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New gas chromatographic–electron-capture detection method for the determination of atmospheric aldehydes and ketones based on cartridge sampling and derivatization with 2,4,6-trichlorophenylhydrazine

David W. Lehmpuhl, John W. Birks*

Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309-0216, USA

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Abstract

The derivatizing reagent 2,4,6-trichlorophenylhydrazine (TCPH) was applied for the first time to the determination of atmospheric aldehydes and ketones using gas chromatography (GC) with electron-capture detection. TCPH is volatile enough to be used with GC without the problems of thermal decomposition or complex procedures associated with other derivatives such as 2,4-dinitrophenylhydrazine. Small cartridges packed with octadecyl silica impregnated with TCPH had collection efficiencies greater than 99% for all carbonyls tested, except for acetaldehyde and propionaldehyde which had collection efficiencies of 80 and 94%, respectively. TCPH requires only 6 min at 100°C for complete reaction with low-molecular-mass carbonyls in the absence of an acid catalyst. Detection limits were determined by the blank and were 0.1 ppb (v/v) for formaldehyde in a 10-l sample and much lower (typically 0.02–0.03 ppb, v/v) for many other carbonyls. As with other cartridge methods, a negative interference from ozone at 300 ppb (v/v) was found for the reagent and positive interferences were found for several other carbonyls. These interferences were eliminated through the use of sodium thiosulfate as an ozone scavenger.

Keywords: Derivatization, GC; Air analysis; Environmental analysis; Aldehydes; Ketones; Carbonyl compounds; Thiosulfate; Ozone

1. Introduction

The most popular means of determining carbonyl compounds in the atmosphere makes use of derivatization with 2,4-dinitrophenylhydrazine (DNPH) followed by reversed-phase high-performance liquid chromatographic (HPLC) separation of the corresponding hydrazones and UV detection near 360 nm [1–7]. The carbonyl compounds are typically collected in impingers or, more commonly, in solid-phase extraction cartridges impregnated with an acidic DNPH solution. Impinger samples are usually preconcentrated through evaporation or some other means to a few milliliters, while cartridges are eluted with a few milliliters of solvent. Typically, a 20-μl aliquot is then injected onto the HPLC column.

Perhaps the most important other derivatizing agent used with HPLC analysis is dansylhydrazine

*Corresponding author.

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(DNSH), which forms fluorescent hydrazones [8–10]. In recent work, microcartridges packed with particles impregnated with DNSH were used to collect atmospheric carbonyls, and the entire sample was injected 'on-line' onto an HPLC column, thus eliminating all sample handling and preconcentration steps. The detection limits of formaldehyde and acetaldehyde were 0.1 ppb (v/v) for 1-l air samples obtained at a sampling rate of 100 ml/min for 10 min using this method [9,10]. However, a significant interference was found for both the DNSH and DNPH cartridge methods from ozone at ozone concentrations exceeding 150 ppbv, thereby limiting the techniques to relatively clean air [11,12].

Analysis using gas, rather than liquid, chromatography is more desirable for a number of reasons. First, the resolution achievable with gas chromatography (GC) is greater than with HPLC, thereby allowing more accurate identification and quantification of carbonyl compounds in complex air samples. HPLC resolution problems include the co-elution of methyl ethyl ketone and butyraldehyde [13], as well as very poor resolution among acrolein, acetone and propionaldehyde [14]. Second, temperature programming in GC is generally faster than gradient elution in HPLC, with shorter equilibration times between injections. Samples can be analyzed at about twice the rate of the DNSH/HPLC method developed earlier in our laboratory [9,10]. Third, GC produces no disposable waste, while large volumes of waste solvents result from HPLC applications. Since GC alleviates the need to transport solvents, it is also more adaptable to field studies with small, portable gas chromatographs commercially available. GC analysis of DNP-hydrazones has been unsatisfactory due to their low volatility and tendency to decompose at temperatures necessary for the chromatography [15–17]. Oxime derivatives have been prepared and used with a nitrogen–phosphorus detector for determination of carbonyls, but decomposition at injection port temperatures and the relatively complex procedure as compared to DNPH/HPLC analysis have prevented oxime derivatization from becoming widely used in atmospheric analyses [18].

In this work, derivatization of aldehydes and ketones using 2,4,6-trichlorophenylhydrazine (TCPH) followed by GC separation and electron-capture detection (ECD) to determine atmospheric aldehydes and ketones is evaluated. This GC method for carbonyl determination has the advantage of simplicity and sensitivity over other methods. In addition, by using thiosulfate as an antioxidant, the ozone interference can be eliminated. The primary disadvantage is a problem with formaldehyde contamination in the blank, which limits its sensitivity for this carbonyl to 0.1 ppbv in a 10-l sample.

2. Experimental

2.1. Principle

Hydrazines (-NH-NH_2) react specifically towards aldehydes and ketones. The reaction involves a nucleophilic attack by the hydrazine on the partially positive carbon of the carbonyl followed by an acid-catalyzed dehydration to form a hydrazone [19]. Since the carbonyl carbon found in aldehydes has a larger positive charge than in ketones, the reactions of hydrazines with aldehydes are usually much faster and proceed to a greater degree of completion. In order to specifically detect aldehydes and ketones, various tags can be attached to the hydrazine for sensitive and selective detection in HPLC or GC. TCPH has a melting point of 141–143°C and is volatile enough to be separated by GC. It also has three chlorines, which provide for high detection sensitivity in an electron-capture detector.

