. After approximately 10 min of combustion, when the aerosol optical density in the chamber is high, the whole aerosol emissions were collected at 3.0 L/min by bubbling the outflow of the combustion chamber through the acidic ethanolic DNPH solution (Figure 1A) for 5 and 120 s. Each timed collection was analyzed separately in order to estimate the effect of aerosol loading on carbonyl quantification.

2.3. Secondary Organic Aerosol Generation. Secondary organic aerosols (SOA) were generated by the reaction of 100 parts-per-billion by volume limonene ($C_{10}H_{16}$) and 300 parts-per-billion by volume of ozone (Figure 1D) in a 10 m^3 atmospheric Teflon chamber in the dark. The details of the chamber and its operation were described in previous works.[83,84] Briefly, *d*-limonene (Sigma-Aldrich, 97%) was injected in a gas flow of dry ultrazero air into the chamber; its concentration in the chamber was detected by a gas chromatograph with a flame ionization detector (Agilent 6890N). Ozone was produced by an ozone generator (A2Ozone Inc.), and its concentration in the chamber was detected via a photometric ozone analyzer (Thermo Environmental Instruments Inc., 49i). The reaction proceeded for approximately 2 h in the dark, after which most of the limonene reacted away. The SOA was collected on a 0.2 μm pore Omnipore hydrophilic poly(tetrafluoroethylene) (PTFE) filter (Millipore Sigma Corp.) for 2 h at 1 L/min, extracted in 1.5 mL of the acidic ethanolic DNPH solution, and shaken for 1 h at room temperature.

2.4. UV−Vis Total Carbonyl Assay. Aerosols from test sources were bubbled through an acidic (pH < 2) DNPH solution in a 30 mL glass impinger (Figure 1A and Scheme 1). 10 mg of recrystallized DNPH (97%, Sigma-Aldrich) and 100 μL of hydrochloric acid solution (6 M, HCl, Sigma-Aldrich) were added to the impinger containing 10 mL of absolute ethanol (Sigma-Aldrich). Aerosols from test systems were bubbled through the impinger for various collection times or captured onto a filter and extracted into the same solution. Excess DNPH is suggested for quantitative determination; the amount used in this work (10 mg) is higher than that used in commercial DNPH cartridges (∼1 mg), and we verify both

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visually (color change) and in HPLC-HRMS that the DNPH concentration remains higher than a factor of 10 compared to carbonyls/acids (i.e., was in excess). The impinger solution was transferred to a new vial and shaken for 1 h in the dark. This reaction time between the aerosol samples and DNPH was determined to be optimal for complete reaction for the tested aldehydes, ketones, and acids with DNPH (Figure S1).

DNPH-hydrazones were then converted to the quinoidal ion by diluting an aliquot from the impinger 1:10 with 0.5 M potassium hydroxide (KOH, 85%, from Fisher Scientific) in ultrapure water (Optima LC-MS grade, Fisher Scientific) and ethanol. Samples were left to stand for 6 min at room temperature to form the quinoidal ion (Scheme 1) and decompose excess DNPH,[85] after which, the UV−vis absorption spectra were measured using a Shimadzu UV-1800 UV−vis spectrophotometer system with a wavelength range of 190−1100 nm. It is important to note that some quinoidal ions are unstable, and therefore all measurements were taken within 10 min of the addition of alkali.[51,52] All measurements were performed by using 4 mL glass cuvettes with a path length of 1 cm. Ethanol was used as a reference blank, and all spectra were baseline corrected.

The absorbance at 530 nm (A_{530}) for each aerosol sample, representing the effective absorbance of the total quinoidal ions, was used for quantification.[85,86] The sample A_{530} was used to quantify the total molar concentration of carbonyls in the samples ($C_{carbonyl}$), using an effective molar extinction coefficient at 530 nm (ε_{530}) with 1 cm path length (l), according to the Beer−Lambert Law

$$A_{530} = \varepsilon_{530}\ (\mathrm{M^{-1}\ cm^{-1}}) \times C_{carbonyl}\ (\mathrm{M}) \times l\ (\mathrm{cm}) \quad (1)$$

