DEVELOPMENT AND EVALUATION OF AIRBORNE CARBONYL MEASUREMENT METHODS

by

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ABSTRACT OF THE DISSERTATION

Development and Evaluation of Airborne Carbonyl Measurement Methods

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The overall goal of the current dissertation work was to further develop and optimize the Passive Aldehydes and Ketones Sampler (PAKS) method, and compare the PAKS method to the United States (U.S.) Environmental Protections Agency's (EPA) Compendium Method TO-11A (active sampling with 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbents).

The PAKS method was optimized to have improved collection efficiencies (~100%) and sample stabilities (on cartridge and in extract) for acrolein and crotonaldehyde (as opposed to Method TO-11A's acrolein collection efficiency of ~20%). Subsequently, the PAKS sample processing procedures were optimized so as to provide the most efficient, accurate, precise, and cost effective techniques. In addition, the PAKS method blank contamination sources and concentrations were identified, and then minimized as best as possible. In the end, the final PAKS method demonstrated stable blank and sample concentrations for almost a half year; method and analytical precisions, expressed as coefficient of variation from replicate samples, of ~20% and <10%, respectively for formaldehyde, acetaldehyde, and acrolein; and analytical detection limits ranging from 0.28 to 4.81 μg/m³ and method detection limits ranging from 0.00 to 9.87 μg/m³, for a 24-hour sampling period.

Extensive laboratory experiments indicated that U.S. EPA Compendium Method TO-11A had long-term (i.e., ≥24 hours) acetaldehyde sampling collection efficiencies that were substantially less than 100% at 30% and 60% relative humidity.

The Active Acrolein Sampler (AAS) method was developed based on the principles of the PAKS methods. The AAS method was suitable for short-term (i.e., 30 minutes) and long-term (i.e., ≥24 hours) acrolein sampling at sampling rates from 50 to 250 mL/min. Relative humidity from 30 to 90%, temperature from 20 to 40°C, and the presence of ozone up to 250 ppb did not affect the performance of the AAS method for short-term acrolein sampling (i.e., 1 to 2 hours). The AAS method had an acrolein LOD of 0.24 μg/m³ for a 30 minute sampling duration @ 250 mL/min, which was comparable to other acrolein measurement methods; however, the AAS method is a significant advantage over other methods when one considers the AAS for its simplicity and ease of use.

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Dedication

To my loving father and mother, Peter Shepard and Kathleen Ann Herrington

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Chapter 1

Background and Introduction

Airborne carbonyl compounds (carbonyls) including aldehydes (RCHO) and ketones (R_1COR_2) are of great interest, because of their ubiquitous presence in indoor, outdoor, and personal air (*1,2*); and because carbonyls and their atmospheric reaction products have well known adverse human health effects (*3,4*). The aims of the present dissertation research were to optimize the PAKS method for the measurement of unsaturated carbonyls (particularly acrolein); evaluate and optimize the PAKS method sample processing procedures; evaluate and minimize the PAKS method blanks; evaluate the "final" PAKS method performance; evaluate the U.S. EPA's Compendium Method TO-11A for long-term (i.e., ≥24 hours) carbonyl sampling; and develop a short-term (i.e., minutes to a few hours), DNSH-based active sampling method for measuring airborne acrolein. The following discussion covers carbonyl sources, carbonyl exposure, carbonyl health effects, and carbonyl exposure measurement, in relation to the aims of the present dissertation research.

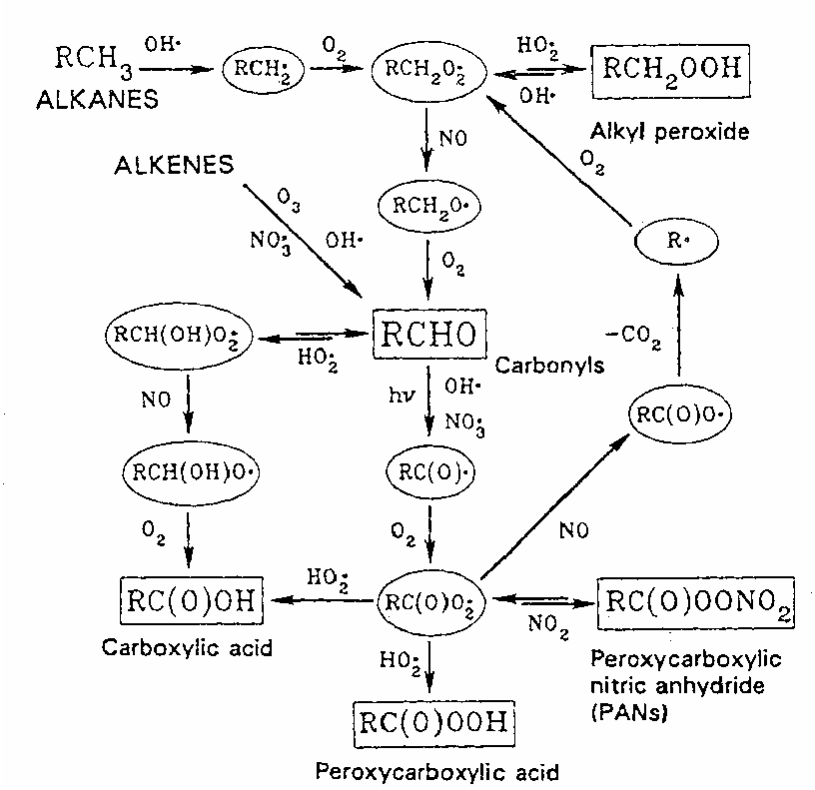
1.1 Background

1.1.1 Carbonyl Sources

Airborne carbonyls are produced from both primary and secondary sources. Primary sources, either natural or anthropogenic, are directly emitted from the source to the air; while secondary sources result from atmospheric reactions. Natural primary sources of carbonyls include plant respiration (*5*), food (*6*), and forest fires (*7*). Primary

anthropogenic sources of carbonyls are virtually countless; however, some examples include combustion sources (*8*), disinfectants (*8*), fumigants (*8*), preservatives (*8*), and resins (*8*). Secondary sources of carbonyls mainly results from the photooxidation of natural and anthropogenic hydrocarbons (see Scheme 1). For example, the hydroxyl radical oxidation of 1,3-butadiene yields acrolein, and continued oxidation yields glyoxal, glycol-aldehyde, and malonaldehyde (*9,10*). Due to the numerous primary and secondary sources, carbonyls are ubiquitously present in indoor, outdoor, and personal air (*2,11*).

In addition to being produced from photochemical reactions, some carbonyls are involved in photochemical reactions that are responsible for initiating and sustaining the photochemical radical pool that produces tropospheric smog (*3*). For example, the oxidation of formaldehyde by OH will form an HCO radical, which rapidly reacts with atmospheric O_2 to form CO and HO_2 radicals. Carbonyls act as precursors to carboxylic acids and oxidants including ozone, peroxycarboxylic nitric anhydrides (PANs), and peroxycarboxylic acids (*3*). Scheme 1 illustrates the major tropospheric photochemical reactions involving carbonyls. Exposure to carbonyls and their reaction products have well known adverse human health effects (*3,4*), thereby necessitating accurate and precise measurement methods for environmental concentrations of carbonyls.



Scheme 1: Major tropospheric reactions involving carbonyls. Adopted from Vairavamurthy et al. (*3*).

1.1.2 Carbonyl Exposure

Although airborne carbonyl exposure can occur via liquid-phase skin absorption, the following discussion focuses on inhalation exposure. Because of their ubiquitous presence in indoor, outdoor, and personal air environments, inhalation exposure to carbonyls is virtually unavoidable. However, as with any airborne constituent, carbonyl exposure will often be at its highest when in the presence of the highest concentrations for the longest periods of time. For example, photochemical oxidation of hydrocarbons (*9,10*) and the burning of fuel (*12*) are major sources of acrolein. Acrolein is an aldehyde that has recently received considerable attention, because it is extremely acrid and irritating to mucous membranes (*11*), and the U.S. EPA considers acrolein to be a hazardous air pollutant (HAP) (*13,14*). Acrolein has been measured in exhaust gases as high as 0.05 - 27.7 mg/m^3 from

gasoline engines and 0.12 - 0.21 mg/ m^3 from diesel engines (*13*). Due to the secondary sources and high concentrations in exhaust gases, the U.S. EPA has reported mean ambient acrolein concentrations of 14.3 μg/m³ (6.2 ppb), ranging from 8.2 to 24.6 μg/m³ (3.6 to 10.7 ppb), for two urban locations based upon data from 1961 to 1980 (*15*). The burning of tobacco is another major source of acrolein (*6*), consequently indoor acrolein concentrations have been measured from 2.3 to 275 μg/m^3 in the smoky environments of bars and restaurants (*13*). Therefore, someone who spends a couple hours in a bar in the presence of environmental tobacco smoke (ETS) is more than likely to have their highest acrolein exposure at that point in time, as opposed to the several minutes they spent waiting for a bus (in the presence of urban ambient air) to get to the bar.

Considering the above scenario, an ideal measure of personal exposure to carbonyls is personal sampling; therefore, a main aim of the present dissertation research was to develop the PAKS method, so as to provide a personal sampling method capable of measuring several saturated and unsaturated (particularly acrolein) carbonyls. The current body of literature has consistently demonstrated that personal exposure to numerous airborne constitutes is underestimated by area sampling (*16-20*). Furthermore, one of the major conclusions from Relationships of Indoor, Outdoor, and Personal Air (RIOPA) study was that with a few important exceptions, the indoor and personal concentrations of 10 carbonyls was higher than outdoor concentrations (*21*); thereby further emphasizing the need for accurate and precise measurement methods for personal exposure to environmental concentrations of carbonyls.

1.1.3 Carbonyl Health Effects

Short- and long-term inhalation of several carbonyls have been associated with various acute and chronic adverse human health effects, including: respiratory symptoms; eye, nose and throat irritation; reproductive and developmental effects; genetic damage; and cancer (*22*,*23*). Accordingly, several carbonyls (e.g., formaldehyde, acetaldehyde, propionaldehyde, acrolein, and methyl-ethyl ketone (MEK)) have been classified as HAPs by the 1990 amendments of the Clean Air Act (*14*). A chemical is classified as a HAP if its presence in the atmosphere is associated with adverse human health outcomes (*22*). Furthermore, the U.S. EPA considers formaldehyde to be a Group B1 probable human carcinogen (*24*) and acetaldehyde to be a Group B2 probable human carcinogen (*25*). Recently, the International Agency for Research on Cancer (IARC) has classified formaldehyde as a known human carcinogen (*13*). Again, it is important to note that the health concerns associated with carbonyls is not limited to strictly carbonyl exposure, but also includes exposure to the compounds that result from atmospheric reactions involving carbonyls. As mentioned earlier, ozone is one of the several products from atmospheric reactions with carbonyls, and ozone has been linked to several adverse human health effects (*22*).

Considering the above, there was a need to develop the PAKS method so as to provide an accurate and precise; personal carbonyl measurement method. The knowledge base on human health effects from carbonyl exposure is largely founded on epidemiological data (*21*,*26*). Very little research has been conducted to understand the possible adverse human health effects of exposure to HAPs such as carbonyls, especially at environmental concentrations (*21*,*26*) and especially for unsaturated carbonyls; largely due to the lack of personal carbonyl measurement methods. In order to establish more reliable health risks

for exposure to carbonyls (in particular unsaturated carbonyls) at environmental concentrations, the PAKS method needed to be further developed.

1.1.4 Carbonyl Exposure Measurement

Over the past 4 decades, numerous carbonyl sampling and analytical methods have been developed. These methods include colorimetric techniques (e.g., chromotropic acid) (*27*), canister sampling (*28*), spectroscopic systems (*in situ* monitoring) (*29*), solid sorbent sampling (e.g., Tenax GC and molecular sieve 13X) (*30,31*), and chemical derivatization (e.g., 2,4-dinitrophenylhydrazine (DNPH)) (*32,33*). It is important note that the aforementioned collection methods are coupled with a wide array of analytical techniques. The first widespread carbonyl measurement method appears to be the use of impingers filled with DNPH (*34*). Impinger-based sampling was often utilized for carbonyl sampling from the late 1960's to the early 1980's (*34-37*). However, impinger techniques are often cumbersome (*3*) and typically require the use of a glass impinger filled with a liquid (a hazard to subjects in the event of a break or spill) (*38*); this makes personal sampling with impingers in the breathing zone impractical (*39*).

In the late 1970's, researchers began to develop carbonyl measurement methods that utilized solid sorbents, which were relatively small and durable. The majority of these methods relied on a substrate impregnated with a reagent that reacted with carbonyls to form stable derivatives. The derivatives retained on the substrate were subsequently extracted and analyzed. Some of the substrates include Amberlite XAD-2 (*39*), silica gel (*38*), glass beads (*40*), C_{18} coated silica gel (*41*), florisil (*42*), and glass fiber filters (*43*). Some of the carbonyl derivatization reagents include o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) (*44,45*),

5-(dimethylamino)naphthalene-1-sulfohydrazide (DNSH, also known as dansylhydrazine) (*46*), and DNPH (*33*). Some of the analytical techniques include high pressure liquid chromatography (HPLC) coupled with UV detection (*33*), fluorescence detection (*46*) or mass spectrometry (MS) (*47*); and gas chromatography (GC) coupled with an electron capture detector (ECD) (*39*), or MS (*48*).

Inarguably, the most frequently utilized method for measuring carbonyls at typical environmental levels is the U.S. EPA's Compendium Method TO-11A (*33*). This method utilizes a DNPH impregnated substrate (most often silica gel), and sample collection is achieved using a sampling pump. This method has been established as a technique for the short-term (i.e., minutes to a few hours) measurement of multiple saturated carbonyls and for the long-term (i.e., ≥24 hours) measurement of formaldehyde. However, the method requires the use of a pump, which is generally noisy; can become blocked and/or malfunction; is often not suitable for use in flammable environments; and needs to be calibrated, therefore requiring a more knowledgeable operator (*49*). Pumps also require a power source (permanent or battery), which can cause problems due to power loss or weak batteries. In addition, a pump may inhibit a subject's activity due to its restrictive size and weight, which may produce non-representative exposure estimates; and is not suitable for use on small children (*50*). As an alternative, several passive samplers have been developed based on the principles of Method TO-11A (*51-55*); however, these samplers have only been evaluated for formaldehyde and a couple of other carbonyls. Furthermore, DNPH-based methods have been shown to have interferences from the presence of ozone (*56*).

An alternative method for the measurement of carbonyls is the Passive Aldehydes and Ketones Sampler (PAKS) method (*46*). The PAKS method was developed and evaluated during the RIOPA study (*21*), so as to provide a passive sampler for 24- to 48-hour indoor, outdoor, and in particular, personal sampling of multiple saturated and unsaturated carbonyls. The RIOPA study was one of the first large-scale (i.e., 309 adults and 188 children) studies to evaluate personal exposure to multiple carbonyls. Initially, the RIOPA investigators measured carbonyls with an active DNPH-based method (*57*,*58*) based on U.S. EPA's Compendium Method TO-11A (*33*); however, the above mentioned short-comings of this method acted as a catalyst for some of the RIOPA researchers to develop the PAKS method.

PAKS (Figure 1) is a diffusive, tube-type, passive sampler, which utilizes DNSH to derivatize carbonyls onto a silica-based bonded C_{18} solid sorbent. The PAKS cartridges (modified solid phase extraction (SPE) tubes) are cleaned with acetonitrile (ACN); coated with a solution of DNSH, acetic acid, and ACN; and dried with nitrogen (*46*).

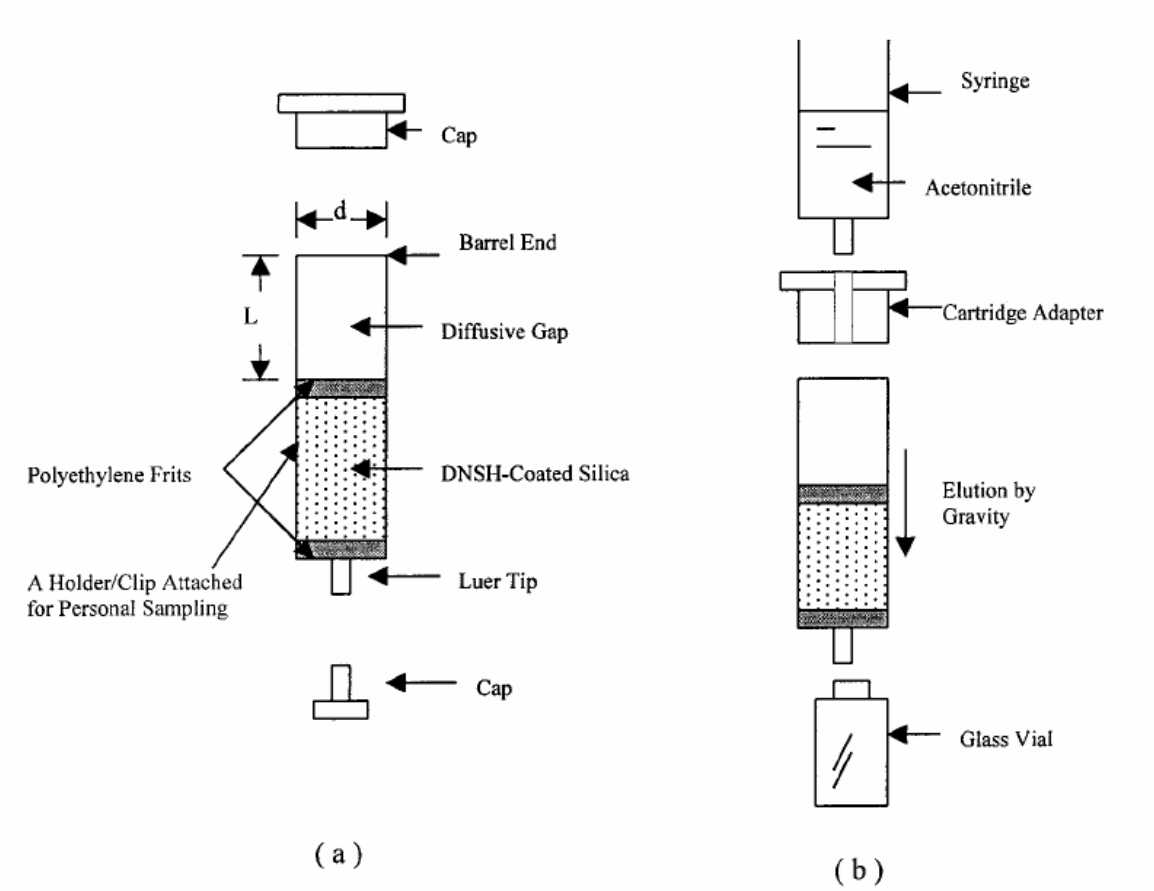


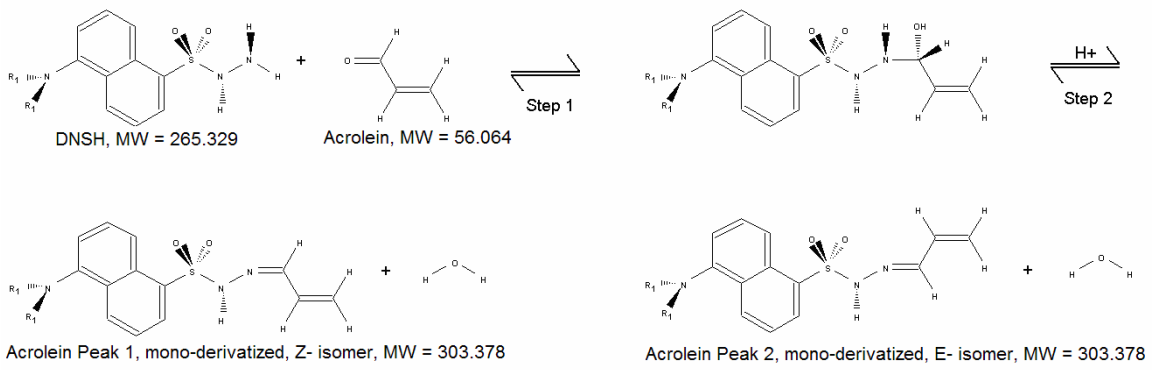
Figure 1: (a) PAKS configuration and (b) extraction schematic adopted from Zhang et al. (*46*).

Since the PAKS works on molecular diffusion, Fick's law can be approximated to the following form if the rate-limiting step for sample collection is molecular diffusion:

Equation 1: Fick's Law for the PAKS $M = D\frac{A}{L}tC_{air}$

where M = mass uptake (g), D = diffusion coefficient (cm^2/sec), A = cross sectional area of diffusion path (cm^2), L = length of diffusion path (cm), C_{air} = concentration at the end of gas gap chamber (g/cm^3), and t = time of sampling (sec) (*46*).

Once a carbonyl has diffused onto the PAKS sorbent, the carbonyl and DNSH coated on the PAKS sorbent will undergo a derivatization reaction (Scheme 2). Derivatization of carbonyl compounds with a single hydrazine (DNSH) molecule begins with a nucleophilic addition reaction at the C=O bond of the carbonyl, and the nitrogen of the hydrazine, resulting in an alcohol intermediate (Scheme 2, Step 1) (*21,40,59,60*). Subsequently, a dehydration (1,2-elimination) reaction ensues and a C=N bond is formed between the carbonyl and hydrazine, resulting in the corresponding hydrazone derivative (Schiff Base) (Scheme 2, Step 2) (*61-63*). Carbonyls, with the exception of formaldehyde and other symmetrical carbonyls, form acid catalyzed E- and Z-geometrical isomers with respect to the C=N bond, with the E isomer being the dominant hydrazone derivative (*63-65*).



Scheme 2: Carbonyl (acrolein)-DNSH derivatization reaction.

Subsequent to sampling, the carbonyl–DNSH derivatives are extracted (Figure 1) with ACN and analyzed using an HPLC-fluorescence technique, as described in detail previously (*46*). The PAKS method has been shown to have collection efficiencies of ~100% for formaldehyde and 80 - 108% for 6 other saturated aldehydes (acetaldehyde, propionaldehyde, benzaldehyde, hexaldehyde, glyoxal, and methylglyoxal) (*46*).

The PAKS method has several significant advantages over DNPH-based methods. As a passive sampling method, the PAKS method is based on diffusion principles and does not require a sampling pump to draw air through the cartridge. Therefore, the PAKS method does not suffer from the aforementioned limitations associated with a sampling pump. Although several passive DNPH-based methods do exist (*51-55*), as mentioned earlier, these methods are generally limited to the analysis of only one or two carbonyls. In addition, the PAKS method has increased sensitivity (afforded by fluorescence detection versus the UV detection often utilized for DNPH-based methods), which provides lower detection limits for the same target compounds. Furthermore, as mentioned previously, current DNPH-based methods suffer from ozone interferences (*56*), and thereby require the use of ozone scrubbers. The PAKS method is not affected by the presence of ozone (*46*) and therefore does not require the use of ozone scrubbers. Most importantly, current DNPH-based methods have proven to be unreliable for measuring unsaturated carbonyls (e.g., acrolein and crotonaldehyde) (*66-74*), as explained in a recent study that has examined the mechanisms of DNPH reactions with unsaturated carbonyls (*74*). The PAKS method indicated improved stability and recovery for acrolein (60%) and crotonaldehyde (76%) (*46*). Despite this, more development and evaluation needed to be conducted on the relatively new PAKS method (specific limitations to be discussed later), so as to optimize the method for the measurement of unsaturated carbonyls; optimize the method's sample processing procedures; optimize the method's blanks; and evaluate the method's performance.

1.1.5 Study Objectives, Rationales, and Overview

Although the PAKS method has several significant advantages over DNPH-based methods, in particular improved stability and capability of measuring unsaturated carbonyls; there was room for improving the method with additional development and evaluation. The overall goal of the current study was to further the development and optimize the PAKS method, compare the PAKS method to U.S. EPA's Compendium Method TO-11A, and to develop a DNSH-based active sampling method. The specific aims of this research were to:

Specific Aim I: Optimize the PAKS method for the measurement of unsaturated carbonyls.

Specific Aim II: Evaluate and optimize the PAKS method sample processing parameters.

Specific Aim III: Evaluate and optimize the PAKS method blanks.

Specific Aim IV: Evaluate the "final" PAKS method performance.

Specific Aim V: Evaluate the U.S. EPA's Compendium Method TO-11A for the long-term (i.e., ≥24 hours) sampling of carbonyls.

Specific Aim VI: Develop a short-term (i.e., minutes to a few hours), DNSH-based active sampling method for measuring airborne acrolein.

As part of the U.S. EPA's national air toxics monitoring program, HAPs are measured at 23 National Air Toxics Trends Stations (NATTS) in 22 cities (*75*). In addition, State and local agencies are monitoring HAPs at over 300 air toxics monitoring stations nationwide (*75*). Formaldehyde, acetaldehyde, and acrolein are three of the volatile organic compounds (VOCs) the U.S. EPA requires these sites to monitor once every 6 days, for a 24-hour period. Carbonyl concentrations are usually derived from 24-hour time-integrated samples collected with DNPH-coated solid sorbent methods based on U.S. EPA

Compendium Method TO-11A (*33*). The goal of the air toxics monitoring program is to provide data that elucidates spatial and temporal trends; supports exposure assessments; and aids in the evaluation of air quality models; all of which is ultimately aimed at supporting the reduction of public exposure to HAPs such as formaldehyde, acetaldehyde, and acrolein (*76*). Therefore, the 24-hour time-integrated carbonyl concentrations reported from air toxics monitoring sites must be accurate and reliable. However, U.S. EPA Compendium Method TO-11A, which is virtually unanimously utilized across the nation, does not have adequate acrolein collection efficiencies (~20%) (*74*). As an alternative, the PAKS method has demonstrated improved stability and recovery for acrolein (60%) and crotonaldehyde (76%) (*46*); however, for obvious reasons there was a desire to increase the acrolein and crotonaldehyde collection efficiencies to ~100%. Specific Aim I was addressed in Chapter 2, where the PAKS method was optimized so as to provide approximately 100% collection efficiencies for acrolein and crotonaldehyde while; at a minimum, maintaining the current reported collection efficiencies and limits of detection for the other carbonyls analyzed by the method. Jason Herrington, with the help of Drs. Lin Zhang and Junfeng (Jim) Zhang, accomplished this by modifying the PAKS preparation, sampling, handling, storage, analytical methods, and combinations thereof.

Although the PAKS sample processing procedures had been established in the original method (46) and during Specific Aim I, it was believed that there was room for improving these procedures by evaluating aspects that had not been assessed. Specific Aim II was addressed in Chapter 3, where Jason Herrington conducted laboratory experiments to evaluate and optimize the PAKS sample processing procedures such as the sample baking

duration, sample baking temperature, sample extraction volume, standard preparation, calibration curve, and calculations methods.

Subsequent to accomplishing Specific Aim I, the modified PAKS method was field tested in the U.S. EPA's Detroit Exposure Aerosol Research Study (DEARS); during which issues arose from the PAKS blanks. Specifically, the formaldehyde concentrations in field blanks were almost equivalent to the concentrations observed in field samples. Therefore, Specific Aim III was addressed in Chapter 4, where Jason Herrington and Dr. Lin Zhang conducted laboratory experiments to evaluate and optimize the PAKS cartridge, solvent, reagent, acid catalyst, drying procedures, and storage procedures; in an attempt to provide the lowest blank concentrations.

Considering the PAKS method had undergone several significant modifications in Specific Aims I, II, and III, the "final" (i.e., most up-to-date) PAKS method performance needed to be established. Specific Aim IV was addressed in Chapter 5, where laboratory experiments were conducted by Jason Herrington; and with the help of collaborators at the U.S. EPA and the RTI, field samples were collected during the DEARS to assess the "final" PAKS method stability, accuracy, precision, and detection limits.

DEARS was a three-year field monitoring study conducted by the U.S. EPA with the collaboration of researchers at RTI. Completed in February 2007, the study was designed to characterize spatial and temporal exposure relationships involving air toxics (in particular, formaldehyde, acetaldehyde, and acrolein), particulate matter (PM) components, PM from specific sources, and criteria pollutants in Wayne County, Michigan. As part of the study, daily (24-hour) personal, residential indoor, residential outdoor and community-based outdoor measurements were collected; with approximately 1200

participant monitoring days. Jason Herrington, Jian Tong, and Dr. Lin Zhang were responsible for preparing, shipping, extracting, and analyzing the PAKS samples for DEARS. Although DEARS produced an extensive database of indoor, outdoor, and personal formaldehyde, acetaldehyde, and acrolein concentrations; only the PAKS quality assurance (QA)/quality control (QC) data was used in this dissertation.

The original PAKS method (*46*) was compared with the U.S. EPA Compendium Method TO-11A during the RIOPA study (*21*); and results indicated that the two methods agreed reasonably well for some saturated carbonyls. However, due to the significant method modifications made for Specific Aim I, the U.S. EPA indicated there was a desire to reconfirm the PAKS agreement with U.S. EPA Compendium Method TO-11A via a field study. Considering the PAKS method had been shown to have acceptable collection efficiencies for the 24- to 48-hour collection of multiple saturated carbonyls (*46*), and the current body of literature did not demonstrate the same capabilities for U.S. EPA Compendium Method TO-11A; Specific AIM V was addressed in Chapter 6, where laboratory experiments were conducted by Jason Herrington, with the help of Shamayne Cumberbatch, to evaluate the 24- and 48-hour formaldehyde and acetaldehyde collection efficiencies for DNPH-based methods.

Although the original PAKS method (*46*) was modified for improved measurement of acrolein (Specific Aim I, Chapter 2), because the method is passive (with relatively low sampling rates) it can not provide the time-resolution that may be needed to understand temporal acrolein variations. Given that the active DNPH-based methods do not work well for unsaturated carbonyls, it was believed using DNSH as an alternative substrate may prove to be effective for measuring acrolein, based on the PAKS success in measuring

acrolein. With the help of Vaibhav Kadakia, Jason Herrington conducted laboratory and field experiments to address Specific Aim VI in Chapter 7, which reports the experimental designs, methods, results, and discussion on the suitability of a DNSH-based active sampling method for measuring acrolein.

Chapter 2

Optimization of the PAKS Method for Measuring Airborne Acrolein and Other Unsaturated Aldehydes*

2.1 Abstract

The PAKS method was developed to measure airborne carbonyls by derivatizing the carbonyls with DNSH on a solid sorbent (*46*). The method collection efficiencies were ~100% for most saturated carbonyls, but were significantly lower for unsaturated carbonyls. In this chapter, the mechanisms of DNSH reactions with unsaturated carbonyls were examined, with a focus on acrolein. With a better understanding of these mechanisms, modifications were made to the sampling substrate conditions and HPLC analysis conditions of the original PAKS method, resulting in substantially improved collection efficiencies for acrolein and crotonaldehyde. Evaluated under a variety of conditions (temperature, humidity, presence of ozone), the modified PAKS method had a collection efficiency of 99% ± 5% for acrolein (N = 36) and 96% ± 20% for crotonaldehyde (N = 6). The acrolein-DNSH derivative was stable within 9.6% of the initial amount, after 14 days of storage at 4°C, on the collection medium; and stable within 2.8% of the initial amount, after 16 days of storage at room temperature, in extract.

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* This chapter was modified from Herrington, J.; Zhang, L.; Whitaker, D.; Sheldon, L.; Zhang, J. J. Optimizing a dansylhydrazine (DNSH) based method for measuring airborne acrolein and other unsaturated carbonyls. *J. Environ. Monit.* **2005**, *7*, 969-976.

2.2 Introduction

Airborne acrolein is produced as a byproduct from the combustion of fuel and tobacco, and is released from several manufacturing processes (*6,77*). Acrolein is extremely acrid and irritating to mucous membranes (*11*). Reported values for odor thresholds range from 0.16 ppm (0.4 mg/m^3) to 0.21 ppm (0.5 mg/m^3) (*78,79*). Airborne acrolein is considered by the U.S. EPA to be HAP (*12*). The health risks from environmental acrolein exposure are poorly understood, largely due to the lack of suitable methods for measuring this compound at typical environmental levels.

The PAKS method shows promise for analyzing environmental levels of acrolein, as well as nine other carbonyls (*46*). However, the method has relatively low collection efficiencies for acrolein (60%) and crotonaldehyde (76%) (*46*). The objective of the current chapter was to optimize the PAKS method for the measurement of acrolein and crotonaldehyde. In the present chapter, the chemical mechanisms that affect the PAKS method collection efficiencies for unsaturated carbonyls were investigated in detail, and the optimal reaction conditions for measuring acrolein and crotonaldehyde were determined.

2.3 Materials and Methods

2.3.1 Sampling Medium Optimization

To increase the PAKS method collection efficiencies for unsaturated carbonyls, a number of in-depth experiments were conducted. With regard for the carbonyl-DNSH reaction mechanisms, substrate conditions such as acidity, DNSH coating amount, and the presence of a hygroscopic agent and/or inhibitor were investigated. The experiments are described below.

