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SAMPLING OF ATMOSPHERIC CARBONYL COMPOUNDS FOR DETERMINATION BY LIQUID CHROMATOGRAPHY AFTER 2,4-DINITROPHENYLHYDRAZINE LABELLING

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1. INTRODUCTION

Determination of carbonyl compounds in the ambient atmosphere is receiving increasing attention because of the critical role these compounds play as pollutants and as key participants in tropospheric photochemistry. Carbonyls are involved in photochemical reactions as products of the oxidation of hydrocarbons, precursors of oxidants including ozone and peroxycarboxylic nitric anhydrides (PANs), and as sources of free radicals and organic aerosols. Formation of carbonyls in the atmosphere and in internal combustion engines proceeds through analogous channels and the mechanisms are dealt with in several recent reviews.[1-4] The series of reactions is initiated by the formation of a carbon-centered radical (R·), usually through reaction of hydroxyl radical (OH·) with a hydrocarbon, although photolysis of labile compounds (such as another carbonyl), or reaction with nitrate radical (NO_3·) is also possible. Reactions of OH·, O_3 or NO_3· with alkenes proceed through addition to the double bond, forming a carbon centered radical on the adjacent carbon. In addition to the in situ photochemical generation, a number of carbonyls are emitted directly in auto exhaust, and a variety of both anthropogenic and biogenic sources.[5,6] In this regard, there is a potential for increased carbonyl emissions resulting from changes in technology such as use of methanol, ethanol etc. as gasolene substitutes.[7,8]

A correct understanding and assessment of the role of carbonyls in tropospheric chemistry requires the accurate and precise measurement of these compounds along with their parent and product compounds. However, measurement of carbonyl compounds in the ambient atmosphere poses challenging problems because of their trace concentrations (sub-ppb or low-ppb in clean air[9] to higher ppb in urban and polluted air[10]) and interferences arising from atmospheric co-pollutants[11] (e.g. ozone). In the 1970s, chromatographic techniques in conjunction with chemical derivatization methods paved the way for sensitive and selective determination of carbonyls in ambient air. Although many chromatographic methods have been proposed, derivatization with 2,4-dinitrophenylhydrazine (DNPH) coupled to liquid chromatographic separation has received widespread acceptance.[12]

Chromatographic methods for ambient carbonyl measurements, such as the DNPH-LC, involve two separate, operational steps: (1) integrated collection of target carbonyls, and (2) chromatographic analysis of the collected sample. Since chromatography allows simultaneous separation of individual species, interference problems arising from analogous compounds are greatly minimized. However, air sampling remains the most critical step affecting the accuracy and precision of the measurements. The goal of integrated sampling is to concentrate the sample in order to improve the sensitivity of the method. A classical method used for sampling and preconcentration of airborne organics is cryogenic collection. Since many other components present in air are also concentrated along with the target molecules, the concentration effect may accelerate many reactions which are kinetically not significant in the ambient air. In DNPH methods for carbonyls, this problem has been alleviated, at least partially, by simultaneous derivatization and collection, which also improves collection efficiency. This selective enrichment has usually been achieved by sampling with reagent-loaded, solid-phase cartridges or impingers charged with reagent.

In spite of the numerous studies concerned with integrated air sampling, especially with the DNPH method, several questions regarding interferences and sampling artifacts have not yet been adequately addressed. The major concerns with air sampling of carbonyls which can affect the accuracy of the method are: (1) incomplete collection of carbonyls, (2) loss of carbonyls by physical processes such as adsorption or chemical reaction with ambient compounds such as SO_2 and O_3, (3) generation of carbonyls as sampling artifacts, (4) formation of various interfering compounds, and (5) variable blanks resulting from contamination of the reagent and sampling instrument. Here we discuss some of these important issues along with the different techniques used for time-integrated collection of carbonyls in the DNPH based liquid chromatographic methods because of their complexity, variability and as well their importance; we emphasize the principles, advantages, and limitations of these techniques.

2. DNPH DERIVATIZATION AND LIQUID CHROMATOGRAPHY

The acid-catalyzed derivatization of DNPH proceeds by nucleophilic addition to the carbonyl followed by 1,2-elimination of water to form the 2,4-dinitrophenylhydrazone (Figure 1). Although GC can be used for separation and determination of DNPHydrazones,[13-15] the GC methods have not found widespread acceptance because of the low volatility of the derivatives, the relative insensitivity of the common flame ionization detector, and the formation of double peaks (due to *syn*- and *anti*- isomers) by some derivatives, which may hamper identification and quantitation of compounds in complex samples. In contrast to GC methods, liquid chromatographic separation of hydrazones combined with UV detection has become the most popular method for determination of carbonyls in air samples.[16-27]

Usually, separation of hydrazones has been accomplished with a reversed-phase C_{18} column (4.6 mm i.d. x 150 mm long) using either isocratic or gradient elution and a water-acetonitrile solvent combination (Figure 2). A major problem has been co-elution or poor resolution of certain compound combinations (e.g. acrolein, acetone, propionaldehyde, and furfural; iso-butyraldehyde, n-butyraldehyde and 2-butanone; and iso-valeraldehyde and 2-methylbutyraldehyde. Smith, Kleindienst, and Hudgens[28] showed that the use of a ternary gradient mobile phase results in good separation of the C_3 carbonyls acrolein and acetone as well as butanal and the isomers of 2-butanone (Figure 3). Elevated column temperatures (e.g. 60 ^{0}C) provided adequate separation of acrolein, propionaldehyde, and furfural but not for other combinations.[29]

In methods focused specifically on HCHO, a variety of wavelengths have been used for the detection of HCHO-DNPHydrazone. In a recent study, Grömping and Cammann recommended 345 nm for formaldehyde, based on the UV spectrum of the derivative which shows 2 peaks, a small peak at 250 nm and a larger one at 345 nm.[30] In contrast to the case with formaldehyde, the detector wavelength used for simultaneous analysis of many carbonyls (usually in the 360-375 nm range) reflects a compromise, because the absorption maxima of the different hydrazone derivatives vary significantly (Table 1). In some recent studies, the use of a diode-array detector allowed the full spectra to be stored and processed later, thus aiding in the identification of the compounds.[25,31] In a few studies mass spectromeric detection was used for confirmation of identification made by LC, determination of compounds in unresolved chromatographic peaks, and characterization of unidentified peaks.[32,33]

3. SAMPLING PROCEDURES WITH DNPH

3-1. Impinger Sampling

Impinger sampling of carbonyls involves 2 mechanisms: (1) physical dissolution, and (2) formation of less-volatile hydrazones by derivatization. The derivatization reaction will not be quantitative within the very short residence time (order of seconds) of air in the sampling solution and, therefore, dissolution plays an important role in controlling carbonyl collection. The dissolved carbonyls will subsequently undergo derivatization. Since organic solvents are better than aqueous solution for dissolution of carbonyls, they result in increased collection efficiency. Furthermore, the reduced surface tension of the organic solvent enhances mixing of the air stream with the liquid reagent during collection.

The first application of microimpinger sampling for determination of carbonyls by the DNPH-LC method was that of Kuwata et al.[16] who used DNPH reagent (5 mM) in 2N HCl as sampling solution. Two bubblers (each containing 10 mL) in series were found adequate for quantitative trapping of carbonyls in air mixtures. For LC analysis, the sampling solutions were combined, extracted with chloroform, and in the final step, after evaporating the chloroform, the residue was reconstituted in 2 mL acetonitrile for injection into the LC. Later investigators introduced several modifications in the preparation of the sampling solution, which include: (1) using a different acid, (2) trapping carbonyls with an organic solvent (e.g. acetonitrile) compatible with LC analysis, (3) trapping carbonyls in a two-phase, aqueous-organic system. The main reasons for these modifications were: (a) to improve collection efficiency, (b) to reduce the volume of collecting solution, and (c) to minimize sample handling steps between collection and LC analysis.

In the modified method by Kuntz et al.,[17] the impinger solution used was a 1.25 mM DNPH in acetonitrile, acidified with concentrated H_2SO_4 (0.2 mL per L). In this case, quantitative collection was claimed with a 4 mL solution at a flow rate of 0.5 L/min for 1 hour. The use of acetonitrile also allows direct injection of the sample into the LC system. In some studies, perchloric acid was used instead of sulfuric acid to acidify the DNPH solution.[23,24] De Bortoli et al.[35] observed an increase in the rate of derivatization for ketones, when phosphoric acid was used in place of perchloric acid. The use of hydrochloric acid in acetonitrile produces a white precipitate (DNPHydrazine hydrochloride); a similar effect has not been found with other acids used. To determine formaldehyde, acetaldehyde and benzaldehyde in ambient air Tanner and Meng[22] used DNPH in acetonitrile as impinger solution and claimed a detection level of < 1 ppb. They cooled the microimpinger to ice temperature, which further enhanced collection efficiency by the dissolution mechanism.

Grosjean used a two-phase system containing 10 mL of an aqueous, acidic (2 N HCl) solution of DNPH and 10 mL of a 9:1 by volume mixture of cyclohexane and isooctane as opposed to using a relatively polar organic solvent as acetonitrile.[10,36] A major advantage of using a two-phase system is that the derivatization reaction is accelerated because of the in situ organic phase extraction of hydrazones, which shifts equilibrium towards hydrazone formation. Grosjean claimed that the two-phase system was required to obtain quantitative recovery of aliphatic and aromatic carbonyls other than formaldehyde. In contrast, work by Van Langenhove et al.[21] who compared derivatization in a one-phase system with that in a two-phase system, indicated no advantage of using a two-phase system for C_2-C_9 carbonyls. However, higher carbonyls showed a decreasing conversion due to their hydrophobicity.

