List of known needed updates to US Compendium Method TO-11A

General Area	Specific Issue(s)	Proposed Action
Section 1 – Scope	Other chemistries (e.g., dansylhydrazine [DNSH]), analysis techniques (gas chromatography with flame ionization detection [GC/FID] or mass spectrometry [MS]), and sampling approaches (e.g., passive monitoring) may also be applicable for measurement of carbonyls in ambient air (Kim & Pal, 2010; Liu, Dills, Paulsen, & Kalman, 2001; Maypole, 2007; Rodier, Nondek, & Birks, 1993)	Retain method's focus on measurement of carbonyls in ambient air using dinitrophenylhydrazine (DNPH) derivatization chemistry and active sampling onto commercially available silica-gel cartridges followed by separation of the hydrazone derivatives with high-performance liquid chromatography (HPLC) with UV detection at ~360 nm.
Section 1 – Scope	Target compound for method is formaldehyde, other carbonyls are only mentioned	Clarify in Section 1 and throughout how to apply the method for measurement of other important carbonyls such as acetaldehyde
Section 1 – Scope	Method is unsuitable for the measurement of unsaturated carbonyls (e.g., acrolein, crotonaldehyde) (Ho et al., 2011); may be inadequate for other important carbonyls (e.g., acetaldehyde) (J. S. Herrington, Fan, Lioy, & Zhang, 2007; Jason S. Herrington & Hays, 2012; Karst, Binding, Cammann, & Witting, 1993; Potter & Karst, 1996; Uchiyama, Ando, & Aoyagi, 2003); suffers from interferences with co-collected moisture (e.g., (Grosjean & Grosjean, 1996) and NO_2 (Karst, Binding, Cammann, & Witting, 1993; Potter & Karst, 1996)	Discuss and present latest knowledge of various method performance issues; clarify that method is not suitable for the measurement of acrolein and crotonaldehyde; present recommendations for measuring acetaldehyde and understanding the impacts of co-collected moisture and NO_2
Section 2 – Applicable documents	References are out of date, including those from the peer-reviewed literature, ASTM standards/practices, PAMS TAD, etc.	Update all references to include latest publications in the scientific literature, standards, and Photochemical Assessment and Monitoring Stations (PAMS) and National Air Toxics Trends Stations (NATTS) Technical Assistance Documents (TADs)
Section 3 – Summary of Method	Many details require updating, including, for example, air sampling rate, elution volume, HPLC detector, method sensitivity, potential method performance variations by type of air sampling cartridge	Update to include best practices and guidance on air sampling rates (< ~ 1.25 L/min), 2 mL elution volumes as acceptable, choice of detectors (diode array detector [DAD], MS), detection limits (<0.1 ppb is attainable for formaldehyde), and information on method performance variations with different sampling media
Section 4 – Significance	Updated details necessary, including, for example, carbonyl sources; their health hazards; significance of carbonyls such as formaldehyde to inhalation risk in ambient air; and that impingers and C18 cartridges are no longer widely used	Revise section to provide information on cancer and non-cancer risks from carbonyls such as formaldehyde and acrolein; on formaldehyde as the most important air toxic risk driver in ambient air (Strum & Scheffe, 2016); and to remove discussion of impingers and C18 cartridges