2.3.1.1 (1) Coating Solution Acidity

Carbonyl derivatization with hydrazines (e.g., DNSH) is a reversible reaction, and thereby requires an acidic pH to catalyze the forward derivatization reaction (*59,60,80*). To evaluate the effects of coating solution acidity on the PAKS performance, cartridges were coated with 2 mL of ACN (J.T. Baker, Phillipsburg, NJ) solutions containing 5 mg/mL DNSH (97%, Fluka, Suwanee, GA, USA) and glacial acetic acid (J.T. Baker, Phillipsburg, NJ) in concentrations of: 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, and 0.5% (v/v). In addition cartridges were coated with 2 mL of ACN solutions containing 5 mg/mL DNSH and the following pH buffer solutions: pH 3 buffer at 10 mM concentration, and pH 4 buffers at 10, 20, and 40 mM concentrations. These pH buffer strengths and concentrations were chosen based on what the literature indicated worked well for carbonyl-hydrazine derivatization (*53*). It is important to note that the buffer solutions were first made in deionized (DI) water, 0.1 M sodium citrate-dihydrate and 0.1 M citric acid-monohydrate, and then added into the ACN solutions at the necessary ratios to achieve the desired buffer pH and strength.

2.3.1.2 (2) DNSH Coating Amount

The reversibility of the carbonyl-DNSH reaction requires a sufficient number of DNSH molecules to promote the forward derivatization reaction. To evaluate the effects of DNSH coating amount on the PAKS performance, cartridges were coated with 2 mL of ACN solutions containing 1, 2.5, 5, 10, 20, and 40 mg/mL DNSH. All of the coating solutions contained 0.1% glacial acetic acid. In addition, the amount of DNSH retained on each cartridge was indirectly quantified by collecting and analyzing the coating eluates. The amount of DNSH retained on the cartridge was determined by subtracting the DNSH eluate concentration from the DNSH coating solution concentration. Subsequent to determining the optimum DNSH coating amount, the optimum coating volume was determined by

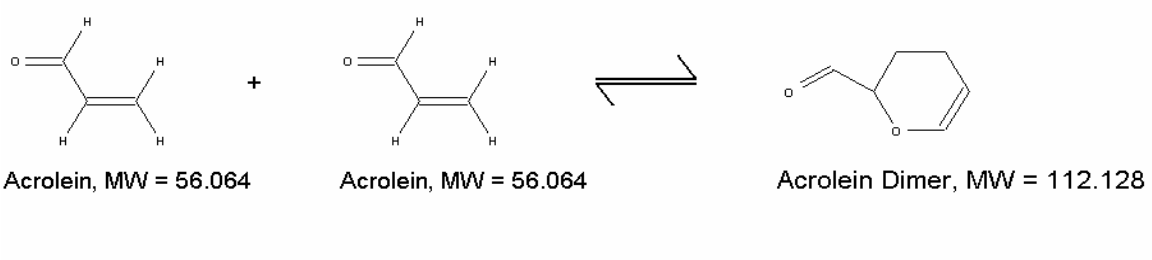
coating cartridges with 1.0, 1.5, 2.0, 2.5, and 3.0 mL of an ACN solution containing 5 mg/mL DNSH and 0.1% glacial acetic acid.

2.3.1.3 (3) 1,3-Butanediol

The absence or presence of water vapor may negatively affect the reaction between hydrazines and carbonyls (*60,64*). Therefore a set of experiments were conducted to evaluate whether the addition of a hygroscopic agent, 1,3-butanediol, can facilitate the reaction and consequently improve the PAKS collection efficiency for acrolein. In this set of experiments, cartridges were coated with 2 mL of ACN solutions containing 1,3-butanediol (99+%, anhydrous, ALDRICH Chemical Co., Inc.) in concentrations of 1, 5, and 10% (v/v). All coating solutions contained 5 mg/mL DNSH and 0.1% glacial acetic.

2.3.1.4 (4) Hydroquinone

Acrolein is prone to forming a cyclic dimer (*71,72*) (Scheme 3), which may inhibit its ability to react with DNSH. Hydroquinone is typically used as a polymerization inhibitor for acrolein. To evaluate whether the addition of hydroquinone and the concentration of hydroquinone added to the collection medium facilitates the reaction between acrolein and DNSH, cartridges were coated with 2mL of ACN solutions containing hydroquinone (99%, ALDRICH Chemical Co., Inc.) in 0, 1, 2.5, and 5% (w/w) concentrations. All the coating solutions for this set of experiments contained 5 mg/mL DNSH and 0.1% glacial acetic in ACN.



Scheme 3: Acrolein cyclic dimer formation.

2.3.1.5 (5) 1,3-Butanediol & Hydroquinone

To evaluate the combined effects of the hygroscopic agent and the polymerization inhibitor, cartridges were coated with 2 mL of an ACN solution containing 5% hydroquinone (w/w) and 10% 1,3-butanediol (v/v), which were the optimum concentrations determined from the experiments above. The solution contained 5 mg/mL DNSH and 0.1% glacial acetic acid.

In all of the above experiments, carbonyl-DNSH derivatives were prepared *in situ*, by spiking a known amount of carbonyls into the DNSH-coated cartridges. In doing so, the cartridges were spiked with 10 μL of ACN solutions containing known concentrations of carbonyls using a 25 μL GASTIGHT (HAMILTON CO.) syringe.

2.3.1.6 Analysis Optimization

Sample analysis was performed using an HPLC system (Waters 600E System Controller, Waters 717 Autosampler, Waters 470 Programmable Fluorescence Detector, and Waters Nova-Pak C_{18} column (3.9×300 mm, 60 Å, 4 um) and a guard cartridge (Nova-Pak, 4 μm, 60Å, C_{18} Guard-Pak, SUPELCO). Although the principle of the PAKS analysis method remained unchanged from its original method (*46*), several modifications were made in the current analysis method. Numerous tests were conducted on the mobile phase gradient program, in order to best resolve the elution of 15 carbonyl-DNSH derivatives. These tests

included the addition and/or alteration of dibasic potassium phosphate powder (K_2HPO_4) (98%, J.T. Baker), monobasic potassium phosphate crystal (KH_2PO_4) (99.6%, J.T. Baker), HPLC-grade tetrahydrofuran (THF) (99.9%, Fisher Scientific), triflouroacetic acid (TFA), ACN, DI water, analytical columns, and the excitation and emission wavelengths of the fluorescence detector. The final analytical program (Table 1) was able to resolve 15 carbonyl-DNSH derivatives (Figure 2).

Acrolein-DNSH and other carbonyl-DNSH derivatives were identified and quantified using their corresponding carbonyl-DNSH derivatives (standards) that were prepared *in situ*, by spiking a known amount (typically ~1.5 µg) of carbonyl(s) onto a PAKS cartridge. Although labor intensive and time consuming, this method of standard preparation takes into account matrix effects that may otherwise be missed when using pure derivative solutions. For example, the formation of E- and Z- geometrical isomers; which if unaccounted for, could result in quantitative errors (*53,65,81*) . In addition, there are no methods or sources available for pure carbonyl-DNSH derivatives, as there are for carbonyl-DNPH derivatives. The spiked PAKS cartridge was then capped and stored for 24 hours at room temperature. The PAKS was then baked in an oven at 50°C for 1 hour to promote the forward carbonyl-DNSH derivatization reaction. Subsequently, the PAKS was extracted and a series of calibration standards was generated by diluting the primary standard to generate a secondary standard. This series of dilution was repeated to generate a series of calibration standards with concentrations of 0.750, 0.375, 0.188, 0.094, 0.047, and 0.023 µg/mL.

Table 1: HPLC-fluorescence analytical conditions for the optimized PAKS method.

Time (min)	% A (pH 7.80): Water/Acetonitrile/Tetrahydrofuran 80/10/10 v/v with 0.68 g/L KH_2PO_4 and 3.48 g/L K_2HPO_4	% B (pH 8.70): Water/Acetonitrile/Tetrahydrofuran 40/30/30 v/v with 0.68 g/L KH_2PO_4 and 3.48 g/L K_2HPO_4
0	100	0
30	70	30
60	60	40
80	60	40
85	100	0
Flow rate	1 mL/min	
Injection volume	20 µL	
Detector	Excitation wavelength 250 nm	Emission wavelength 525 nm

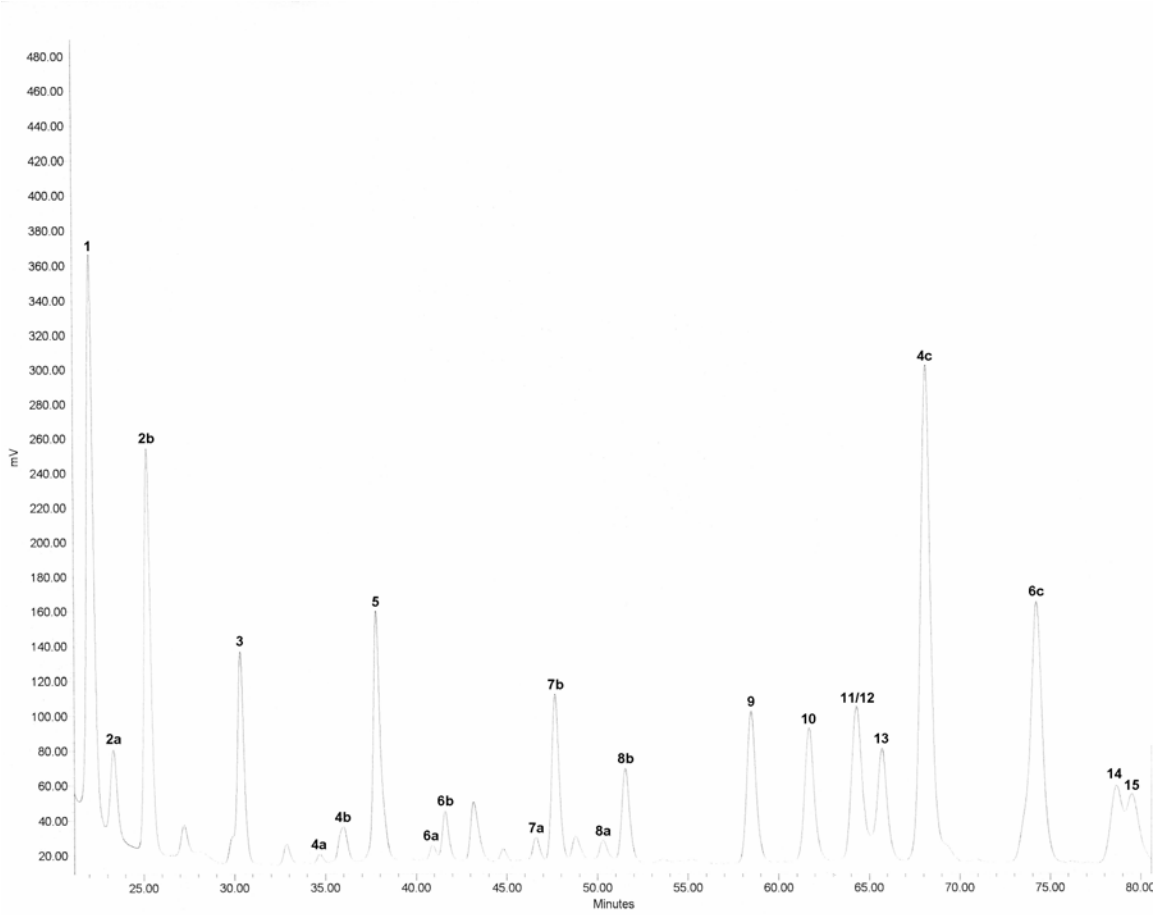


Figure 2: HPLC chromatograph of 15 carbonyl-DNSH derivatives analyzed with the optimized PAKS method. 1. Formaldehyde, 2a. Acetaldehyde (Z-isomer), 2b. Acetaldehyde (E-isomer), 3. Acetone, 4a. Acrolein (mono-derivatized, Z-isomer), 4b. Acrolein (mono-derivatized, E-isomer), 4c. Acrolein (di-derivatized), 5. Propionaldehyde, 6a. Crotonaldehyde (mono-derivatized, Z-isomer), 6b. Crotonaldehyde (mono-derivatized, E-isomer), 6c. Crotonaldehyde (di-derivatized), 7a. Butyraldehyde (Z-isomer), 7b. Butyraldehyde (E-isomer), 8a. Benzaldehyde (Z-isomer), 8b. Benzaldehyde (E-isomer), 9. Isovaleraldehyde, 10. Valeraldehyde, 11. o-Tolualdehyde, 12. m-Tolualdehyde, 13. p-Tolualdehyde, 14. Hexaldehyde, 15. 2,5-Dimethylbenzaldehyde.

2.3.2 Evaluation

2.3.2.1 Stability

Previous studies have indicated that poor acrolein collection efficiencies were associated with instability of the derivatives on the collection medium or in the extract (*68,71,72,74*). Therefore, tests were conducted to determine the stability of the acrolein-DNSH

derivatives on the PAKS cartridges and in the ACN extracts. For the cartridge stability experiment cartridges were coated with the finalized optimal coating procedure (2 mL of an ACN solution containing 5 mg/mL DNSH, 0.1% glacial acetic acid, and 5% (w/w) hydroquinone) and then spiked the cartridges with an acrolein standard. These cartridges were then stored at 4° C. Two of these spiked cartridges were extracted and analyzed at a time on days 1, 4, 7, 10, and 14 post spiking. For the extract stability experiment, several cartridge extracts containing acrolein-DNSH derivatives were analyzed (on Day 1). These same extracts, stored at room temperature (~25° C), were reanalyzed at 2, 6, 9, 12, and 16 days post extraction.

2.3.2.2 Collection Efficiency

A dynamic atmosphere generation system, as schematically shown in Figure 3, was used to generate test atmospheres of acrolein and crotonaldehyde. Gas-phase acrolein and crotonaldehyde were generated with capillary diffusion tubes (VICI Metronics Inc.). The diffusion tubes were placed in Oven #2, which was set at the desired temperature. The concentrations delivered were determined by the mass lost from the diffusion tube and the total flow rate of the dynamic atmospheric generation system. The collection efficiency was defined as the ratio of the carbonyl concentration, determined using the PAKS method, to the known carbonyl concentration generated in the dynamic atmosphere generation system. Using this system, the collection efficiencies of the modified PAKS method were determined for acrolein and crotonaldehyde (i.e., using the optimized cartridge coating procedures and the optimized analysis procedures) under four conditions (see Table 2).

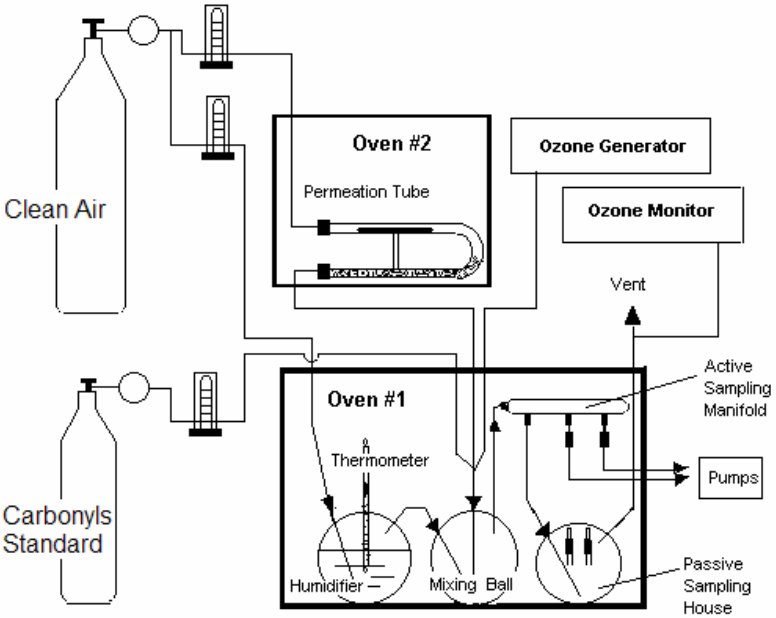


Figure 3: Dynamic atmosphere generation system.

Table 2: Experimental conditions and collection efficiencies for the optimized PAKS method. Determined using the dynamic atmosphere generation system.

Experimental Condition	Concentration Generated ($\mu g/m^3$)	Mean Concentration Measured ($\mu g/m^3$)	Collection Efficiency (%)[f]	95% Confidence Interval
Acrolein (High Concentration)[a, c]	340	326	96	(92, 100)
Acrolein (Low Concentration)[b, c]	77.0	79.3	103	(100, 105)
Acrolein (Ozone)[b, c, d]	77.0	77.8	101	(98, 104)
Acrolein (Relative Humidity) [a, e]	69.0	66.9	97	(89, 104)
Crotonaldehyde[a, c]	89.0	85.4	96	(81, 112)

[a] Three (3) pairs of samples (n = 6) with temperature = 30°C, face velocity = 0.01 m/s, and exposure duration = 24 hr.
[b] Six (6) pairs of samples (n = 12) with temperature = 30°C, face velocity = 0.01 m/s, and exposure duration = 24 hr.
[c] Relative humidity = 10%.
[d] Ozone concentration = 250 ppb.
[e] Relative humidity ranging from 10 – 95%.
[f] Collection Efficiency (%) = Mean Concentration Measured / Concentration Generated x 100.

2.4 Results and Discussion

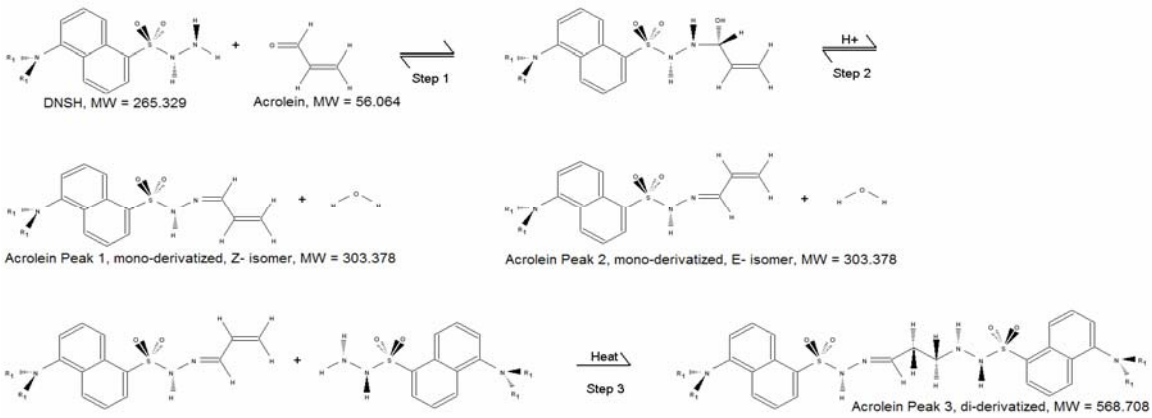
2.4.1 Carbonyl-DNSH Derivatization

Recall that derivatization of carbonyl compounds with a single hydrazine (DNSH) molecule begins with a nucleophilic addition reaction at the C=O bond of the carbonyl, and the nitrogen of the hydrazine, resulting in an alcohol intermediate (Scheme 4, Step 1) (*21,40,59,60*). Subsequently, a dehydration (1,2-elimination) reaction ensues and a C=N bond is formed between the carbonyl and hydrazine, resulting in the corresponding hydrazone derivative (Schiff Base) (Scheme 4, Step 2) (*61-63*). However, unsaturated carbonyls can be further derivatized with a second hydrazine molecule via another addition

reaction at the C=C bond (Scheme 4, Step 3). This reaction mechanism was not well understood in the original study for developing the PAKS method (*46*).

A more careful HPLC analysis of acrolein-DNSH derivatives found three chromatographic peaks (see Figure 2). Pereira et al. also noticed three chromatographic peaks corresponding to the acrolein-DNSH derivative (*61*). LC-MS/MS analysis confirmed that the first two peaks corresponded to the E- and Z- isomers of an acrolein derivative with one DNSH molecule (mono-derivatized acrolein, MW = 303) and the third peak corresponded to the acrolein derivative with two DNSH molecules (di-derivatized acrolein, MW = 568). (The same di-derivatized product has recently been suggested for acrolein-DNPH derivatization (*74*). Schulte-Ladbeck and coworkers also observed tri-DNPH derivatives and another uncharacterized product; however, similar carbonyl-DNSH products were not observed in the current study or in the study by Pereira et al. (*61*).

In the original PAKS method, only one peak was observed because the E- and Z-isomers were not resolved and the third peak was not recognized. Hence, in the original PAKS method the determination and quantification of acrolein was based only on the peak of the mono-derivatized acrolein, which may undergo further derivatization during cartridge and/or extract storage. Switching the analysis from the mono-derivatized acrolein to the ultimate derivative (i.e., the di-derivatized acrolein) seemed to be a better approach to getting more stable results for acrolein analysis. Moreover, the di-derivatized acrolein afforded increased analytical sensitivity, because of the additional fluorescing DNSH molecule. Consequently, the majority of this chapter focuses on optimizing various conditions to maximize the formation and stability of the di-derivatized acrolein.



Scheme 4: Acrolein-DNSH derivatization. Step 3 may be a reversible step; however, this was not evaluated in the current chapter.

2.4.2 Acidity Effects

Carbonyl-DNSH derivatization is a reversible reaction, and thereby requires a sufficient number of hydrogen ions to catalyze the dehydration reaction (Scheme 4, Step 2) and promote the forward derivatization reaction (*59,60,80*). In the original PAKS method development, Zhang and coworkers tested several acids stronger than acetic acid, including phosphoric (H_3PO_4) and hydrochloric (HCl), for their abilities to promote carbonyl-DNSH derivatization. However, the test results were not reported in the original paper (*46*). These stronger acids were found to have resulted in both a visible (loss of characteristic yellowish color) and analytical (loss of active DNSH in HPLC analysis) destruction of DNSH. Consequently, DNSH treated with stronger acids decreased the ability to form stable hydrazone derivatives. Glacial acetic acid was shown to be a more ideal acid for carbonyl-DNSH derivatization (*46*). Acetic acid and pH buffers were further evaluated for their ability to maximize the reactions to form stable di-derivatized acrolein. The results from the acetic acid and citrate buffer tests strongly supported the notion that acids and pH buffers provide acrolein-DNSH derivatization reactions with the essential

hydrogen ions. Both an increase in buffer strength (concentration) and/or an increase in acidity resulted in an increase in di-derivatized acrolein and a proportional decrease in mono-derivatized acrolein. It is important to note that hydrogen ions only catalyze the dehydration reaction (Scheme 4, Step 2) and promote the forward derivatization reaction at Step 2; thereby providing the opportunity for the mono-derivatized acrolein to then engage in an addition reaction at the C=C bond with an additional DNSH molecule (Scheme 4, Step 3).

The pH buffers and acetic acid both appeared to be suitable hydrogen donors for the acrolein-DNSH derivatization reaction; however, it was important to determine which hydrogen donor provided the most stable acrolein-DNSH derivative. As stated earlier, previous studies associated lower acrolein collection with the instability of acrolein and/or the acrolein-hydrazone derivative on the collection medium (cartridge) and/or the extract (*68,71,72,74*). Therefore, the stability of the acrolein-DNSH derivative on the cartridge for both the optimum pH buffer (pH 3, 10 mM) and the optimum acetic acid concentration (0.1%) were evaluated.

The addition of pH buffers resulted in a decay of the acrolein-DNSH derivative, and the acetic acid provided a relatively more stable di-derivatized acrolein-DNSH derivative. This observation was consistent with the fact that highly exothermic acrolein polymerization may occur in the presence of traces of acids or strong bases (*82*). For this reason, pH buffers were not selected for the PAKS coating solution. Beyond 0.1% glacial acetic acid the effects were negligible; hence the optimum acetic acid concentration in the coating solution was determined to be 0.1% (v/v).

2.4.3 DNSH Coating Amount Effects

As shown in Scheme 4, the formation of di-derivatized carbonyls requires an additional DNSH molecule (Step 3). Results indicated that an increase in DNSH concentration in the PAKS coating solution promoted an increase in di-derivatized acrolein and a proportional decrease in mono-derivatized acrolein. However, increasing the DNSH coating solution concentration beyond 5 mg/mL posed a problem for chromatography, as this resulted in a large DNSH peak, which overlapped with the formaldehyde peak. Given the fact that the mono-derivatized acrolein was negligible (i.e., virtually non-detect) in samples, concentration calculations were based only on the di-derivatized acrolein.

Results demonstrated that all of the coating volumes had relatively similar affects on the PAKS performance. Considering the above observation and the fact that the PAKS cartridge can hold approximately 2 mL of the coating solution in the diffusion gap; a coating solution with 5 mg/mL DNSH, and a coating volume of 2 mL was chosen as the optimal conditions for the modified PAKS method.

Results demonstrated that the DNSH concentration of eluate collected from coated PAKS during the coating procedure was ~80% of the DNSH concentration in the PAKS coating solution. This correlates to ~20% of the DNSH in the coating solution retaining on the silica-based bonded C_{18} sorbent. A 5 mg/mL DNSH coating solution concentration and a 2-mL coating volume correlates to 2.52 mg or ~ 9.51×10^{-6} moles of DNSH coated on each PAKS cartridge. The retained DNSH was ~100% extractable with ACN.

2.4.4 Hydroquinone Effects

Current literature indicates that vapor-phase acrolein will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals, ozone, and nitrate radicals; the half-lives for these reactions in air are estimated to be 20 hours, 15 days, and 28 days,

respectively (*77*). Liquid-phase acrolein is very reactive and in the absence of an inhibitor, highly exothermic polymerization occurs at room temperature, catalyzed by light and air. Highly exothermic polymerization also occurs in the presence of traces of acids or strong bases (*82*). Risner and Martin, and Risner attributed poor acrolein-DNPH collection efficiency to the formation of a dimer between two acrolein molecules (2-formyl-3,4-dihydro-2H-pyran) (Scheme 3) prior to derivatization (*71,72*). Hydroquinone is often used as an inhibitor, stabilizer, antioxidant, or intermediate; and is typically added to liquid acrolein as an inhibitor of polymerization (0.1 - 0.25% by weight) (*83,84*). In 1978, Hurley and Ketcham described the use of hydroquinone-treated carbon as a means for determining airborne acrolein (*85*).

Considering hydroquinone acts as an inhibitor of acrolein polymerization, and mimicking Hurley and Ketcham's technique, hydroquinone was added to the PAKS coating solution. As shown in Figure 4, the addition of hydroquinone in the PAKS coating solution promoted an increase in di-derivatized acrolein and a proportional decrease in mono-derivatized acrolein. Hydroquinone was only soluble in the ACN coating solution up to 5% (w/w). Therefore, 5% hydroquinone was added to the coating solution. The enhancement in the di-derivatized acrolein response by the hydroquinone addition may result from hydroquinone polymerization inhibition, antioxidant capability, and/or simply H-bonding stabilization of ionic transitions states.

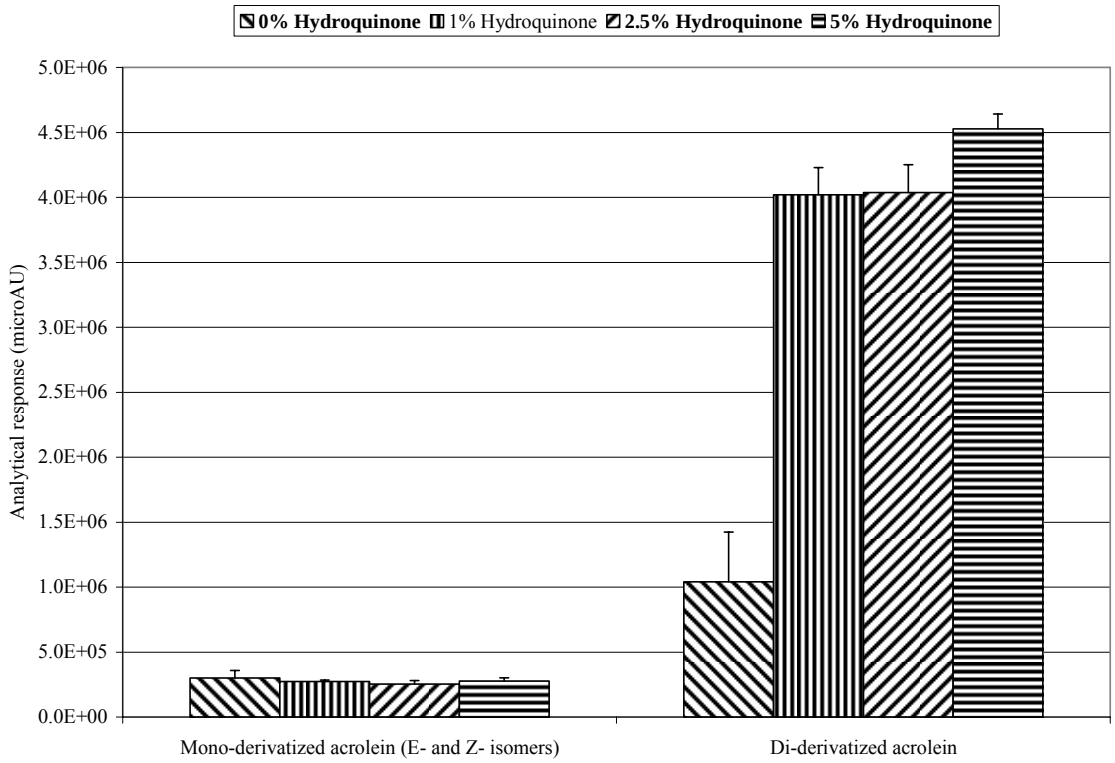


Figure 4: Effects of hydroquinone on the PAKS performance. Cartridges (N = 2 for each concentration) were coated with 2 mL of ACN solutions containing 5 mg/mL DNSH, 0.1% glacial acetic acid, and the polymerization inhibitor hydroquinone in 1, 2.5, and 5% (w/w) concentrations. All cartridges were spiked, stored (4°C), extracted, and analyzed under the same conditions. Y error bars represent difference amongst duplicate samples.

2.4.5 Collection Efficiency and Stability

The optimum PAKS coating procedures were determined to be 2 mL of an ACN solution containing 5 mg/mL DNSH, 0.1% acetic acid (v/v), and 5% (w/w) hydroquinone. As shown in Table 2, the optimum PAKS method provided close to 100% collection efficiencies for both acrolein and crotonaldehyde, under all RH levels (10% – 95%) and in the presence of ozone (250 ppb). Di-derivatized acrolein on the PAKS cartridge was stable within 9.6% of the initial amount, after 14 days of storage at 4°C (Figure 5). Di-derivatized acrolein in the extract was stable within 2.8% of the initial amount, after 16 days of storage at room temperature (Figure 6).

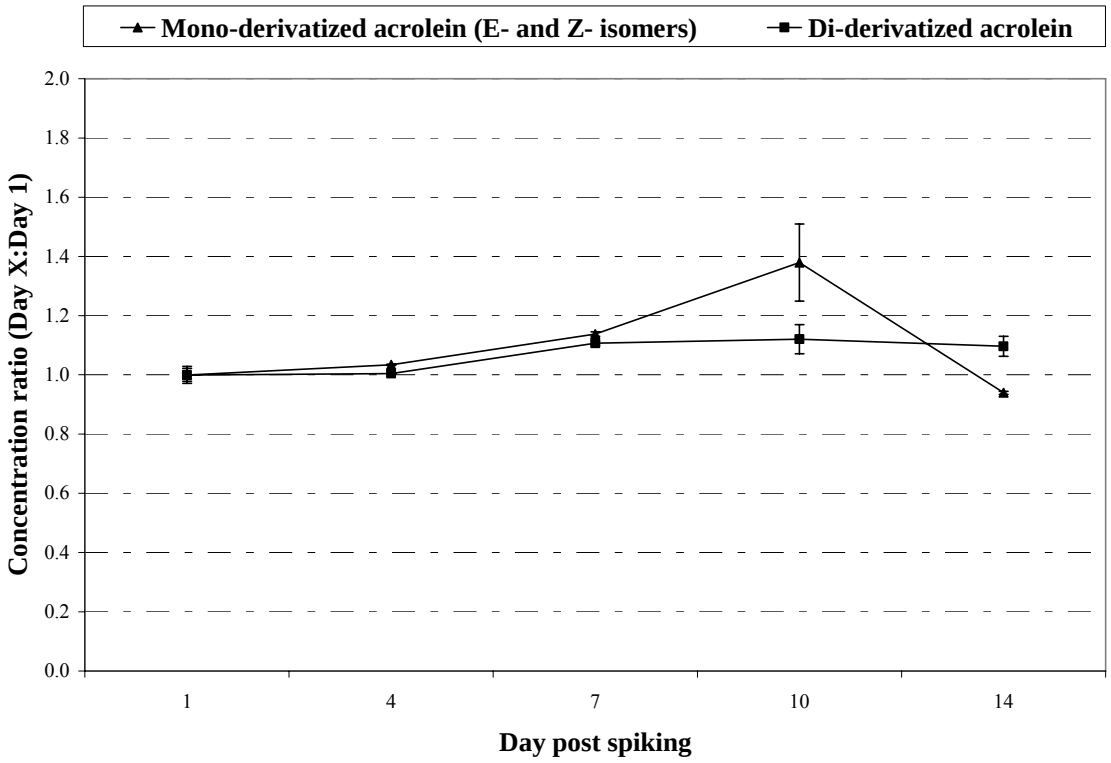


Figure 5: Stability of acrolein-DNSH derivative on the PAKS cartridge. All cartridges (N = 2 for each day) were spiked, stored (4°C), extracted, and analyzed under the same conditions. Y error bars represent the difference amongst duplicate samples.