3-2. Sampling with DNPH Coated Solid Sorbents

Although DNPH based impinger techniques have been used in many studies to determine atmospheric carbonyls, they are cumbersome and not well-suited to large field studies or for sampling at remote locations when samples have to be stored and transported to a central laboratory for analysis. The solid sorbent technique results in much higher sensitivity than the impinger method because the derivatives are usually preconcentrated to a high degree in the sample. For these reasons, the DNPH-coated solid sorbents are a convenient alternative to impinger sampling and have recently been increasingly used.[24-27] A number of solid sorbents, both commercial and laboratory made, have been used for this purpose. The solid sorbents include glass beads, glass fiber filters, silica gel, Chromosorb P, Florisil, Carbopack B, XAD-2, and C_{18}(silica). Several solid sorbents, including silica gel, Florisil and C_{18}(silica) are now commercially available as prepacked cartridges or syringe columns with polypropylene or polyethylene casings (e.g. Sep-Pak brand cartridges manufactured by Waters Associates, Milford, MA), which have several advantages including convenience of use, reproducibility and low blanks. Recently, inert sampling devices, made with only glass and teflon parts, have also been introduced (Inert Columns, Burdick and Jackson, Muskegon, MI).

3-2-1. Glass Beads and Glass Fiber Filters

Grosjean and Fung examined DNPH coated glass beads (20 mesh size) packed in glass tubes (100 mm length x 6 mm i.d.) for carbonyl sampling.[18,36] The glass beads were coated with DNPH by immersing in a DNPH reagent (a saturated, acidic solution with added polyethylene glycol to increase viscosity) and evaporating the reagent to obtain a film around the bead. Hydrazones were extracted with a mixture of hexane and methylene chloride (7:3 v/v), which was then washed with water to remove excess DNPH and acid. The extract was then evaporated and reconstituted in methanol prior to injection into the LC. The collection efficiency was found to be highly variable, especially affected by humidity variations. Carbonyl collection using DNPH coated glass fiber filters (organic- and binder-free) were also affected by humidity variations.[37,38] As in the case with glass beads, the preparation of DNPH coated glass fiber filters was cumbersome and they performed poorly at HiVol sampling rates.[22]

In a recent study de Andrade and Tanner[39] reported that bisulfite-coated cellulose filters can be used for ambient air sampling of formaldehyde at high-volume flow rates. The hydroxymethanesulfonate formed is then extracted and treated with base to regenerate formaldehyde, which is then determined by DNPH derivatization and LC.

3-2-2. Silica Gel Cartridge

DNPH-coated silica gel was used initially by Beasley et al.[40] for sampling formaldehyde in air. Later Tejada[24] simplified the silica gel technique by using commercial Sep-Pak silica gel cartridges (contains ca. 0.7 g of silica gel) and also examined the technique for sampling other carbonyls. In this study by Tejada, the DNPH cartridges were prepared by passing an acidified (with HCl) DNPH solution through a pre-washed cartridge, which produced DNPH loading of ca. 1.9 mg per cartridge. Typical blank concentrations, when a DNPH cartridge was eluted with 5 mL acetonitrile, ranged 0.1-0.3 nmol/mL, 0.05-0.1 nmol/mL, and 0.1-0.25 nmol/mL for formadehyde, acetaldehyde and acetone respectively. The hydrazone derivatives formed during sampling were eluted with acetonitrile and analyzed by LC.

The silica gel cartridge technique was compared with the validated DNPH-acetonitrile impinger technique for sampling carbonyls in ambient air and in diluted automotive exhaust emissions. Results indicated a discrepancy in the two methods with respect to olefinic aldehydes such as acrolein and crotanaldehyde, but stable species, including formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde and acetone correlated very well. The acrolein derivative degraded partially on the cartridge and formed an unknown product. For stable carbonyls, the sample integrity on cartridge was maintained for over a month under refrigerated storage. The cartridge technique was found to provide adequate preconcentration for sampling carbonyls at sub to low ppbv level in ambient air. However, recent work by Arnts and Tejada showed a dramatic negative interference by ozone in the determination of formaldehyde and put in question the validity of silica gel sampling technique unless a carbonyl-passive ozone scrubber is employed.[11] The effect of ozone on sampling with DNPH coated solid sorbents is discussed in section 5-2.

3-2-3. Florisil Cartridge

Florisil is the brand name of purified magnesium silicate, manufactured by Floridian Company. Commercial, prepacked Florisil cartridges of the make Thermosorb/F (Thermoelectron Corporation, Waltham, MA) coated with DNPH was used by Lipari and Swarin[41] for determination of formaldehyde in ambient air and in diluted automotive exhaust emissions. The cartridges are constructed of polyethylene tubing (2.0 cm long x 1.5 cm o.d.) and contain about 1.2 g of dry sorbent. These cartridges allow high sampling rates up to 4.0 L/min.

In the method by Lipari and Swarin, the sorbent was coated with DNPH by filling the cartridge with a DNPH solution in methylene chloride, without any acid, which resulted in a 3 mg loading. The formaldehyde hydrazone was extracted with acetonitrile and analyzed by HPLC. The hydrazone was found stable on cartridges kept for more than 3 weeks at 21 ^{0}C, as long as the end caps were properly installed. The detection limit, which was ca. 1 ppb in 100 L air, was limited by the blank level of 0.5 ppb in 100 L air. Excellent agreement between the cartridge and the DNPH/acetonitrile impinger sampling methods was obtained for formaldehyde. However, no comparative results were presented for the other carbonyls, such as acetaldehyde, acetone, acrolein etc., that are known to be present in these sample types. Interference from NO_2 (550 ppb), SO_2 (100 ppb) and humidity were examined and found to have no effect. However, the effect of ozone has not been studied.

3-2-4. C_{18} Cartridge (octadecylsilane bonded silica)

As opposed to silica gel and Florisil, which are polar sorbents, C_{18} provides non-polar, hydrophobic and relatively inert surface characteristics. Because of these surface properties, C_{18} sorbents easily retain relatively non-polar organic compounds by hydrophobic interactions. The adsorbed molecules can be eluted quantitatively from the sorbent with organic solvents. Due to these advantages, C_{18} sorbents have been used successfully to enrich and cleanup trace organic compounds in many environmental and biological applications involving aqueous samples. Recently, there has been an increasing interest in the use of C_{18} cartridges to sample organics in air, especially carbonyls in conjunction with DNPH.

The use of a DNPH impregnated C_{18} cartridge for sampling carbonyls in air was first introduced by Kuwata et al.,[20] who used the Sep-Pak C_{18} cartridges (Waters Associates, Milford, MA). The study focused on aldehydes, with no results on ketones presented. The cartridge was coated with DNPH by passing through a 2 mL acetonitrile solution containing 0.2 % DNPH and 1 % phosphoric acid, which produced a 1.0-1.2 mg coating. Blank levels for formaldehyde and acetaldehyde were in the range 0.2-0.5 ppb for 100 L air sample. The collection efficiency was found to be >95 % on the first cartridge, when two were used in series, for 100 L of sample at 0.7-1.2 L/min of sampling rate. This study highlighted the simplicity and usefulness of the method, but did not address questions regarding possible interferences and sampling artifacts.

Later, some shortcomings were observed, when Tejada[24] attempted to duplicate the method: (1) significant acetone contamination from the cartridge and (2) formation of carbonyls with molecular weight greater than hexanal and their increase with storage of cartridge. However, no systematic study was undertaken to reevaluate Kuwata's method. Recently Druzik et al.[25] essentially followed the sampling procedure of Kuwata et al. in their method using diode array detection of the hydrazones following LC separation. This study did not report of any major problem in the method and was in agreement with that of Kuwata et al. Furthermore, based on indirect evidence, Druzik et al. noted that co-pollutants including ozone do not interfere in the sampling with C_{18} cartridges.

Most recent work on the C_{18} sampling technique has been that of Zhou and Mopper.[27] Important modifications were proposed in this study regarding reagent purification and cartridge preparation in order to reduce blank levels for clean, marine air applications. An aqueous DNPH solution (ca. 0.15 mM) was used for cartridge loading, instead of an acetonitrile solution used by previous workers. The use of aqueous reagent allowed effective removal of hydrazone blanks by solvent extraction. With two cartridges in series and a flow rate of 0.7 L/min, greater than 96 % collection efficiecy was obtained for all compounds of interest, except acetone (92 %). The study claimed detection limits in the 0.01-0.02 ppb range for most carbonyl compounds for a 100 L air sample.

In agreement with other studies, humidity was found to have no effect on the collection efficiency. The authors claimed no interference by ozone at ca. 50 ppb, based on a comparison study with and without stripping of ozone by a KI solution. About 20 % difference in results was found and considered to be within experimental error and no other data were presented. Exposure of cartridges to sunlight was found to cause significant production of carbonyls and was eliminated by wrapping the cartridges in aluminum foil during sampling and storage.

3-2-5. XAD-2, Carbopack B, and Chromosorb P

In contrast to silica gel, Florisil, and C_{18}, these sorbents are not commercially available as prepacked cartridges and thus, have to be laboratory-packed, which is a marked disadvantage in large field studies. XAD-2 is a styrene-divinylbenzene polymer and requires tedious procedures for cleanup. Andersson et al.[42,43] used DNPH coated XAD-2 for sampling formaldehyde, acrolein and glutaraldehyde. The sorbent appeared to contribute high carbonyl blanks, especially acetaldehyde. XAD-2 has not been used in any recent study for sampling carbonyls in air.