The A_{530} of an air blank, i.e., lab air that was bubbled through the DNPH impinger using the same flow rate and collection time as the sample (containing carbonyls or small organic acids present in lab air), was subtracted from all samples. In this work, effective ε_{530} values were determined for 8 representative carbonyl-DNPH or acid-DNPH standards (formaldehyde-DNPH, acetaldehyde-DNPH, acetone-DNPH, glycolaldehyde-DNPH, hydroxyacetone-DNPH, acrolein-DNPH, diacetyl-DNPH, and acetic acid-DNPH) after conversion to quinoidal ions. Individual ε_{530} were obtained by plotting observed A_{530} with known concentrations of the added hydrazone standard and extracting a linear least-squares fit. The average of the inverse of the ε_{530} for n numbers of hydrazone standards was used as a unified calibration factor (CF), as concentration $C \propto (1/\varepsilon)$ and thus $C_{avg} \propto (1/\varepsilon)_{avg}$

$$\mathrm{CF} = \left[\frac{1}{\varepsilon_{530}}\right]_{avg} = \frac{\sum\left(\frac{1}{\varepsilon_{530_i}}\right)}{n} \quad (2)$$

$$\mathrm{mol}_{carbonyl} = (A_{530_{aerosol}} \times \mathrm{CF}) \times \mathrm{vol} \quad (3)$$

$$Y = \frac{\mathrm{mol}_{carbonyl}}{m_{aerosol}} \quad (4)$$

Application of the CF affords a molar concentration of hydrazones in the aerosol solution, equimolar with carbonyls, after accounting for the volume of the impinger solution (vol) and any dilution factors. While the factor of 10 dilution is minimum due to the original addition of impinger solution to the KOH mixture, we used dilution factors up to 200 for some samples that produce high yields of quinoidal ions in order to maintain linearity with the Beer−Lambert Law in the spectrometer. The mass of the collected aerosol ($m_{aerosol}$) was used to normalize both the UV−vis and HPLC-HRMS data in order to understand the carbonyl yield (Y), or efficiency with which carbonyls are produced, from individual aerosol sources in order to compare them. Aerosol mass was estimated gravimetrically via filter collection for SOA and woodsmoke (for which a separate collection was performed) and via mass loss from the disposable e-cigarette. The predicted total molar yields of carbonyl in the aerosol mixture using the spectroscopic method were then compared to a "bottom-up" method, which sums the molar concentrations from each speciated carbonyl that was quantified by a calibrated HPLC-HRMS analysis (Section 2.5).[17,80] Assumptions about gas and particulate collection efficiencies of the aerosol into the impinger solution impact the accuracy of the absolute yield estimates; however, as the aerosol mass is used to normalize both types of data, it is not a source of error for the relative intercomparison.

2.5. Carbonyl Characterization via HPLC-HRMS. The methods for the analysis of carbonyl-DNPH hydrazones using HPLC-HRMS in this work have been described previously.[17,34] Unmodified contents from the DNPH impinger were analyzed with HPLC-HRMS. Separation took place on an Agilent 1100 HPLC instrument equipped with an Agilent Poroshell EC-C18 column (2.1 mm × 100 mm, 2.7 μm, 120 Å) coupled with a linear trap quadrupole-Orbitrap (LTQ-Orbitrap) mass spectrometer (Thermo Corp., Waltham, MA). Analysis used a mass resolving power of 30,000 m/Δm at m/z 400. Commercial analytical standards of formaldehyde-DNPH, acetaldehyde-DNPH, acetone-DNPH, acrolein-DNPH, propionaldehyde-DNPH, crotonaldehyde-DNPH, methacrolein-DNPH, 2-butanone-DNPH, butyraldehyde-DNPH, benzaldehyde-DNPH, valeraldehyde-DNPH, tolualdehyde-DNPH, hexaldehyde-DNPH, diacetyl-bis-DNPH, methylglyoxal-bis-DNPH, and glyoxal-bis-DNPH (AccuStandard, New Haven, CT) were used for calibration and quantification. Acetic acid-DNPH and glycolaldehyde-DNPH standards were synthesized and purified by recrystallization as previously described,[30] and were diluted into standards for quantification. Other carbonyl hydrazones (e.g., formic acid-, glyceraldehyde-, propionic acid-, lactaldehyde-, dihydroxyacetone-, and others) were quantified using an empirically weighted theoretical model as previously described.[17] HPLC-HRMS peak areas of individual hydrazone peaks, identified both by retention time and accurate mass, were corrected for any dilution and converted to concentration using empirical calibration factors. With analytical standards, the uncertainty of analysis is 10−20%, while the theoretical model provides an uncertainty of 30−50%. Carbonyl and acid concentrations were normalized by the amount of aerosol mass collected from each aerosol source, as determined gravimetrically.