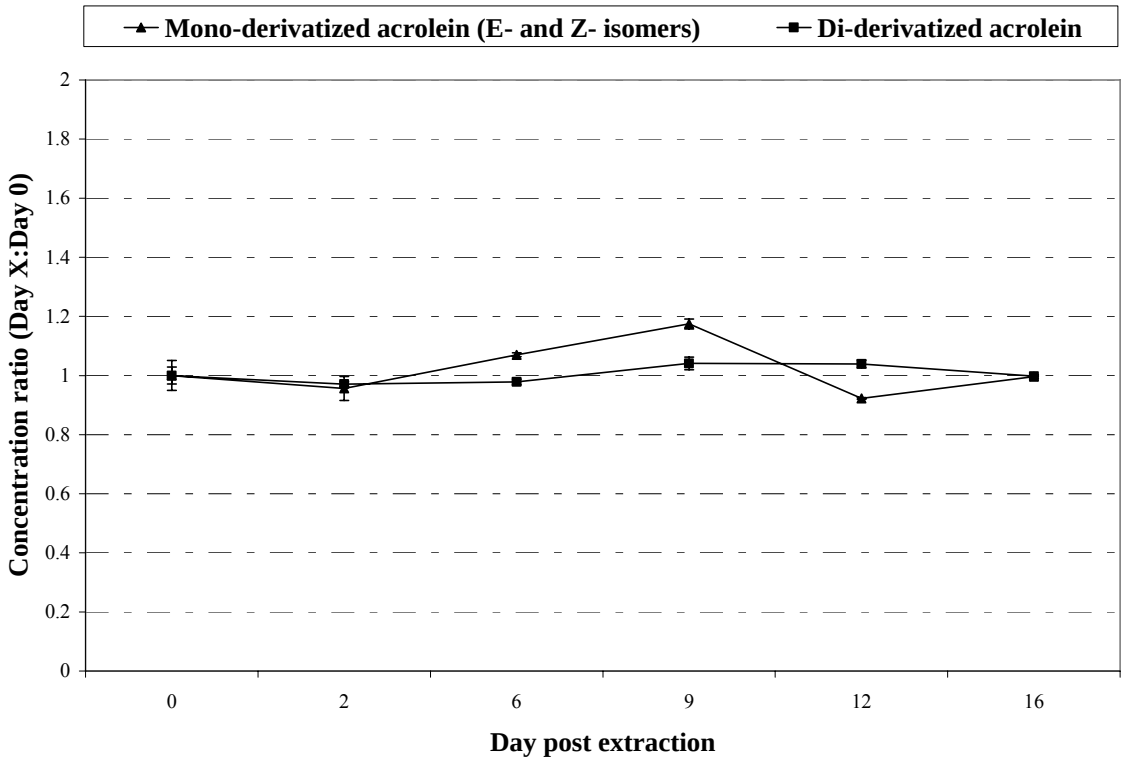


Figure 6: Stability of acrolein-DNSH derivative in ACN extract. All cartridges (N = 2 for each day) were spiked, stored (~25°C), extracted, and analyzed under the same conditions. Y error bars represent the difference amongst duplicate samples.

Arnst and Tejada, and Smith et al. demonstrated that ozone reacts and interferes negatively with both DNPH and its hydrazone derivatives (*56,86*). However, Arnst and Tejada also demonstrated that C_{18} cartridges did not appear to exhibit this phenomenon, but the presence of ozone did produce extraneous HPLC peaks (*56*). As shown in Table 2, the presence of ozone at 250 ppb did not have adverse effects on the collection efficiency of di-derivatized acrolein. This is consistent with the observation by Rodler et al. that ozone is not a significant interference so long as DNSH is in substantial excess over the carbonyl compounds being derivatized (*64*). In addition, the presence of ozone at 250 ppb did not appear produce extraneous HPLC peaks in blank cartridges.

Zhang et al. previously determined the relative humidity (RH) effects on the PAKS sampling rates, using the dynamic dilution system (*46*). The results from those experiments indicated that the changes in the PAKS sampling rates were within 8% for a wide range of RH (10% to 90%). The results from the present research indicated that the modified PAKS collection efficiency for di-derivatized acrolein was stable within ±9.2% over a relative humidity range of 10% - 95%. This was consistent with the fact that the silica in PAKS is coated with reversed phase (non-polar/hydrophobic) C_{18}; therefore, water vapor is repelled from the surface (on which DNSH is coated) and sorbed into the bulk silica, such that water vapor interference is kept to a minimum.

Grosjean and Grosjean demonstrated poor collection efficiency of carbonyls on C_{18} cartridges when the RH was low (i.e., 3 - 7%) (*60*); however, this should only be of concern in a limited number of applications. Levin and coworkers' described the process where glycerin was added to sampling cartridges for water retention to resolve the low RH phenomena (*87*); and Liu and coworkers' observed an increase in acrolein collection efficiency when an alternative hygroscopic agent, 1,3-butanediol, was added in replace of glycerol (*53*). In the present study, the addition of the hygroscopic agent 1,3–butanediol had limited effects on the acrolein collection efficiency. In a set of experiments, 1,3-butanediol was added to the coating solution, and as shown in Figure 7, the addition of 1,3-butanediol did promote an increase in the di-derivatized acrolein and a proportional decrease in mono-derivatized acrolein. It is not clear if this observation was the direct result of 1,3-butanediol's hygroscopic properties or 1,3-butanediol has some H-bonding stabilization of ionic transition states. However, results from the 1,3-butanediol and hydroquinone experiments, indicated that when both agents were present, the effects of

1,3-butanediol was negligible compared to the effect of hydroquinone alone (see Figure 8). Since an additional agent may have the potential for adverse side effects, which were not tested in the current study, it was determined that there were no compelling benefits to include 1,3-butanediol on the sampling medium.

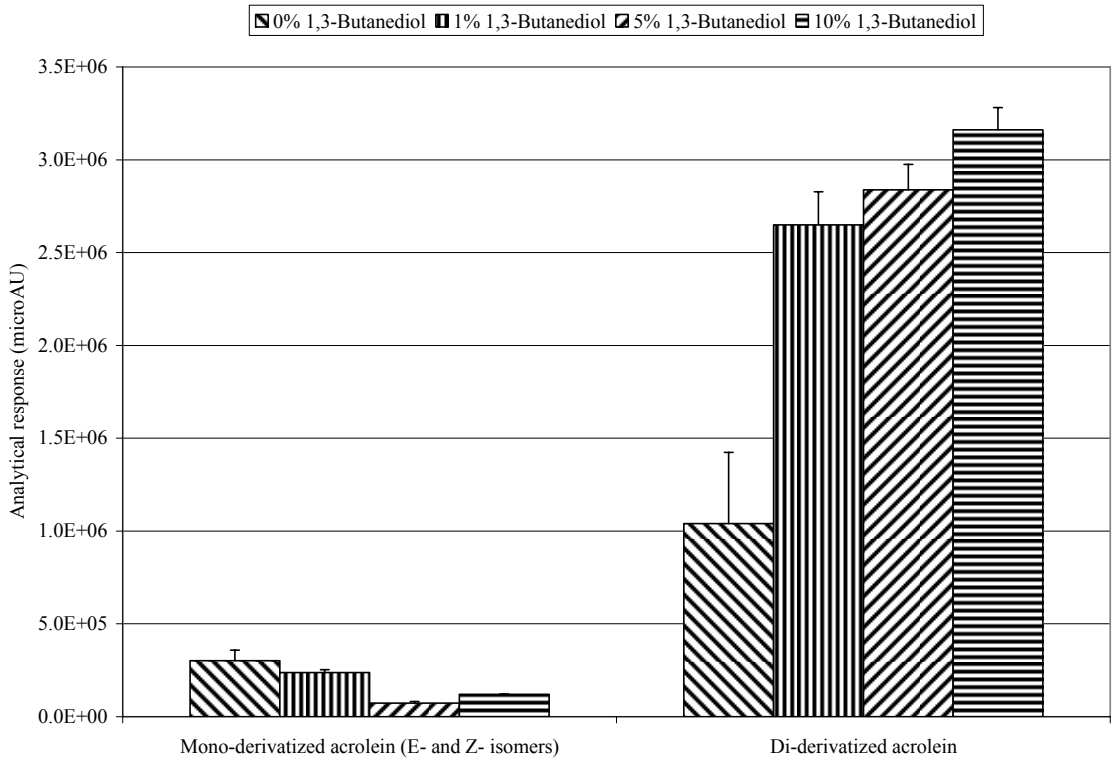


Figure 7: Effects of 1,3-butandiol on the PAKS performance. Cartridges (N = 2 for each concentration) were coated with 2 ml of coating solutions containing 5 mg/mL DNSH, 0.1% glacial acetic acid, and 1,3-butanediol in 1, 5, and 10% (v/v) concentrations. All cartridges were spiked, stored (4°C), extracted, and analyzed under the same conditions. Y error bars represent the difference amongst duplicate samples.

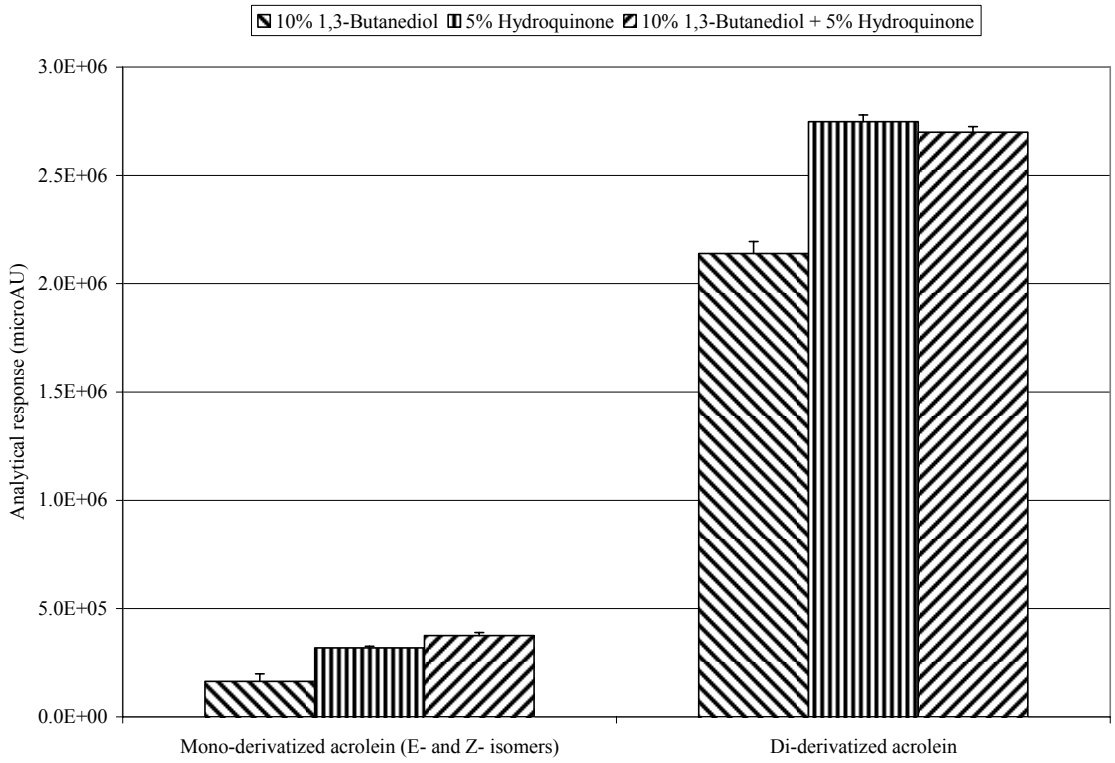


Figure 8: Combined effects of 1,3-butanediol and hydroquinone on the PAKS performance. Cartridges (N = 2 for each condition) were coated with 2 mL of ACN solutions containing 5% hydroquinone (w/w), and 10% 1,3-butanediol (v/v); 5% hydroquinone, and 10% 1,3-butanediol (v/v), with 5 mg/mL DNSH, and 0.1% glacial acetic acid. All cartridges were spiked, stored (4°C), extracted, and analyzed under the same conditions. Error bars represent standard deviation. Y error bars represent the difference amongst duplicate samples.

Zhang and coworkers previously determined the temperature effects on the PAKS sampling rates, using the dynamic atmosphere generation system at three temperature levels (*46*). The results indicated excellent agreement between the experimentally determined sampling rates and theoretically calculated sampling rates within a tested temperature range of 20°C to 40°C. It is believed that the modifications of the PAKS coating and analysis procedures should not change the sampling rates of the PAKS (Table 3). Recall Chapter 1, Equation 1, where the PAKS sampling rates are governed by the carbonyl diffusion coefficient (cm^2/sec), the cross sectional area of the PAKS diffusion

path (cm^2) and the length of the PAKS diffusion path (cm) (D(A/L) is considered the sampling rate as it is in units of cc/sec). The current modifications did not affect the carbonyl diffusion coefficient, the cross sectional area of the PAKS diffusion path, and the length of the PAKS diffusion path. Therefore, the PAKS sampling rates should remain the same.

Table 3: Theoretical PAKS sampling rates (mL/min)[a] at 0 – 40°C.

Carbonyl Compound	Theoretical PAKS Sampling Rate (mL/min)[a]						
	0°C	10°C	20°C	25°C	30°C	35°C	40°C
Acrolein	4.08	4.31	4.54	4.66	4.78	4.89	5.01
Crotonaldehyde	3.53	3.73	3.92	4.03	4.13	4.23	4.33

[a] Theoretical PAKS sampling rate is equal to D(A/L), where D is the diffusion coefficient (cm^2/s), A is the cross sectional area of the diffusion path (cm^2), and L is the length of the diffusion path (cm); which can be calculated from Gilliland's Approximation (*88*).

In addition to acrolein, fourteen other carbonyls were evaluated with the new analytical method. The other carbonyls evaluated include: acetaldehyde, acetone, benzaldehyde, butyraldehyde, crotonaldehyde, 2,5-dimethylbenzaldehyde, formaldehyde, hexaldehyde, isovaleraldehyde, valeraldehyde, propionaldehyde, m-tolualdehyde, p-tolualdehyde, and o-tolualdehyde. As shown in Figure 2, all of these compounds were successfully separated with the modified chromatographic procedures. It is important to note that the new method had substantially increased the collection efficiency and stability for crotonaldehyde, due to its derivatization chemistry, which is similar to the acrolein derivatization. The optimized PAKS method is expected to work well for other unsaturated carbonyl compounds, utilizing the ultimate products of their reactions with DNSH.

2.4.6 Method Sensitivity and Operational Range

The original PAKS method had an acrolein detection limit of 7.50 ng/cartridge. The modified PAKS method sensitivity had been increased to 1.80 ng/cartridge for acrolein. This correlates to an estimated acrolein concentration detection limit of 0.25 μg/m³, calculated based on a 24 hr sampling period at 25°C. This increase in sensitivity was afforded by the new analysis carried out on the di-derivatized acrolein, which has the additional fluorescing DNSH molecule. Furthermore, the analytical program (i.e., detector wavelengths) was optimized specifically for the detection of acrolein, while maintaining comparable sensitivities for the other carbonyls. It is important to note that the same observation was made for crotonaldehyde sensitivity.

Although no formal range tests were conducted, the PAKS method has been evaluated for acrolein in the range of 2.34 – 340 μg/m³ (1.02 – 149 ppb). In addition, based on stoichiometry the PAKS should have a carbonyl capacity of approximately 9.51×10^{-6} and $4.76 \times \times 10^{-6}$ moles for saturated and, unsaturated and di-carbonyls, respectively. This correlates approximately to an acrolein capacity of 270 μg, which is equivalent to a nominal acrolein concentration of 40,100 μg/m³ (17,500 ppb) over a 24 hr sampling duration at 25°C.

2.5 Conclusions

The PAKS method was optimized for the measurement of unsaturated carbonyls. By careful examination and a better understanding of the mechanisms of DNSH reactions with unsaturated carbonyls, modifications were made to the sampling substrate conditions and HPLC analysis conditions of the original PAKS method. These modifications resulted in an optimized PAKS method that when evaluated under a variety of conditions (temperature, humidity, presence of ozone), the method had a collection efficiency of 99%

± 5% for acrolein (N = 36) and 96% ± 20% for crotonaldehyde (N = 6). In addition, the acrolein-DNSH derivative was stable within 9.6% of the initial amount, after 14 days of storage at 4°C, on the collection medium; and stable within 2.8% of the initial amount, after 16 days of storage at room temperature, in extract. The PAKS method is now the first passive method of its kind, which can meet the U.S. EPA's requirement of NATTS to monitor formaldehyde, acetaldehyde, and acrolein for 24 hour sampling durations. This is a significant advantage of U.S. EPA Compendium Method TO-11A, and should be strongly considered by future investigators.

Chapter 3

Evaluation and Optimization of the PAKS Method Sample Processing Procedures

3.1 Abstract

The original and optimized PAKS methods utilized virtually identical sample processing procedures. Both method developments focused relatively little on optimizing the PAKS sample processing procedures; therefore, there were some sample processing procedures that warranted further evaluation and optimization. Experiments were conducted to further evaluate and optimize the following PAKS sample processing procedures: sample baking duration, sample baking temperature, sample extraction volume, standards preparation, calibration curve preparation, and concentrations calculation methods. Through these experiments and the PAKS developmental work performed so far, a set of optimal conditions for processing PAKS samples and determining sample concentrations were identified and recommended in this chapter.

3.2 Introduction

The original (*46*) and optimized (*89*) PAKS methods' sample processing procedures may be found in detail in their respective manuscripts. Briefly, subsequent to sampling, shipping, and storage, PAKS samples were extracted with 2 mL of ACN and then analyzed with an HPLC-fluorescence technique. The standards used for HPLC analysis were prepared by spiking known concentrations of carbonyl(s) standard *in situ* on a PAKS cartridge. The HPLC-fluorescence technique was optimized in Chapter 2 (*89*); however, sample processing procedures including sample baking, extraction, standards preparation,

and calibration curve preparation were not evaluated and may not be optimal; therefore, it was believed that there was some possible room for improving these aspects of the PAKS method.

In the original PAKS method (*46*) samples were baked in an oven at 50°C for 1 hour. This was done to promote the forward carbonyl-DNSH derivatization reaction(s) (Chapter 2, Scheme 4) (*89*). However, it was later discovered that when samples were baked, the DNSH derivatives for unsaturated carbonyls (e.g., acrolein and crotonaldehyde) disappeared from the HPLC chromatographs (*90*). It was then discovered by Herrington et al. (*89*) (Chapter 2) that this was the result of the unsaturated carbonyls undergoing a third derivatization step to produce di-derivatized carbonyl-DNSH derivatives (Chapter 2, Scheme 4), which are facilitated by an addition reaction that is promoted by heat. Therefore, experiments were conducted to determine optimum sample baking duration and temperature, which would provide the highest yield of saturated and un-saturated carbonyl-DNSH derivatives.

Subsequent to sampling and baking, PAKS are extracted with ACN. It is imperative that the extraction volume is large enough to extract all of the carbonyl-DNSH derivatives from the cartridge; while ensuring that the sample is not diluted unnecessarily, thereby raising the PAKS LODs. The original (*46*) and optimized (*89*) PAKS methods used an extraction volume of 2 mL; however, the reason for choosing this volume was not reported. Therefore, an experiment was conducted to determine the optimum extraction volume.

Once a sample has been extracted, the sample extract is ready for HPLC analysis. However, prior to sample analysis a standard calibration curve needs to be established for the HPLC system. Unlike DNPH-based methods, there are no commercially available pure

carbonyl-DNSH derivatives, and there are no standard methods for crystallizing pure carbonyl-DNSH derivatives. Therefore, the original (*46*) and optimized (*89*) PAKS methods utilized standards generated from *in situ* spiking of known concentrations of pure carbonyl solutions onto PAKS cartridges. As with any analytical method, it is important to establish the appropriate range of calibration samples, so as to encompass the linear range of the collected sample concentrations. Once that is established, it is important to determine the appropriate means for delivering the standard concentration to the PAKS cartridge. Dr. Morandi at the University of Texas School of Public Health (UTSPH) spiked calibration standards onto PAKS cartridges with a relatively large volume (500 μL) of a low concentration standard (*91*). Whereas the original (*46*) and optimized (*89*) PAKS methods utilized a relatively small spiking volume (10 to 20 μL) of a high concentration standard. Because the 500 μL of standard saturates the entire bed of the PAKS cartridge, it was believed that this would result in reduced reaction efficiency between the standard(s) and the DNSH, because the reaction efficiency of DNSH in solution is relatively poor (*90*). Whereas a relatively smaller spiked volume would react more efficiently due to rapid volatilization on the PAKS medium, and the surface area of the PAKS cartridge would promote the carbonyl-DNSH derivatization reaction(s). Therefore, an experiment was conducted to determine which method of standard spiking provided the highest carbonyl-DNSH derivative yield. In addition, an experiment was conducted to determine which method was most appropriate for generating a calibration curve from the spiked PAKS cartridge. Lastly, because the calibration standards are prepared from *in situ* spiking of a standard(s) on a PAKS cartridge, some of the standard concentration(s) is derived from the laboratory blank concentration(s), due to contamination. Therefore, an experiment was

conducted to determine the best method for accounting for the PAKS laboratory blank concentrations in the calibration curve(s)

3.3 Materials and Methods

3.3.1 Sample Baking

The following experiment was conducted to determine the optimum sample baking duration, which would provide the highest yield of saturated and un-saturated carbonyl-DNSH derivatives. For this experiment, 16 PAKS cartridges were prepared, spiked with a known standard (AccuStandard (New Haven, CT, USA) Option 2 Testing Mix, M-8315-R2, 1.0 mg/mL of carbonyls in ACN), and allowed to sit for 24 hours. Subsequently, 2 PAKS cartridges were baked at 1, 2, 3, 4, 5, 6, 7, and 8 hours, and then extracted for analysis.

In addition, an experiment was conducted to determine the optimum sample baking temperature, which would provide the highest yield of saturated and un-saturated carbonyl-DNSH derivatives. For this experiment, 12 PAKS cartridges were prepared, spiked with a known standard, and allowed to sit for 24 hours. Subsequently, 2 PAKS cartridges were baked at 50, 55, 60, 65, 80, and 95°C for 3 hours, then extracted for analysis.

3.3.2 Sample Extraction

The following experiment was conducted to determine the optimum extraction volume. For this experiment, 8 PAKS cartridges were prepared and 2 PAKS cartridges each were extracted with 1, 1.5, 2, and 2.5 mL of ACN.

3.3.3 Sample Analysis

3.3.3.1 Standard Preparation

The following experiment was conducted to determine which method of standard spiking providing the highest carbonyl-DNSH derivative yield. For this experiment, 2 PAKS cartridges each were spiked with equivalent concentrations of standard (AccuStandard (New Haven, CT, USA) Option 2 Testing Mix, M-8315-R2, 1.0 mg/mL of carbonyls in ACN); however, via injection volumes of 10 and 500 µL (above standard diluted accordingly). The PAKS cartridges were then extracted, analyzed, and compared to see which method provided the best reaction efficiencies..

3.3.3.2 Calibration Curve

Once the appropriate standard preparation method was established, it was then important to establish the appropriate means for developing the calibration curve. The calibration curve could be prepared from one of the two following methods: 1) One high standard (encompassing the upper end of the calibration curve's linear range) is prepared and then serially diluted to generate the entire calibration curve down to lower end of the linear range; 2) A series of PAKS cartridges (encompassing the upper and lower linear range of the calibration curve) are spiked with different levels of standards to generate the entire calibration curve. To evaluate which method was more appropriate, calibration curves were prepared with each method and the slopes, intercepts, and R^2 values were compared.

3.3.3.3 Calculations

Once the appropriate calibration curve method was established, it was then important to establish the appropriate means for calculating concentrations. Because the calibration standards are prepared from *in situ* spiking of a standard(s) on a PAKS cartridge, some of the standard concentration(s) is derived from the laboratory blank concentration(s), due to

contamination (Note: This primarily only applies to formaldehyde, acetaldehyde, and acetone, because these are the only carbonyls commonly found in the PAKS laboratory blanks). Therefore, the laboratory blank concentration(s) should be subtracted from the standard concentration(s). However, laboratory blank concentration(s) could be subtracted from the standard concentration(s) using one of the two following methods: 1) A laboratory blank can be serially diluted in parallel with the standard serial dilutions, and then each concurrent concentration level is subtracted; 2) The laboratory blank concentration(s) can be subtracted at each point based on a uniform percentage (i.e., the starting laboratory blank concentration / the starting standard concentration). To evaluate which method was more appropriate, calibration curves were prepared with each method and the slopes, intercepts, and R^2 values were compared.

3.4 Results and Discussion

3.4.1 Effects of Sample Baking

Results from the sample baking duration experiment (Figure 9) indicated that 3 hours of baking provided the highest yield of formaldehyde- and acetaldehyde-DNSH derivatives. Although the results indicated that 2 hours was the optimum sample baking duration for the acrolein-DNSH derivative, it was deemed more important to have the ~30% increase (i.e., in sampling baking for 3 hours over 2 hours) in both formaldehyde and acetaldehyde, with a concurrent ~30% decrease in acrolein, than vice versa. Especially when one considers the relative importance of formaldehyde. Propionaldehyde did not appear to have any noteworthy trend between sample baking duration and derivative yield, and was overshadowed by the other carbonyls importance. Considering the above, a sample baking duration of 3 hours was chosen for the final PAKS method.

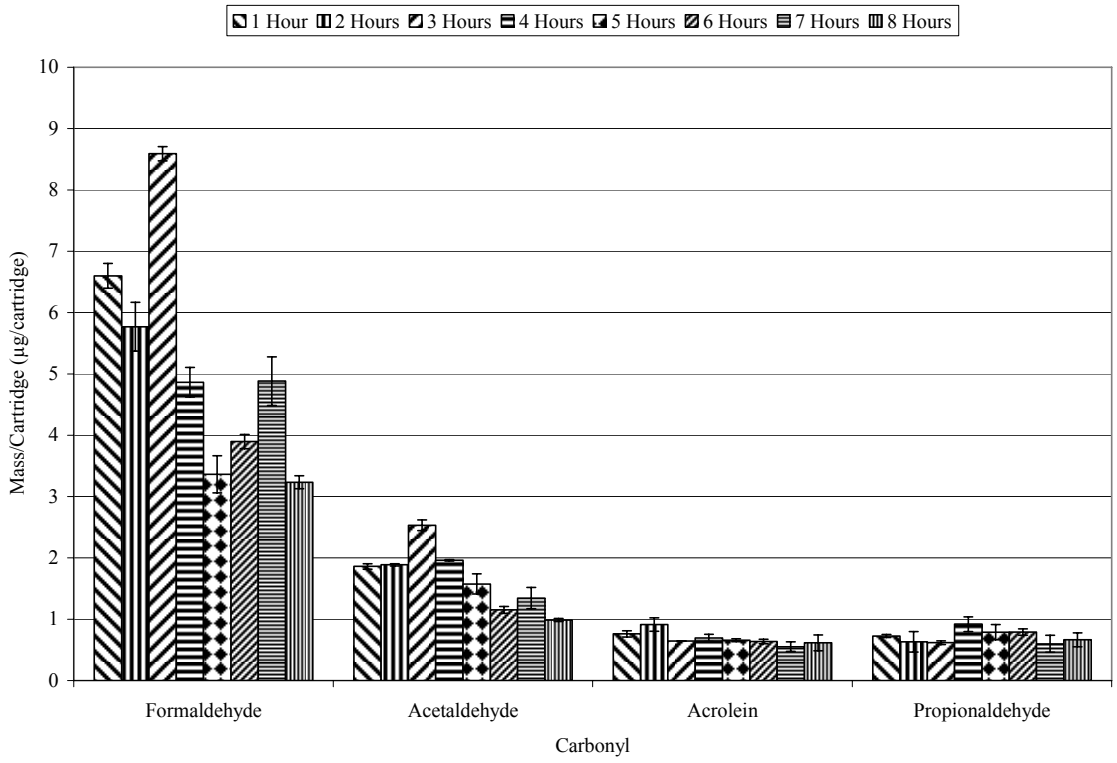


Figure 9: Effects of sample baking duration on PAKS baked at 50°C. N=2 for each duration and Y error bars represent the difference amongst duplicate samples.

Results from the sample baking duration experiment (Figure 9) indicated that the optimum sample baking duration was 3 hours. The sample baking duration experiment was conducted at 50°C, because the original PAKS method (*46*) had used 50°C. However, it was important to establish if 50°C was the optimum sample baking temperature. Therefore, a sample baking temperature experiment was conducted. Results from the sample baking temperature experiment (Figure 10) indicated that with the exception of formaldehyde, there were no large increases in the carbonyl-DNSH derivatives with increasing baking temperature. However, due to the small decreasing trend for acrolein- and propionaldehyde-DNSH derivatives, 50°C was chosen as the optimum baking temperature for the final PAKS method.

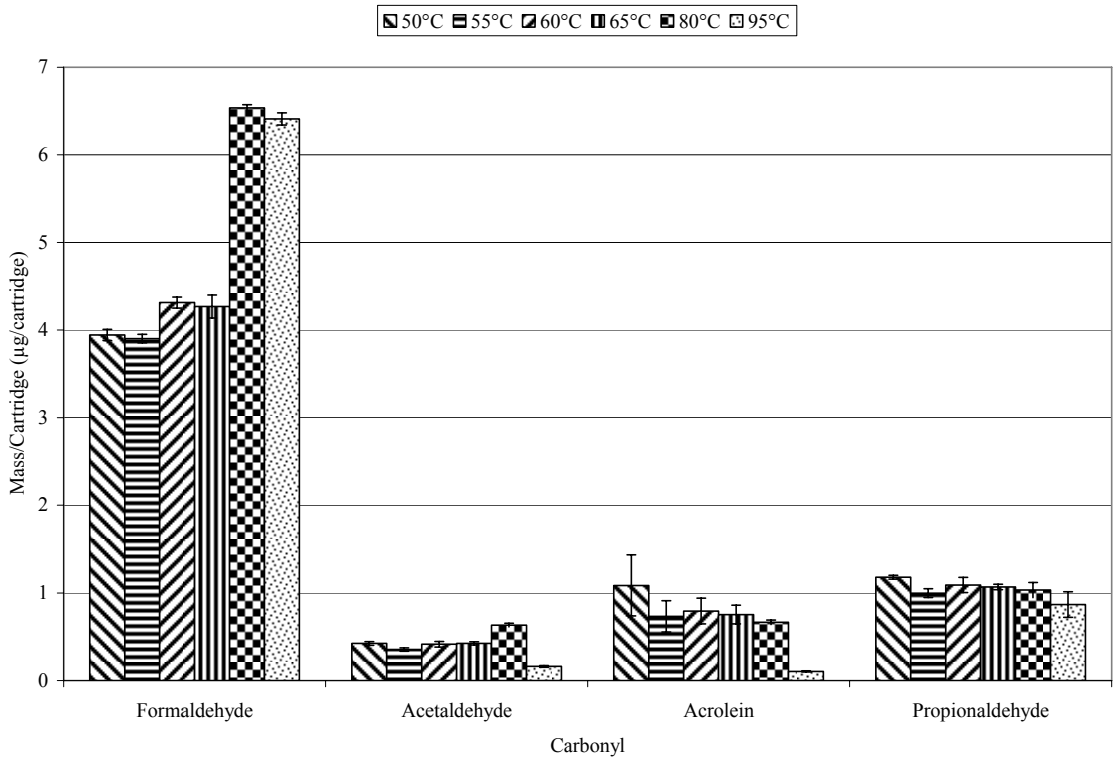


Figure 10: Effects of sample baking temperature on PAKS baked for 3 hours. N=2 for each temperature and Y error bars represent the difference amongst duplicate samples.

3.4.2 Sample Extraction Volume

Results from the sample extraction experiment (Figure 11) indicated that approximately 1.5 mL of ACN was a sufficient volume to extract the formaldehyde- and acetone-DNSH derivatives; however, the trend for the acetaldehyde-DNSH derivatives was more ambiguous, due to variability amongst the duplicate samples for the 1 and 1.5 mL extraction volumes. Extracting with more than 2 mL of ACN resulted in the unnecessary dilution of the sample for all three carbonyl-DNSH derivatives. An extraction volume of 2 mL of ACN was used in the original (*46*) and optimized (*89*) PAKS methods, and was chosen as the extraction volume for the final PAKS method.

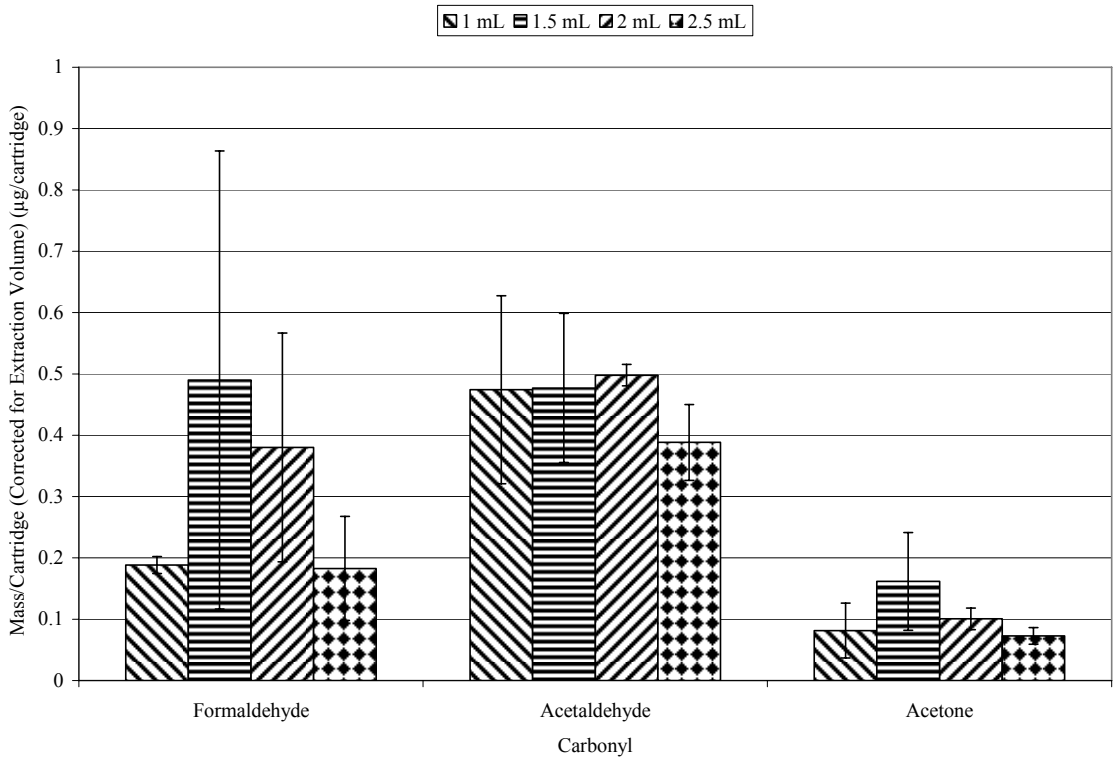


Figure 11: Effects of sample extraction volume on PAKS sample recovery. N=2 for each volume and Y error bars represent the difference amongst duplicate samples.