Carbopack B, a graphitized carbon black of specific surface area (ca. 100 m^2/g) and supplied by Supelco (Bellefonte, PA) was used by Ciccioli et al.[44] as the solid sorbent with DNPH/H_3PO_4 to sample carbonyls in air. The hydrazones formed during sampling were eluted with acetonitrile (5-10 mL) and determined by LC and UV detection. Carbopack B cartridges were made by packing 20-40 mg of material in glass tubings (0.5 cm i.d. x 5 cm long); the sorbent was held in place by a 100 mesh, stainless steel screen at the trap inlet and by glass wool plug at the outlet. The cartridges, despite their very small size allowed quatitative collection of formaldehyde, acetaldehyde, acrolein, propionaldehyde and acetone and made possible their determination at sub-ppb levels when about 100-200 L air were sampled.

Recently, Chromosorb P coated with DNPH has been used by Grömping and Cammann[30] for determination of formaldehyde in air. Chromosorb P is diatomaceous silica which is acid and base washed to remove both inorganic and organic contaminants and was found suitable for coating with acids. For formaldehyde, the collection efficiency on the Chromosorb cartridge was >95 %, and the data agreed well with the standard impinger technique. The study did not report on collection efficiency for other carbonyls or problems related to interferences from other airborne pollutants, including ozone.

3-2-6. Kinetics of DNPH Derivatization in Aqueous Medium and on Solid Phase

As discussed previously, in impinger sampling, both derivatization and physical dissolution aid in the initial trapping of airborne carbonyls into the collecting solution. Subsequently, derivatization proceeds to completion. Therefore, an understanding of the effects of variables on derivatization is important in order to optimize sample collection and analysis in impinger based methods. In solutions, the derivatization yield depends on many variables including reaction pH, reagent concentration, and temperature. Some of these questions have been addressed with formaldehyde. Although other low-molecular weight aldehydes are expected to behave similarly, the results may not be extended for ketones.

The effect of pH on reaction yield was studied for formaldehyde and acetaldehyde.[45] For formaldehyde, a smooth relationship was observed over the pH range of 1.7 to 7.0, with maximum around pH 4 (Figure 4). The reaction yields did not change significantly over the 3 to 5 pH range. These results were remarkable because most studies used very low pH

(<3) for derivatization. In contrast, for acetaldehyde, maximum yield was observed at pH 1.7 and the yield was nearly constant between pH 3 and 5. Protonation of the carbonyl group at low pH promotes the nucleophilic addition, but concurrently reduces the amount of un-protonated DNPH, which is the reactive nucleophile. Because of these competing effects, the rate passes through a maximum at a characteristic pH.

Tuß et al.[46] studied the effect of temperature on reaction yield at pH 3 for formaldehyde. Their results are summarized in Figure 5. At 25 ^{0}C the reaction was nearly complete after 20 min. Similar results were obtained by Lowe et al.[47] However, results obtained by Cofer et al.[48] indicated that longer derivatization times (ca. 2 h) were required for completion at pH 2. The reaction yield was also dependent on the molar ratio of reagent (DNPH) to carbonyls. The data by Tuß et al.[46] showed that a DNPH molar ratio in excess of 40 was required for quantitative derivatization. An interesting observation was that when HCHO-DNPHydrazone was added to a DNPH solution, the added hydrazone dissociated to variable extent, forming HCHO and DNPH, if the DNPH was present in less than 40 molar ratio. However, the added hydrazone was fully recovered at DNPH molar ratios > 40.

In contrast to liquid phase derivatization, the mechanism of carbonyl trapping with DNPH coated solid sorbent is not well-understood. The derivatization can take place in a liquid phase film or as a gas-solid phase reaction. In analogy to liquid phase derivatization, probably both derivatization and dissolution are involved in initial trapping, followed by time dependent derivatization of dissolved carbonyls. Past studies, which documented collection efficiency using two cartridges in series, assumed complete derivatization immediately. Because of the high degree of DNPH enrichment on cartridges, the derivatization may proceed faster on solid sorbents than in liquid medium. Furthermore, the reduced water activity on cartridges may facilitate equilibrium towards hydrazone formation.

3-3. Miscellaneous Sampling Techniques

3-3-1. Cryogenic Collection

This sampling is based on the principle that soluble species (which include carbonyls) are collected along with condensed or solidified water vapor and CO_2 which are present in the sample air. Since the collection solution is derived entirely from the small amount of condensable water present in air, cryogenic collection results in very high air/water ratios. This approach was used by Neitzert and Seiler[49] and Tuß et al.[46] to sample clean air for formaldehyde determination by DNPH derivatization. For preconcentration, air was passed (1 L/min) through a glass trap (200 mL) cooled with liquid nitrogen, thereby separating HCHO from atmospheric nitrogen and oxygen and fixing it in the ice and CO_2 matrix. After sampling the cooling trap was warmed up and the DNPH solution added to the sample at a temperature of 5 ^{0}C for the derivatization of formaldehyde. The derivative (DNPHydrazone) was then extracted with carbon tetrachloride and the extract used for analysis by HPLC or GC.

Tests performed by using two traps in series indicated that the collection efficiency in the first trap was >95 % at a sampling rate of 1 L/min. Excellent agreement was observed between this sampling technique and the standard impinger technique suggesting no production or destruction of formaldehyde in the cold trap. No loss of HCHO was observed during the warm-up step because of the ease with which HCHO dissolves in liquid water. However, this step may lead to losses for higher molecular weight carbonyls. The collection devices are not simple to construct and operate, and especially, great care must be taken to keep all collection surfaces clean to promote uniform wetting.

3-3-2. High-volume, Rotating Cylinder Sampling

The high volume, high efficiency rotating flask sampler was used by Lowe et al.[47,50] as the device to strip formaldehyde from air at high flow rates (ca. 40 L/min), into DNPH solution acidified with sulfuric acid. The HCHO-DNPHydrazone was determined by HPLC. The sampler was a pyrex cylinder (ca. 9 cm i.d. x 24 cm long) packed with raschig rings (1 L of 4 x4 mm) and held in place by two glass sieve plates. Tight packing of the rings are required to avoid channeling effects that would affect sampling efficiency. About 40-100 mL DNPH solution (0.3 mM) was added. During sampling, the cylinder was rotated at an optimum speed of ca. 30 rpm, ensuring that all raschig rings are wet with the DNPH solution, thereby facilitating efficient scrubbing of carbonyls. The collection efficiency was found to be >80 % with 40 mL DNPH solution and at an air flow rate of 40 L/min. About 1000 L air were processed for each sample. The method was found to be useful for formaldehyde determination at low mixing ratios of the order of 0.1 ppb.

3-3-3. Nebulization/Reflux Concentration

In common with impinger sampling, the nebulization/reflux concentration is based on the extraction of target molecules present in air into a liquid scrubber, but presents a marked improvement in extraction efficiency. In nebulization/reflux concentration the scrubbing solution is dispersed into fine drops (a mist), generating large interfacial surface area, which promotes extremely effective mass transfer between the gas and liquid phases.[51,52] The collection process is described as consisting of sorption onto the droplet surface, rather than dissolution. A method based on this technique has been used by Cofer and Edahl,[48] in conjunction with DNPH derivatization, for collection and determination of formaldehyde in air.

In the nebulizer method, during sampling, air is drawn through a commercially available (DeVilbiss 40) glass-nebulizing nozzle at ca. 7.5 L/min, aspirating the DNPH solution from the reservoir into the air stream, where the solution is atomized by impaction into small droplets, forming an air/droplet mist (Figure 6). The DNPH solution (4-6 mL total) was aspirated at a rate of ca. 2mL/min. The upward drawn air/droplet mist impinges on a teflon filter (Zeflour, 1-μm diameter) which traps the solution droplets while allowing the scrubbed sample air to pass out of the collector. The trapped solution droplets containing the scrubbed compounds coalesce into larger droplets, which subsequently roll back down the collector into the reservoir to be recycled. After 15-20 min scrubbing runs, followed by a 1-min rinse with 3-4 mL fresh DNPH solution using ultrapure nitrogen, the solutions were withdrawn, mixed and prepared for HPLC analysis.

The nebulization/reflux concentration technique presents a marked advantage over other liquid scrubbing methods because of the highly efficient collection mechanism. Since maximum flow (V_g) through the minimum volume (V_x), achievable without causing loss of trapped analytes, translates into the most concentrated solution, the extraction efficiency can be represented as V_g/V_x. For polar gases, this ratio is ca. 300 for impingers but with nebulizer collectors a value of >3000 can be achieved.[52] A problem encountered in these devices is the evaporation of the collecting solution when sampling low humidity air, because of the high gas to liquid ratio. This problem can be minimized by placing the collector in an ice bath. Further studies are required in order to use the nebulizer collector for sampling and analysis of carbonyls other than formaldehyde. Furthermore, modifying and adapting the nebulizer/collector design for high-repitition analysis is highly desirable.

4. REAGENT BLANKS

In DNPH based methods, method detection limits (MDL) for different carbonyl compounds are limited either by the analytical detection limit (i.e. the lowest quantifiable limit) or by the blank level. For the most common carbonyl compounds, namely formaldehyde, acetaldehyde and acetone the blank level determines the detection limit. Therefore, reducing the blank to the lowest possible level is necessary to achieve the lowest detection limit, especially for clean, marine air applications. Several different sources including the reagent, water, chemicals, solvents, and apparatus used for sampling and subsequent sample preparatory steps can contribute to the carbonyl concentrations appearing in the blank. Air contact with prepared reagents, gradual leaching from plastics as well as formation by unidentified mechanisms during storage increase blank levels. It is difficult to eliminate carbonyl blanks completely, but they can be minimized to allow ppt level detection. Important ways to achieve lowest blanks are: (1) to use highest purity DNPH (usually recrystalized twice in acetonitrile), (2) to purify the reagent solution thoroughly, (3) to avoid air and light contact with prepared reagent, and (4) to use highest purity solvents (sometimes distilled with DNPH).