3. RESULTS AND DISCUSSION

3.1. Method Optimization. Figure 2 shows the wavelength-dependent UV−vis absorbance spectra of quinoidal ions of hydrazones detected in laboratory air and aerosol samples. The measurement wavelength of 530 nm is free from interference from both DNPH and its hydrazones in the sample (Figure 2, black line). DNPH itself absorbs around 350 nm and its hydrazones have absorption maxima ~350−380.[55,86] Due to the high overlap in absorption maxima

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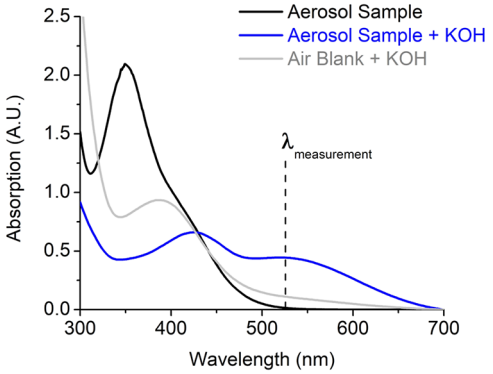

Figure 2. Absorption spectra for vaped aerosol sampled through the acidic ethanolic DNPH impinger prior to (black) and after reacting with KOH (blue). An air blank sampled identically to the aerosol sample after adding KOH (gray) is shown to demonstrate the magnitude of the blank correction. The vertical hashed line is at 530 nm, where measurements were collected.

between DNPH and its hydrazones, and the fact that DNPH is in excess, the absorption spectrum prior to the addition of alkali is not distinguishable between sample and blank; thus, spectrometric analysis cannot be performed without the addition of alkali to decompose DNPH and convert hydrazones to quinoidal ions.

Eight analytical standards for carbonyl-DNPH and acid-DNPH hydrazones were chosen to develop a CF to convert sample A_{530} to a molar concentration of hydrazones. Besides being important compounds in nature, the selected calibration standards represent various classes of functionalized carbonyls and acids that may be present in an environmental complex mixture of aerosols: acetic acid for small organic acids (RC(O)OH, where R can be H), formaldehyde for the smallest carbonyl (HC(O)H), acetaldehyde for simple aldehydes (RC(O)H), acetone for simple ketones ($R_1C(O)-R_2$), glycolaldehyde for hydroxyaldehydes ($R_1-HC(OH)-C(O)-H$), hydroxyacetone for hydroxyketones ($R_1-HC(OH)-C(O)-R_2$), acrolein for unsaturated carbonyls ($R_1-HC{=}CH-C(O)-R_2$), and diacetyl for dicarbonyls ($R_1-C(O)-C(O)-R_2$, where R can be H).

Figure 3 and Table 1 show that the hydrazone standards have effective ε_{530} values (the slope of the linear least-squares fit) that can vary substantially. The term "effective" indicates that individual ε_{530} slopes can reflect both the conversion efficiency of the hydrazone to the quinoidal ion and the true molar absorptivity of the product quinoidal ion. To our knowledge, the conversion efficiency to the quinoid has not been reported, and thus, it is not clear if the observed ε_{530} values represent the true molar absorptivity. The average of the inverse ε_{530} for the 8 hydrazone calibration standards is 5.16×10^{-5} M cm, which was used as the unified calibration factor (CF). The three ε_{530} values in this work that are much larger than the others are those for acrolein-DNPH, acetone-DNPH, and diacetyl-DNPH. While the absorptivity of the acrolein-DNPH quinoidal ion is anticipated to be high due to the additional unsaturation, the other high absorptivity values are unexpected. Thus, it is probable that the conversion efficiency to the quinoid plays a significant role in the observed ε_{530}. Aimanant and Ziemann used 10 simple and functionalized carbonyls (C_5-C_{18}) for calibration compared to this work and obtained a range of 6600−15 600 M^{-1} cm^{-1}; they obtained a single CF that is approximately 1×10^{-4} M cm.[53] Although a detailed comparison between this work and that of Aimanant and Ziemann may not be possible due to the differences in assumptions and absence of validation in that study, it can be noted that the usage of a single spectroscopic CF for different organic aerosols appears to be a robust approach in general.