3.4.3 Sample Analysis

3.4.3.1 Standard Preparation

Results from the standard preparation experiment (Figure 12) indicated that there were differences between the two methods of spiking standards into PAKS cartridges. The 10 µL spike appeared to result in considerably larger amounts of formaldehyde than the 500 µL spike; which would be consistent with the idea that a smaller spiked volume would allow for rapid volatilization of the carbonyl(s) and take advantage of the PAKS cartridge surface area to promote the carbonyl-DNSH derivatization reaction(s). Whereas the 500 µL spike would be similar to spiking in solution, which has slower reaction rates for the carbonyl-DNSH derivatization reactions (*90*). The 10 µL spikes appeared to have acetaldehyde concentrations that were lower than the 500 µL spikes; however, it is

believed that the large volume of ACN associated with the 500 µL spikes introduced a relatively large amount of acetaldehyde (contaminant in ACN), thereby increasing the acetaldehyde concentrations. This idea would be consistent with what is observed with the PAKS laboratory blanks in extract (Chapter 4, to be discussed later). The 10 µL spikes had lower propionaldehyde and acrolein concentrations than the 500 µL spikes; however, the 10 µL spike concentrations were heavily dominated by one low spike out of the three spikes. In the first 10 µL spike the concentrations measured appeared to be abnormally low, relative to the concentrations from the other two spikes. Considering this, and the fact that spiking with 500 µL requires the dilution of the standards, thereby introducing a possible source of error; a 10 µL spike was chosen for preparation of the final PAKS standards. It is important to note that administering the standard for a 24-hour period would be ideal, because it would mimic the PAKS field sampling durations; however, this is entirely not feasible.

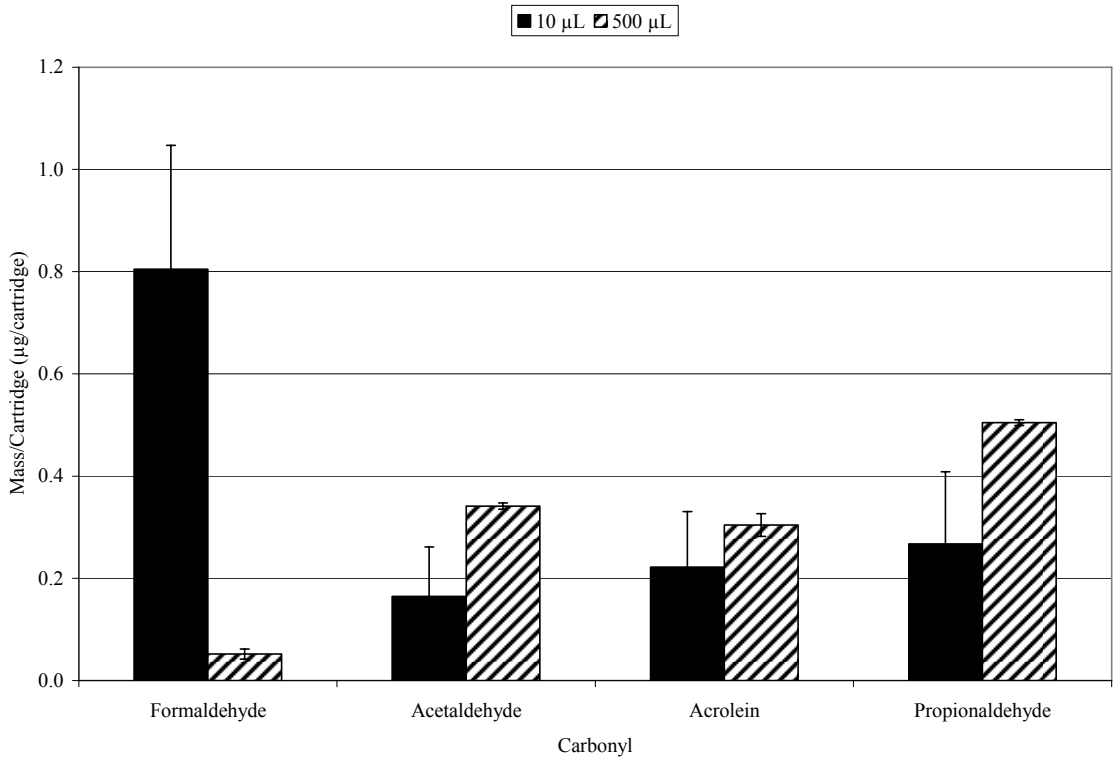


Figure 12: Comparison of in-situ spiking volume for PAKS standard preparation. N=3 for each volume and Y error bars represent the standard deviation amongst replicate samples.

3.4.3.2 Calibration Curve

Results from the calibration curve experiment (Table 4) indicated that spiking and extracting 1 PAKS and serially diluting it to make the entire calibration curve is similar to spiking multiple PAKS to make the entire calibration curve for formaldehyde. The two calibration curves had similar slopes, intercepts, and correlation coefficients for formaldehyde. However, the other three carbonyl calibration curves did not agree as well. The spiked calibration curves for acetaldehyde, propionaldehyde, and acrolein consistently had smaller slopes, larger intercepts, and smaller correlation coefficients. The relatively smaller correlation coefficients for the calibration curves prepared by spiking multiple PAKS is easily explained by the error introduced by the variation amongst multiple PAKS,

multiple spikes, and multiple extractions. However, the relatively smaller slopes and larger intercepts for the calibration curves prepared by spiking multiple PAKS is a little more ambiguous. It is believed that the relatively smaller slopes and larger intercepts for the calibration curves prepared by spiking multiple PAKS were attributed to spiking error. Not spiking error on the human/technician's behalf, but just a result of spiking a solution onto the PAKS solid sorbent.

More specifically, it is believed that the PAKS solid sorbent acted like a sponge during spiking, and upon completing a full injection of the standard solution onto the PAKS solid sorbent, the PAKS sponge-like properties drew out some of the remaining standard solution in the dead volume of the syringe. This resulted in relatively higher amounts of the standard solution spiked onto the PAKS; however, this effect was not seen as readily except when spiking relatively smaller amounts of standard solution onto the PAKS. When spiking smaller amounts of standard solution (i.e., the lower end of the calibration curve) onto the PAKS, the relative contribution from excess solution drawn out of the syringe's dead volume became greater. This relative increase in concentration at the lower ends of the calibration curves caused the relatively lower slopes and higher intercepts. It is important to note that the same trend was observed with formaldehyde; however, the trend was not as pronounced. It is believed that the formaldehyde trend was not as pronounced, because it was compensated by formaldehyde's relatively higher reaction rate and volatility, and/or formaldehyde was the anomaly in these results.. Considering the above, and considering the following; serially diluting 1 standard is less labor intensive than spiking multiple PAKS; spiking multiple PAKS introduces more possible sources of error; extracting multiple PAKS introduces more possible errors; and spiking multiple PAKS

uses more resources; serially diluting 1 PAKS was chosen for the final PAKS method calibration curve.

Table 4: Comparison of generating the calibration curve via serially diluting one spiked PAKS vs. spiking multiple PAKS.

Curve	Formaldehyde	Acetaldehyde	Propionaldehyde	Acrolein
Diluted Slope	8.03×10^6	3.83×10^6	5.17×10^6	6.09×10^6
Diluted Intercept	1.24×10^6	2.09×10^4	4.66×10^4	6.02×10^4
Diluted R^2	0.994	0.999	0.999	0.990
Spiked Slope	6.18×10^6	2.04×10^6	2.59×10^6	4.58×10^6
Spiked Intercept	1.33×10^6	3.44×10^6	8.53×10^5	4.56×10^6
Spiked R^2	0.975	0.972	0.982	0.936

3.4.3.3 Calculations

Results from the calculations experiment (Table 5) indicated that calibration curves prepared by applying uniform (percentage) laboratory blank subtractions across the calibration curves were similar to calibration curves prepared by serially diluting laboratory blanks across the calibration curves and subtracting the laboratory blanks at each point in the curves. (Acrolein is not shown, because acrolein was not present in laboratory blanks). The calibration curves had similar slopes, intercepts, and correlation coefficients. Considering that there were little differences between the calibration curves; applying uniform laboratory blank subtractions is less labor intensive than serially diluting laboratory blanks; and serially diluting laboratory blanks introduces more possible sources of error from the additional processing; applying uniform laboratory blank subtractions was chosen for the final PAKS method calculations.

Table 5: Comparison of applying a laboratory blank correction to the calibration curve via a uniform percentage vs. serially diluting a laboratory blank in parallel.

Curve	Formaldehyde	Acetaldehyde	Propionaldehyde
Percentage Slope	6.51×10^6	1.09×10^7	5.56×10^6
Percentage Intercept	9.89×10^4	1.44×10^5	4.80×10^4
Percentage R^2	0.996	0.995	0.999
Diluted Slope	6.61×10^6	1.10×10^7	5.55×10^6
Diluted Intercept	7.83×10^4	5.77×10^4	5.22×10^4
Diluted R^2	0.994	0.996	0.999

3.5 Conclusions

The above experiments evaluated and optimized the following PAKS sample processing procedures: the sample baking duration, sample baking temperature, sample extraction volume, standard preparation method, calibration curve, and calculations method. The final PAKS sample processing procedures are as follows: PAKS cartridges are baked at 50°C for 3 hours; baked PAKS cartridges are extracted with 2 mL (~1.45 mL twice, as the sorbent retains ~0.9 mL) of ACN; standards are prepared by *in situ* spiking of ≤10 µL of un-diluted pure carbonyl standard (AccuStandard Option 2 Testing Mix (M-8315-R2), New Haven, CT, USA) on a PAKS cartridge; calibration curves are prepared by serially diluting the extract of 1 PAKS cartridge spiked with a relatively high concentration of pure carbonyl standard(s); and laboratory blank concentrations are subtracted from the calibration curves at each point based on the laboratory blank's percentage of the first (highest) standard. These procedures are deemed to be optimal through the PAKS method developmental work performed to date; and should help to improve the PAKS method accuracy and precision.

Chapter 4

Evaluation and Minimization of the PAKS Method Blanks

4.1 Abstract

Shortly after the PAKS method was optimized for the collection of acrolein (Chapter 2) (*89*), it became apparent that the method had relatively elevated formaldehyde and acetaldehyde blank concentrations. Therefore, the following work was conducted to determine the sources and magnitudes of the PAKS blank contamination, and to reduce the blank contamination levels to ~10 fold less than expected sample concentrations. Experiments were conducted to evaluate the PAKS cartridge, solvent, reagent, acid catalyst, drying procedures, and storage procedures. Through these experiments, the sources of PAKS blank contamination were identified, remediation actions were implemented, and optimum blank preparation and handling protocols have been made in this chapter. These remediation actions resulted in a significant reduction in PAKS blank levels for formaldehyde and acetaldehyde.

4.2 Introduction

The limits of detection (LOD) for the PAKS method are derived from either the 1111analytical detection limits (ADLs) or the method detection limits (MDLs). The latter are dictated by the field blank contamination. Like 2,4-dinitrophenylhydrazine (DNPH)-based methods, the PAKS field blank contamination (MDLs) drives the LODs (*3*). During initial field sampling with the optimized PAKS method (*89*) the field blanks had relatively elevated formaldehyde and acetaldehyde concentrations, and large amounts of variability across field blanks (e.g., 0 – 31 μg/m³ for formaldehyde); therefore, the LODs

were considered unacceptably high. In some cases the formaldehyde and acetaldehyde field blank concentrations were higher than the field sample concentrations. Therefore, reducing the field blank contamination and variability to the lowest possible levels was necessary to achieve acceptable LODs.

All PAKS cartridges start as laboratory blanks; therefore, reducing the PAKS laboratory blank contamination levels was the first step to reducing the PAKS field blank levels. There are several possible sources of contamination for the PAKS laboratory blanks including the PAKS cartridge, solvent, reagent, acid, storage, etc.

The PAKS cartridge itself is a possible source of contamination for the PAKS laboratory blanks. The PAKS cartridge is a modified Supelclean™ LC-18 Solid Phase Extraction (SPE) Tube (Supelco (Bellefonte, PA, USA)). The LC-18 cartridge uses a polypropylene syringe barrel containing silica-based bonded C18 (Octadecyl, ~10% C) packing material. The polypropylene, packing material, pore size, pore space, and pore volume are all controlled by Supelco's manufacturing processes. Because of the ubiquitous nature of carbonyls such as formaldehyde (especially in the manufacturing of plasticizers), some free carbonyls may be present in and/or on the PAKS cartridge from the polypropylene and/or packing material. Considering this, experiments were conducted in an attempt to identify the presence of any quantifiable contamination from the PAKS cartridge, and attempt to reduce the contamination.

Another possible source of contamination for the PAKS laboratory blanks is the solvent ACN. ACN is used to clean the PAKS cartridges, make the PAKS coating solution, and extract all samples. HPLC grade ACN from J.T. Baker (Phillipsburg, NJ, USA) was used, which is assayed to contain "< 20 ppb of carbonyl compounds (as Acetone)". This

means that ACN has the potential to contribute ~ 25 ng/mL of acetone to a PAKS laboratory blank (calculated based on a 2 mL ACN coating volume; assuming 100% derivatization of the available 20 ppb (~20 μg/L) acetone; and a 2 mL extraction volume). Note that this is approximately half of the typical acetone concentration observed in the PAKS laboratory blanks (typical acetone concentrations range from 40 ng/mL to 80 ng/mL). In addition, this is equivalent to ~7.8 μg/m³ for a 24 hour sampling duration at 25°C. Therefore, it is imperative that the ACN be as pure as possible to reduce the chance of ACN contributing to the PAKS laboratory blank level. A criteria of ≤25% contaminant contribution from ACN was adopted from EPA Compendium Method TO-11A (*33*). Considering this, experiments were conducted in an attempt to identify the presence of any quantifiable contamination from the ACN, and attempt to reduce the contamination.

Another possible source of contamination for the PAKS laboratory blanks is the reagent 5-(dimethylamino)naphthalene-1-sulfohydrazide (DNSH), also known as dansylhydrazine. DNSH is a hydrazine reagent coated on the PAKS cartridge, which reacts with carbonyls to form stable carbonyl-DNSH derivatives. (Please refer to Zhang et al. (*46*) and Herrington et al. (Chapter 2) (*89*) for more specific details on the carbonyl-DNSH derivatization reaction.) Therefore, it was necessary to determine which commercially available DNSH provided the lowest contamination levels, and attempt to reduce the contamination. In addition, it was necessary to evaluate the variability in contamination levels across DNSH batches to see if PAKS users could expect consistent contamination levels from batch to batch.

Another possible source of contamination for the PAKS laboratory blanks is the acid catalyst. An acid catalyst is required in the PAKS method to promote the forward

carbonyl-DNSH derivatization reaction (Chapter 1,Scheme 2). In the original PAKS method (*46*), Zhang et al. tested several acids stronger than acetic acid (the final acid chosen), including phosphoric (H_3PO_4) and hydrochloric (HCL) acid for their abilities to promote the acid-catalyzed carbonyl–DNSH derivatization reaction. These test results were not reported in the original manuscript (*46*). These relatively stronger acids resulted in both a visible (loss of characteristic yellowish color) and analytical destruction of DNSH (loss of active DNSH in HPLC chromatographs) (*90*). These results suggested that DNSH and stronger acids decreased the ability to form stable carbonyl-DNSH derivatives. Glacial acetic acid was shown to be a more suitable acid for carbonyl-DNSH derivatization, and was therefore chosen.

In Chapter 2 (*89*), acetic acid and pH buffers were further evaluated for their ability to maximize the acrolein-DNSH derivatization reaction to form stable di-derivatized acrolein-DNSH derivatives. The pH buffers and acetic acid both appeared to be suitable acid catalysts for the acrolein–DNSH derivatization reaction; however, it was important to determine which acid catalyst provided the most stable acrolein-DNSH derivative. Glacial acetic acid provided the most stable acrolein-DNSH derivative and was therefore selected for the optimized PAKS method (Chapter 2) (*89*).

Acetic acid was used in the original (*46*) and modified (*89*) PAKS methods. However, in the acetic acid manufacturing process, acetaldehyde is oxidized by oxygen to produce acetic acid (*92*). Using modern catalysts, the reaction can have an acetic acid yield greater than 95% (*92*). In addition to residual reactant (acetaldehyde), the major side products are ethyl acetate, formic acid, and formaldehyde (*92*). Although all of these compounds have lower boiling points than acetic acid and are readily separated by distillation; the presence

of these compounds even at a ppm or ppb level could still have significant effects on the PAKS laboratory blank contamination levels. Considering this, experiments were conducted to evaluate an alternative acid, which could reduce the PAKS laboratory blank levels of acetaldehyde and formaldehyde. The goal was to find an acid with low volatility and a similar pKa to acetic acid (pKa = 4.76), with lower impurity levels for formaldehyde and acetaldehyde and similar reaction efficiencies.

Another possible source of contamination for the PAKS laboratory blanks is nitrogen (N_2). Subsequent to being coated, PAKS cartridges are dried with ultra-high purity (UHP) nitrogen. The nitrogen is supplied by Airgas East (Piscataway, NJ, USA) and therefore the purity of the nitrogen is governed by their manufacturing, bottling, storage, and transportation processes. Considering this, experiments were conducted in an attempt to identify the presence of any quantifiable contamination from the nitrogen, and attempt to reduce the contamination. The only method to minimize contamination during drying was to determine the optimum and minimum drying time.

Another possible source of contamination for the PAKS laboratory blanks is during storage and shipping. Subsequent to coating and drying, the PAKS cartridges are sealed with caps and stored in glass amber jars. Note that in 1980, Beasley et al. (*38*) recommended that Bakelite bottles be avoided for any method used in the determination of formaldehyde. Bakelite is a polymer prepared from formaldehyde and phenol and may release free formaldehyde. In addition, in 1981 Lowe et al. (*36*) proposed that formaldehyde contamination originated from polyethylene. Based on the above information, PAKS cartridges were only stored and shipped in amber (reduces UV light

exposure, which is important due to the fact that UV light can artificially increase background concentrations) glass jars with Teflon lined caps.

The original PAKS method (*46*) required the male lure end (extraction end) to be capped with a syringe cap and the female end (exposure end) to be capped with a polypropylene cap that covered the end in a manner similar to that of a garbage can lid and garbage can. It was believed that these caps did not hermetically seal the PAKS; therefore, contamination could potentially occur during storage and shipping. In an attempt to hermetically seal the PAKS and reduce the possibility for contamination, alternative caps were evaluated.

The objective of the current chapter was to evaluate each of these possible sources of contamination. Based on the evaluation, optimal conditions were selected to achieve the lowest PAKS method blank concentrations. The work was limited to formaldehyde, acetaldehyde, and acetone; like DNPH-based methods, these were the three most abundant carbonyls in the PAKS laboratory blanks. Although other carbonyls (e.g., propionaldehyde) were occasionally present in the PAKS laboratory blanks; their infrequent presence and low contamination levels did not warrant discussion. Note that acrolein was not present in the PAKS laboratory blanks.

4.3 Materials and Methods

The following is a start-to-finish evaluation of the PAKS laboratory blank contamination sources, levels, variability, and reduction strategies.

4.3.1 Cartridge

The following 2 experiments were conducted in an attempt to identify the presence of any quantifiable contamination from the PAKS cartridge, and attempt to reduce the contamination. The idea behind the following two experiments was that if there were free carbonyls present on the PAKS cartridge, by coating or soaking the cartridge with DNSH and allowing the cartridges to sit for an extended period of time; the free carbonyls would be consumed by the DNSH and then extracted off to leave a relatively cleaner cartridge.

4.3.1.1 Coat and Recoat

For this experiment, 3 PAKS cartridges were cleaned with 4 mL of ACN, coated with an ACN solution containing 5 mg/mL DNSH and 1.3% (w/w) citric acid, and dried with UHP nitrogen. The PAKS cartridges were then allowed to sit for 30 days, so as to ensure the carbonyl-DNSH derivatization reactions were complete. Subsequently, the PAKS cartridges were cleaned with 8 mL of ACN. The idea behind this experiment was that if any free carbonyls were present from the PAKS cartridge, they would be consumed by the DNSH over the 30 day period and then extracted off with the 8 mL of ACN. Subsequent to extraction, the PAKS cartridges were then recoated, extracted, and analyzed in parallel with 3 PAKS cartridges that had not gone through the coating and sitting period.

4.3.1.2 Soak and Recoat

For this experiment, 3 PAKS cartridges were allowed to soak in the PAKS coating solution (5 mg/mL DNHS and 1.3% (w/w) citric acid) for 30 days. The idea behind this experiment was that soaking the cartridge may be more efficient and thorough at scavenging contaminants than coating the cartridge (previous experiment, 4.4.1.1). Like the Coat and Recoat experiment (4.3.1.1), the PAKS cartridges were then cleaned with 8 mL of ACN,

recoated, extracted, and analyzed in parallel with 3 PAKS cartridges that had not been through the soaking and sitting period.

4.3.2 Solvent (ACN)

The following experiments were conducted in an attempt to identify the presence of any quantifiable contamination from the ACN, and attempt to reduce the contamination

4.3.2.1 Purity

Before reducing any laboratory blank contamination from the ACN, the level of contamination contributed by the ACN (purity) needed to be quantified. There were no standard operating procedures (SOPs) for testing the purity of ACN for carbonyls for use in the PAKS method; however, there are SOPs for testing the purity of ACN for use in DNPH-coated solid sorbent methods (*93*). Considering that the SOPs for testing the purity of ACN for use in DNPH-coated solid sorbent methods are based on a criteria of percent contaminant contributions from ACN; the method was adopted for the PAKS method. For this experiment, a Waters (Milford, MA, USA) Sep-Pak DNPH-silica cartridge was gravimetrically eluted with 3 mL of ACN. The eluate was then analyzed with an HPLC system within 3 minutes. Subsequently, 1 drop of concentrated hydrochloric (HCl) acid was added to the eluate and allowed to sit at room temperature for 30 minutes. This was done to catalyze the acid-catalyzed carbonyl-DNPH derivatization reaction (Figure 13). The eluate was then re-analyzed. The difference in carbonyl-DNPH derivative concentrations from each measurement was then compared. The percent hydrazone contributed by the ACN was calculated using a criteria of ≤25% contaminant contribution (calculated using Equation 3) from ACN was adopted from EPA Compendium Method TO-11A (*33*).

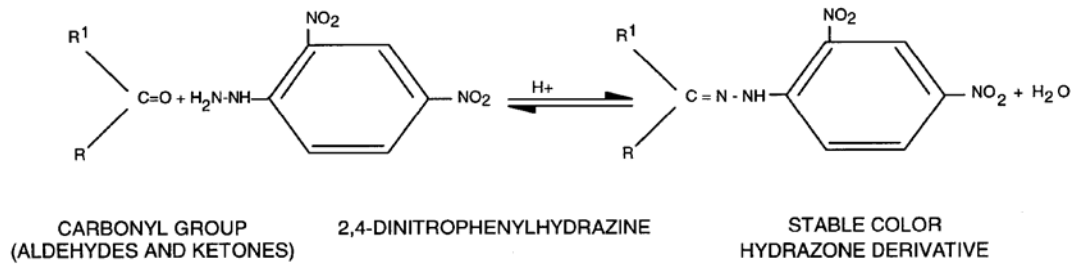


Figure 13: Carbonyl-DNPH derivatization reaction.

Equation 2: Concentration after reaction – Concentration in blank = Contribution from ACN

Equation 3: Contribution from ACN / Background x 100 = % Contribution from ACN

4.3.2.2 Distillation

Results from the ACN purity experiment indicated that ACN contributed unacceptable levels of contaminants to the PAKS blanks. Therefore, in an attempt to reduce the amount of contamination present in the ACN, ACN was triply distilled. The purity of the distilled ACN was then compared to the same batch of un-distilled ACN using the purity test outlined in section 4.3.2.1 (*93*). However, it is important to note that the purity test and criteria for acceptable ACN was adopted from the DNPH-based EPA Compendium Method TO-11A (*33*); and the criteria for acceptable ACN is derived from a relative comparison to the total background contamination, which is low for DNPH-coated solid sorbents. Therefore, it was also important to establish how much improvement would be observed in the PAKS laboratory blanks from using distilled ACN. Therefore, PAKS coating solutions (5 mg/mL DNSH and 1.3% (w/w) citric acid) were made from

un-distilled and distilled ACN, and 2 PAKS laboratory blanks from each coating solution were prepared and compared.

4.3.2.3 Extracts

The above experiments focused on determining and reducing ACN's contaminant contribution to laboratory blanks; however, because ACN is used to extract laboratory blanks, there is possibility for ACN contaminating the extracts. Therefore, an experiment was conducted to evaluate and reduce ACN's contaminant contribution to extracts. For this experiment, PAKS were prepared and 2 PAKS each were extracted with un-distilled ACN and triple distilled ACN on 0, 1, 2, 8, 12, and 17 days post preparation. In addition, 2 PAKS were extracted with ACN that had been refluxed and distilled from DNPH on 0, 1, 2, 8, 12, and 17. ACN refluxed from DNPH was evaluated as an alternative to distillation. The procedure for refluxing the ACN from DNPH was adopted from the methanol purification procedures outlined in the American Society of Testing and Material's Method E411-00 (*94*). For this experiment, 200 mL of ACN was combined with 1 g of DNPH and 100 µL of HCL. This solution was then refluxed for 3 hours and then distilled. The first 25 mL of distillate was discarded. The distillation was then continued until approximately 75% of the ACN was distilled over.

4.3.3 Reagent (DNSH)

The following two experiments were conducted to determine which commercially available DNSH provided the lowest contamination levels, and attempt to reduce the contamination. The first experiment (4.4.3.1 Brand Purity/Variability) evaluated which commercially available DNSH had the lowest contaminant concentrations; and then evaluated the variability amongst batches for lowest commercially available DNSH, to see

if PAKS users could expect consistent contamination levels from batch to batch. The second experiment (4.4.3.2 Purification) attempted to purify the DNSH to provide lower contaminant concentrations.

4.3.3.1 Brand Purity/Variability

The following 3 commercially available DNSH brands were evaluated: ALDRICH's DNSH (assayed at 98% purity), SIGMA's (assayed at 95% purity), and Fluka's (assayed at 97% purity). For this experiment, a coating solution (5 mg/mL DNSH and 1.3% (w/w) citric acid) was prepared from each brand of DNSH, from the same parent acidified ACN solution. From each coating solution, 3 laboratory blanks were prepared and compared.

Once the DNSH brand with the lowest laboratory blank contamination levels was determined, it was necessary to evaluate the variability in contamination levels across batches to see if PAKS users could expect consistent contamination levels from batch to batch. For this experiment, 4 coating solutions were made with the same parent acidified ACN solution using 4 different batches of the same brand of DNSH (determined in the previous experiment). From each coating solution, 3 PAKS (5 mg/mL DNSH and 1.3% (w/w) citric acid) laboratory blanks were prepared.

4.3.3.2 Purification

Numerous studies evaluated the effectiveness of purifying DNPH to lower the contamination levels and variability, thereby lowering LODs (*95*). Several studies determined that re-crystallizing DNPH from warm ethanol was an effective means of lowering contamination levels (*95*). Based on the above, it was believed that re-crystallizing DNSH may be an appropriate means of lowering the PAKS laboratory blank contamination levels and variability. The current body of literature does not provide

a method for re-crystallizing DNSH. However, it was believed that the chemistry of DNPH and DNSH was analogous; therefore, the method of re-crystallizing DNPH was adopted from EPA Compendium Method TO-11A (*33*). For this experiment, a supersaturated solution of DNSH was prepared by boiling excess DNSH in 50 mL of ethanol for one hour. Subsequently, the supernatant was transferred to a covered beaker on a hot plate and allowed to gradually cool to 40-60°C. This solution was then maintained at this temperature (40-60°C) until 95% of solvent was evaporated. The solution was then decanted to waste, and the crystals were rinsed three times with cold ethanol. The crystals were then transferred to another clean beaker and 50 mL of ethanol was added, brought to a boil, and allowed to cool as previously done. The DNSH from this experiment was then used to prepare 3 laboratory blanks.

4.3.4 Acid Catalyst

The following experiment was conducted to find alternative acid catalyst to acetic acid. Citric acid was evaluated, because citric acid is relatively non-volatile and has pKa values of 3.15, 4.77, and 6.40, which is very similar to acetic acid. For this experiment, coating solutions were prepared with acetic and citric acid. 2 Laboratory and 2 field blanks were evaluated for each coating solution. In addition, the reaction efficiencies of the acids were compared by spiking 2 cartridges from each coating solution with known carbonyl standards.

4.3.5 Cartridge Drying

The following experiment was conducted in an attempt to identify the presence of any quantifiable contamination from the nitrogen, and attempt to reduce the contamination. For this experiment, PAKS were coated and dried at a constant flow rate (~500 mL/min) for 10,

20, 30, and 40 minutes post coating. 2 laboratory blanks were analyzed from each batch. It is important to note that the drying flow rate should not affect the contamination levels, rather contamination levels would be dictated by total volume passed over the cartridge.

4.3.6 Blank Storage/Shipping

The following experiment was conducted in an attempt to hermetically seal the PAKS and reduce the possibility for contamination. For this experiment, polypropylene plugs (inserted into the exposure end) were purchased from Supelco (Supelco product # 52173-U). In addition, Teflon caps (for the extraction end) were purchased from Supelco (Supelco product # 57098). A vacuum gauge hooked up in line with a pump and a PAKS cartridge was used to qualitatively evaluate the degree of seal. 3 of the polypropylene caps (original method) were compared to 3 of the polypropylene plugs. In addition, 3 of each of the 2 different syringe caps (original method) were compared to 3 of the Teflon caps.

4.4 Results and Discussion

4.4.1 Laboratory Blanks

4.4.1.1 Cartridge

Results from the cartridge experiments indicated that there was no quantifiable contamination from the PAKS cartridge. For the coat and recoat experiment (Figure 14) there was no large difference between the controls and the experiments for all 3 carbonyls (formaldehyde, acetaldehyde, and acetone). For the soak and recoat experiment (Figure 15) the contamination levels for the experiments were relatively higher than the contamination levels for the controls, for all three carbonyls. These results suggest that soaking the PAKS cartridges with the DNSH coating solution had the opposite anticipated effect and concentrated the contaminants on the cartridge. It is important to note that there was the

assumption that if there was quantifiable contamination from the PAKS cartridge, this contamination would be reduced by coating/soaking the cartridge, allowing the cartridge to sit, and then cleaning the cartridge with ACN.

It is possible that there was contamination from the cartridge; however, this contamination was not quantifiable by these experiments and/or the contamination could not be removed by these methods. It is also important to note that the results from the coat and recoat experiment (Figure 14) suggest that a blank stored for an extended period of time could possibly be cleaned, recoated, and reused; as there was no increase in contamination levels over the control; however, this would have to be further evaluated in the future. This also indicates that there is the possibility that sampled cartridges could be reused; however, again this would have to be evaluated in the future.