Several solvents including hexane, chloroform, and carbon tetrachloride have been used to purify aqueous DNPH reagent by extracting hydrazones. The relative polarity of the solvent is an important factor that determines extraction efficiency. Hexane is non-polar and, therefore, less efficient than chloroform and carbon tetrachloride in extracting polar hydrazones. Chloroform being more polar than carbon tetrachloride removes appreciable amounts of the reagent (DNPH) along with hydrazones[46]. Thus, chloroform is less suitable than carbon tetrachloride. Tuß et al.[45] studied the extraction efficiency of hydrazones with carbon tetrachloride and their results (Table 2) suggest that quantitative extraction can be achieved by extracting 3 times using a 10:1 ratio of DNPH solution to carbon tetrachloride. Once purified, the aqueous DNPH solution can be maintained for at least 2 weeks in glass containers, if air contact is avoided. This can be achieved by purging the headspace with highest purity nitrogen, which will also allow dispensing the reagent (Figure 7).

Recently, Zhou and Mopper[27] used CCl_4 to purify the DNPH reagent in their C_{18} cartridge based technique. Three successive extractions of the reagent (500 mL) with 5-10 mL CCl_4 resulted in lower blanks of ca. 0.3 nmol for formaldehyde and acetone, and undetectable for other carbonyls per cartridge with ca. 0.9 mg loaded DNPH. These blanks corresponded to 0.07 ppb for formaldehyde and acetone and less than 0.02 ppb for other carbonyl compounds for a 100 L sample. This was a significant improvement over previous studies. It was observed that when prepared cartridges were stored at ambient temperature, blank values for formaldehyde and acetone increased with time at ca. 0.5 nmol/day, probably due to leaching from cartridges. For this reason, cartridges were prepared within 2 hours prior to use.

Beasley et al.[40] recommended that Bakelite bottle caps should be avoided in any utensils used in the determination of formaldehyde. Bakelite is a polymer prepared from formaldehyde and phenol and may contain enough free formaldehyde to cause a low level background. New glass bottles should not be used to store DNPH derivatized samples because of adsorption loss on new glass surfaces, which requires conditioning with DNPH prior to use. Polyethylene bottles do not exhibit this negative interaction, but results in an increase of the formaldehyde signal with time. Lowe et al.[47] explained this HCHO contamination as originating from the polyethylene, but another possible source could be diffusion through the plastic.

5. INTERFERENCES

In air samples, potential interfering compounds for the determination of carbonyl compounds include ozone, nitrogen dioxide and sulfur dioxide. Ordinarily, NO_2 does not interfere with determination of carbonyls in ambient air. For example, Lipari and Swarin[41] studied the effect of nitrogen dioxide on HCHO sampling using Florisil cartridges coated with DNPH and found no interference at concentrations as high as 550 ppb and NO_2/HCHO ratios of 7 to 1.

5-1. SO_2 Interference

The interference by sulfur dioxide is due to the formation of carbonyl-bisulfite addition compound (hydroxyalkane sulfonic acid) which can reduce the recovery of the carbonyl compound.[53] It appears that SO_2 has no effect on sampling gas-phase HCHO with DNPH containing impingers or cartridges. For example, at gas-phase concentrations of 1000 ppb SO_2 and 92 ppb HCHO no interference was observed for HCHO collection on DNPH coated Florisil cartridges.[41] However, SO_2 could potentially affect the DNPH derivatization in atmospheric water depending on the physico-chemical conditions influencing the formation-dissociation of hydroxymethane sulfonic acid. It was shown that the yield of HCHO-

DNPHydrazone was reduced when derivatization reaction was carried out by addition of HCHO to a DNPH solution in the presence of sulfite and at near neutral pH. However, under acidic conditions (pH less than 3) the derivatization of HCHO was complete despite added sulfite corresponding to a SO_2 mixing ratio in air of 90 ppbv, suggesting that DNPH reaction with HCHO dominated over the formation of hydroxymethanesulfonate under these conditions.[47] In contrast, if hydroxymethanesulfonate is already formed, the bound HCHO does not react with DNPH. To determine this bound HCHO, hydroxymethanesulfo-nate must be dissociated first at high pH (ca. pH 13) prior to DNPH derivatization.[54]

5-2. Effect of Ozone

Ozone is one of the most abundant reactive gases in air, hence could potentially cause sampling artefacts. The effect of ozone on DNPH based methods for carbonyls can be three-fold: (1) formation of carbonyls as artefacts from reaction with sampling substrates, (2) degradation of DNPHydrazones and (3) formation of interfering compounds. The reagent (DNPH) itself reacts with ozone. For example, a DNPH solution rapidly became colorless when high concentrations of ozone in air (0.1%) was passed through, but the reaction products were not identified.[47] In contrast, the reactions of ozone with simpler hydrazines including hydrazine, monomethylhydrazine and dimethylhydrazine have been studied and products including hydrogen peroxide, formaldehyde have been shown to form under simulated atmospheric conditions.[55] Formation of formaldehyde from the reaction of ozone with DNPH has not been studied, but cannot be ruled out.

In a recent study by Arnts and Tejada[11] the reaction of ozone with HCHO-DNPHydrazone was identified as a potential problem when DNPH coated silica cartridges were used for formaldehyde sampling. In this study synthetic mixtures of humidified air containing formaldehyde (20 ppb to 140 ppb) and ozone (0 to 770 ppb) were sampled. The loss of HCHO-DNPHyrdazone increased markedly with increase in ozone concentration, at 25 ppb of HCHO and 120 ppb O_3, about 48% of HCHO was lost (Table 3). Also noticed on silica cartridges were concurrent large losses of DNPH. In contrast to the silica cartridges, impingers charged with DNPH acetonitrile solutions did not show any loss of HCHO-DNPHydrazone but DNPH was markedly reduced. It was concluded that the silica cartridge exhibited such large reductions in formaldehyde response because the DNPH derivative, which is largely formed at the front of the cartridge and immobilized, was being destroyed by O_3. In the case of impingers, the HCHO-DNPHydrazone is protected by the DNPH, which is always present in excess and well-dispersed. However, a matter of concern in the impinger technique is that the products formed from the DNPH-O_3 reaction can interfere with the resolution of formaldehyde peak in HPLC separation. Recently, this problem was addressed by Smith, Kleindienst, and Hudgens[28] who used a ternary gradient mobile phase (refer to Figure 3) to obtain good chromatographic separation of the formaldehyde peak from interfering artifact peaks (Figure 8). In contrast to the silica cartridges, C_{18} cartridges (Sep-Pak brand by Waters Associates, Milford, MA) exhibited no loss of the HCHO derivative up to 120 ppb of O_3. In this case, it was reasoned that C_{18} substrate itself was the target of O_3 reaction, thereby preventing attack on formaldehyde-DNPHydrazone.

The mechanism of ozone initiated reactions in the above cases are not clearly understood. Atkinson and Carter[56] suggested that a chain of free-radical reactions can be initiated when ozone reacts with hydrazines, either by addition to a nitrogen, or abstraction of a hydrogen from a weak N-H bond. Arnts and Tejada[11] pointed out that under the acidic conditions of the DNPH reaction, O_3 addition to the protonated nitrogen is restricted and hydrogen abstraction could be the preferred route. The following pathway has been proposed by Atkinson and Carter[56] for hydrogen abstraction:

$$RHNNH_2 + O_3 \rightarrow RNNH_2 \text{ (or RHNNH)} + O_2 + OH$$

$$RNNH_2 \text{ (or RHNNH)} + O_2 \rightarrow RN{=}NH + HO_2$$

$$RN{=}NH + O_3 \text{ (or OH)} \rightarrow RN{=}N + OH + O_2 \text{ (}+H_2O\text{)}$$

$$RN{=}N \rightarrow R + N_2$$

Arnts and Tejada suggested that when DNPH coated C_{18} substrate is used for sampling, the radicals generated by O_3 attack can be scavenged by the C_{18}, thus limiting further attack on DNPH or the hydrazones. In recent studies by Vairavamurthy and Roberts[57] using O-(pentafluorobenzyl)hydroxylamine (PFBOA) for carbonyl derivatization, it has been observed that when O_3 was passed through PFBOA coated C_{18} cartridges several carbonyl compounds were generated (Figure 9). An increased production was observed with inert glass columns packed with C_{18} material as against polypropylene cartridges containing C_{18}, suggesting that O_3 was partially quenched in the case of polypropylene cartridge, before it impinged on the C_{18} material.

From the above discussion it is clear that ozone is a serious interferent in almost all the methods using solid phases for sampling carbonyls in the ambient air. Arnts and Tejada[11] reported that they have obtained encouraging results in a preliminary study using potassium iodide coated copper tubing inlet to remove O_3 prior to collection with a DNPH coated silica gel cartridge. Vairavamurthy and Roberts[57] obtained complete removal of ozone up to 500 ppb by using a CuO cartridge in front of the sampling cartridge. Studies with gas-phase standards indicate that concentrations of carbonyl compounds are not affected by using the

CuO cartridge. Gas-phase titration of O_3 with nitric oxide (NO), as used by Tanner et al.[58] in the determination of hydrogen peroxide in the ambient atmosphere, is also a potential technique to overcome ozone interference.