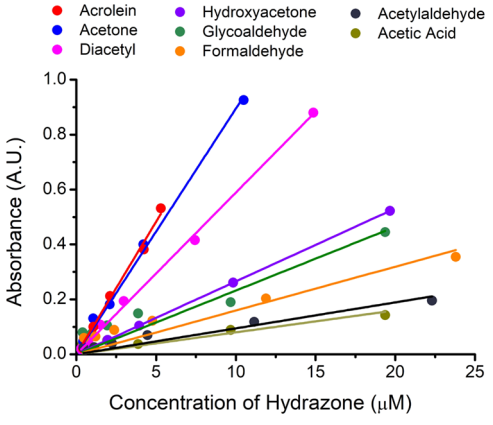

Figure 3. Absorbance at 530 nm, associated with the absorption of quinoidal ions, after various concentrations of carbonyl-DNPH and acid-DNPH hydrazone standards were reacted with KOH according to the experimental protocols.

3.2. Validating UV−Vis Data with HPLC-HRMS. Using a CF of $\sim 5.16 \times 10^{-5}$ M cm (eq 2), the total carbonyls detected with the spectroscopic method were converted to an aerosol molar yield (eqs 3 and 4). The sums of the speciated carbonyls that were individually quantified via HPLC-HRMS are compared to the UV−vis results in Figure 4, and the data are tabulated in Table 2. It is apparent from Figure 4 that each aerosol source has a different distribution of carbonyls and acids. A fairly large range of aerosol masses were tested (2−650 mg), with each source having yields from 4 to 1300 μmol carbonyls per gram aerosol. Yet, despite this heterogeneity, the molar yields of carbonyls characterized by UV−vis and HPLC-HRMS from the different aerosol sources tested agree to within 40%. The correlation coefficient (R^2) between the two methods is strong (>0.99, Figure 5). This is especially noteworthy given that myriad sources of uncertainty exist in both mass spectrometric and spectroscopic measurements; in particular, each empirical or estimated calibration factor performed for carbonyl-DNPH and acid-DNPH hydrazone is subject to its own uncertainty, which may add or cancel in unpredictable ways when the individual components are summed to a total carbonyl concentration. For example, we may expect the uncertainties for the determination of formaldehyde to dominate for the nicotine salt e-cigarette (Figure 4F) or for the uncertainties of acetaldehyde and acrolein to dominate for the woodsmoke aerosol (Figure 4H). Yet, as a whole, spectroscopic determinations of carbonyls in different aerosol sources tested here appear to be well described by a single governing relationship. The best agreement is found with the benzoic acid nicotine salt vape aerosol, for which the distribution of carbonyls is dominated by well-calibrated analytes. Poorer agreements between the two techniques appear to be from analytes labeled as "other carbonyls," (Section 3.3 and Table S1) for which HRMS sensitivities were estimated.

Although an average CF determined from quinoidal ions for 8 hydrazone standards was used (Figure 3), the development of the method does not require assumptions about the most

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Table 1. Carbonyl-DNPH and Acid-DNPH Hydrazones Used for Calibrating the Production of Quinoidal Ion and the Effective Molar Absorption Coefficient (ε_{530}) for Each Hydrazone, Which May Represent both the Absorption of the Quinoidal Ion and the Conversion of Hydrazone to Quinoid

hydrazone	$MW_{hydrazone}$ (g/mol)	eff. ε_{530} (M^{-1} cm^{-1})	type of acid or carbonyl	general structure
formaldehyde-DNPH	210	15 900	formaldehyde	H−C(O)−H
acetaldehyde-DNPH	224	9500	simple aldehydes	R−C(O)−H
acetone-DNPH	238	87 200	simple ketones	R_1−C(O)−R_2
glycolaldehyde-DNPH	240	23 200	hydroxyaldehyde	R_1−HC(OH)−C(O)−H
hydroxyacetone-DNPH	254	26 550	hydroxyketone	R_1−HC(OH)−C(O)−R_2
acrolein-DNPH	236	96 600	unsatd. carbonyls	R_1−HC═CH−C(O)−R_2
diacetyl-DNPH	266	58 000	dicarbonyl	R_1−C(O)−C(O)−R_2
acetic acid-DNPH	240	8000	organic acid	R−C(O)−OH