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Section 5 – Definitions	Definitions missing and/or out of date for, among others, method detection limit (MDL), trip blank, field blank, collection efficiency	Update MDL to explicitly require assessment of blank levels as described in revision 3 of the NATTS TAD (Battelle, 2016); add definitions of field and trip blanks; and define collection efficiency as the ratio of the measured concentration divided by the expected concentration
Section 6 – Extended Methodology and Common Interferences	Many details out of date. For example: the method's focus on formaldehyde; use of older column technology; need to purify DNPH reagent; use of granular potassium iodide (KI) scrubber for ozone (O_3) removal	Update information on separation and measurement of range of carbonyls, new and ultra-high-performance LC (UHPLC) instrument column technologies; remove discussion of recrystallization of DNPH; and remove option to use granular KI O_3 scrubbers
Section 7 – Apparatus	Information on instrumentation, cartridge media, air samplers, and ancillary equipment must be updated to reflect modern practice	Provide details on UHPLC/MS or DAD; new column technology (smaller particle sizes, shorter columns); sampling media vendors (e.g., Supelco, Waters, SKC) and cartridge expiration dates; vendors of carbonyl samplers (ATEC, Tisch); and current state of the art flow rate control and measurements and with mass flow controllers and meters
Section 8 – Reagents and Materials	Information such as need for high-purity DNPH, use of perchloric and ortho-phosphoric acids, high-purity aldehydes and ketones for preparation of derivatized standards, etc. no longer reflects current practice	Remove unnecessary details
Section 9 – Preparation of Reagents and Cartridges	Cartridges, reagents and carbonyl-hydrazone derivatives are no longer prepared in-house but instead are purchased commercially	Revise section throughout to, for example, explain how to assess acetonitrile (ACN) contamination by periodic analysis of system blanks (injection of ACN solvent only) and cartridge method blanks; remove information on recrystallization of DNPH, preparation of derivatized carbonyls, and preparation of DNPH-coated cartridges
Section 10 – Sampling Procedure	Various operational details no longer reflect current practice, including need for collection of backup cartridges; impact of humidity on collection efficiency; and use of a dry gas meter for flow rate measurements	Update section to present latest information on observed lack of compound breakthrough at typical ambient concentrations; impact of co-collected moisture on carbonyl collection efficiencies; recent work on confirming the O_3 removal capacity of the KI-coated denuders and on understanding of the impact of O_3 denuders on method performance; and to provide best practices on cartridge handling and methods to improve sampling performance such as: selection of compatible inlet and manifold materials, routine cleaning of inlets and manifolds, preference for flow rate control with mass flow controllers, flow rate measurement with volume displacement-type flow meters, and periodic

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		demonstration of acceptably low sampling system contamination and bias by way of zero air and known concentration challenges of carbonyls at low ppb levels
Section 11 – Sample Analysis	Many details are out of date, such as that sample extraction is only performed with 5 mL ACN with an injection volume of 25 µL onto a 25 cm column followed by single wavelength detection.	Update method to allow cartridge extraction with 2 mL ACN; injection volumes of 5 to 10 µL that account for increased HPLC sensitivity; and use of: latest reversed-phase column technology (shorter columns, smaller particle sizes), shorter runtimes < 1 h, modern multiple wavelength DAD, MS detection, and commercially-purchased derivatized carbonyl-hydrazone standards. Include best practices on HPLC analysis such as degassing of solvents, use of guard columns, and backflushing of the LC column. Recommend a typical calibration range of 0.03 to 5 µg/mL for ambient air analysis and remove requirement for triplicate injections. Explain that calibration standards are typically already given in units of carbonyl equivalent concentrations thereby obviating the need to calculate such for calibration curves
Section 12 – Calculations	Calculations assume y-intercept = 0 for linear best fit calibration model (response factor model, area = slope * concentration)	Update to include data treatment for linear regression models that include non-zero y-intercepts
Section 13 – Performance Criteria and Quality Assurance	Method precision and accuracy requirements require review, as does the requirement for a 50% frequency for collocated sampling. The MDL procedure must account for the impact of media blank levels	Review and solicit input on current method capabilities and needs with respect to precision and accuracy for various ambient air monitoring applications. Relax collocated sampling guidance. Require MDL Method Update Rule (MUR) procedure, or similar, as given in NATTS TAD revision 3 (Battelle, 2016).
Section 14 – Detection of Other Aldehydes and Ketones	Monitoring is routinely performed with this method for carbonyls in addition to formaldehyde.	Incorporate relevant details of this section, such as gradient elution, into Sections 10 and 11 on Sampling Procedure and Sample Analysis
Section 15 – Precision and Bias	Information is out of date.	Update with the latest results from the NATTS proficiency testing (PT) program, the Urban Air Toxics Monitoring Program (UATMP) program, and other round robin studies and information in the literature sources
Tables and Figures	Information is out of date.	Update Tables 1, 2 and 4; retain Table 2; Delete Figures 1, 3, 4, 5, 7; update Figures 2, 6, 8, 9, 10, 11, 12, 13, and 15; retain Figure 14.

References

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