6. CONCLUSION

DNPH labelling followed by liquid chromatographic separation and UV detection is currently the most popular chromatographic technique used for the determination atmospheric carbonyls. Among the variety of sampling techniques that have been used with this derivatization, carbonyl collection with DNPH coated solid phase cartridges such as C_{18} have been preferred in recent studies because of convenience and other logistic reasons. Although the DNPH method has been in widespread use, it is surprising that some important analytical problems (e.g. ozone interference) have not been resolved yet. Because of the increasing demand for time-series measurements in field studies, an automated method for continuous sampling and analysis of carbonyls is very much required. The DNPH method employing a commonly used sampling technique (e.g. cartridge sampling) may not lend itself for this purpose due to the lengthy collection times required to achieve sub-ppbv detection limits. Because of this inherent problem, the DNPH-LC method is also unsuitable for studies in which short time resolution is required or for sampling from aircraft, unless a suitably designed high volume sampler (e.g. the nebulization/reflux concentrator) is used. It appears that new analytical approaches are required in the development of a suitable field method with real-time capabilities for carbonyls measurement in the ambient air. However, when sampling problems associated with ozone interference are resolved, the DNPH-LC method employing cartridge sampling will provide a convenient batch method for atmospheric measurements.

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FIGURE CAPTIONS

Figure 1. Reaction of carbonyls with 2,4-dinitrophenylhydrazine to form hydrazone derivatives.

Figure 2. Chromatogram of various DNPH derivatives separated on a Zorbax-ODS column; mobile phase: acetonitrile-water (67:33) at 0.7 mL/min for 8 min, then 1.0 mL/min and gradient to acetonitrile-water (90:10) over 17 min, then gradient to 100% acetonitrile over 3 min. Peaks: 1, formaldehyde; 2, acetaldehyde; 3, furfural; 4, acrolein; 6, propanal; 7, salicylaldehyde; 8, crotanaldehyde; 9, butanal; 10, glyoxal; 11, benzaldehyde; 12, glutaraldehyde; 13, pentanal; 14, p-tolualdehyde; 15, hexanal; 16, 3-heptanone; 17, heptanal; 18, octanal; 19, nonanal. Source: Lipari and Swarin, 1982.[34]

Figure 3. A. Ternary gradient mobile phase composition. B. Standard chromatogram. Peaks: 1, formaldehyde; 2, acetaldehyde; 3, acrolein; 4, acetone; 5, propanal; 6, butanal; 7, *anti-* and *syn-* 2-butanone; 8, cyclopentanone (internal standard); 9, benzaldehyde; 10, glyoxal; 11, pentanal; 12, cyclohexanone (internal standard); 13, p-tolualdehyde; 14, methyl glyoxal. Source: Smith, Kleindienst and Hudgens, 1989.[28]

Figure 4. Effect of reaction pH on percent yield of HCHO-DNPHydrazone. Symbols: circles, phosphate buffer; square, acetate buffer. Source: Bicking et al., 1988.[45]

Figure 5. Reaction yield of DNPH derivatization of formaldehyde as function of temperature and time (corrected for incomplete extraction recovery). Source: Tuß et al., 1982.[46]

Figure 6. Schematic diagram of the nebulization/reflux concentrator as reported by Cofer et al., 1986.[48]

Figure 7. Apparatus for maintaining and dispensing the purified DNPH or PFBOA reagent.

Figure 8. Ternary gradient separation of HCHO-DNPHhydrazone from ozone-DNPH reaction artifacts at constant HCHO concentration. A. High-level ozone (514 ppbv); B. low-level ozone (16 ppbv). Peaks: 1, DNPH reagent; 2, formaldehyde; 3-8, ozone-DNPH reaction artifacts. Source: Smith, Kleindienst and Hudgens, 1989.[28]

Figure 9. Ozone effect on C_{18} cartridges loaded with PFBOA.

A. Carbonyls generated by passiong 10 L zero air containing 100 ppb through a C_{18} cartridge (900 mg, Burdick & Jackson Brand) loaded with 3 mL of 5 mM PFBOA in pH 3.2 buffer. 1, acetaldehyde; 2, internal standard (2-bromochlorobenzene); 3, acetone; 4, propanal; 5, 2-butanone; 6, n-butanal; 7, n-pentanal; 8, n-hexanal; 9, n-heptanal; 10, n-octanal; 11, n-nonanal; 12, n-decanal; 13, n-undecanal; 14, n-dodecanal.

B. Ozone removed with a CuO (5 g) cartridge attached in front of the C_{18} cartridge.

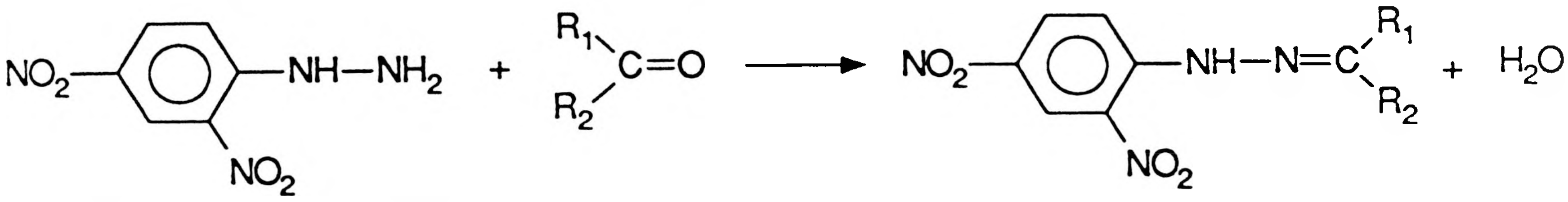

Figure 1

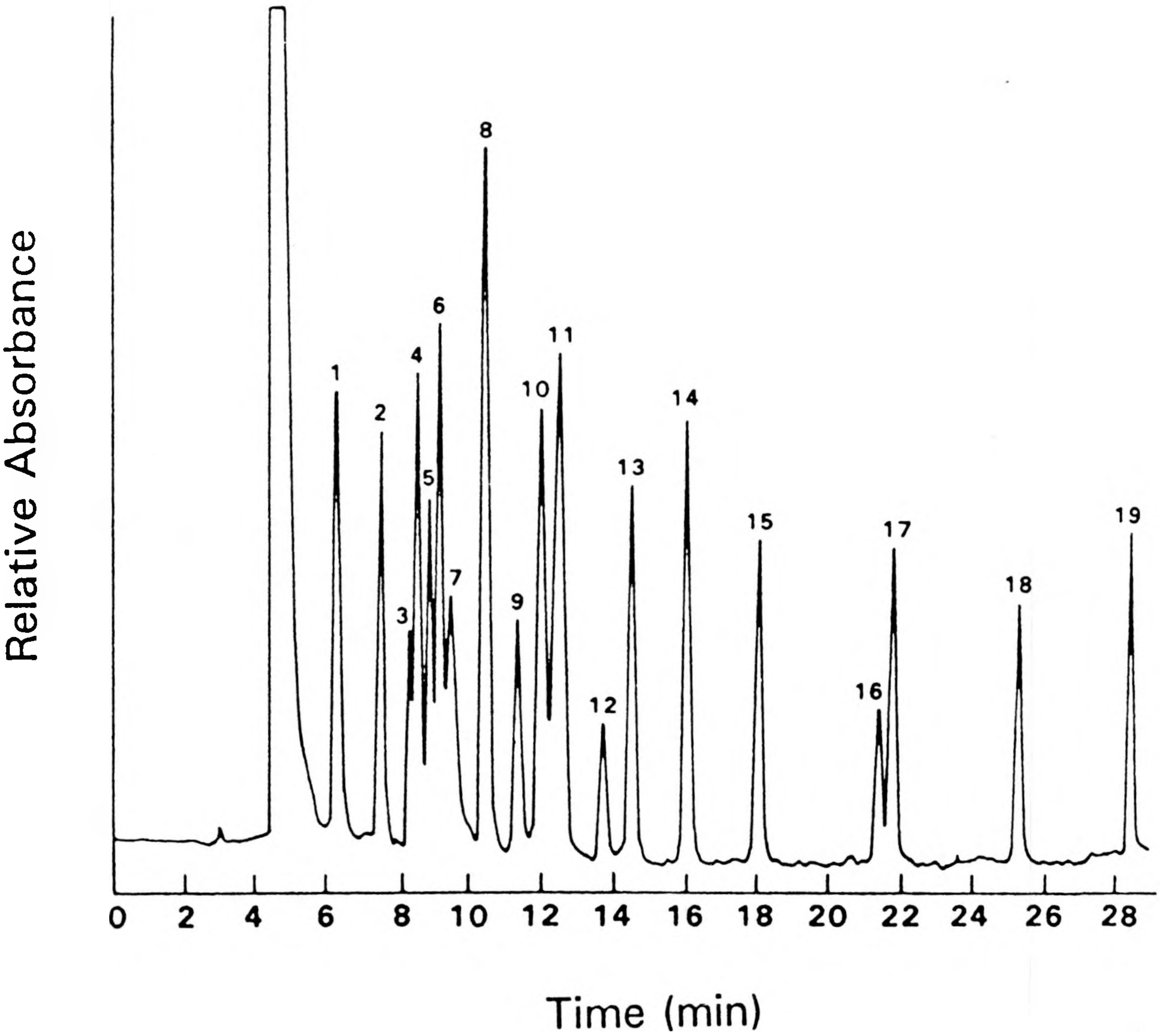
Relative Absorbance
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
Time (min)