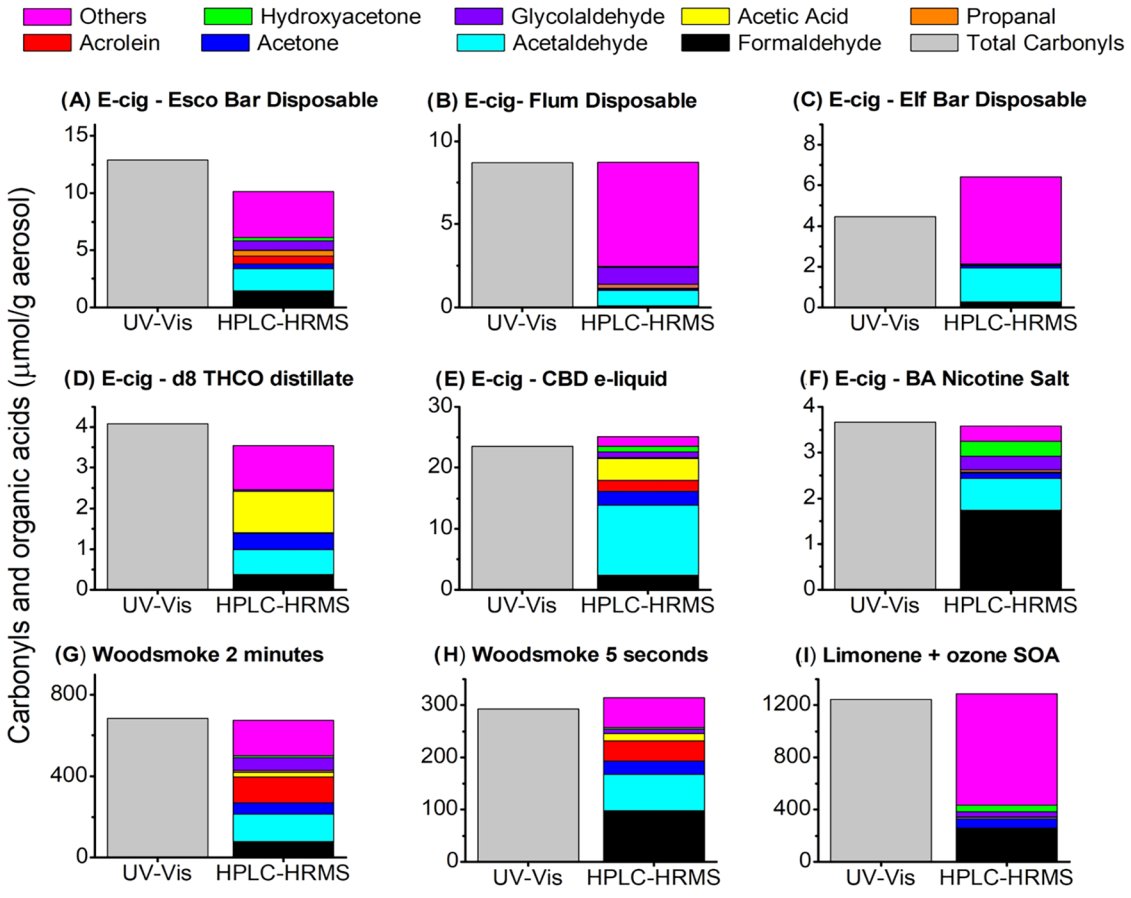

Figure 4. Total carbonyl molar yields (μmol/g) in aerosols detected from different electronic cigarettes, including: (A−C) disposable nicotine devices; (D) cannabinoid distillate, (E) refillable pod with 50 mg/mL CBD in 7:3 PG/VG, and (E) refillable pod with benzoic acid (BA) nicotine salt (1:1) in 3:7 PG/VG; and from laboratory generated models of atmospheric aerosols, including whole smoldering woodsmoke aerosols collected for (G) 2 min and (H) 5 s; and (I) limonene ozonolysis secondary organic aerosol (SOA) generated under dry conditions without inorganic seed particles. Gray bars indicate the total carbonyls determined via UV−visible spectroscopy of the same sample used for HPLC-HRMS analysis.