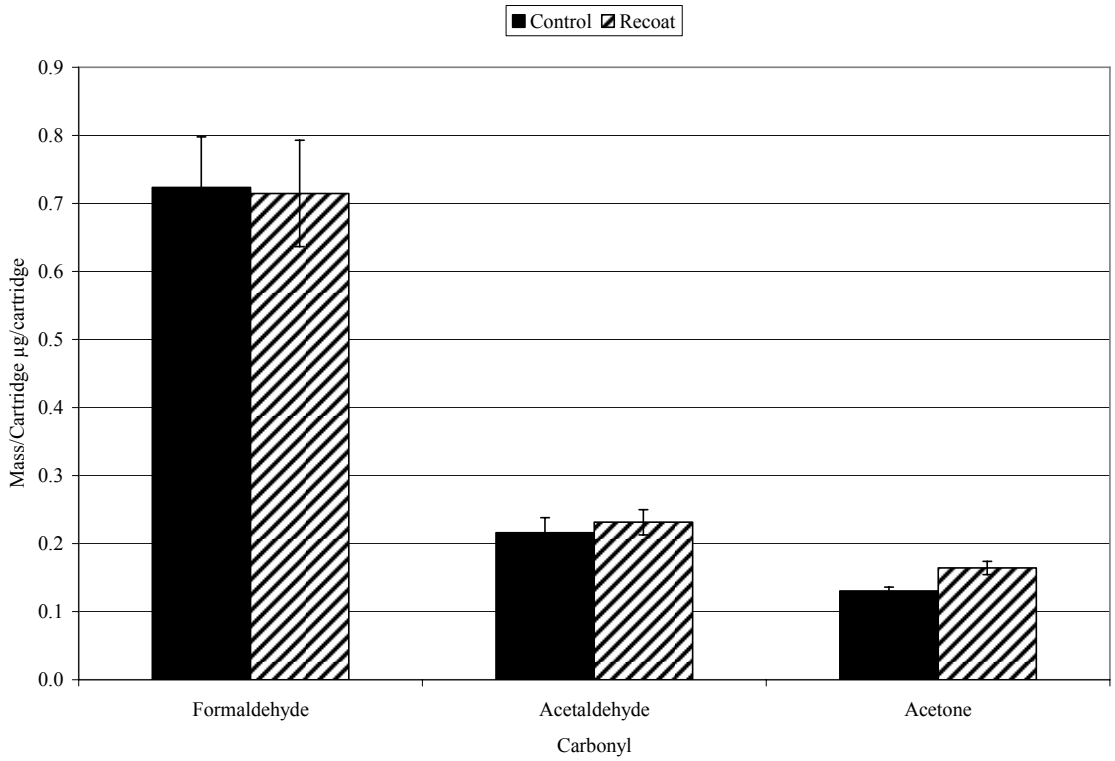


Figure 14: Effects of coating, cleaning, and re-coating PAKS cartridges on the PAKS laboratory blank concentrations. N= 3 for each condition and Y error bars represent the standard deviation amongst replicate samples.

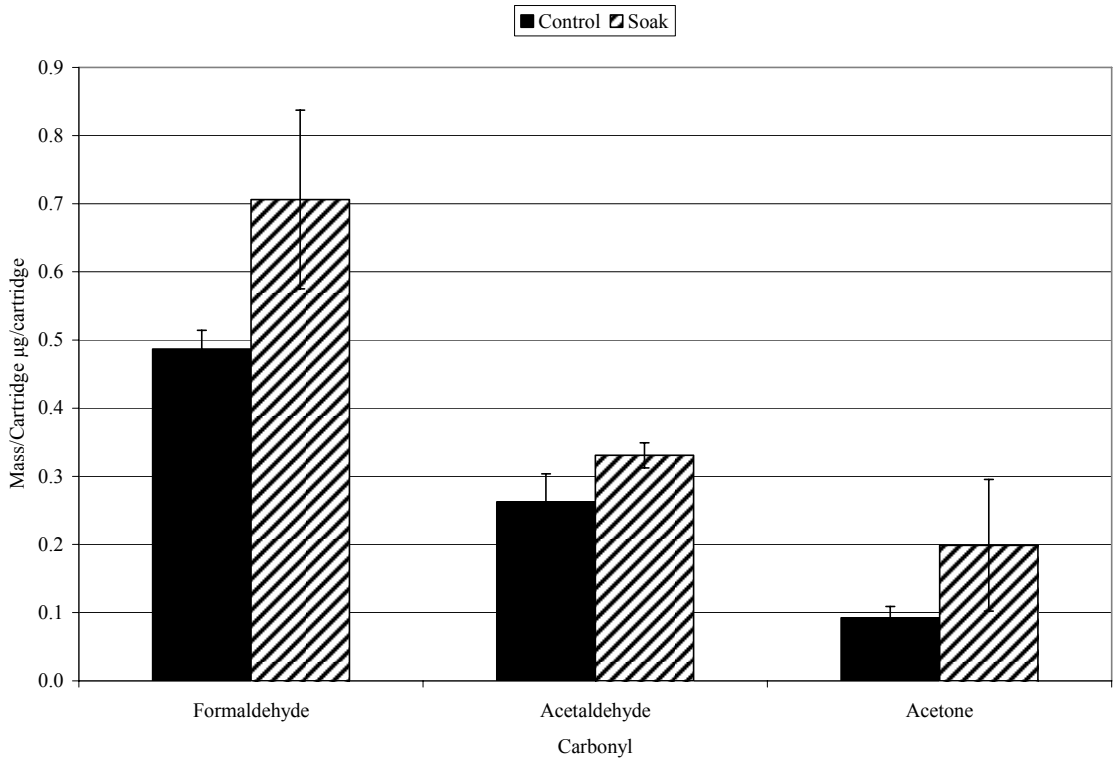


Figure 15: Effects of soaking, cleaning, and re-coating PAKS cartridges on the PAKS laboratory blank concentrations. N= 3 for each condition and Y error bars represent the standard deviation amongst replicate samples.

4.4.1.2 Solvent (ACN)

Results from the ACN purity test (Table 6) indicated that there was a relatively large and unacceptable (>25%) contribution of all 3 carbonyls from the ACN. In particular, the results indicated that the ACN contributed 525% (calculated using Equations 1 and 2) of the acetaldehyde. Therefore, the ACN was triple distilled in an attempt to remove these impurities. Results from the ACN distillation experiment (Table 7) indicated that distilling the ACN was a successful method for reducing the ACN contribution for all 3 carbonyls to acceptable levels (≤25%). However, results from utilizing distilled ACN for preparing the PAKS laboratory blanks (Table 7) indicated that distilled ACN was not successful in reducing the PAKS laboratory blank contamination levels for all 3 carbonyls.

The distillation of ACN reduced the contribution of all 3 carbonyls from ACN to acceptable levels based on a purity test for EPA Compendium Method TO-11A (*33*). This purity test/criteria is dependent on ACN's relative contribution to the total background contamination of DNPH-coated solid sorbents, which is relatively low. These results suggested that although there is contaminate contribution from the ACN, this contribution level is relatively low for the PAKS method, suggesting that the majority of the PAKS laboratory blank contamination comes from another source (e.g., the reagent (DNSH)).

It is important to note that these experiments focused on ACN's contaminant contribution to the laboratory blank, and ACN's contact time with the laboratory blanks is relatively short. For example, the ACN is used to make the coating solution. Shortly thereafter the PAKS cartridges are cleaned with ACN and then coated with the coating solution. Immediately afterwards the cartridges are dried with nitrogen to remove the ACN. In order for the ACN to contribute contamination to the laboratory blank, the contamination in the ACN needs to react with the DNSH and acid catalyst to undergo the carbonyl-DNSH derivatization reaction. This reaction is relatively slow and the aforementioned coating procedures take ~10 minutes. Therefore the contamination in the ACN probably does not have enough time to react and contribute to the laboratory blank cartridge.

Table 6: PAKS solvent (ACN) purity.

Derivative	Concentration prior to reaction with HCL (µg/mL)	Concentration after reaction with HCL (µg/mL)	Contribution from ACN (µg/mL)	Contribution from ACN (%)
Formaldehyde-DNPH	0.30	0.54	0.24	79
Acetaldehyde-DNPH	0.08	0.51	0.43	525
Acetone-DNPH	0.31	0.47	0.16	50

Table 7: Effects of distillation on the purity of ACN.

Derivative	Concentration prior to reaction with HCL (µg/mL)	Concentration after reaction with HCL (µg/mL)	Contribution from ACN (µg/mL)	Contribution from ACN (%)
Formaldehyde-DNPH	0.20	0.20	0	0
Acetaldehyde-DNPH	0.66	0.77	0.11	17
Acetone-DNPH	0.64	0.79	0.15	25

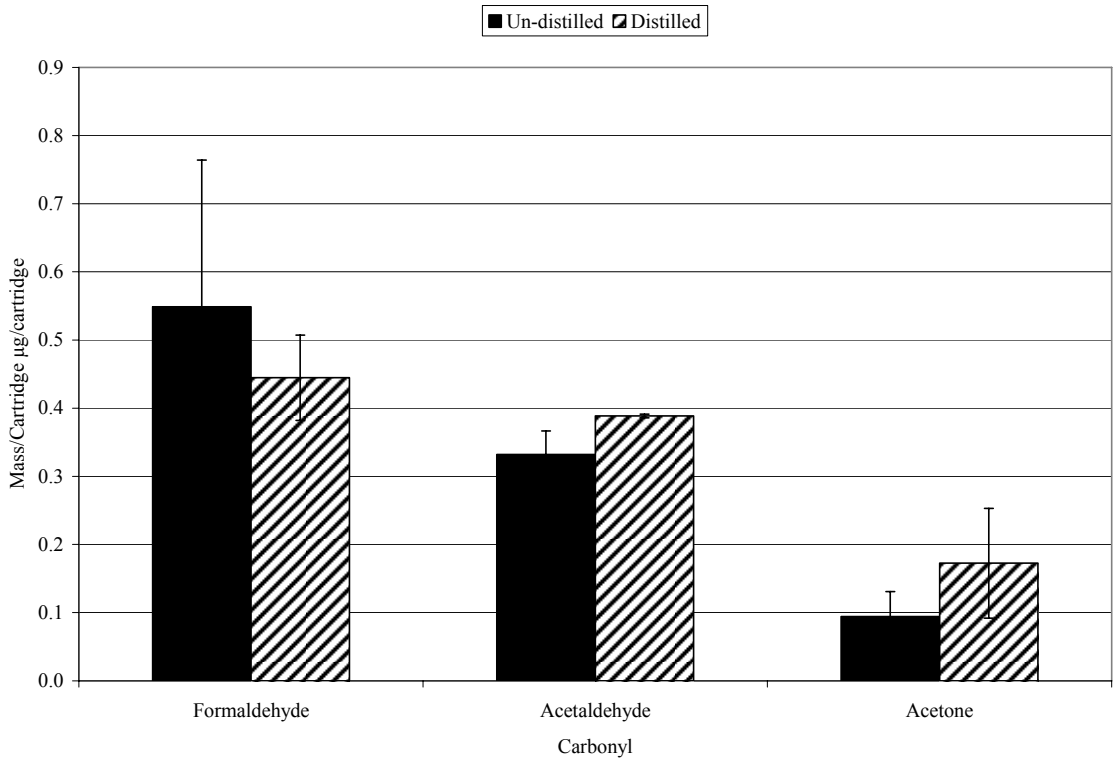


Figure 16: Effects of ACN distillation on the PAKS laboratory blank concentrations. N= 2 for each condition and Y error bars represent the difference amongst duplicate samples.

However, ACN does have a relatively and substantially longer period of time (hours to days) to react with the laboratory blanks in extract. Therefore, an experiment was conducted to evaluate un-distilled, distilled, and refluxed from DNPH ACN contaminant contribution to laboratory blanks in extract. Results from the extract experiment (Figure 17) indicated that with time the contamination levels of a laboratory blank in the extract increased, because contaminants were afforded time to react with the DNSH in extract.. It is important to note that Dr. Morandi at the UTSPH also observed an identical phenomenon with PAKS standards (*96*). This was consistent for the three types of ACN evaluated. These results indicated that distilled and refluxed ACN were unsuccessful in reducing extract contamination. Therefore, these results indicated that if samples are not going to be

analyzed immediately (i.e., within a day or two) the samples should not be extracted to avoid the increase in contaminant concentration associated with storage time.

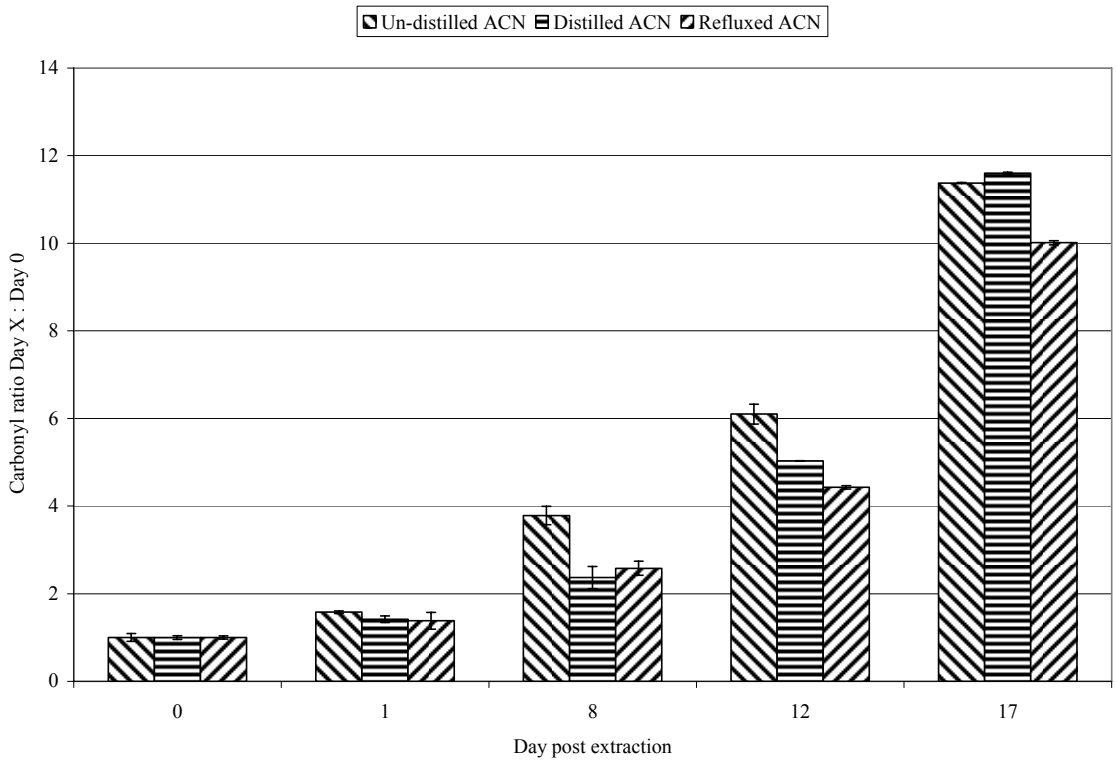


Figure 17: Effects of different ACNs on the acetaldehyde concentrations in PAKS extracts stored at 25°C. N = 3 for each ACN and Y error bars represent the standard deviation amongst replicate samples.

4.4.1.3 Reagent (DNSH)

Results from evaluating the purity of the 3 commercially available brands of DNSH (Aldrich, Fluka, an Sigma) (Table 8) indicated that Sigma had much larger acetaldehyde and acetone contamination levels than the other two DNSH brands and was therefore not considered for the PAKS method. Aldrich and Fluka had very similar contamination levels for all 3 carbonyls. Fluka was chosen to be used in the PAKS method, because Fluka costs ~$36/gram, whereas Aldrich costs ~$105/gram. Once Fluka was chosen as the most

economical DNSH for the PAKS method, the variability amongst Fluka batches was evaluated, and results (Figure 18) indicated that there were no large differences amongst the batches of Fluka DNSH.

Although Fluka was chosen to have the lowest economical contamination levels and very little variability amongst batches, researchers had shown large improvements in contamination levels and variability for DNPH-based methods by purifying the DNPH via re-crystallization from warm ethanol (*3*). Therefore, DNSH was re-crystallized from warm ethanol with the same procedures; however, results (Table 9) indicated that with the exception of acetone the contamination levels increased drastically after re-crystallization. These results suggested that DNSH is not subject to the same purification procedures as DNPH, which has also been confirmed by other researchers (*96*,*97*). The DNSH itself appears to a large source of contamination to the PAKS blanks, and future work on the PAKS method will need to address the DNSH contamination levels and develop a method to purify the DNSH.

Considering that other studies effectively purified DNPH (*95*) to lower the contamination levels and variability, and that DNSH is analogous in structure and chemistry; theoretically one should be able to develop a method for purifying DNSH. The problem is that the PAKS method and other methods for sampling carbonyls with DNSH have only been developed and evaluated by a relatively small number of researchers over the past decade. In contrast, countless researchers have worked on the development and evaluation of DNPH-based sampling methods for over two and a half decades. In addition, the widespread acceptance of DNPH-based methods attracted the commercial industries, which drastically helped with the contaminant levels and variability found in DNPH-based

methods. It is believed that the PAKS method would greatly benefit from the same attention.

In the meantime, current and near future users need to be aware of the PAKS limitations. Specifically, they need to be aware of the contaminant levels and variability in the PAKS. The following precautionary measures are recommended:

1. All batches of PAKS should be evaluated with at least 5% laboratory blanks. The laboratory blank(s) should be analyzed and the contaminant level(s) should be subtracted from all field samples on a batch-specific basis.
2. All batches of PAKS deployed to the field should be accompanied with at least 10% field blanks for the day, to account for batch and field trip variability. The field blank(s) should be transported, stored, extracted, and analyzed in the exact same manner all accompanying field samples are. The field blank(s) contaminant level(s) should be subtracted from all field samples on a batch-specific basis.
3. In order to provide the lowest PAKS detection limits, a batch of 7 PAKS field blanks (prepared at the same time) should be deployed to the field at the same time and place.

It is anticipated that with widespread acceptance, in particular from the commercial sector, the PAKS method blank levels and variability will be reduced, so as to eliminate the need for such stringent laboratory and field practices.

It is important to note that the PAKS formaldehyde blank concentrations typically range around ~0.150 – 0.200 µg/cartridge (Table 8), which is not ~10 fold less than a typical field sample concentration (~0.200 – 1.000). Therefore, the PAKS blank

concentration need to be reduced; however, it is interesting to note that the PAKS formaldehyde blank concentrations are comparable to what is observed in the DNPH-coated solid sorbents used for U.S. EPA Compendium Method TO-11A (~0.15 µg/cartridge) (Page 11A-34, Table 2, and page 11A-35, Table 4) (*33*). This is significant when one considers the PAKS method has not benefited from purification procedures and commercialization that DNPH-coated solid sorbents have. However, in the case of DNPH-coated solid sorbent methods, a background formaldehyde concentration of ~0.15 µg/cartridge is not of concern, because the sampling rates of these methods are generally at least 10 to 20 fold higher than the PAKS method.

Table 8: Comparison of PAKS laboratory blank concentrations for different commercially available DNSH brands**.**

DNSH Supplier	Formaldehyde (µg/cartridge)	Acetaldehyde (µg/cartridge)	Acetone (µg/cartridge)
Aldrich A	0.151	0.042	0.041
Aldrich B	0.142	0.046	0.011
Aldrich C	0.128	0.025	0.016
Mean ± Stdev.	0.140 ± 0.012	0.037 ± 0.011	0.023 ± 0.016
Fluka A	0.192	0.052	0.002
Fluka B	0.175	0.058	0.011
Fluka C	0.177	0.062	0.043
Mean ± Stdev.	0.181 ± 0.009	0.057 ± 0.005	0.018 ± 0.022
Sigma A	0.190	0.146	0.202
Sigma B	0.197	0.165	0.213
Sigma C	0.186	0.167	0.212
Mean ± Stdev.	0.191 ± 0.006	0.159 ± 0.012	0.209 ± 0.006

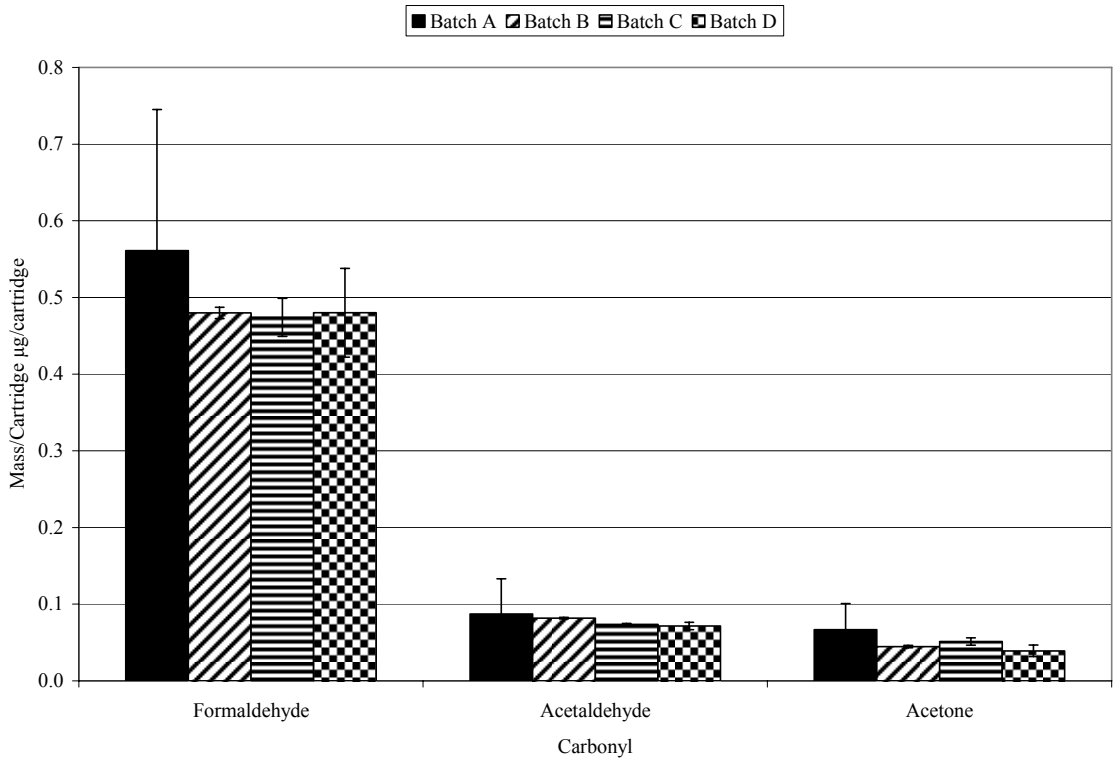


Figure 18: PAKS laboratory blank concentration variability across several different batches of Fluka DNSH. N=2 for each batch and Y error bars represent the difference amongst duplicate samples.

Table 9: Effects of DNSH purification on the PAKS laboratory blank concentrations. Compare with Table 8 concentrations.

Cartridge	Formaldehyde (µg/cartridge)	Acetaldehyde (µg/cartridge)	Acetone (µg/cartridge)
A	2.322	1.158	0.084
B	2.511	1.266	0.086
C	2.403	1.188	0.102
Mean ± Stdev.	2.412 ± 0.095	1.204 ± 0.056	0.091 ± 0.010

4.4.1.4 Acid Catalyst

Results from the acid comparison (Table 10) indicated that citric acid would be a good replacement for acetic acid. The citric acid laboratory blanks had much lower levels of formaldehyde and acetaldehyde contamination than the acetic acid laboratory blanks. Furthermore, the reductions in contamination levels from citric acid were magnified in the

field blanks. Lastly, the citric acid provided comparable reaction efficiencies (Table 11) to acetic acid. Therefore, 1.3% (w/w) citric acid was chosen for use in the final PAKS method coating solution.

Table 10: Comparison of two acid catalysts on the PAKS laboratory and field blank concentrations.

Cartridge	Formaldehyde (µg/cartridge)	Acetaldehyde (µg/cartridge)
Acetic Acid Lab Blank A	0.262	0.319
Acetic Acid Lab Blank B	0.274	0.336
Mean	0.268	0.328
Citric Acid Lab Blank A	0.175	0.184
Citric Acid Lab Blank B	0.213	0.196
Mean	0.194	0.190
Acetic Acid Field Blank A	0.422	0.453
Acetic Acid Field Blank B	0.347	0.411
Mean	0.384	0.432
Citric Acid Field Blank A	0.256	0.195
Citric Acid Field Blank B	0.233	0.196
Mean	0.244	0.195

Table 11: Comparison of two acid catalysts on the reaction efficiency of spiked PAKS cartridges.

Cartridge	Formaldehyde (µg/cartridge)	Acetaldehyde (µg/cartridge)	Propionaldehyde (µg/cartridge)	Acrolein (µg/cartridge)
Acetic Acid Spike A	0.527	0.924	0.946	0.537
Acetic Acid Spike B	0.546	0.928	0.943	0.451
Mean	0.537	0.926	0.945	0.494
Citric Acid Spike A	0.548	0.907	0.877	0.721
Citric Acid Spike B	0.560	0.909	0.791	0.666
Mean	0.554	0.908	0.834	0.694

4.4.1.5 Cartridge Drying

Results from the cartridge drying experiment indicated that at ~500 mL/min a cartridge would dry in ~5 to 7 minutes. The only method to determine if a cartridge was dry was to rotate the cartridge and see if the packing material tumbled freely. In addition, a cartridge that was not dry would have condensation on the outside of the cartridge due to evaporative cooling as the ACN evaporated. Results from the cartridge drying experiment (Figure 19) indicated that the N_2 is not a large source of contamination for the PAKS laboratory blanks. As the drying time increased from 10 to 40 minutes there was very little change in the laboratory blank contamination levels for all 3 carbonyls. It was unclear as to why there was a relatively large amount of acetone variability amongst duplicate samples. It is important to note that shorter drying times are preferable for the following two reasons: 1) shorter drying times use less N_2, which is economically beneficial; 2) shorter drying times reduce the possibility of evaporating the acid catalyst, which could reduce the PAKS reaction efficiency. Therefore, a PAKS drying time of 10 minutes at a flow rate ~500 mL/min was selected for the final PAKS method.

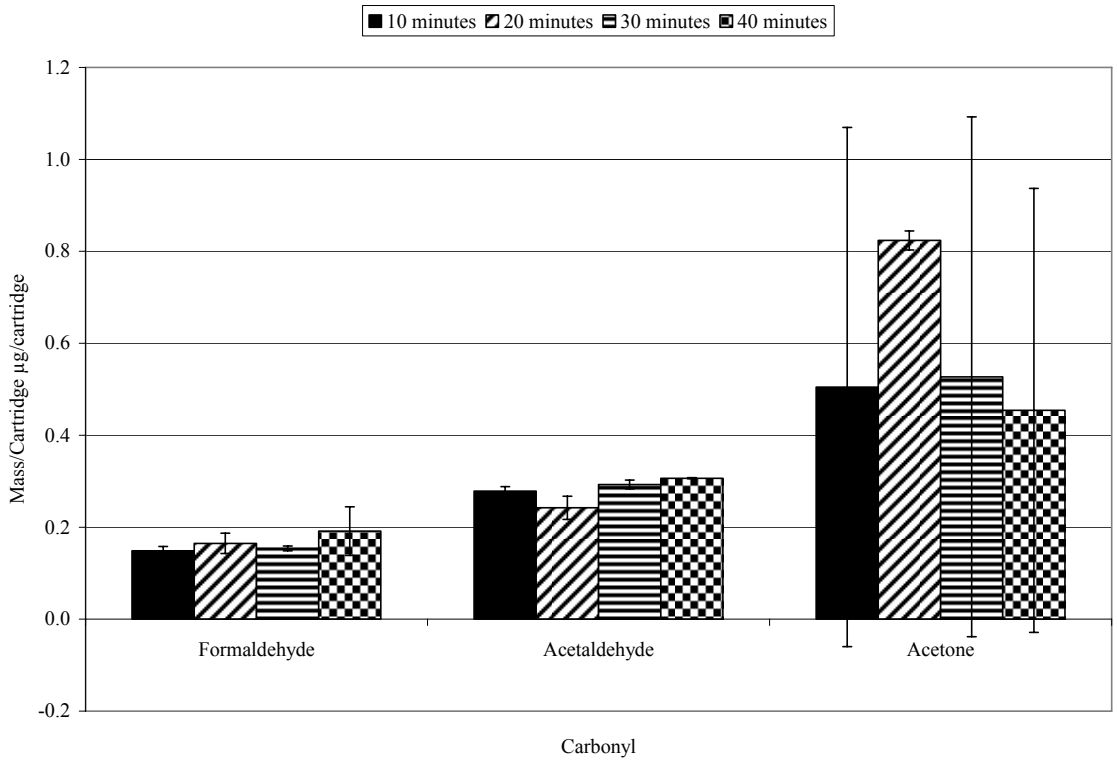


Figure 19: Effects of cartridge drying time on PAKS laboratory blank concentrations. N=2 for each drying time and Y error bars represent the difference amongst duplicate samples.

4.4.1.6 Blank Storage/Shipping

Results from the caps experiment indicated that the original PAKS extraction end caps were not able to hermetically seal the PAKS. When placed under vacuum, all 3 caps would leak immediately. The original PAKS exposure end caps were able to hermetically seal the PAKS for 2 of the 3 caps evaluated. All of the new caps (extraction and exposure) purchased from Supelco were able to hermetically seal the PAKS, and were therefore chosen for the final PAKS method.

4.5 Conclusions and Recommendations

Results from the cartridge experiments indicated that the PAKS cartridge is not a quantifiable source of contamination for the PAKS laboratory blanks (based on the methods used in this study). Results from the solvent experiments indicated that the ACN

is not a large source of contamination for the PAKS laboratory blank cartridges; however, ACN is a large source of contamination for the PAKS laboratory blank extracts, especially over time. Therefore, samples should not be extracted until immediately prior to HPLC analysis. Results from the ACN purification experiments were unsuccessful in reducing the ACN contamination levels, and this should be addressed in future work. Results from the reagent experiments indicated that Fluka provided the lowest economical PAKS laboratory blank contamination levels; however, the DNSH purification methods mimicked from DNPH-based methods were unsuccessful in reducing the PAKS laboratory blank contamination levels. As discussed in section 4.5.1.3, future work needs to address the contamination levels in the DNSH. Results from the acid catalyst experiment indicated that citric acid is a suitable replacement for acetic acid that resulted in a large decrease in the laboratory blank contamination levels, while still providing comparable reaction efficiencies. The acid catalyst results are the most significant findings of this study and had the largest impact on the PAKS laboratory blanks to date. The change from acetic to citric acid result in a ~37% and ~55% reduction in formaldehyde and acetaldehyde field blank concentrations, respectively. Results from the cartridge drying experiments indicated that the nitrogen was not a large source of contamination for the laboratory blanks and cartridge drying time of 10 minutes at a flow rate of ~500 mL/min is optimum. Results from the blank storage/shipping experiments indicated that the new PAKS caps were able to provide a more effective hermetic seal than the original PAKS caps.

Chapter 5

Evaluation of the Final PAKS Method

5.1 Abstract

The PAKS method has evolved significantly over the past several years. Starting with the original method (*46*) developed and evaluated during the RIOPA study (*21*); the method was then modified for improved measurement of acrolein (Chapter 2) (*89*); followed by optimization of the method's sample processing procedures (Chapter 3); and lastly optimization of the method for the reduction of blank contamination levels (Chapter 4). This significant evolution dictated that the final (i.e., most up-to-date) PAKS method performance be evaluated. Experiments were conducted and field samples were collected to assess the final method stability, accuracy, precision, and detection limits. The final PAKS method was shown to have stable laboratory blanks and samples for up to 20 weeks of storage; accuracies close to 100%; method and analytical imprecision, expressed as coefficient of variation from duplicate samples, being <20% and <15%, respectively; and detection limits in the low ppb range for 24-hour sampling.

5.2 Introduction

The original PAKS method (*46*) development evaluated the PAKS performance for parameters such as accuracy, relative humidity effect, ozone effect, and limits of detection (LOD). When the method was modified for the improved measurement of acrolein (Chapter 2) (*89*) those same parameters were re-evaluated to confirm that the method continued to perform well. However, shortly after the modified method was developed it became apparent that the PAKS field blanks had relatively elevated and variable

formaldehyde and acetaldehyde concentrations, and therefore the LODs were unacceptably high. Therefore, the method was reevaluated and optimized for the reduction of blank contamination levels (Chapter 4). During the blank development work the method was modified drastically by changing the acid catalyst. Like Chapter 2 (*89*) this method change dictated that PAKS method performance be re-evaluated to: 1) see that the method continued to perform well (i.e., collection efficiency was ~100%, sample stability was acceptable, etc.); and 2) to provide future users with an idea of what performance they could expect (i.e., method precision values, LODs, etc.) from the final method. It is important to note that throughout the PAKS modifications, the PAKS has remained the same physically and therefore Figure 1 in Chapter 1 is valid for the final PAKS method This chapter reports on an evaluation of the final (most up-to-date) PAKS method performance.

5.2.1 Method Performance Criteria

The objective of the current chapter was to evaluate the performance of the final (i.e., most up-to-date) PAKS method with an emphasis on formaldehyde, acetaldehyde, and acrolein; therefore, it was imperative to establish the following set of criteria for evaluating the method's performance:

1. Laboratory Blank Stability
    - Ideally, the criteria for the PAKS laboratory blank stability (i.e., shelf-life) would be indefinite; however, this is not necessarily feasible. An extensive literature search did not provide any specific benchmark as to an expected laboratory blank stability; however, a few studies (e.g., Tsai and Hee, (*98*)) suggested 3 months. Therefore, a criteria of a

laboratory blank stability (i.e., no change in concentration >±20%) was adopted for 3 months for the final PAKS method.

2. Sample Stability
    - Again, a criteria for the PAKS sample stability to be indefinite would be ideal; however, this is not necessarily feasible. Again, the literature did not provide any specific benchmark as to an expected sample stability; however, a criteria of sample stability (i.e., no change in concentration >±20%) was adopted for 1 month for the final PAKS method. One month was deemed reasonable for samples to be collected, stored, shipped back to the laboratory, stored in the laboratory, and then finally analyzed.
3. Method Accuracy
    - A method accuracy or efficiency (This is often referred to as collection efficiency or recovery rate in literature; however, these two terms do not take into account the efficiency of the method as a whole) criteria of 100% ± 20% was adopted for the final PAKS method.
4. Method Precision
    - A method precision (or more accurately imprecision, as it is reported as the CV amongst duplicate pairs.) criteria of ≤±20% was adopted for the final PAKS method.
5. Method Detection Limits
    - The current body of literature indicates that the majority of environmental ambient concentrations of carbonyls are in the low

μg/m^3 (ppb) range; with personal exposure often much higher. For example, the RIOPA study reported a median ambient formaldehyde concentration of 6.5, 6.2, and 7.1 μg/m^3 in Los Angeles, Houston, and Elizabeth, respectively (*21*). Therefore, a method detection limit (MDL) criteria of low to sub μg/m^3 was adopted for the final PAKS method.