Figure 2

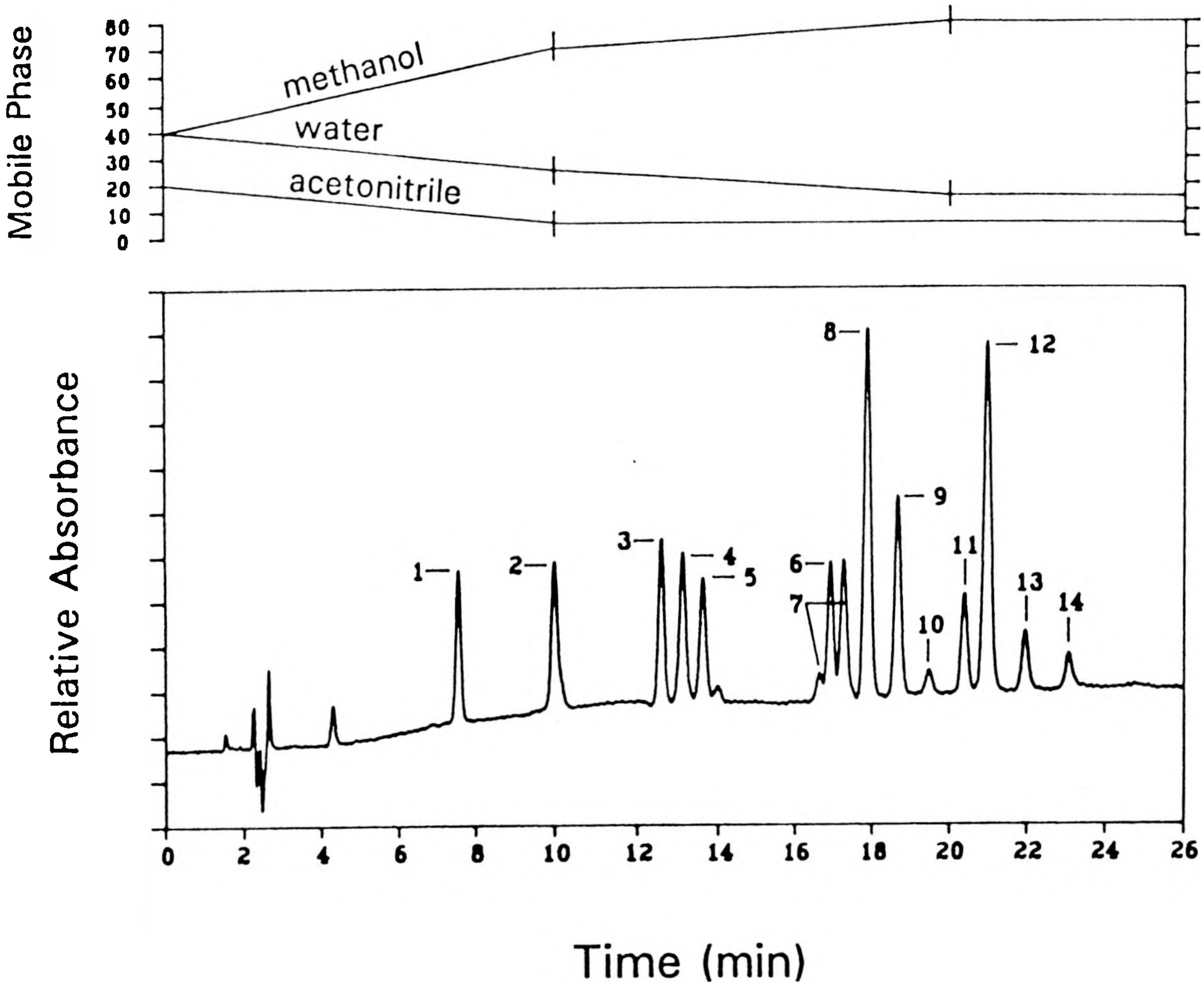
Mobile Phase
80
70
60
50
40
30
20
10
0
methanol
water
acetonitrile
Relative Absorbance
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
2
4
6
8
10
12
14
16
18
20
22
24
26
Time (min)

Figure 3

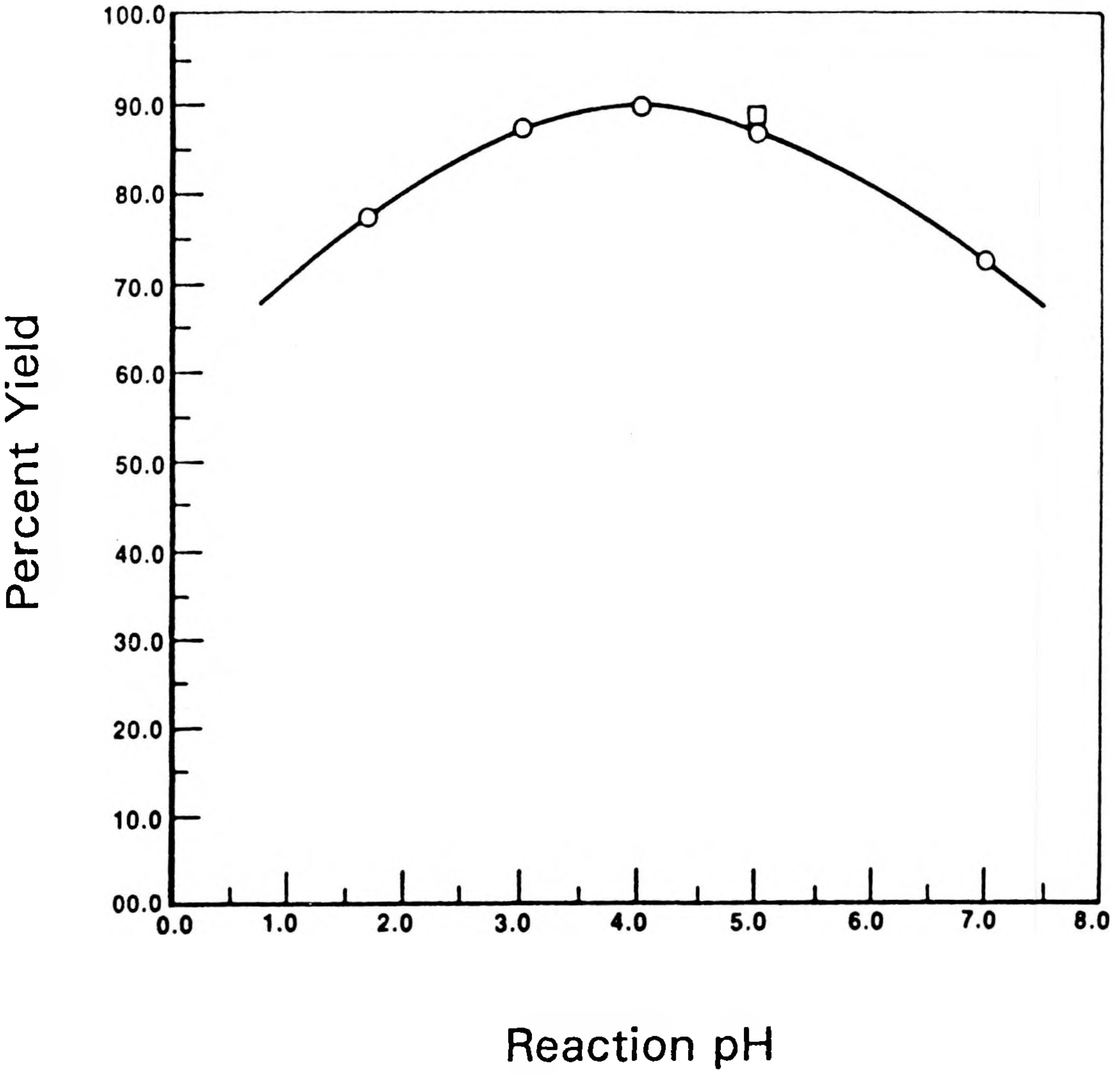
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
00.0
Percent Yield
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Reaction pH