appropriate hydrazone standards to represent complex mixtures to be made. Different choices for calibrant hydrazones (Table 1) will yield different CFs, and the agreement shown in Figure 5 is likely serendipitous. In fact, no calibrant hydrazones need to be selected. The relationship between the dilution-corrected A_{530} as directly observed from the "top-down" UV−vis method and the molar concentrations of carbonyls analyzed by the "bottom-up" HPLC-HRMS method that is independently calibrated for each carbonyl-DNPH hydrazone (Section 2.5) may be used to derive an empirical CF with no knowledge of the aerosol systems tested. The slope of concentration (in M) versus dilution-corrected A_{530} is simply the effective CF $(1/\varepsilon_{530})_{avg}$ that best represents the quinoidal ions derived from the carbonyl-DNPH hydrazones in solution (Figure 6). The dilution-corrected A_{530} had a similarly strong relationship with the total concentration of carbonyls obtained from HPLC-HRMS ($R^2 \sim 0.997$) and a CF of 5.34×10^{-5} M cm can be extracted. This is similar to the CF value of 5.16×10^{-5} M cm obtained using calibration compounds (Table 1) that was used to calculate the total carbonyl values in Figure 4 and Table 2.

3.3. Carbonyl Distribution from HPLC-HRMS. While this paper focuses on validating a spectroscopic method for the detection of total carbonyls, the data shown here for speciated carbonyls from different aerosol sources are novel and thus

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Table 2. Determination of the Molar Concentration of Carbonyls and Acids (Equivalent to That of the Carbonyl-DNPH and Acid-DNPH Hydrazones) in Various Aerosol Samples Collected with an Acidic Ethanolic DNPH Impinger via the UV−Vis and the HPLC-HRMS Methods[a]

							yield (μmol/g)	
sample name	A_{530} (blank corr.)	dilution	[carbonyl] (μM)	volume (mL)	carbonyl (μmol)	aerosol (mg)	UV−vis	HRMS
disposables (Flum SM)	0.503	10	259.6	10	2.60	298.7	8.69	8.73
disposables (Elf Clear)	0.192	10	99.1	10	0.99	222.9	4.45	6.42
disposables (Esco TRB)	0.335	20	345.9	10	3.46	268	12.91	10.15
d_8-THCO distillate	0.263	10	135.9	4	0.54	132.8	4.09	3.55
CBD 50 mg/mL in PG/VG (7:3)	0.748	40	1544.5	10	15.44	656.8	23.52	25.12
nicotine Salt BA in PG/VG	0.236	10	121.8	10	1.22	332	3.67	3.58
woodsmoke 5 s	0.275	40	567.8	10	5.68	19.4	292.69	329.34
woodsmoke 2 min	0.116	200	1197.6	10	11.98	17.5	684.34	744.44
limonene + ozone SOA	0.354	60	1096.4	2.5	2.74	2.2	1245.92	1294.43

[a]The A_{530} value for samples in UV−vis has been corrected for air blanks (Figure 1). The volume column refers to the volume of DNPH solution in the impinger or the volume of DNPH solution used to extract a filter, depending on the method of aerosol collection.