6. Analytical Detection Limits
    - Similar to DNPH-based methods, the PAKS limit of detections are driven by the MDLs and therefore an analytical detection limit (ADL) criteria of sub μg/m^3 was adopted for the final PAKS method.
7. Analytical Precision
    - A criteria of ≤±10% precision (or more accurately imprecision, as it is reported as the CV amongst replicated HPLC injections) of response for replicate HPLC injections was adopted for the final PAKS method.

5.3 Materials and Methods

5.3.1 Stability

5.3.1.1 Laboratory Blank Stability

The PAKS laboratory blank stability had never been evaluated for more than 1 month, and the criteria for acceptable laboratory blank stability had been adopted as no change in concentration >±20% for 3 months; therefore, the final PAKS laboratory blank stability needed to be evaluated. Because formaldehyde, acetaldehyde, and acetone are ubiquitous throughout the environment, particularly in laboratory settings, it was important that the laboratory blanks were stored in a relatively clean environment. The freezer offered several advantages. There was a relatively air-tight seal to prevent the intrusion of carbonyls into

the freezer; the freezer provided a dark environment (shielding the PAKS cartridges from UV light); and the colder temperatures reduced the diffusion and reaction rates of the PAKS. However, the longer a laboratory blank is stored the more chance for contamination and/or reactions to take place. Therefore, experiments were conducted to evaluate the maximum duration a laboratory blank could be stored without a large change (>±20%) in contamination level. For this experiment, PAKS cartridges were prepared and then stored in a freezer at -21°C. Two PAKS cartridges were extracted for analysis at 0, 1, 2, 3, 4, 6, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, 48, and 52 weeks post storage

5.3.1.2 Sample Stability

The optimized PAKS sample stability had never been evaluated for more than 2 weeks, and the criteria for acceptable samples stability had been adopted as no change in concentration >±20% for 30 days; therefore the final PAKS sample stability needed to be evaluated. Like the laboratory blanks, the longer sample storage durations pose the possibility for increased contamination over time. In addition, PAKS samples may be prone to reactions such as degradation; therefore, experiments were conducted to evaluate the maximum duration a sample could be stored without a large change (>±20%) in the concentrations. For this experiment, PAKS cartridges were prepared, spiked with a known standard, and stored in a freezer at -21°C. Two PAKS cartridges were extracted for analysis at 0, 1, 2, 3, 4, 6, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, 48, and 52 weeks post spiking

5.3.2 Method Performance

5.3.2.1 Method Accuracy

The PAKS method accuracy, commonly referred to as recovery or collection efficiency (CE), is defined as the ratio of the carbonyl concentration measured using the PAKS

method to the known carbonyl concentration (often generated in a dynamic atmosphere generation system) ((Measured/Known) × 100). The final PAKS method accuracies were determined for formaldehyde, acetaldehyde, and acrolein by collecting 15 duplicate pairs (N=30) of 24 hour samples from the dynamic atmosphere generation system described in the original (*46*) and modified (Chapter 2, Figure 3) (*89*) PAKS method developments.

5.3.2.2 Method Precision

The final method precisions were determined using data collected from the U.S. EPA's Detroit Exposure and Aerosol Research Study (DEARS). The PAKS results were compiled from DEARS Season V (Summer, 2006) for formaldehyde, acetaldehyde, and acrolein. From theses results, the PAKS method precisions were calculated from 70 indoor, outdoor, and personal duplicate samples. The PAKS method precision was defined as the coefficient of variation (CV) (determined using Equation 4) amongst the duplicate samples. However, since the method uses duplicate samples over varying concentrations, a pooled standard deviation (SD_P) must be calculated using Equation 5, and the SDp is substituted in Equation 4 for SD.

Equation 4: $$CV = \frac{SD}{Mean}$$

Equation 5: $$SD_P = \sqrt{\frac{\sum diff^2}{2 \times N}}$$

5.3.2.3 Method Detection Limits (MDLs)

The MDLs for the final version of the PAKS method were determined using data collected during DEARS Season V. The formaldehyde, acetaldehyde, and acrolein MDLs were calculated from 120 indoor, outdoor, and personal field blanks. The PAKS MDL(s) were

calculated as 3 times the standard deviation of the field blank concentration(s). In addition to these MDLs, MDLs were calculated for formaldehyde and acetaldehyde with a "best case" scenario. For this experiment, 7 PAKS laboratory blanks were baked, extracted, and analyzed. This was done to eliminate the PAKS field blank variability, which is introduced from shipping, sampling, and storage. This experiment examined the variability amongst PAKS blanks strictly. The "laboratory blank MDLs" were calculated as 3 times the standard deviation of the 7 PAKS laboratory blanks.

5.3.3 Analytical Performance

5.3.3.1 Analytical Detection Limits (ADLs)

The final PAKS ADLs were calculated as three times the standard deviation of repeat analyses of a low concentration standard. At least 7 repeat analyses of the lowest concentration standard were executed in order to determine the ADLs for the following 15 carbonyls: acetaldehyde, acetone, acrolein, benzaldehyde, butyraldehyde, crotonaldehyde, 2,5-dimethylbenzaldehyde, formaldehyde, hexaldehyde, isovaleraldehyde, valeraldehyde, propionaldehyde, m-tolualdehyde, p-tolualdehyde, and o-tolualdehyde.

5.3.3.2 Analytical Precision

The PAKS analytical precision was defined as the coefficient of variation (CV). The CV was defined as the standard deviation (SD) divided by the mean (Equation 4). The analytical precision was determined by performing at least 7 multiple analyses of a single sample (near the ADL).

5.3.4 Results and Discussion

Note that discussion involving blanks was limited to formaldehyde, acetaldehyde, and acetone; because these were the three most abundant carbonyls in the PAKS laboratory

blanks; acrolein was not present in the PAKS laboratory blanks. However, discussion involving field samples and field blanks was limited to formaldehyde, acetaldehyde, and acrolein, because acrolein was present in the PAKS field blanks.

5.3.4.1 Stability

Results from the laboratory blank stability experiment (Figure 20) indicated that the formaldehyde laboratory blank contamination was relatively stable (i.e., within ±20% of the starting level). However, results from the laboratory blank stability experiment (Figure 20) indicated that the acetaldehyde, and to a lesser extent acetone, contamination levels were erratic. Upon closer review, it appeared that there was a correlation with the acetaldehyde and acetone contamination, and the number of days that passed between extraction and analysis (Figure 21). This observation suggested that with time ACN present in the extract had contaminations of acetaldehyde, and, to a lesser extent, acetone. It appeared that the phenomenon took place somewhere around 7 days post extraction (Figure 21). It is important to note that Dr. Morandi also observed an identical phenomenon with PAKS standards (*96*). This was also evaluated in Chapter 4 with the extract experiment and the results exhibit a similar trend. However, when the laboratory blank stability was evaluated for samples analyzed within 5 days of extraction (Figure 22) the blanks exhibit fairly (i.e., ±20%) constant contamination levels over time up to 36 weeks of storage. Note that acetone was not stable for the first 4 weeks (Figure 22); however, this was not of concern, because acetone was not one of the "key" carbonyls evaluated. If PAKS laboratory blanks are analyzed within 5 days of extraction, the method satisfactorily meets the criteria (no change in concentration >±20% for 3 months) set forth

for laboratory blank stability. As stated in Chapter 4, these results indicated that a sample should not be extracted until ready for analysis.

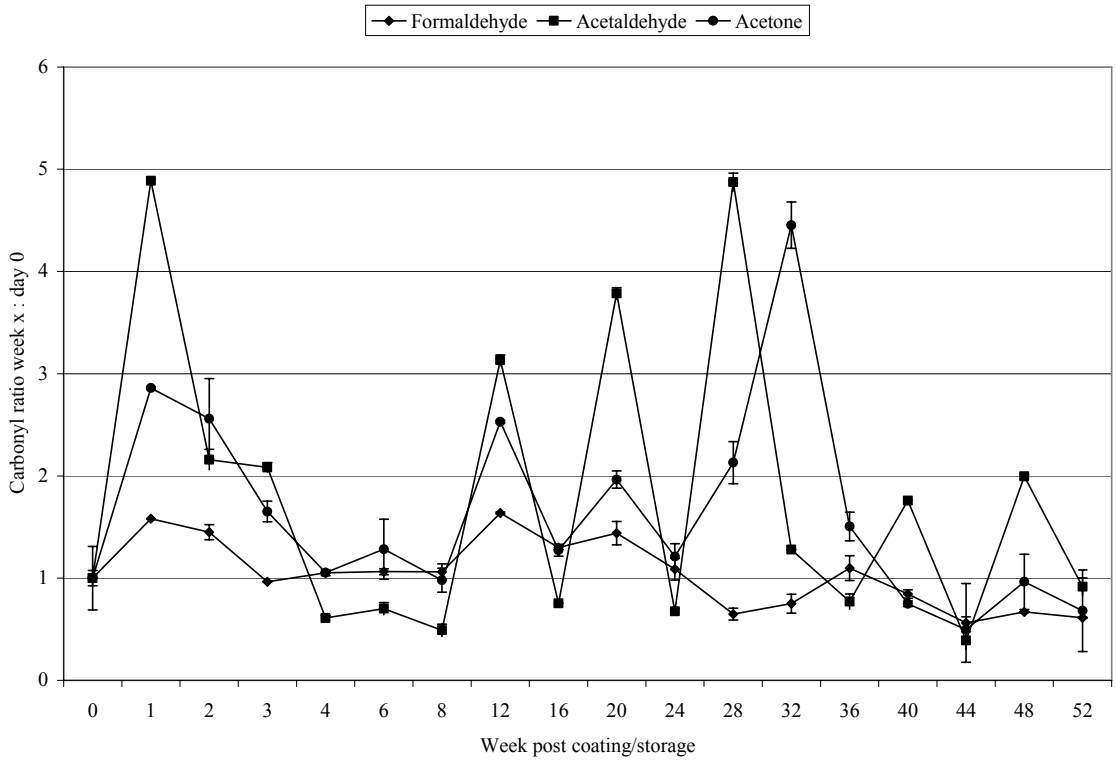


Figure 20: PAKS laboratory blank stabilities at -21°C. N=2 for each data point and Y error bars represent the difference amongst duplicate blanks.

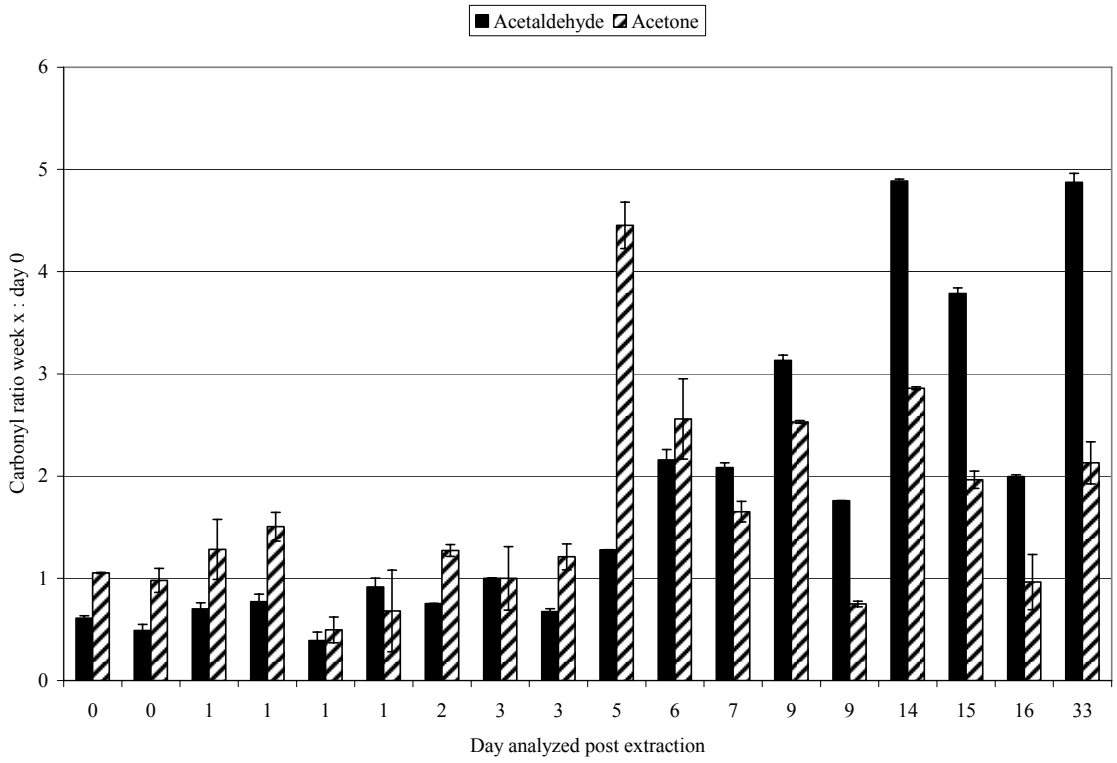


Figure 21: Relationship between PAKS laboratory blank concentrations in extract and number of days between extraction and analysis. N=2 for each day and Y error bars represent difference amongst duplicate blanks.

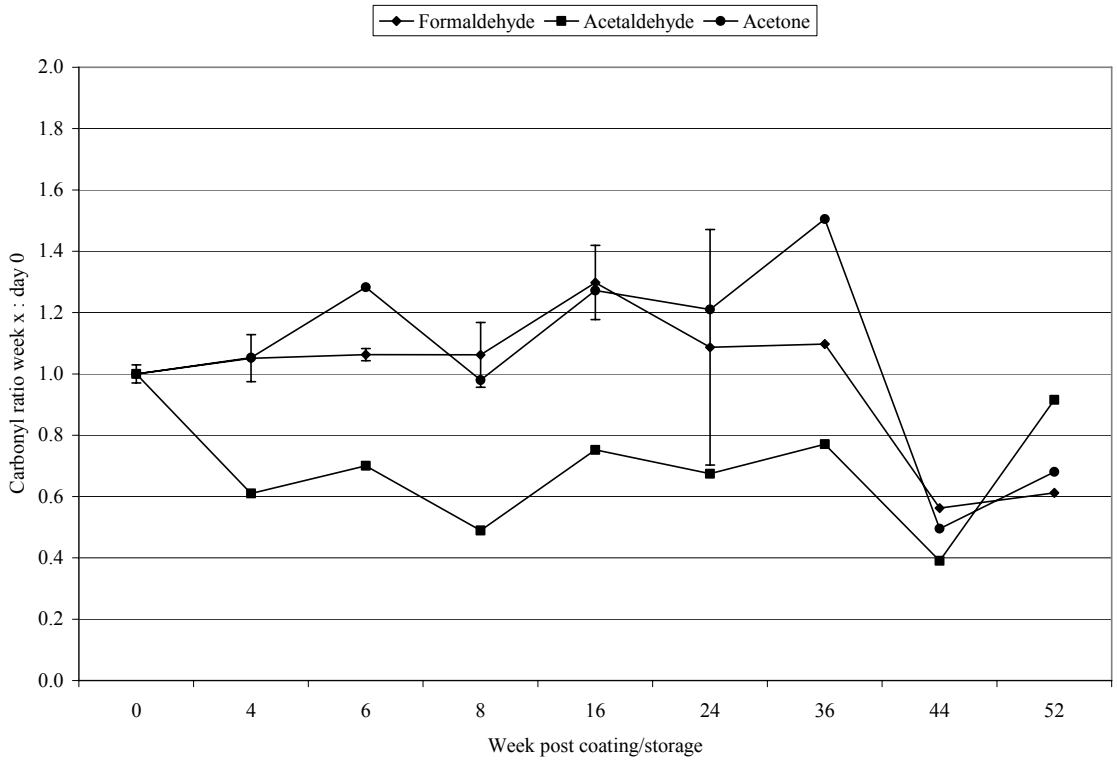


Figure 22: PAKS laboratory blank stabilities at -21°C for samples analyzed within 5 days of extraction. N=2 for each data point and Y error bars represent the difference amongst duplicate blanks.

Results from the sample stability experiment (Figure 23) indicated that all 3 carbonyls were stable on the cartridge up to ~20 weeks of storage at -21°C. Beyond 20 weeks of storage it appeared that all 3 carbonyl-DNSH derivatives degraded. Considering the samples are stable on the cartridge for such extended periods of time, and samples stored in extract are subject to increased acetaldehyde and acetone contamination (as discussed in the previous section and Chapter 4); it is more appropriate to keep samples on the cartridge and only extract immediately before HPLC analysis. If PAKS samples are analyzed within 5 days of extraction, the method more than satisfactorily meets the criteria (no change in concentration >±20% for 30 days) set forth for sample stability.

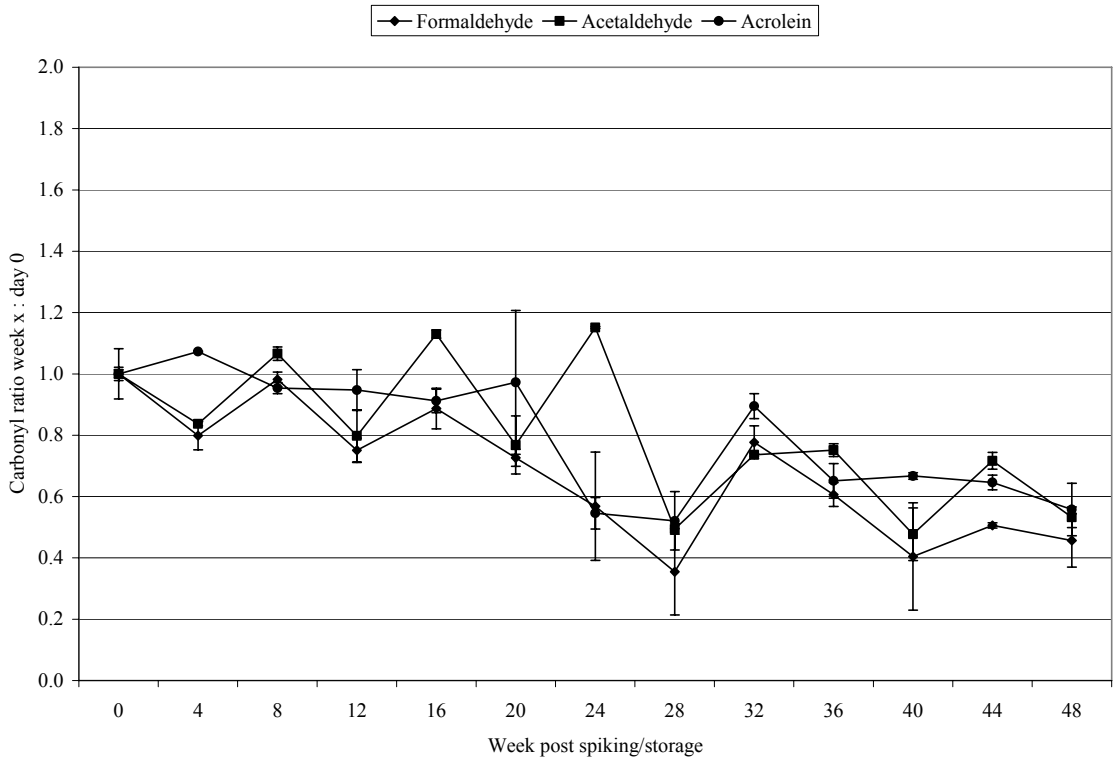


Figure 23: PAKS sample stabilities at -21°C. N=2 for each data point and Y error bars represent the difference amongst duplicate blanks.

5.3.4.2 Method Performance

Results from the method accuracy (collection efficiency) experiment (Table 12) indicated that the final PAKS method had ~100% collection efficiencies for formaldehyde, acetaldehyde, and acrolein, and meets the criteria (100% ± 20%) set forth. These values are consistent with what was observed in the original (*46*) and modified (Chapter 2) (*89*) PAKS methods. Future users could expect to see comparable accuracy values for other carbonyls analyzed by the PAKS method, based on the results for the earlier versions of the PAKS. This, however, remains to be confirmed.

Table 12: PAKS method accuracies determined using the dynamic atmosphere generation system.

Carbonyl	Collection Efficiency (%)[a]	Coefficient of Variation (CV (%))
Formaldehyde	115.5	11.02
Acetaldehyde	105.8	9.12
Acrolein	87.5	4.71

[a] Based on 15 tests (N = 30) with temperature = 30°C, face velocity = 0.05 m/s, relative humidity = 10%, and sampling duration = 24 hours.

Results from DEARS Season V duplicate samples (Table 13) indicated that the PAKS method precisions (expressed as coefficient of variations amongst duplicate samples) for formaldehyde, acetaldehyde, and acrolein were 17.6, 22.5, and 15.9%, respectively. Although the acetaldehyde precision is slightly higher than the criteria set forth (±20%), most would argue this is acceptable. These precision values are consistent with what was observed for the original method during the RIOPA study (*21*). Although only formaldehyde, acetaldehyde, and acrolein were evaluated, future users could probably expect to see comparable precision values for other carbonyls analyzed by the PAKS method.

Table 13: PAKS method precisions determined from duplicate samples collected during DEARS Season V.

Carbonyl	Coefficient of Variation (CV (%)) (N)
Formaldehyde	17.6 (67)
Acetaldehyde	22.5 (69)
Acrolein	15.9 (67)

Results from DEARS Season V field blanks indicated that the PAKS MDLs for formaldehyde, acetaldehyde, and acrolein were 20.0, 8.53, and 0.62 μg/m³, respectively; when the MDLs were calculated based on the SD of all the field blanks collected during the season. Based on these calculations, with the exception of acrolein, the final PAKS MDLs do not meet the criteria set forth. However, it is imperative to have the following discussion.

As outlined by the United States U.S. EPA's in Title 40, Appendix B to part 136 (Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11), the MDL is defined as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte". Simply put, the MDL is the level at which one can confidently separate a "true" signal from the method's "noise".

Considering the above, the first step in determining the PAKS MDLs is to establish what is the "noise" of the PAKS method, which includes field sampling activities. Very often, researchers define the noise of such a passive sampling method as the variation amongst field blanks. Therefore, determining the MDL from the standard deviation of at least 7 (as stipulated by the EPA) field blanks would be a sound method. However, in the event that at least 7 field blanks are not deployed to the field simultaneously, rather at least 7 field blanks are deployed over several field sampling trips, this approach is not feasible. In the later situation, the noise would not be limited to the method's noise, rather the noise would now include the noise of field sampling activities; which could be heavily influenced by the variation of such field sampling variables such sampling duration,

temperature, relative humidity, human activities, etc. This is exactly the case of the MDLs mentioned previously (i.e., formaldehyde, acetaldehyde, and acrolein were 20.0, 8.53, and 0.62 μg/m³, respectively). The MDLs mentioned previously were calculated from indoor, outdoor, and personal field blanks; in addition, the field blanks came from different batches; and the field blanks were deployed at different locations and times. The MDLs mentioned previously do not accurately represent the "noise" of the PAKS method; however, they do represent the noise attributed by different PAKS batches (as discussed in Chapter 4), the noise attributed by different ambient temperatures, the noise attributed by different human activities, etc. The following two approaches should be used to appropriately determine the PAKS MDLs:

1. PAKS field blanks are deployed during every field sampling trip. Therefore, the field blank levels and variability are accounted for every trip. Furthermore, all sample concentrations will then be corrected with the appropriate field blank (i.e., that day's field blank). This means for each field sampling trip, sample concentrations above the field blank are above zero, because the field blank is zero for that given day; and this also means that all sample processing steps have been accounted for. (Recall, the deployment of field blanks during every field sampling trip was recommended in Chapter 4.) Therefore, the noise of the PAKS method can now be reduced to the analytical noise, whereby the PAKS MDLs can be calculated according to the EPA's guidelines. In short, the PAKS MDLs are reduced to the PAKS analytical detection limits (Section 5.3.4.3), which are defined as the 3 times the standard deviation of 7 repeat analyses of a low concentration standard.

2. At the start of a field sampling study, 7 PAKS field blanks from the same batch should be deployed to the field at the same time and in the same location. This approach would represent the PAKS "true" "noise" and would appropriately meet the EPA's guidelines for determining the PAKS MDLs. This approach would also be a relatively more conservative method (i.e., the MDLs should be slightly higher) for determining the PAKS MDLs. In addition, as stipulated in the EPA guidelines, batches of 7 field blanks should be deployed throughout an extended field sampling campaign to reconfirm the PAKS MDLs.

It is recommended that for small (i.e., ~25 samples or less) field studies, approach 1 be used, because it may not be feasible to deploy 7 field blanks; and approach 2 be used for large field studies.

In an attempt to demonstrate what one might expect as the PAKS "true" "noise" based on blanks, the "laboratory blank MDL" experiment was conducted. Results from the "laboratory blank MDL" experiment (Table 14) indicated that the PAKS MDLs would be 8.53 and 2.85 $\mu g/m^3$ for formaldehyde and acetaldehyde, respectively (Acrolein was not present in the blanks). These results are on the cusp of the range of the criteria set forth for the PAKS method, and therefore they need to be lower for ambient sampling. However, they would probably be sufficient for indoor and personal sampling. In addition, there were batches of 7 PAKS field blanks deployed during DEARS Season V. Although the batches were never deployed from the same batch of PAKS and in the same location (i.e., they were a mix of indoor, outdoor, and personal), these batches of 7 could give one a rough, but very conservative of the PAKS "noise" based on field blanks. The results from these 4 batches of 7 field blanks indicate the PAKS MDLs would range from 0 – 9.87, 1.15 – 7.30,

and 0.24 – 0.64 µg/m³ for formaldehyde, acetaldehyde, and acrolein, respectively. Note that these would be the recommended MDLs; however, they relatively conservative as they were determined from indoor, outdoor, and personal field blanks. Again, these results are on the cusp of the range of the criteria set forth for the PAKS method, and therefore they need to be lowered for ambient sampling. It certainly does not mean the method is not suitable for use, it just means that current and future users need to be aware of this limitation. However, these results do further support the fact that the PAKS laboratory blank contamination arising from the ACN and DNSH needs to be reduced in future studies.

Table 14: PAKS "laboratory blank method detection limits" determined from 7 PAKS laboratory blanks. Expressed as µg/m³ based on a 24-hour sampling duration @ 25°C.

Carbonyl	µg/m³ (N = 7)
Formaldehyde	8.53
Acetaldehyde	2.85

Table 15: PAKS method detection limits determined from indoor, outdoor, and personal field blanks collected during DEARS Season V. Samples were collected over the same 24-hour period in batches of 7.

Carbonyl	07/22/06 µg/m³ (N = 7)	07/29/06 µg/m³ (N = 7)	08/12/06 µg/m³ (N = 7)	08/19/06 µg/m³ (N = 7)
Formaldehyde	9.87	0.00	9.03	4.89
Acetaldehyde	3.81	1.15	7.30	7.12
Acrolein	0.24	0.25	0.51	0.64

5.3.4.3 Analytical Performance

Results from the ADL experiment (Table 16) indicated that the final PAKS method had ADLs in the low µg/m³ **(**ppb) range. These ADL values are consistent with what was

observed during the RIOPA study (*21*), and meet the criteria set forth for the final PAKS method

Table 16: PAKS analytical detection limits.

Carbonyl	ng/cartridge (μg/m^3)[b]
Formaldehyde	5.42 (0.53)
Acetaldehyde	2.12 (0.28)
Acetone	4.06 (0.63)
Propionaldehyde	6.81 (1.06)
Butryaldehyde	5.40 (0.97)
Benzaldehyde	8.49 (1.73)
Isovaleraldehyde	12.4 (2.47)
Valeraldehyde	9.81 (1.95)
o-/m-Tolualdehyde	6.99 (1.55)
p-Tolualdehyde	7.48 (1.66)
Acrolein	3.06 (0.46)
Crotonaldehyde	3.63 (0.63)
Hexaldehyde	2.02 (4.40)
2,5-Dimethylbenzaldehyde	2.02 (4.81)

[a] Determined from 7 repeat analyses of a low concentration standard.
[b] Estimated air concentration for 24 hr sampling @ 25°C

Results from the analytical precision experiment (Table 17) indicated that the final PAKS method had precision values, or more accurately, imprecision values based on the coefficient of variation (CV), generally less than 15%. The relatively high CV values for hexaldehyde and 2,5-dimethylbenzaldehyde were the result of inconsistent co-elution of these two compounds. These precision values were consistent with what was observed for the original PAKS method during the RIOPA study (*21*), and meet the criteria set forth for the final PAKS method.

Table 17: PAKS analytical precisions.

Carbonyl	Coefficient of Variation (%)[a]
Formaldehyde	2.28
Acetaldehyde	1.55
Acetone	2.81
Propionaldehyde	11.3
Butryaldehyde	10.3
Benzaldehyde	9.69
Isovaleraldehyde	18.8
Valeraldehyde	13.3
o-/m-Tolualdehyde	14.5
p-Tolualdehyde	7.61
Acrolein	7.78
Crotonaldehyde	9.48
Hexaldehyde	28.8
2,5-Dimethylbenzaldehyde	28.8

[a] Determined from 7 repeat analyses of a low concentration standard.

5.4 Conclusions and Recommendations

The final (i.e., most up-to-date) version of the PAKS method had relatively stable blank levels when the PAKS cartridges were stored in a -21^{0}C freezer for up to 20 weeks. When samples (cartridges) were stored in a freezer, their concentrations remained unchanged (<±20% deviation) within up to 20 weeks. To prevent artifacts during the storage of sample extracts, however, the samples need to be extracted only immediately before HPLC analysis. The final method had accuracies close to 100% for formaldehyde, acetaldehyde, and acrolein. The method and analytical precisions, expressed as coefficient of variation from duplicate samples, were <20% and <10%, respectively for these carbonyls. The analytical detection limits ranged from 0.28 to 4.8 μg/m³; however, method detection limits ranged from 0 to 9.87 μg/m³, for a 24-hour sampling period. The only aspect of the final PAKS method that did not meet the criteria set forth, was the MDLs. Future work

needs to be conducted to further reduce the PAKS field blank levels and variability and thereby to further lower the method detection limits.

Chapter 6

Low Acetaldehyde Collection Efficiencies for 24-Hour Sampling with 2,4-Dinitrophenylhydrazine (DNPH)-Coated Solid Sorbents[†]

6.1 Abstract

Airborne aldehyde and ketone (carbonyl) sampling methodologies based on derivatization with 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbents could unequivocally be considered the "golden" standard. Originally developed in the late 1970s, these methods have been extensively evaluated and developed up to present day. However, these methods have been inadequately evaluated for the long-term (i.e., 24 hours or greater) sampling collection efficiency (CE) of carbonyls other than formaldehyde. The current body of literature fails to demonstrate that DNPH-coated solid sorbent sampling methods have acceptable CEs for the long-term sampling of carbonyls other than formaldehyde. Despite this, such methods are widely used to report the concentrations of multiple carbonyls from long-term sampling, assuming ~100% CEs. Laboratory experiments were conducted in this study to evaluate the long-term formaldehyde and acetaldehyde sampling CEs for several commonly used DNPH-coated solid sorbents. Results from sampling known concentrations of formaldehyde and acetaldehyde generated in a dynamic atmosphere generation system demonstrate that the 24-hour formaldehyde sampling CEs ranged from 83% to 133%, confirming the findings made in previous studies. However, the 24-hour

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[†] This chapter was modified from Herrington, J.; Lioy, P. J.; Fan, T.; Zhang, J. J. Low acetaldehyde collection efficiencies for 24-hour sampling with 2,4-Dinitrophenylhydrazine (DNPH)-coated solid sorbents. *Environ. Sci. Technol.* **2007**, 41, 580-585.

acetaldehyde sampling CEs ranged from 1% to 62%. Attempts to increase the acetaldehyde CEs by adding acid to the samples post sampling was unsuccessful. These results indicate that assuming ~100% CEs for 24-hour acetaldehyde sampling, as commonly done with DNPH-coated solid sorbent methods, would substantially under estimate acetaldehyde concentrations.

6.2 Introduction

Originally developed in the late 1970s, DNPH-coated solid sorbent sampling methods have been extensively evaluated and developed up to present day. The first documented DNPH-coated solid sorbent sampling method appears to be DNPH-coated Amberlite XAD-2 (*39*). Since then, similar methods have been developed and evaluated by numerous researchers (e.g., *38,40-43,47,48,51,56,60,67,68,70,86,95,99-107*). However, a large number of these method evaluations were limited to formaldehyde (*38,39,42,43,56,86,100,105*). Although method evaluations were extended to other carbonyls (*40,41,47,48,51,60,67,68,70,95,99,101-104,106,107*), they were only evaluated for short-term sampling durations that were on the order of minutes to a few hours (*40,41,48,51,60,67,70,95,99,101,102,104,107*), with the longest sampling duration being 12 hours (*68*). Through an extensive literature search, only three studies were found during which carbonyls other than formaldehyde were evaluated on DNPH-coated solid sorbents for long-term sampling (i.e., 24 hours or greater) (*47,103,106*). Lazarus (*106*) reported low CEs; and Grosjean (*103*), and Grosjean and Grosjean (*47*) evaluated breakthrough of the collection media, which does not necessarily reflect CE. The breakthrough tests were conducted using cartridge-impinger or cartridge-cartridge sampling trains, and no breakthrough simply means that the downstream sample did not collect a measurable

amount of carbonyl(s). The absence of breakthrough can not automatically be translated in to ~100% CE on the upstream cartridge; because CE is defined as the ratio of the carbonyl concentration determined from the collection media, to the actual (know) concentration. In the case of DNPH-coated solid sorbents, CE is largely dependent on the reaction efficiency of the reversible acid catalyzed carbonyl-DNPH derivatization reaction (*3,40,51,60,80,107*). In fact, Grosjean and Grosjean (*60*) noted that although there was no breakthrough observed by Grosjean and Grosjean (*47*), the CEs for DNPH-coated solid sorbents sampled in dry air were low.