Figure 4

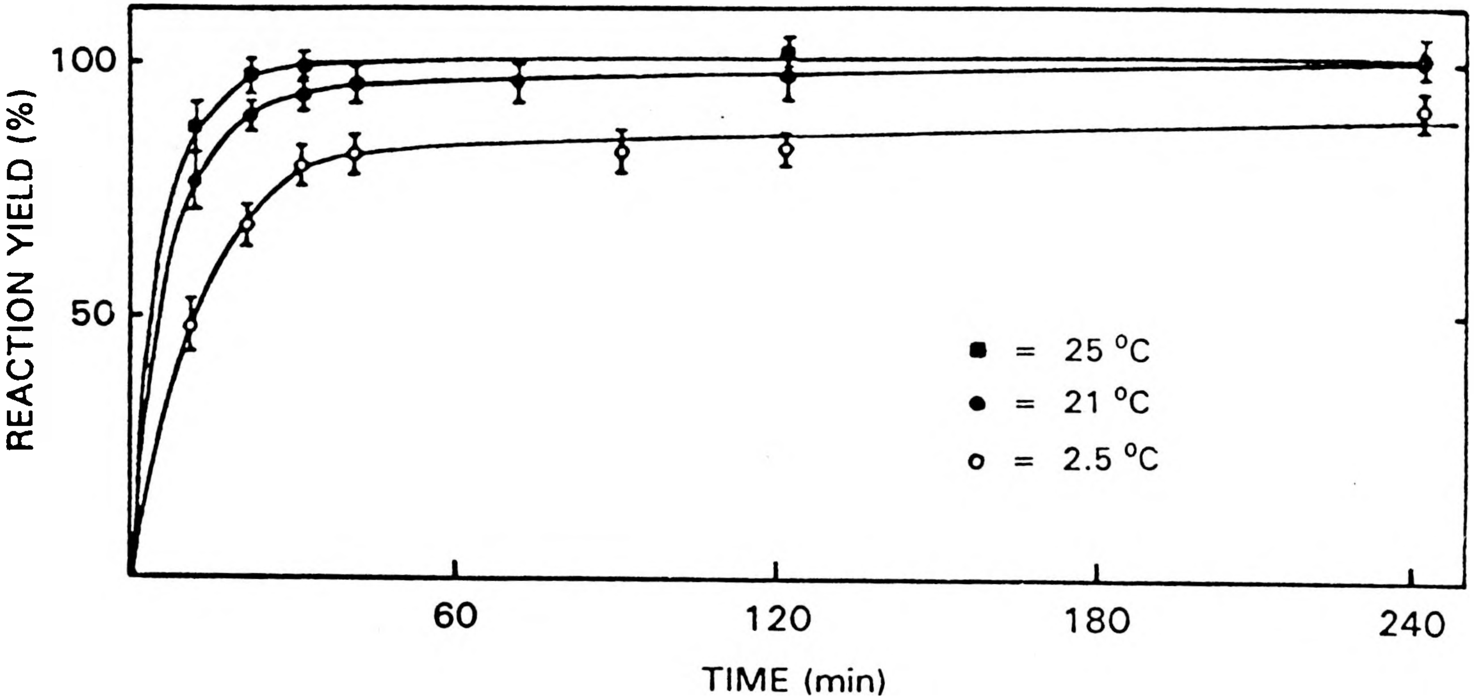

Figure 5

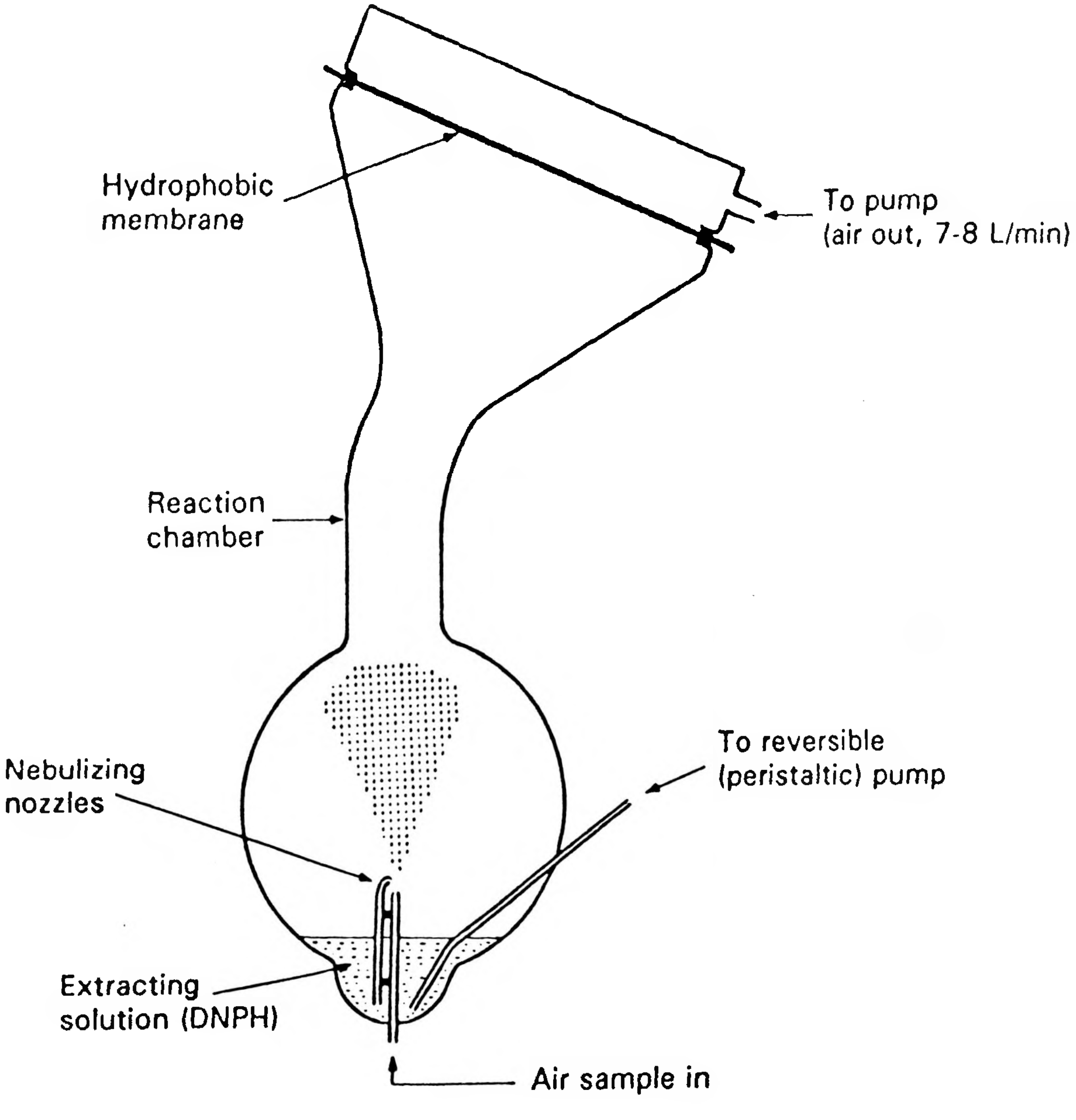
Hydrophobic membrane
To pump (air out, 7-8 L/min)
Reaction chamber
To reversible (peristaltic) pump
Nebulizing nozzles
Extracting solution (DNPH)
Air sample in