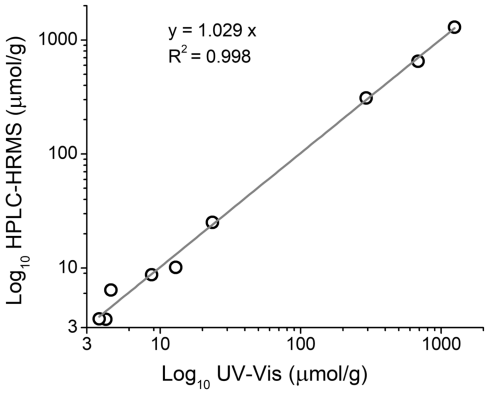

Figure 5. Correlated relationship between total carbonyl molar yields (μmol carbonyl/g aerosol) determined using the same aerosol samples derivatized with acidic DNPH, as quantified by UV−vis spectroscopy (total carbonyls) and HPLC-HRMS (speciated carbonyls, summed) methods, using an unified calibration factor (CF) obtained by eq 2 using the effective molar absorption coefficient (ε_{530}) data shown in Figure 3. Data are plotted on a log−log scale to better showcase range; the relationship and fit are identical to linear scale.

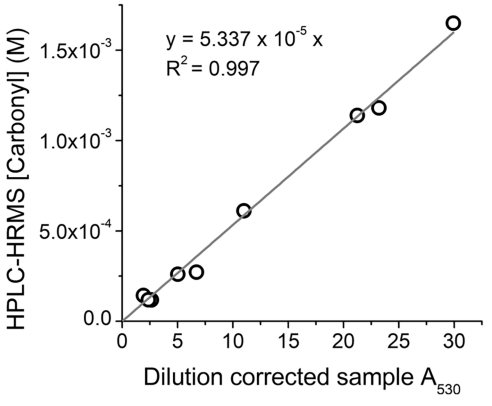

Figure 6. Relationship between the quantified carbonyl concentrations, in molar, using HPLC-HRMS and the dilution-corrected A_{530} for each aerosol sample tested in this work. The slope is the effective calibration factor (eq 2) that best represents the quinoidal ions obtained from carbonyls in the samples.

worthy of discussion. Table S1 lists concentrations for all of the carbonyl species detected from the aerosols studied in this work. Figure 7 shows an extracted ion chromatogram for the carbonyls detected in woodsmoke aerosols after collecting for 5 s through the acidic DNPH impinger.

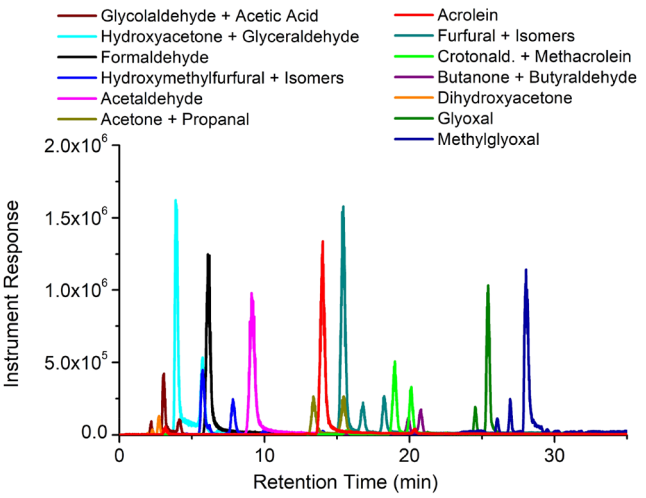

Figure 7. Representative HPLC-HRMS extracted ion chromatograms for the exact masses of carbonyl-DNPH hydrazones detected in the woodsmoke aerosol sample. The raw instrument response in counts/s is shown. Structural isomers of carbonyl species, with the same exact mass, are differentiated by retention time. Individual calibration factors are applied to peak areas to obtain the concentration.

Small simple carbonyls such as formaldehyde and acetaldehyde are abundant in many types of aerosol mixtures, including e-cigarette aerosols and woodsmoke aerosols. The disposable e-cigarettes had substantial acetaldehyde content as well; however, their carbonyl distribution had significant quantities of additives such as 1-amino-ethanal. We infer that this product comes from the oxidation of monoethanolamine (MEA), which is used in many consumer products,[87] and is either an impurity or purposefully added to buffer the pH of the e-liquid against the added organic acids.[88] The small hydroxycarbonyls, glycolaldehyde and hydroxyacetone, were important components of nearly all tested aerosol systems. The d_8-THCO distillate contained a significant portion of acetic acid, potentially due to the dissociation of the acetate group on the THCO. Acetone was found in sizable quantities in both the cannabinoid e-cigarettes as well as in limonene ozonolysis SOA, likely due to the decomposition of the C_3 tail of