It is not the intent of this chapter to be a review of every DNPH-coated solid sorbent sampling method. However, an exhaustive literature search failed to produce any documentation from the body of readily available literature, which appropriately evaluated the long-term sampling CEs of DNPH-coated solid sorbent sampling methods for carbonyls other than formaldehyde. Due to the lack of appropriate evaluations; can one assume that DNPH-coated solid sorbent sampling methods have ~100% CEs for long-term sampling of carbonyls other than formaldehyde? The goal of the current chapter was to provide an answer to the above by determining the long-term formaldehyde and acetaldehyde sampling CEs for several commonly found DNPH-coated solid sorbents. A dynamic atmosphere generation system was employed to generate formaldehyde and acetaldehyde gas standards to determine CEs. This is a significant, because in 1998 Kleindienst et al. (*86*) noted that with the exception of a few studies (*105* and now *86*), relatively few studies had systematically evaluated the performance of DNPH-coated solid sorbent methods with the use of formaldehyde gas standards; and none evaluated long-term sampling of acetaldehyde gas standards. Efforts were focused on formaldehyde

and acetaldehyde, because they are ubiquitous in indoor and outdoor air, and are of significant health concerns (In June 2004, formaldehyde was classified as a human carcinogen based on sufficient evidence from epidemiological studies (*13,108*). Acetaldehyde has been classified as probable human carcinogen by the U.S. EPA (*109*). In addition, both aldehydes are potent eye and the respiratory tract irritants).

6.3 Materials and Methods

6.3.1 DNPH-coated solid sorbents

The following commercially available DNPH-coated cartridges were used in this study: SUPELCO's (Bellefonte, PA, USA) LpDNPH Air Monitoring Cartridge (referenced as SUPELCO in tables and figures); Waters (Milford, MA, USA) Sep-Pak DNPH-Silica Cartridge (referenced as WATERS in tables and figures); and Waters Sep-Pak XPoSure™ Aldehyde Sampler (referenced as XPOSURE in tables and figures). These cartridges were selected based on their ubiquitous citation in the literature. In addition to the commercially available DNPH-coated cartridges, an "in house" cartridge (referenced as HOUSE in tables and figures) was evaluated. The DNPH-coated cartridges prepared in house have been reported in detail earlier by Zhang et al. (*57*) and Zhang and Smith (*58*). Briefly, C_{18} Sep-Pak cartridges (Waters Corporation) were freshly coated with twice-re-crystallized DNPH, as per a method adopted from EPA Compendium Method TO-11A (*33*).

6.3.2 Sample extraction and analysis

All laboratory samples were extracted and analyzed using the following procedures. All sample cartridges and extracts were stored in the dark at -20°C. Sampled cartridges were gravimetrically eluted with 4 mL of acetonitrile (ACN). Sample extracts were analyzed using an HPLC system (Spectra Physics P4000 Mobile Phase Pump, Spectra Physics

AS3000 Autosampler, Spectra Physics UV2000 Programmable UV Detector; and Waters Nova-Pak C_{18} column (3.9×150 mm, 60 Å, 4 µm) and guard cartridge (Nova-Pak, 4 µm, 60Å, C_{18} Guard-Pak)). The use of the analytical program, as described in Table 18, (was able to clearly resolve the formaldehyde- and acetaldehyde-DNPH derivatives from all other carbonyl-DNPH derivatives. Carbonyl concentrations were determined through calibration curves prepared using commercially available standard solutions of pure carbonyl-DNPH derivatives purchased from SUPELCO.

Table 18: HPLC-UV analytical conditions

Time (min)	% A: Water/Acetonitrile/Tetrahydrofuran 60/30/10 v/v	% B: Water/Acetonitrile 60/40 v/v
0	100	0
5	100	0
33	0	100
50	0	100
55	100	0
Flow rate	1 mL/min	
Injection volume	20 µL	
Detector wavelength	360 nm	

6.3.3 Experiments

6.3.3.1 Sample breakthrough

Prior to conducting any CE experiments for short-term and long-term sampling CE experiments, an appropriate sampling flow rate was estimated based on molar stoichiometry and the carbonyl concentrations in the dynamic atmosphere generation system. This would allow for sufficient collection (approximately 10 times greater than the blank concentrations) of the carbonyls present in the dynamic atmosphere generation system (Figure 3) (*46,89*); while avoiding sample breakthrough. Based on the

concentrations in the dynamic atmosphere generation system, and the longest sampling period of 48 hours at a nominal flow rate of 150 mL/min; the consumption of DNPH, based on molar stoichiometry, would be ~16% and ~32% for the commercial and in house cartridges, respectively. This is well below the manufacturers' loading recommendations based on 50% consumption. Therefore, there should be a sufficient amount of DNPH to promote the forward carbonyl-DNPH derivatization reaction to completion. In addition, sample breakthrough experiments were conducted to demonstrate any correlations, or lack there of, with CE. Similar to Grosjean and Grosjean, (*47*) the four types of DNPH cartridges were sampled with cartridge-cartridge sampling trains for 24 hours at a nominal flow rate of 150 mL/min. For all of the experiments the sampling flow rate was regulated by an SKC Adjustable Low Flow Regulator (Houston, TX, USA) and the sampling flow rate was verified at the start and end of each experiment with a DryCal® DC-Lite primary flow controller (Bios International Corp., NJ, USA). The mean sampling flow rate accuracy was ±6.5%.

6.3.3.2 Collection efficiency

The dynamic atmosphere generation system (Chapter 2, Figure 3) was used to generate atmospheres of formaldehyde and acetaldehyde gas standards (*46,89*). Formaldehyde and acetaldehyde were generated with permeation devices (VICI Metronics, WA, USA). Once equilibrated at their operating temperature, the permeation devices were found to be constant over a period of several months. The concentrations delivered were determined by the mass delivered from the permeation device and the total flow rate of the dynamic atmosphere generation system (Table 20). Concentrations were cross checked by collecting samples with the PAKS method (*46,89*). Using this system, the formaldehyde

and acetaldehyde sampling CEs were determined for DNPH-coated solid sorbents, for both short-term and long-term sampling (Table 19).

Table 19: Dynamic atmosphere generation system parameters

Parameter	Mean ± SD
Oven #1 temperature (°C)	30.4 ± 0.5
Oven #2 temperature (°C)	29.9 ± 1.2
System flow rate (L min-1)	0.98 ± 0.02
Formaldehyde concentration (µg m-3)	22.8 ± 0.5
Acetaldehyde concentration (µg m-3)	47.7 ± 1.1

6.3.3.3 Short-term CE

It was imperative that the CE results, reported in studies referenced earlier, for short-term sampling durations using DNPH-coated solid sorbents were duplicated (Table 20). This was necessary to confirm previous findings, and serve as a cross-check that the dynamic atmosphere generation system was generating the expected carbonyl concentrations. To reduce costs and analytical time, tests were conducted to determine the short-term CEs of Waters Sep-Pak DNPH-Silica Cartridges (WATERS) only. Samples were collected for 3 hours, at a RH of 30%, and at a nominal flow rate of 150 mL/min.

6.3.3.4 Long-term CE

The long-term sampling CEs were determined of all four DNPH-coated solid sorbents. The long-term CEs were determined for 24- and 48-hour sampling durations at 30% RH (Table 20). For these experiments samples were collected at a nominal flow rate of 150 mL/min. In addition, because and Grosjean (1996) observed that DNPH-coated solid sorbents performed poorly at low RH (*60*), the effect of RH was evaluated on the long-term CEs for

a 24-hour sampling duration at 60% RH (Table 20). For these experiments samples were collected at a nominal flow rate of 75 mL/min.

6.3.3.5 CE deviation with sampling time/volume

In an attempt to determine at what time, if any, the CE would begin to deviate from ~100%. For this experiment samples were collected at 2, 6, 12, 16, 18, 20, 22, and 24 hours; at a RH of 30%, and at a nominal flow rate of 100 mL/min. To reduce costs and analytical time, the test was only evaluated for Waters Sep-Pak DNPH-Silica Cartridges (WATERS). In addition, the sample extracts from this experiment were split; one of the sample extracts was analyzed as it was, while ~5 µL (one drop) of hydrochloric acid (HCl) acid was added to the other extract, shaken, allowed to sit for 3 hours, and then analyzed. The samples were allowed to sit for 3 hours, because the current body of literature suggests that carbonyl-DNPH derivatization reactions are complete after a few minutes to hours, for lower molecular weight carbonyls. This experiment was conducted to evaluate if incomplete derivatization was responsible for a reduction, if any, in CE as the sampling duration increased; and if so, whether the addition of HCl acid would push the carbonyl-DNPH derivatization reaction to completion after sample collection.

6.3.3.6 Stability

Sample instability on the DNPH-coated solid sorbent and/or in the ACN extract has been attributed to the poor performance of DNPH-coated solid sorbents for the collection of other carbonyls (e.g., acrolein) (*68*). Therefore, experiments were conducted to determine the stability of acetaldehyde on the DNPH-coated solid sorbents and in the ACN extracts; and attempted to assess what role, if any, sample stability had on the determination of CEs. For the cartridge stability experiment DNPH-coated cartridges were spiked with an

acetaldehyde standard. These cartridges were then stored at 4°C. Two of these spiked cartridges were extracted and analyzed at a time on days 1, 2, 3, 4, 7, 11, and 14 post spiking (Figure 25). For the extract stability experiment, several cartridge extracts containing acetaldehyde-DNPH derivatives from the cartridge stability experiment were stored at room temperature (~25°C), and reanalyzed at 1, 2, 3, 6, 7, 10, 13, and 15 days post extraction (Figure 26). The stability of the XPOSURE cartridge was not evaluated due to its similarity with the WATERS cartridge.

6.3.3.7 Inter-laboratory quality check

To assess the analytical accuracy, an independent, outside laboratory provided (blinded) extracts, which covered a range of samples, field positive controls, standards, and pure ACN. A total of 10 samples were analyzed by the in house laboratory and the outside laboratory. The analytical results were then compared with the outside laboratory's analytical results (Figure 27).

6.4 Results and Discussion

6.4.1 Breakthrough and collection efficiency

Results from the 3-hour CE experiment (Table 20) confirmed that DNPH-coated solid sorbents have ~100% CEs for formaldehyde and acetaldehyde under short-term sampling durations. This observation is consistent with the findings of other researchers who appropriately defined and determined CE for short-term sampling with DNPH-coated solid sorbents (*38,42,86,105,107*). In addition, results from the 3-hour CE experiments confirmed that the dynamic atmosphere generation system was generating the expected formaldehyde and acetaldehyde concentrations.

Table 20: Collection efficiency, ratio of concentration measured to concentration generated in the dynamic atmosphere generation system, reported as mean ± sd, parentheses represent sample number.

Experimental condition	Carbonyl	SUPELCO	WATERS	XPOSURE	HOUSE
3 hours at 30% RH[ab]	Formaldehyde	89 ± 10[c] (3)			
	Acetaldehyde	93 ± 8[c] (3)			
24 hours at 30% RH[ab]	Formaldehyde	83 ± 4 (3)	87 ± 11 (3)	111 ± 4 (3)	104 ± 25 (3)
	Acetaldehyde	39 ± 7 (3)	43 ± 3 (3)	62 ± 7 (3)	1 ± 2 (3)
48 hours at 30% RH[ab]	Formaldehyde	89 ± 8 (3)	93 ± 4 (3)	105 ± 19 (3)	14 ± 8 (3)
	Acetaldehyde	51 ± 22 (3)	43 ± 2 (3)	40 ± 11 (3)	0 (3)
24 hours at 60% RH[ad]	Formaldehyde	101 ± 8 (3)	101 ± 13 (3)	121 ± 32 (3)	133 ± 27 (3)
	Acetaldehyde	27 ± 4 (3)	29 ± 2 (3)	30 ± 2 (3)	9 ± 2 (3)

[a] Temperature = 30°C
[b] Sample flow rate = 150 mL min-1
[c] Only determined with WATERS cartridge
[d] Sample flow rate = 75 mL min-1

Results from the 24- and 48-hour (both 30% RH) CE experiments (Table 20) confirmed that DNPH-coated solid sorbents have ~100% CEs for formaldehyde under long-term sampling durations. For these experiments, the formaldehyde sampling CEs ranged from 83% to 111%. This observation is consistent with the findings of Sirju and Shepson (*105*) who appropriately defined and determined the formaldehyde (only) CE for 24-hour sampling with DNPH-coated solid sorbents. The results from the 24- and 48-hour (both 30% RH) CE experiments (Table 20); however, indicated that DNPH-coated solid sorbent sampling methods consistently poorly measured acetaldehyde concentrations. For these experiments, the acetaldehyde sampling CEs ranged from 0% to 62%.

The CEs amongst the commercial DNPH cartridges appear to agree well with one another, perhaps only reflecting some minor variability across cartridge type and/or the variability of the dynamic atmosphere generation system. However, the "in house" cartridge (HOUSE) did not perform as well as the commercial cartridges for acetaldehyde and for the 48-hour formaldehyde at 30% RH. The discrepancy between the commercial and "in house" cartridges could possibly be the result of different substrates and/or acids. The commercial cartridges' substrate is silica gel and the in house cartridges' substrate is C_{18}. Lazarus (*106*) and Kleindienst et al. (*86*) also observed that under certain conditions C_{18} cartridges would under measure carbonyls relative to silica gel cartridges.

Results from the breakthrough and CE experiments indicate that despite low acetaldehyde sampling CEs, acetaldehyde was never found to be in detectable quantities on the second (downstream) cartridges. This observation is consistent with Grosjean and Grosjean (*60*) observation that the use of two cartridges in series with no breakthrough does not explain low CE. The results are also consistent with the finding of Kleindienst et al. (*86*) that a discrepancy between DNPH-coated silica gel and C_{18} cartridges was not associated with breakthrough. As stated earlier, the absence of breakthrough does not necessarily mean ~100% CE, because DNPH-coated solid sorbents operate on both adsorption and absorption, and the CE of DNPH-coated solid sorbents is largely dependent on the reaction efficiency of the reversible carbonyl-DNPH derivatization reaction (*3,40,51,60,80,107*). The reversible carbonyl-DNPH derivatization reaction is complex; and is dependent upon parameters such as substrate moisture, substrate pH level, and substrate pH strength. An imbalance in these parameters could result in the incomplete carbonyl-DNPH derivatization reaction. For example, protonation of the carbonyl group at

a low pH level will promote the nucleophilic addition, but concurrently reduces the amount of available un-protonated DNPH (*3*). Because of these competing effects, the carbonyl-DNPH derivatization reaction rate passes through a maximum at a characteristic pH level (*3*). Based on these results, the formaldehyde-DNPH derivatization reaction is not adversely affected by longer sampling durations; however, the acetaldehyde-DNPH derivatization reaction is adversely affected, perhaps due to an imbalance as previously discussed. It is believed that the larger sample volumes associated with the longer sampling durations upsets the substrate pH level and/or strength, possibly due to evaporation of the acid catalyst. However, it is possible that the larger sample volumes caused the DNPH to react with the acid to form a salt, as proposed by Grosjean and Grosjean (*60*). The mechanisms behind our observations need further evaluation.

Results from the CE deviation experiment (Figure 24) indicate that the CE drops off gradually from 2 to 16 hours of sampling, and then the CE appears to stabilize from 16 to 24 hours. Figure 24 represents the trend in CE for the current sampling conditions (i.e., temperature, relative humidity, etc.). A decrease or increase in sampling rate, temperature, relative humidity, and/or carbonyl concentration could alter the CE trend. It is worth noting that the apparent tapering off in CE is suggestive that the CE reaches some sort of equilibrium. This observation is consistent with the observation between 24- and 48-hour sampling, where there was no decrease from 24- to 48- hour sampling. Again, illustrating the complex relationship between long-term sampling and CE. The split extracts from this experiment that were treated with HCl acid were not able to provide an increase in CE, and in some cases the CE appeared to decrease slightly. In addition to the split extracts, several samples were treated with HCL acid on the cartridge post sampling (results not shown).

This was done in an attempt to take advantage of increased reaction efficiency afforded by the cartridge surface area; however, the results from this experiment were also unsuccessful in increasing the acetaldehyde CE. Perhaps it would have been more appropriate to add a base, because as Grosjean and Grosjean proposed (*60*), the sampling medium may have become too acidic. It can only be speculated, as these mechanisms are expected to be complex and warrant future investigations. Future investigations would need to evaluate substrate pH level and strength (with various acids and/or pH buffers) on the cartridge pre- and post-sampling; and other reaction parameters (e.g., time, temperature, etc.).

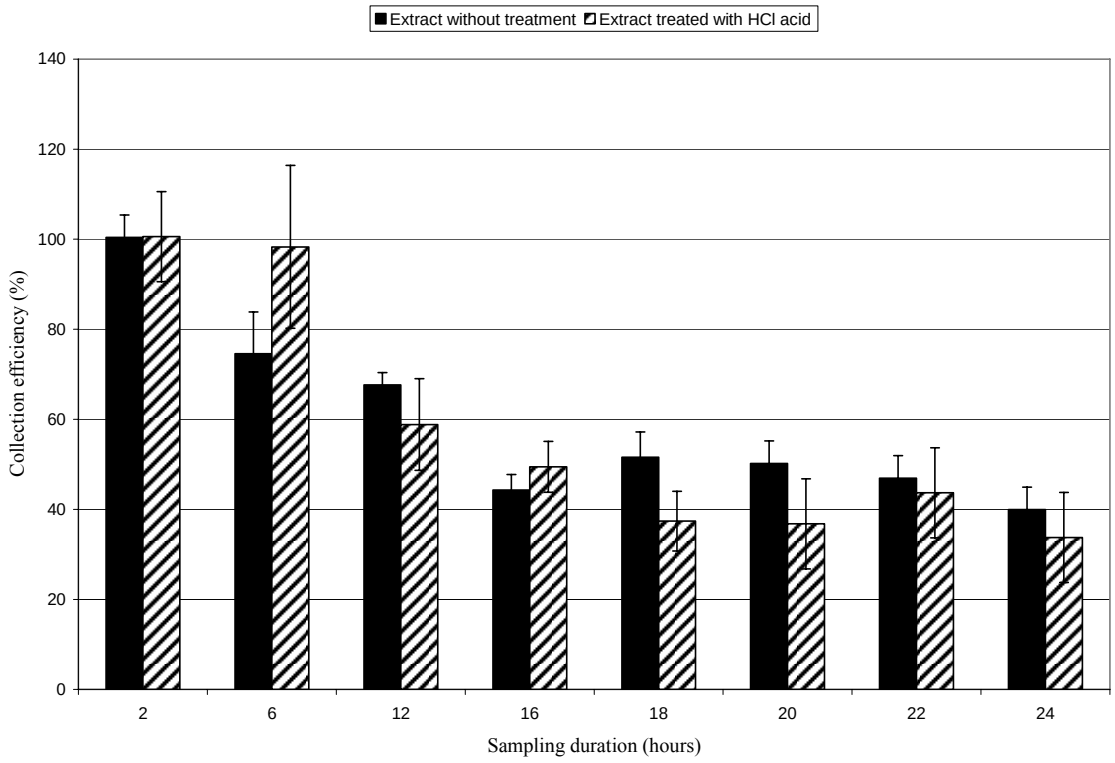

Figure 24: Acetaldehyde CE deviation for un-treated extracts and extracts treated with HCl acid. N = 2 for each data point and Y error bars represent the difference amongst duplicate samples.

Grosjean and Grosjean (*60*) observed that DNPH-coated solid sorbents performed poorly when sampled under relatively low RH (3% - 7%). The authors reasoned that lower RH levels resulted in the DNPH-coated solid sorbent becoming too acidic when sampled in dry air, and possibly resulted in the formation of a salt from a reaction with DNPH and the acid; thereby reducing the reaction efficiency of the carbonyl-DNPH derivatization reaction. Although the RH in first two long-term CE experiments (30%) was not extremely low or unreasonable, 24-hour CE experiments were conducted at 60% RH (Table 20) to examine the effect of RH on the long-term sampling CEs for DNPH-coated solid sorbents. Results from the 24-hour CE experiments at 60% RH (Table 20) continue to indicate that DNPH-coated solid sorbent sampling methods have ~100% CEs for formaldehyde, but substantially under measure acetaldehyde. For these experiments, the formaldehyde sampling CEs ranged from 101% to 133% and the acetaldehyde sampling CEs ranged from 1% to 30%. It was observed that the acetaldehyde sampling CEs decreased with an increase in humidity, which is contrary to what Grosjean (*103*), and Grosjean and Grosjean (*60*) observed. However, it is difficult to make any direct comparisons with Grosjean (*103*), and Grosjean and Grosjean (*60*) observations, because both of these studies evaluated the performance of DNPH-coated C_{18} cartridges; and the DNPH-coated C_{18} cartridges virtually had not detected acetaldehyde for any of the current CE experiments. Regardless, the results indicate that an increase in RH decreases the efficiency of DNPH-coated silica gel cartridges. The mechanism for this remains unclear and needs to be evaluated in future studies.

In an attempt to examine sample instability as a possible cause for the observed low acetaldehyde CEs for long-term sampling with DNPH-coated solid sorbents, the stability

of the acetaldehyde-DNPH derivatives on the collection media and in the ACN extracts was examined. Results from the stability experiments (Figures 25 and 26) indicate that the observed low acetaldehyde CEs were not associated with sample instability on the DNPH-coated solid sorbents or in the ACN extracts. Results from the cartridge experiment (Figure 25) indicate that acetaldehyde was stable on the cartridge within ±20% over 14 days. It should be noted that the cartridge stability results reflect analytical and cartridge spiking variability. Results from the extract experiment (Figure 26) indicate that the acetaldehyde-DNPH derivative was stable in the extract within ±20% over 15 days post extraction. It is important to note that although the sample stability experiments were based on spiked samples, changes in the acetaldehyde-DNPH derivative both on cartridge and in extract were not observed over time for "real" samples. Furthermore, these results are consistent with the findings of other researchers (*42,68,95,104*). These results suggest that the low acetaldehyde CEs were not associated with sample instability.

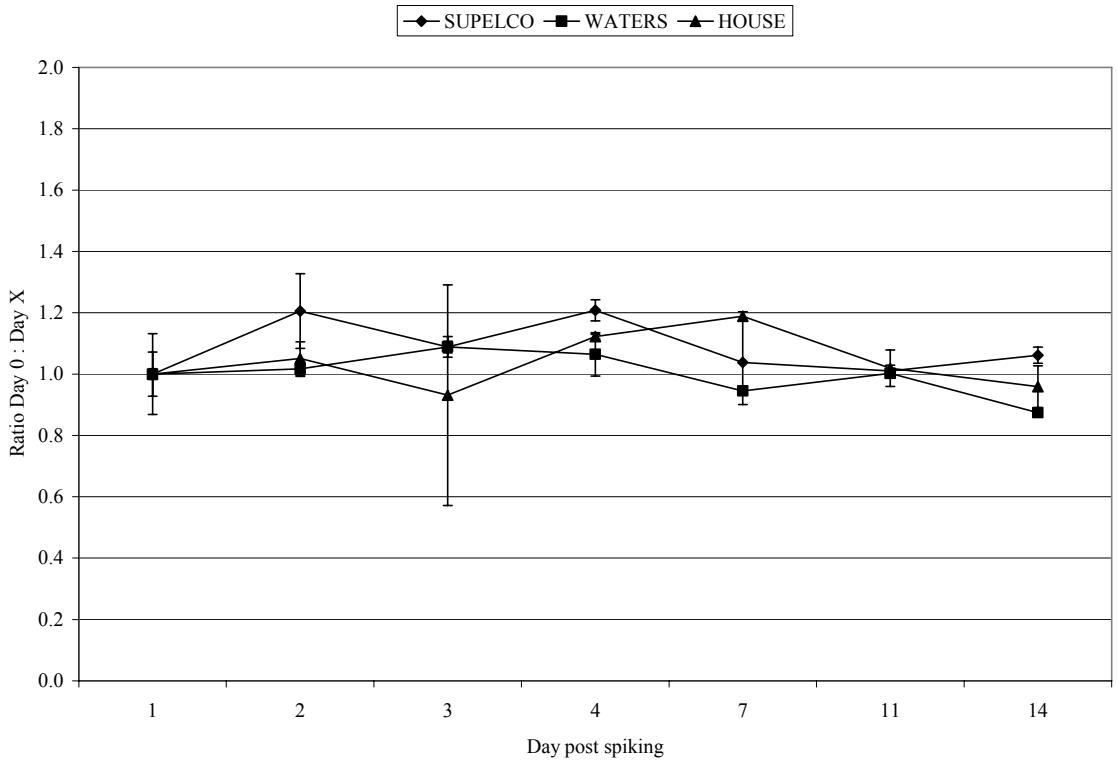

Figure 25: Cartridge acetaldehyde stability. N = 2 for each data point and Y error bars represent the difference amongst duplicate samples.

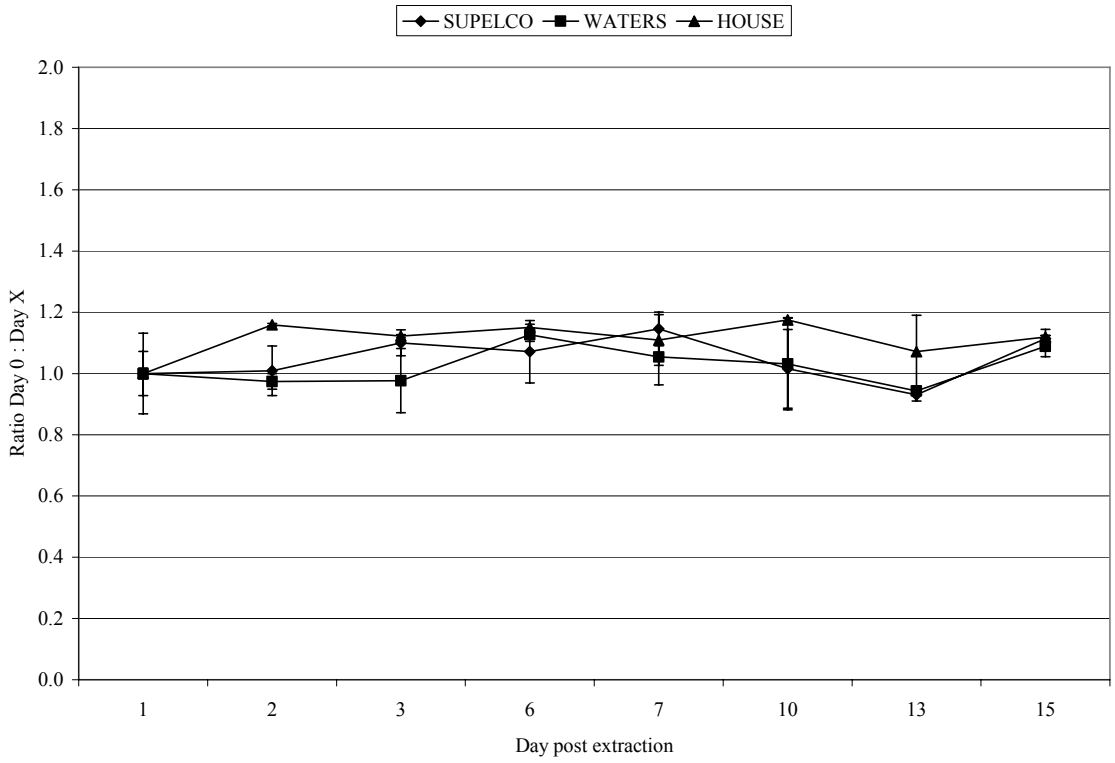

Figure 26: Extract acetaldehyde stability. N = 2 for each data point and Y error bars represent the difference amongst duplicate samples.

Finally, results from the inter-laboratory quality check (Figure 27) indicate that the analytical results are consistent with the results obtained by an outside laboratory. Results from linear least squares regression on the two sets of analytical results demonstrates a slope value close to 1; an intercept value close to 0, and a high R^2. This indicates that the analysis of carbonyl-DNPH derivatives was robust and was not a source of error.

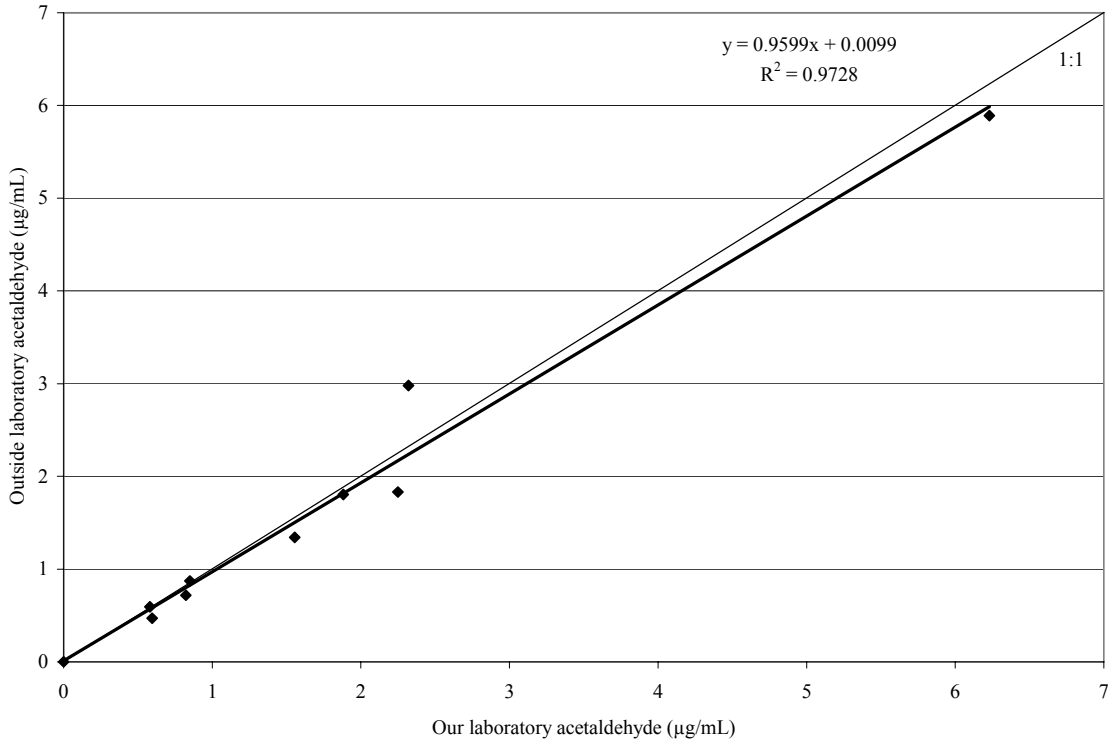

Figure 27: Inter-laboratory quality check

6.4.2 Other evidence of low acetaldehyde CE

Previous work conducted in also provides evidence that DNPH-coated solid sorbent sampling methods have low acetaldehyde CE for long-term sampling. In the Relationships of Indoor, Outdoor, and Personal Air (RIOPA) study (*21*), the 48-hour formaldehyde concentrations determined by DNPH-coated solid sorbents appear to agree reasonably well with the formaldehyde concentrations determined with the PAKS method (*46,89*); however, the acetaldehyde (and other carbonyls) concentrations determined by DNPH-coated solid sorbents appear to be consistently and substantially lower than the acetaldehyde concentrations determined with the PAKS method (*46,89*). In addition, Lazarus (*106*) used a dynamic dilution system to evaluate the 12- and 48-hour CEs of DNPH-coated solid sorbents, and observed a trend similar to what has been observed in the

current study. In his work, Lazarus (*106*) observed a substantially lower (by about 3 fold) CE for acetaldehyde (and for acetone) than for formaldehyde. These independent results support the observation that DNPH-coated solid sorbents have low CEs for long-term sampling of carbonyls other than formaldehyde.

6.4.3 Implications and Recommendations

Results from this chapter have confirmed the findings of other studies that support the short-term sampling of formaldehyde and acetaldehyde, and the long-term sampling of formaldehyde with DNPH-coated solid sorbent sampling methods. However, results from the long-term sampling experiments indicate that DNPH-coated solid sorbent sampling methods have acetaldehyde CEs that are substantially less than 100% under the current experimental conditions. The current observations, along with those of Grosjean and Grosjean (*60*) and Kleindienst et al. (*86*), clearly demonstrate that there can be discrepancies with DNPH-coated solid sorbent sampling methods that are not explained by cartridge breakthrough, although the reaction mechanisms need to be further investigated to explain and "remediate" the observed discrepancies. Assuming that DNPH-coated solid sorbent methods have ~100% acetaldehyde CEs for long-term sampling, simply based on breakthrough results or short-term sampling evaluations, will result in a substantial under-estimation of acetaldehyde concentrations. This is likely to be the case for other carbonyls as well; and evaluations of long-term sampling CEs, using DNPH-coated solid sorbents, needs to be extended to other commonly measured carbonyls in future studies.