Figure 6

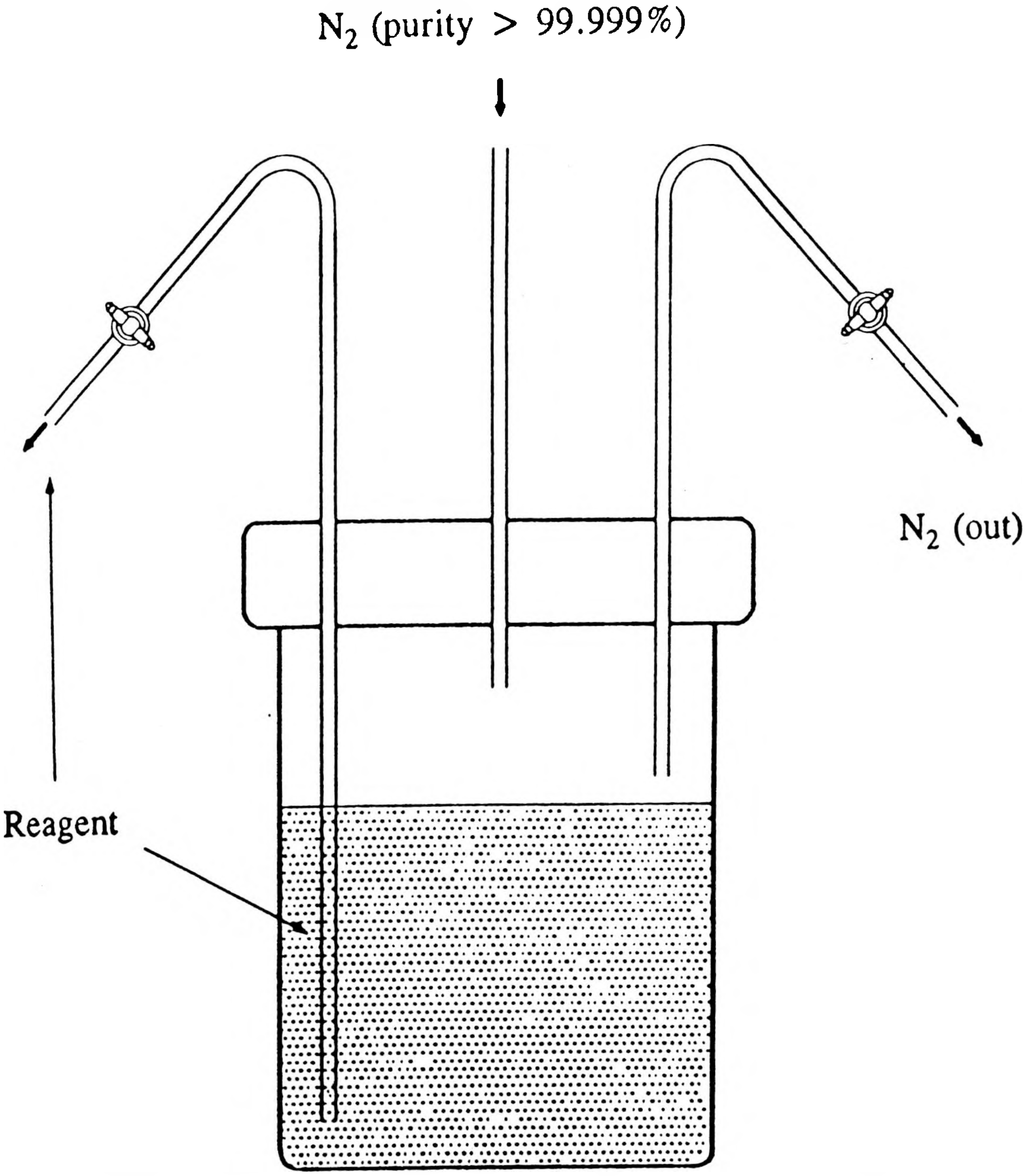

Figure 7

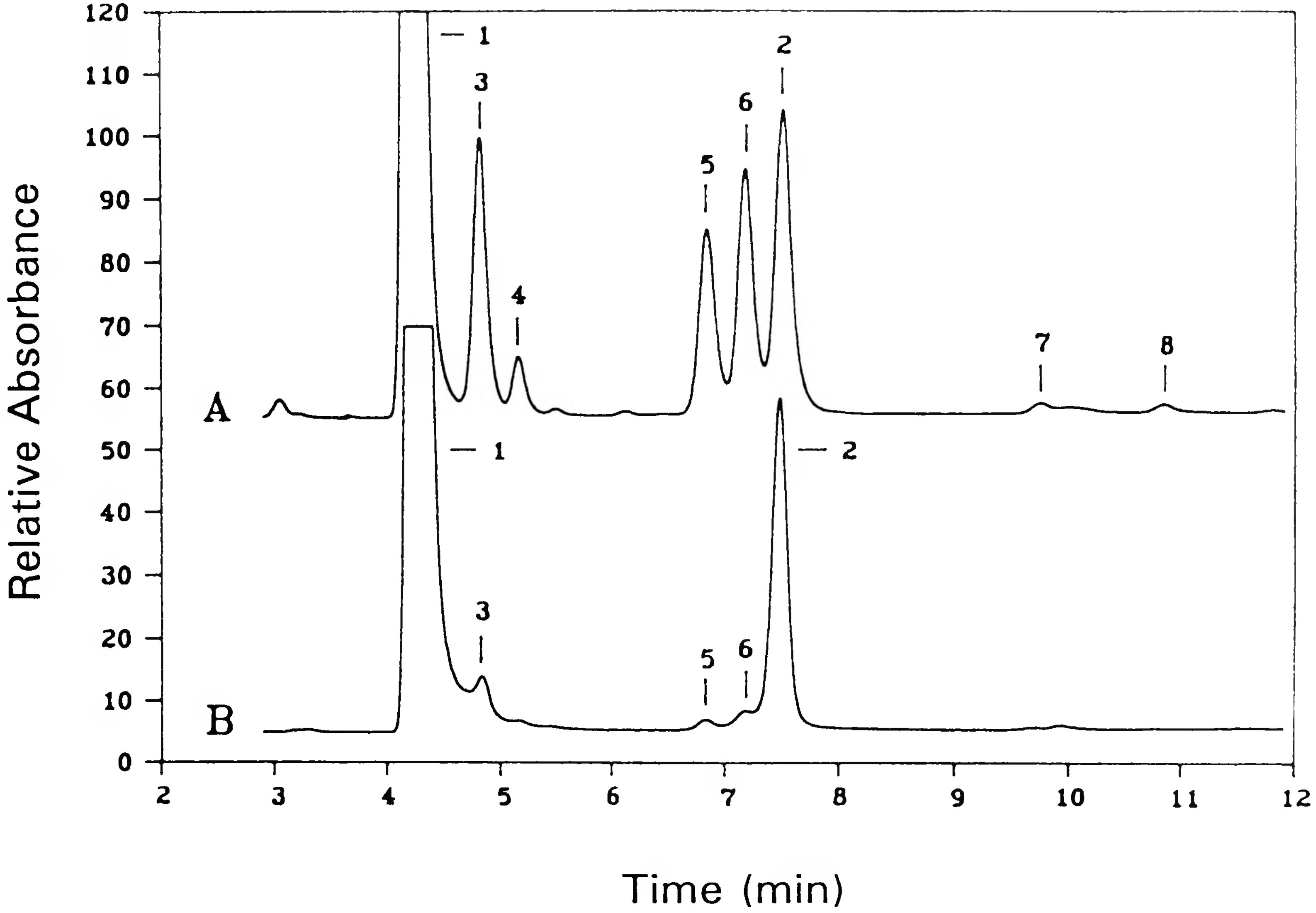
Relative Absorbance
0
10
20
30
40
50
60
70
80
90
100
110
120
Time (min)
2
3
4
5
6
7
8
9
10
11
12
A
B
1
2
3
4
5
6
7
8
1
2
3
5
6

Figure 8

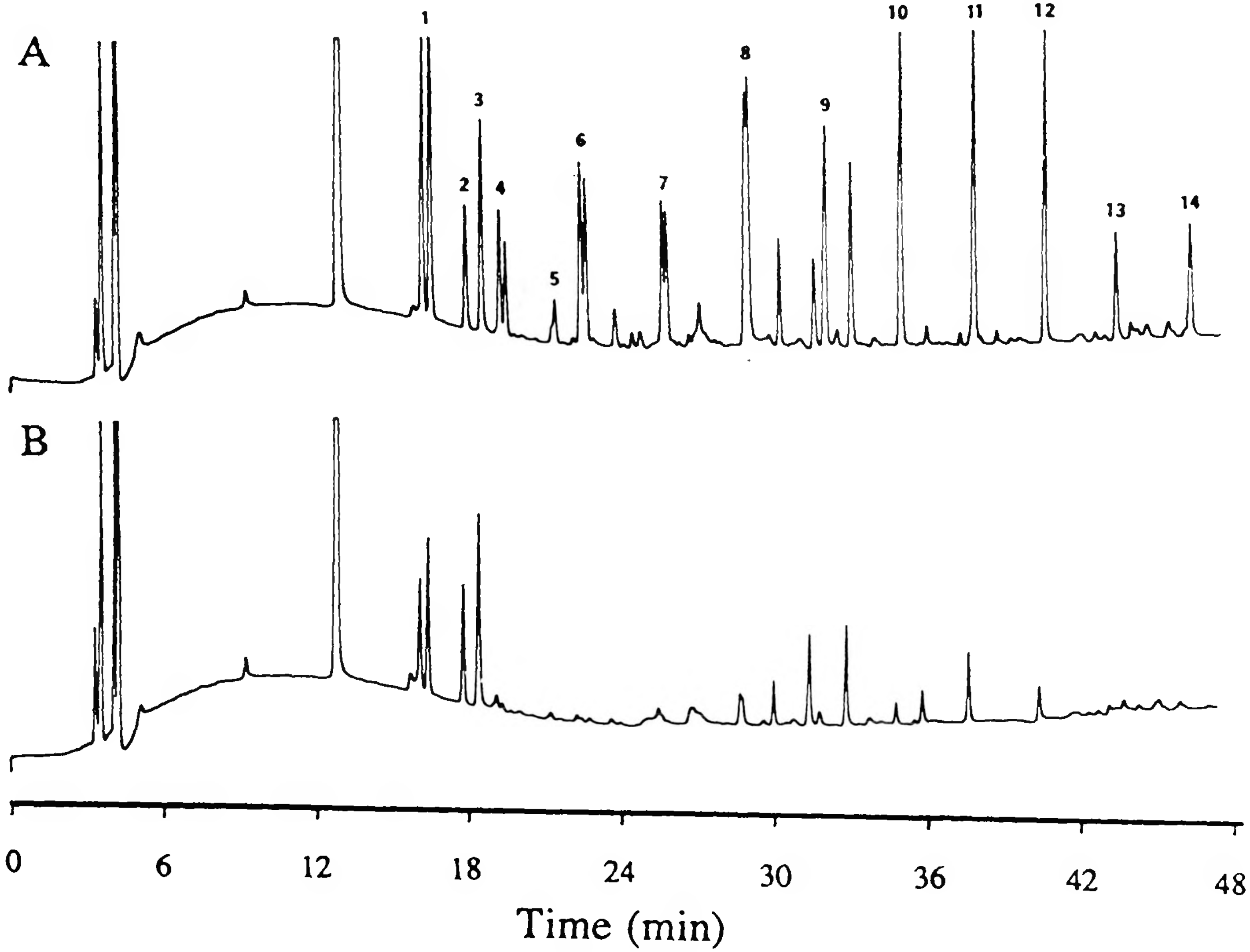

Figure 9

Table 1. Absorption Maxima of Carbonyl DNPHydrazones

Carbonyl Compound	λ-max (nm)	Carbonyl Compound	λ-max (nm)
DNPH reagent	357[a]	Acrolein	373[a], 367[b]
Formaldehyde	353[a], 350[b], 345[c]	Crotanaldehye	378[d]
Acetaldehyde	363[a], 360[b]	Glyoxylate	355[a], 351[b]
Propanal	365[a]	Pyruvate	369[a], 351[b]
n-Butanal	363[a]	Acetoacetate	375[b]
Isobutanal	363[a]	Acetone	367[a]
n-Pentanal	363[a]	Methylethylketone	367[a]
n-Hexanal	363[a], 350[b]	Hydroxyacetone	360[b]
n-Heptanal	359[a]	Dihydroxyacetone	367[b]
Benzaldehyde	385[a]	2-Methylcyclohexanone	371[a]
Hydroxybenzaldehyde	393[b]	5-Hydroxy-2-pentanone	369[a]
Glyoxal	437[a]		
Methylglyoxal	427[a]		

[a] In 55:45 CH_3CN, H_2O medium (Druzik et al.1990).[25]

[b] In 60:40 CH_3CN, H_2O (pH 2.6) medium (Kieber and Mopper, 1990).[31]

[c] In 75:25 CH_3OH, H_2O medium (Grömping and Cammann, 1989).[30]

[d] In 65:35 CH_3CN, H_2O medium (Puputti and Lehtonen, 1986).[29]

Table 2. Extraction Efficiency[a,b]

CCl_4 (mL)	HCHO-DNPH (ng)		Recovery after first extract (%)	Recovery after three extracts (%)
	Added	Found		
50	400	363	94	95
		375		
		384		
5	400	303	76	92
		292		
		318		
1	400	173	34	56
		217		
		136		

[a] Source: Tuß et al., 1982.[46]

[b] A 50 mL DNPH solution containing 400 ng added HCHO-DNPH was used for extraction.

Table 3. Formaldehyde Recovery as a Function of Ozone using the DNPH Coated Silica Gel Cartridge Technique[a]

Added ozone, ppbv	Ratios of HCHO[b] with/without ozone	
	Average response	Std. deviation
0[c]	1.0	0.063
120	0.63	0.084
300	0.39	0.053
500	0.27	0.074
770	0.15	0.077

[a] Source: Arnts and Tejada, 1989.[11]

[b] Formaldehyde concentrations of 20, 40 and 140 ppb were used in the experiment.

[c] Ozone concentration in the ambient background ranged from 0 to 20 ppbv with no ozone addition.