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limonene and similarly structured terpene moieties of the cannabinoid.[89] Acrolein, a highly mutagenic carbonyl,[90] was a significant fraction of total carbonyls in the Esco Bars e-cigarette (~7%) and both woodsmoke samples (~20%). Furfural and hydroxymethyl furfural, two well-known aldehydes in woodsmoke,[91] were also detected and included with the "other" carbonyls in Figure 4. Crotonaldehyde, methacrolein, butanone, butanal, benzaldehyde, and hexaldehyde were notable carbonyls detected in woodsmoke aerosols. The limonene ozonolysis SOA produced the most carbonyls per gram of aerosols tested. Given that this is the only aerosol system that was first collected on a filter before it was derivatized by DNPH, the carbonyl yield should be interpreted different (normalized by the particulate fraction not total aerosol) and it should not be surprising that smaller carbonyls were not as represented in the SOA (Figure 4I) as in other systems. Instead, the limonene-derived carbonyls (mostly C_9 and C_{10}) were found to dominate the carbonyl distribution. For example, the fully ozonized limonene product ketolimonaldehyde ($C_9H_{14}O_3$) was observed as a major product,[91] likely because the aerosol was sampled upon reaction completion when limonene has almost been fully depleted. Despite sampling using a filter, formaldehyde was still the single most abundant carbonyl in the limonene ozonolysis system; it will likely be even more abundant when sampling the whole aerosol.

4. CONCLUSIONS

UV−vis spectroscopic determination of total carbonyls offers a rapid, simple, and cost-effective alternative to speciated carbonyl detection using hyphenated chromatography methods and may be valuable in applications in which detailed speciation of carbonyls is not required. Although the technique has been used for functional group analysis of α-pinene ozonolysis SOA, this work represents the first validation of the technique with liquid chromatography-high-resolution mass spectrometry (HPLC-HRMS) for a diverse range of aerosols for which carbonyls may comprise a significant portion of the composition. An empirical determination of an effective calibration factor (5.34×10^{-5} M cm) was obtained from plotting molar concentrations of carbonyls quantified by HPLC-HRMS and the dilution-corrected absorbances (A_{530}) of the alkali-treated samples, which is remarkably similar to the averaged factor (5.16×10^{-5} M cm) obtained by calibrating the conversion of eight hydrazone calibration standards to quinoidal ions upon treatment with alkali.

While the spectroscopic method lacks the ability to distinguish between individual carbonyl species, it can (a) provide carbonyl functional group apportionment data for model development of complex mixture properties, (b) serve as a preliminary screening tool to identify whether notable concentrations of carbonyls exist before committing to more detailed and resource-intensive LC-MS analysis; and (c) be an effective method in educational settings (e.g., student capstone project or a module at a teaching laboratory) to compare carbonyl content in various environmental, pharmaceutical, or other complex mixture samples. Furthermore, in situations where chemical diversity is low (i.e., when one carbonyl dominates the distribution in a mixture), the total carbonyl analysis can approximate the concentration of the dominant carbonyl with good accuracy. When used as a rapid screening tool for total carbonyls, the combination of the spectroscopic and hyphenated chromatography methods in tandem could provide an efficient workflow that balances speed, cost, and data quality.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestair.5c00123.

Quinoidal ion yield with respect to DNPH derivatization time; tabulated aerosol mass-normalized carbonyl emissions (in μmol carbonyl per gram aerosol); and limits of detection for the HPLC-HRMS and UV−vis methods (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Tran B. Nguyen − *Department of Environmental Toxicology, University of California, Davis, Davis, California 95616, United States;* orcid.org/0000-0001-9206-4359; Email: tbn@ucdavis.edu

Authors

Haylee C. Hunsaker − *Department of Chemistry, University of California, Davis, Davis, California 95616, United States*

Nicholas E. Robertson − *Department of Environmental Toxicology, University of California, Davis, Davis, California 95616, United States*

Brett A. Poulin − *Department of Environmental Toxicology, University of California, Davis, Davis, California 95616, United States;* orcid.org/0000-0002-5555-7733

Complete contact information is available at: https://pubs.acs.org/10.1021/acsestair.5c00123

Notes

The authors declare no competing financial interest.

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