Chapter 7

Development and Evaluation of a Method for Time-resolved Measurement of Airborne Acrolein

7.1 Abstract

Due to its relatively low sampling rate, the PAKS method may not provide the time-resolution (e.g., <24 hours) that is needed to understand the temporal acrolein variations found in various microenvironments. Without an understanding of these temporal variations, it is difficult to understand the correlations between short-term acrolein exposure and acute biological endpoints of concern (e.g., ocular irritation). The Active Acrolein Sampler (AAS) method has been developed based on the PAKS method, and utilizes a dansylhydrazine (DNSH)-coated silica-based bonded C_{18} sorbent to collect airborne acrolein using a sampling pump. Results indicated that the AAS method was suitable for short-term (i.e., 30 minutes) and long-term (i.e., ≥24 hours) sampling durations at sampling rates from 50 to 250 mL/min. Results also indicated that relative humidity from 30 to 90%, temperature from 20 to 40°C, and the presence of ozone up to 250 ppb do not affect the performance of the AAS method for short-term sampling durations. The AAS method had an acrolein limit of detection of 0.24 μg/m³ for a 30 minute sampling duration at 250 mL/min. This method sensitivity is comparable to those of other more complex acrolein measurement methods.

7.2 Introduction

Although the original PAKS method (*46*) was modified for improved measurement of acrolein (Chapter 2) (*89*), it can not provide the time-resolution (e.g., for < 24 hours) that

may be needed to understand temporal acrolein variations due to its passive sampling nature (with relatively low sampling rates). Existing active DNPH-based methods could probably provide the required time-resolution; however, these methods have numerous short-comings as discussed in Chapter 2 (*89*). As an alternative to DNPH-based methods, several acrolein sampling methods have been developed based on derivatization with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) followed by gas chromatography/mass spectrometry (GC/MS) analysis (*48,110,111*). However, these methods also have significant shortcomings. The Destaillats et al. (*111*) method used multiple impingers in-line, and the short-comings of impingers have been expounded upon sufficiently in Chapter 1. The Ho and Yu (*48*) method used Tenax packed in Pyrex glass tubes; however, personal sampling with glass tubes poses a safety issue. Lastly, the Seaman et al. (*110*) method was extremely labor intensive and required relatively large (42-45 cm in length), custom-built glass mist chambers. In addition, the Destaillats et al method and the Ho and Yu method required the use of ozone scrubbers.

The goal of this chapter was to capitalize on the PAKS ability to measure acrolein, while also utilizing the following advantages the PAKS method offers over other acrolein measurement methods: a compact (1.5 x 3.5 cm) and durable (i.e., no glass) design; no interference from the presence of ozone; and relatively simple preparation, sampling, and extraction. This chapter describes the experimental designs and methods utilized to design the Active Acrolein Sampler (AAS) method; presents the evaluation results for the AAS; and discusses the suitability of the AAS method as a sensitive and reliable method for measuring airborne acrolein with an hourly resolution. (The method's suitability for measuring other aldehydes and ketones is a subject of future research.)

7.3 Materials and Methods

7.3.1 AAS Cartridge Preparation, Extraction, and Analysis

The AAS cartridges were prepared, extracted, and analyzed as per the optimized PAKS method (Chapter 1) (*89*); however, the coating solution only contained 5 mg/mL DNSH and 1.3% (w/w) citric acid. Hydroquinone was not added to the coating solution and citric acid was substituted for acetic acid due to formaldehyde and acetaldehyde blank interferences observed subsequent to the optimized PAKS method development (Chapter 4). Because the AAS cartridge preparation, extraction, and analysis procedures remained the same as the PAKS method, future users will have the flexibility of choosing from either AAS (active) or PAKS (passive) when sampling in the field.

7.3.2 Dynamic Atmosphere Generation System

The dynamic atmosphere generation system (Chapter 2, Figure 3) was used to generate atmospheres of acrolein gas standard. Acrolein was generated with a permeation device (VICI Metronics, WA, USA). Once equilibrated at the operating temperature, the permeation device was found to be constant over a period of several months. The concentrations delivered were determined by the mass delivered from the permeation device and the total flow rate of the dynamic atmosphere generation system. See Table 21 for a summary of the dynamic atmosphere generation system parameters. Concentrations were cross checked by collecting samples with the PAKS method (*46*,*89*). This system was used to determine the AAS sampling flow rates, sampling durations, relative humidity effects, temperature effects, and ozone effects. The following 5 sections describe the experimental procedures utilized to evaluate the AAS method, and Table 22 provides a detailed summary of the experimental procedures.

Table 21: Dynamic atmosphere generation system parameters used for generating of acrolein gas standard.

Parameter	Mean ± SD
Oven #1 temperature (°C)[a]	30.4 ± 0.5
Oven #2 temperature (°C)[b]	29.9 ± 1.2
System relative humidity (RH (%))[c]	31.8 ± 1.8
System flow rate (L min^{-1})[d]	0.98 ± 0.02
Acrolein concentration (µg m^{-3})	3.65 ± 0.1

[a] Oven #1 temperature for the permeation device was kept constant for all experiments
[b] Oven #2 temperature for the sample housing was kept constant except for temperature experiments
[c] System RH was kept constant except for during RH experiments
[d] System flow rate was kept constant for all experiments

7.3.3 Sampling Flow Rate

The maximum sampling flow rate of an active sampling method, such as the AAS method, is often evaluated with breakthrough experiments (i.e., samples are collected with cartridge-cartridge sampling trains). However, Chapter 6 (*112*) indicated that breakthrough is not an indicator of sampling efficiency, and that only collection efficiency (CE) should be used to evaluate the performance of such an active sampling method. In this study, the maximum sampling flow rate was defined as the point at which the CE dropped to <85%.

Recall that in Chapter 2 it was believed that the 3rd step of the acrolein-DNSH derivatization reaction (Scheme 4) (an addition reaction) would be promoted by heat. This idea was confirmed by the sample baking experiment in Chapter 3 (Figure 9 and Figure 10), which demonstrated an increase in the acrolein-DNSH derivative when samples were baked at 50°C for 2 hours. Considering this, samples were baked at 50°C for 2 hours, post sampling. For this experiment, 2 samples each were collected at 35, 70, 125, 200, 250, 500,

and 750 mL/min. The sampling duration, RH, and temperature was 0.5 hr, 30%, and 30°C, respectively.

7.3.4 Sampling Duration

An experiment was conducted to determine the minimum and maximum sampling duration an AAS could maintain ~100 ± 15 CE. For this experiment, 3 samples each were collected for 0.5, 1, 2, 4, 8, and 24 hours. The sampling flow rate, RH, and temperature were 205 mL/min, 30%, and 30°C, respectively.

7.3.5 Relative Humidity Effects

Relative humidity has been shown to have effects on hydrazine-derivatization based sampling methods (*60*). Therefore, the effects of relative humidity were evaluated for the AAS method. For this experiment 3 samples each were collected at 30 and 90% RH. The sampling flow rate, sampling duration, and temperature were 250 mL/min, 1 hr, and 30°C, respectively.

7.3.6 Temperature Effects

Sampling temperature could possibly affect the reaction efficiency of the AAS method. Therefore, the effects of temperature were evaluated for the AAS method. For this experiment 3 samples each were collected at 20, 30, and 40°C. The sampling flow rate, sampling duration, and RH were 250 mL/min, 1 hr, and 30%, respectively.

7.3.7 Ozone Effects

Ozone has been shown to have negative effects on the performance of DNPH-coated solid sorbent active sampling methods (*56*). Although the PAKS method has been shown to exhibit very little effects from the presence of ozone up to 250 ppb (*46,89*), ozone effects were evaluated, because the AAS method is an active sampling method and the contact rate

with ozone was much higher than that of the PAKS method. For this experiment 3 samples each were collected without ozone and in the presence of 250 ppb ozone. The sampling flow rate, sampling duration, RH, and temperature were 250 mL/min, 1 hr, 30%, and 30°C, respectively.

Table 22: Summary of laboratory experiments utilized to evaluate the AAS performance.

Experiment	# of Samples/ Condition	Sampling Flow Rate(s) (mL/min)	Sampling Duration(s) (hr)	Relative Humidity(s) (%)	Temperature(s) (°C)
Sampling Flow Rate	2	35, 70, 125, 200, 250, 500, 750	0.5	30	30
Sampling Duration	3	250	0.5, 1, 2, 4, 8, 24	30	30
Relative Humidity Effects	3	250	1	30, 90	30
Temperature Effects	3	250	1	30	20, 30, 40
Ozone Effects	3	250	1	30	30

7.3.8 Method Comparison

7.3.8.1 Laboratory

Considering the PAKS method was the only method readily available to compare the AAS method against, 8 AAS samples were collected in parallel with 8 PAKS samples in the dynamic atmosphere generation system. For this experiment, the AAS sampling flow rate was 50 mL/min and the sampling duration was 24 hours.

7.3.8.2 Field Evaluation

In addition to laboratory samples, 9 AAS field samples were collected in parallel with 9 PAKS field samples. For this experiment, the AAS sampling flow rate was 100 mL/min and the sampling duration was 24 hours. The field samples were collected in an apartment over three weekends during September, 2006. During some of the sampling periods several cigars were smoked and a lot of high temperature frying with oil was conducted. This was done so as to generate acrolein concentrations in the apartment.

7.3.8.3 Analytical Detection Limit and Precision

The AAS analytical detection limit (ADL) was determined as 3 times the standard deviation of 7 repeat analyses of a low concentration standard. The AAS analytical precision was determined as the coefficient of variation (CV) of 7 repeat analyses of a low concentration standard.

7.3.8.4 Method Detection Limit and Precision

The AAS MDL was determined as 3 times the standard deviation of 7 field blanks deployed in the field for 24 hours during the method comparison. The AAS method precision was determined from 7 duplicate field samples collected during the method comparison.

7.4 Results and Discussion

7.4.1 Sampling Flow Rate

Results from the sampling flow rate experiment (Figure 28) indicated that the AAS method could efficiently collect acrolein up to 250 mL/min (with sample baking post sampling), beyond which the acrolein CE appeared to drop off relatively quickly. Based on the acrolein concentration in the dynamic atmosphere generation system, and the highest attempted sampling flow rate of 750 mL/min; the consumption of DNSH, based on molar

stoichiometry, would be <<<1%. Therefore, there should be a sufficient amount of DNSH to promote the forward acrolein-DNSH derivatization reaction. These results suggest that the rate limiting step for the AAS acrolein CE is the reaction rate of the acrolein-DNSH derivatization reaction. Although not necessary from the standpoint of molar stoichiometry, the addition of DNSH my in crease the AAS acrolein CE by having a relatively denser coating of DNSH on the sorbent, thereby increasing the contact rate of acrolein and DNSH.

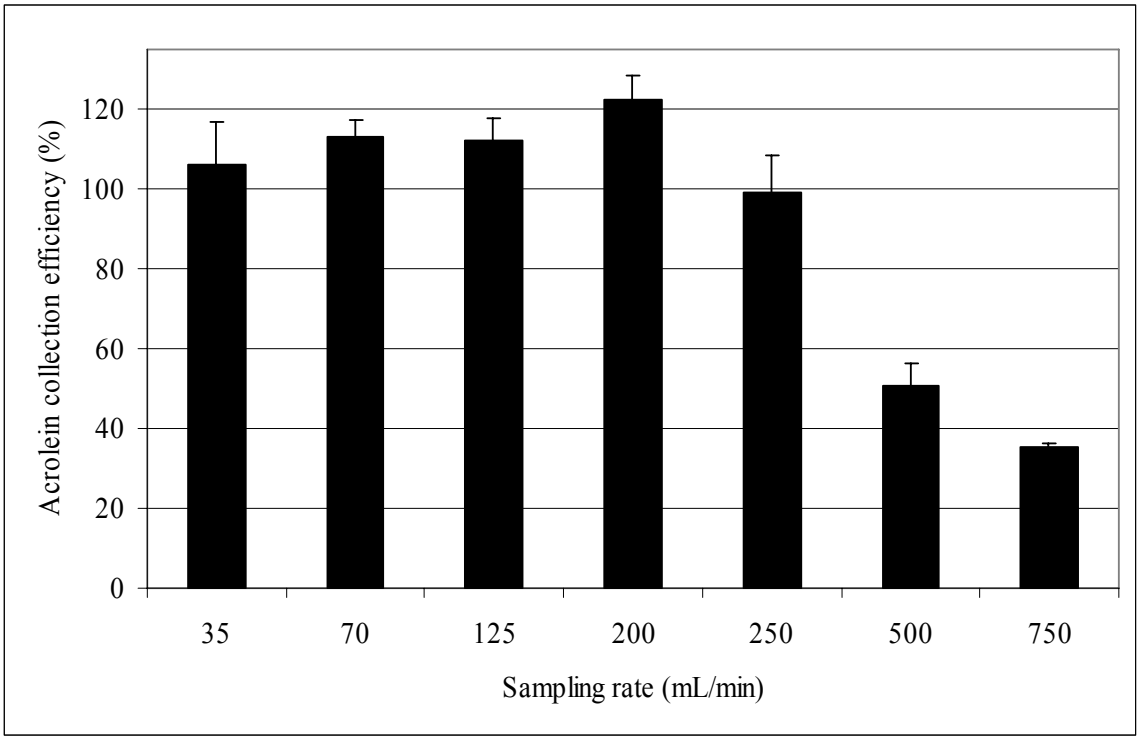

Figure 28: AAS sampling flow rate experiment with sample baking post sampling. N=2 for each data point and Y error bars represent the difference amongst duplicate samples.

7.4.2 Sampling Duration

Results from the sampling duration experiment (Figure 29) indicated that the AAS method could efficiently collect acrolein from 30 minutes to 24 hours. With the exception of the 8 hour samples (~70% CEs with high variability), the acrolein CEs were ≥85%. Although the

original objective of the AAS method was to provide an acrolein measurement for short-term sampling durations, the sampling duration experiment was extended to 24 hours to verify the AAS method would be able to collect 24-hour samples for the field validation experiment (24 hours needed to meet the PAKS limit of detection for acrolein). This is also of significance, because the fact that the AAS maintained ≥ 85% acrolein CE for the 24-hour sampling duration further supports the previous idea that DNSH was in sufficient excess; and that the rate limiting step is the acrolein-DNSH derivatization reaction rate. Furthermore, it suggests that the complex and sensitive nature of pH level and strength on the AAS substrate was not affected by the longer sampling duration.

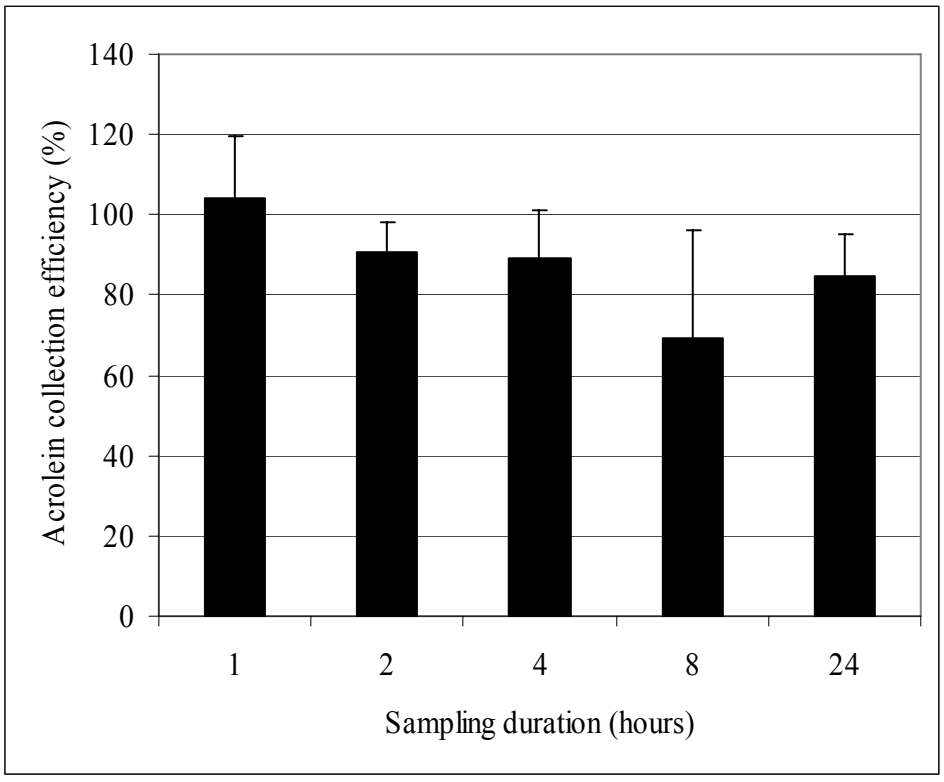

Figure 29: Sampling duration experiment. N=3 for each data point and Y error bars represent the standard deviation amongst replicate samples.

7.4.3 Relative Humidity, Temperature, and Ozone Effects

Note that RH, temperature, and ozone effects were not evaluated long-term sampling durations, because the method was originally developed for short-term sampling durations; and if users want, they have the flexibility to simply switch over from the AAS method to the PAKS method for long-term sampling. Results from the relative humidity experiment (Figure 30) indicated that the AAS sampling efficiency was impacted by RH for a sampling duration of 1 hour. The AAS CE at 90% RH is relatively higher. This is likely due to the fact that water vapor affected the acrolein-DNSH derivatization reaction. As discussed in Chapters 2 and 6, carbonyl-hydrazine reactions are very sensitive to the presence of water vapor. Although the AAS CE at 90% RH was relatively high, it was still within ±20% of 100%, and therefore may be considered acceptable for typical applications.

Results from the temperature experiment (Figure 30) indicated that temperature had relatively little impact on the AAS sampling efficiency. The coefficient of variation from 20 to 40°C was 7.6%.

Results from the ozone experiment (Figure 30) indicated that the AAS sampling efficiency was not impacted by ozone up to 250 ppb for a sampling duration of 1 hour. This is consistent with Rodler et als'. (*64*) observation that ozone is not a significant interference so along as DNSH is in substantial excess over the carbonyl compounds being derivatized.

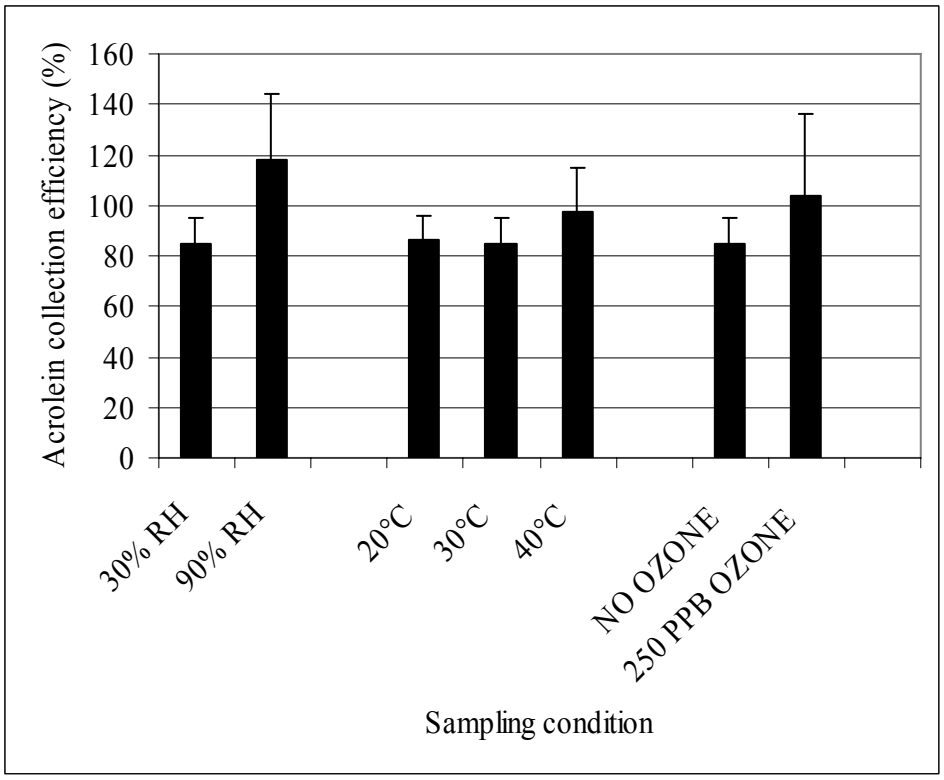

Figure 30: Effects of relative humidity, temperature, and the presence of ozone (250 ppb) AAKS performance. N=3 for each data point and Y error bars represent the standard deviation amongst replicate samples.

7.4.4 Method Comparison

7.4.4.1 Laboratory

Results from the laboratory method comparison (Table 23) indicated that the two methods agree well with each other. The results of a Wilcoxon signed-rank test indicated the two methods' concentrations significantly agree with each other ($p = 0.093$); and the AAS acrolein concentrations were on average only ~13% less than the PAKS acrolein concentrations.

7.4.4.2 Field Evaluation

In the field evaluation, a range of acrolein concentrations were obtained for a linear least-square regression analysis. Results, as shown in Figure 31, indicated that with the exception of one relatively high concentration sample (AAS and PAKS concentrations of

~6 and ~8, respectively), the two methods agree well with each other. For acrolein concentrations ranging from ~0.4 to ~3.7 μg/m³, the results from linear least squares regression demonstrated a slope value close to 1 (0.978); an intercept value close to 0 (0.0656), and a high R^2 (0.8707). However, the present chapter generated inadequate data to evaluate whether the excellent agreement between the PAKS and AAS methods would exist above ~3.7 μg/m³, because the sole data point above ~3.7 μg/m³ was far away from the rest of the data points. The practical implications of this limitation my not be of significance, considering the current literature indicates that acrolein concentrations of above ~3.7 μg/m³ are not commonly encountered, especially in ambient air.

Table 23: AAS vs. PAKS laboratory comparison

Experiment	AAS acrolein concentration (μg/m³)	PAKS acrolein concentration (μg/m³)
1	3.33	3.44
2	4.53	3.99
3	3.97	4.16
4	4.38	5.07
5	3.22	4.10
6	3.37	3.21
7	2.76	4.00
8	3.06	3.81
Mean ± Stdev.	3.58 ± 0.64	3.97 ± 0.56
CV (%)	17.9	14.0

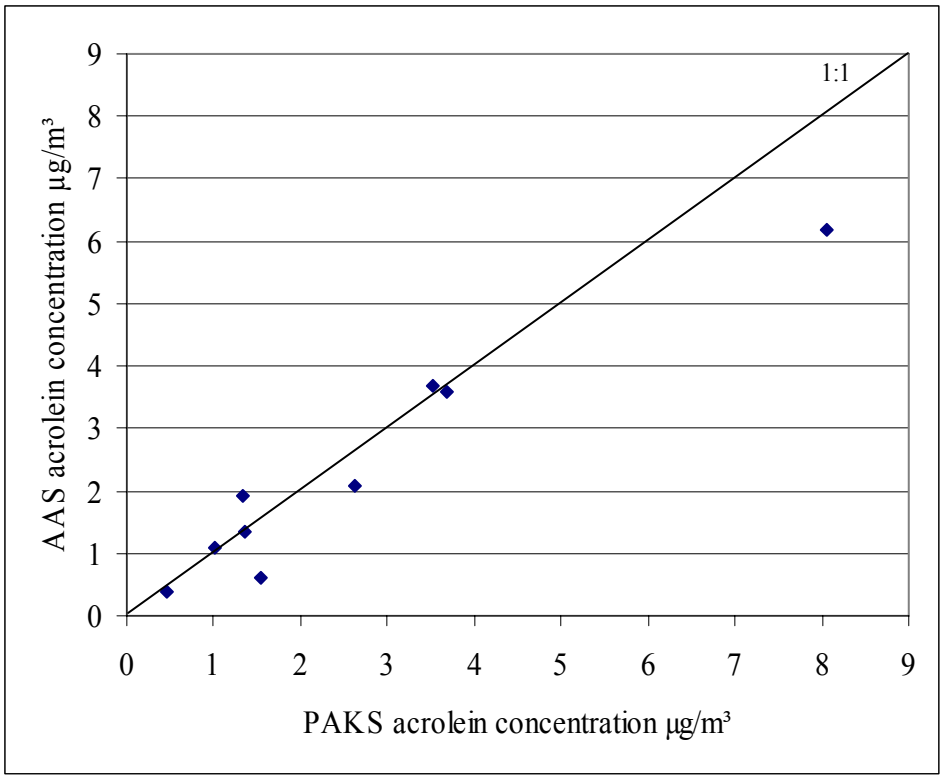

Figure 31: AAS vs. PAKS field comparison.

7.4.5 Detection Limits and Precisions

The AAS analytical detection limit (ADL) was 1.80 ng/cartridge; however, the AAS limit of detection (LOD) is dictated by the method detection limit. The 7 field blanks that were collected during the method comparison did not have any detectable quantities of acrolein. Therefore, in this case the AAS LOD would default back to the AAS ADL. However, in order to get a sense of what one might expect as the highest AAS MDL (a worst case scenario), I have provided an AAS MDL based on field blanks collected during DEARS, which was 5.99 ng/cartridge. This LOD corresponds to 0.80 µg/m³ for a 30 minute sampling duration @ 250 mL/min. With the exception of the Destaillats reported detection limit, the AAS LOD of 0.80 µg/m³ is comparable to the detection limits reported by other methods (see Table 21). Although the AAS LOD is not a significant improvement over the

other methods, the AAS method has the advantage of offering comparable detection limits with a far simpler, safer, and portable sampling method. It is important to note that AAS LOD could be lowered significantly by simply injecting a larger sample (i.e., 100 µL as opposed to the current 20 µL) volume during the HPLC analysis

Table 24: AAS detection limits and comparison with other reported detection limits.

Detection Limits	ng/cartridge (µg/m³)[a]
AAS Analytical	1.80 (0.24)[b]
AAS Method	5.99 (0.80)[c]
Destaillats (*111*)	NR (0.02)[d]
Ho and Yo (*48*)	NR (0.73)[d]
Seaman (*110*)	NR (0.32)[d]

[a] Estimated air concentration for a 30 minute sampling duration @ 250 mL/min (7.5 L).
[b] Determined from 7 repeat analyzes of a low concentration standard.
[c] Determined from 68 indoor, outdoor, and personal field blanks collected (24 hour durations) during DEARS.
[d] Detection limit corrected for an equivalent sample volume (7.5L).
NR – Not reported

7.5 Conclusions and Recommendations

Results indicated that the AAS method will be suitable for short-term (i.e., 30 minutes) and long-term (i.e., ≥24 hours) sampling durations at sampling rates from 50 to 250 mL/min. Results also indicated that relative humidity from 30 to 90%, temperature from 20 to 40°C, and the presence of ozone up to 250 ppb does not affect the performance of the AAS method for short-term sampling durations (i.e., 1 to 2 hours). Although the AAS method can sample for long-term durations, it is recommend that the AAS method only be used for short-term sampling durations (the original purpose of the method) when in the presence of high RH or ozone, because the long-term sampling effects of high RH and ozone were not evaluated in the current chapter.. Results indicated that the AAS method LOD of 0.24 µg/m³ for a 30 minute sampling duration at 250 mL/min is comparable to other acrolein

methods. The AAS method, however, is of significant advantage over other methods when one considers its simplicity and ease of use. The AAS method is likely to work for other carbonyls, but is less attractive than for measuring acrolein, because the conventional DNPH-based methods have proven to work well for short-term sampling (and measurements) of common saturated carbonyls (*112*).

Chapter 8

Conclusions and Recommendations

8.1 Conclusions

The PAKS method has been extensively developed and evaluated to provide a simple and reliable passive sampling method for the 24- to 48-hour time-integrated measurement of multiple saturated and unsaturated carbonyls in indoor, outdoor, and personal air. The most significant attribute of the PAKS method is the fact that the method can now measure unsaturated carbonyls (in particular acrolein) with a ~100% collection efficiency, and provide ample sample stabilities for field samples to be retuned to the laboratory for analysis. This is especially important considering that current DNPH-based methods do not have adequate collection efficiencies and sample stabilities to reliably measure acrolein.

In addition, a set of optimal conditions for processing PAKS samples and preparing calibration curves were identified and recommended. These optimal conditions will provide future users with guidelines to follow, which will provide the most efficient, accurate, and precise PAKS methods. These improvements were further compounded by the development and evaluation work conducted on the PAKS blank levels and variability, which ultimately reduced the PAKS detection limits; and areas of future research were identified, so as to possibly further reduce the PAKS method blank levels and variability.

All of the above work produced the "final" (i.e., most up-to-date) version of the PAKS method. The final PAKS method had relatively stable blank levels when the PAKS cartridges were stored in a -21^{0}C freezer for up to 20 weeks. When samples (cartridges)

were stored in a freezer, their concentrations remained unchanged (<±20% deviation) within up to 20 weeks. To prevent artifacts during the storage of sample extracts; however, the samples need to be extracted only immediately before HPLC analysis. The final method had accuracies close to 100% for formaldehyde, acetaldehyde, and acrolein. The method and analytical precisions, expressed as coefficient of variation from duplicate samples, were <20% and <10%, respectively for these carbonyls. The analytical detection limits ranged from 0.28 to 4.8 μg/m³; however, method detection limits ranged from 0 to 9.87 μg/m³. The method detection limits are above the criteria set forth in this dissertation. Future users must be aware of this limitation, and future work should focus on reducing the method detection limits by reducing the PAKS blank levels and variability. All of the above provides a benchmark for future improvement efforts and aids in the identification of any deviation from expected performance.

This dissertation demonstrated that current DNPH-coated solid sorbent sampling techniques, which are virtually unanimously utilized nationwide, have low collection efficiencies (1% to 62% determined in this dissertation work) for acetaldehyde and thus could lead to significant underestimations of acetaldehyde concentrations for long-term (e.g., 24-hour) sampling.

When in need of higher temporal resolution of acrolein concentrations, the PAKS method can be adapted into an active sampling method (AAS). This method has a detection limit of 0.24 μg/m³ for a 30 minute sampling duration @ 250 mL/min, and is not affected by temperature (20 to 40°C), RH (30 to 90%), and the presence of ozone (up to 250 ppb).

8.2 Recommendations

8.2.1 For the Present

- All PAKS and AAS samples should be analyzed within 5 days of extraction, regardless of the extract storage conditions.
- All batches of PAKS and AAS should be evaluated with at least 5% laboratory blanks. The laboratory blank(s) should be analyzed and the contaminant level(s) should be subtracted from all field samples on a batch-specific basis.
- All batches of PAKS and AAS deployed to the field should be accompanied with at least 10% field blanks for the day, to account for batch and field trip variability. The field blank(s) should be transported, stored, extracted, and analyzed in the exact same manner all accompanying field samples are. The field blank(s) contaminant level(s) should be subtracted from all field samples on a batch-specific basis.
- For small-scale studies or studies were it is not feasible to deploy 7 PAKS or AAS field blanks at one time, a field blank should be deployed during every field sampling trip. Therefore, the field blank levels and variability are accounted for every trip. Furthermore, all sample concentrations will then be corrected with the appropriate field blank (i.e., that day's field blank). This means for each field sampling trip, sample concentrations above the field blank are above zero, because the field blank is zero for that given day; and this also means that all sample processing steps have been accounted for. Therefore, the noise of the PAKS or AAS method can now be reduced to the analytical noise, whereby the PAKS or AAS MDLs can be

calculated according to the EPA's guidelines. In short, the PAKS MDLs are reduced to the PAKS or AAS analytical detection limits (Section 5.3.4.3), which are defined as the 3 times the standard deviation of 7 repeat analyses of a low concentration standard.

- For large-scale studies, at the start of a field sampling study, 7 PAKS or AAS field blanks from the same batch should be deployed to the field at the same time and in the same location. This approach would represent the PAKS or AAS "true" "noise" and would appropriately meet the EPA's guidelines for determining the PAKS or AAS MDLs. This approach would also be a relatively more conservative method (i.e., the MDLs should be slightly higher) for determining the PAKS or AAS MDLs. In addition, as stipulated in the EPA guidelines, batches of 7 field blanks should be deployed throughout an extended field sampling campaign to reconfirm the PAKS or AAS MDLs.

8.2.2 For the Future

- The acetonitrile (ACN) purification experiments conducted in Chapter 4 were unsuccessful in reducing the ACN contamination levels. It is recommended that future work develop ACN purification techniques.
- The reagent experiments conducted in Chapter 4 indicated that the DNSH purification methods mimicked from DNPH-based methods were unsuccessful in reducing the PAKS laboratory blank contamination levels. Researchers demonstrated significant improvements in DNPH-coated solid sorbent blanks when the reagent was purified (*95*). It is recommended that current users follow the

above current use recommendation, and that future work develop DNSH purification techniques.

- The MDL results in Chapter 5 indicated that the PAKS field blank concentrations and variability were still relatively high. Again, it is recommended that future work develop ACN and DNSH purification techniques, which should hopefully remediate this problem.
- The relatively high MDLs reported in Chapter 5 were due to relatively high and variable field blank concentrations. In addition to the previous recommendation, this may be due to variability in the PAKS coating procedures. When the PAKS are coated with the ACN solution of DNSH and citric acid, it is possible that there was channelization of the coating solution through the cartridge. This channelization could result in viable blank concentrations. Barone and Walter found more reproducible DNPH-coated solid sorbents when the DNPH was coated on the sorbent in multi-kilogram quantities and then packed into the cartridges (*113*). It is recommended that future work consider the same cartridge preparation technique for the PAKS method. This may be more readily achieved with the participation of prospective manufactures, based on the DNPH-based method experience.
- It is anticipated that with the aid of ACN and DNSH purification procedures, coupled with widespread acceptance, in particular the commercial sector; the PAKS method blank concentrations and variability will become a “thing of the past” and future users will not need to follow such stringent laboratory and field practices.

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