2.2. The GC system

A Hewlett-Packard 5890 Series II gas chromatograph was used with a J & W Scientific (Folsom, CA, USA) 30 m×0.30 mm I.D., DB-5, fused-silica capillary column (film thickness of 1 μm). Helium was used as the carrier gas (1.5 ml/min) and UHP N_2 was used as a make-up gas (58 ml/min) for the ^{63}Ni electron-capture detector. For comparison, limits of detection were also determined using flame ionization detection (FID). When used, the column was manually switched to the FID port which was held at 250°C. Injections were split with a split ratio of 5:1. The injector and detector temperatures were 220 and 250°C, respectively, and the oven was temperature programmed to begin at 140°C and

increase at 5 C°/min to 250°C, holding at 250°C from 2 to 10 min, depending on the sample being analyzed. The injection volume was 2 μl. Peaks were integrated by a HP 3390A integrating recorder and areas also were obtained simultaneously through chromatography software (Peaksimple, SRI Instruments, Las Vegas, NV, USA) on a personal computer interfaced to the ECD detector.

2.3. Sampling procedure

Sampling of atmospheric carbonyls was accomplished through the use of cartridges constructed in our laboratory (Fig. 1). Each cartridge consists of a 5-cm section of 0.635 cm O.D. glass tubing fitted with a 1/4 inch (0.635 cm) to 1/16 inch Swagelok reducing union on one end (which will be called the bottom of the cartridge) and a 1/4 inch Swagelok union on the other end (which will be called the top of the cartridge). PTFE ferrules were used to seal the fittings. The C_{18} packing was obtained from Sep-Pak C_{18} cartridges from Waters (Milford, MA, USA) and was held in place using two layers of polypropylene cloth (160 mesh) obtained from Small Parts (Miami Lakes, FL, USA). The Sep-Pak cartridges themselves were used until it was found that the frits were a source of contamination. The fittings on our cartridge allow simple, tight connections to the air pump and syringes used for loading and eluting the cartridge.

A typical sample was collected as follows:

1. The cartridge was rinsed with CH_3CN by attaching a syringe filled with 5 ml CH_3CN to the bottom end. This was accomplished through the use of an adapter made of a 1/16 in. Swagelok union attached to a removable 18-gauge Luer Lock needle whose point had been removed. A 0.1-ml volume of 0.2 mg/ml TCPH in CH_3CN was then injected into the top of the cartridge and pulled through the cartridge using another Luer Lock syringe attached to the bottom end. For the elimination of the ozone interference, 40 μl of 30 mg/ml thiosulfate solution adjusted to pH 8.5 with KOH was injected into the top of the cartridge and also pulled through.
2. The cartridge was blown dry with UHP He for 1 min at 350 ml/min. The He was added through the top of the cartridge to help distribute the TCPH through the entire cartridge. A dry cartridge was required to ensure a constant sampling rate. A carbonyl trap using DNPH impregnated C_{18} was placed upstream of the cartridge and was used to remove any carbonyls in the He stream before entering the cartridge.
3. The cartridge was attached to a pump through another 1/16 inch adapter, and air was pulled through the top at 100 ml/min. Air was pulled through the cartridge in the same direction that the derivatizing agent was loaded on the cartridge to ensure a high concentration of derivatizing agent at the point of highest carbonyl concentration. A digital mass flowmeter (Teledyne Hastings-Raydist, Hampton, VA, USA) was connected downstream of the cartridge and monitored every 30 s, while collecting a sample. The exact volume of the sample was determined by integrating the readings from the flowmeter.
4. After sampling, the cartridge was disconnected from the pump, and the ends of the cartridge were covered with aluminum foil. The cartridge was heated at 100°C for 6 min in a GC oven to complete the reaction.
5. The cartridge was sealed with PTFE caps and then cooled to room temperature in a water bath. The TCPH and hydrazones were eluted from the cartridge with 0.50 ml CH_3CN using a glass syringe attached to the bottom end. The highest concentration of carbonyls will be at the top end of the cartridge; therefore, eluting from this end more efficiently removes the hydrazones.
6. A 2-μl aliquot of the solution was injected onto the GC column using the split injection technique.

Blanks were obtained in the same manner by leaving out step 3 (pulling air through the cartridge).

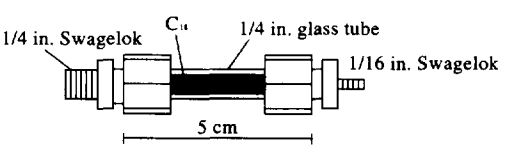


Fig. 1. Schematic diagram of the sampling cartridge used to collect atmospheric carbonyls.

2.4. Gas phase carbonyl generation

For the generation of gas phase carbonyls, a 100-ml glass chamber was employed that had an inlet and an outlet port and a third port connected to a 1/4 inch Cajon glass union which was fitted with a septum. The chamber was wrapped with heating tape and kept between 115 and 120°C. When solutions of carbonyls are injected through the septum, they are vaporized and carried by UHP grade He through the chamber and into the cartridge, which is attached to the outlet. The chamber thus acts similarly to the injection port of a GC. Three to five volumes of He were forced through the sample chamber in order to ensure complete transfer of the carbonyl standard.

2.5. Method of calibration

Absolute calibration of the carbonyl compounds was obtained by preparing a dilute solution of TCPH in CH_3CN followed by addition of an excess carbonyl compound and allowing the solution to stand until the reaction was complete (about 1 h at room temperature with a 1000-fold or greater excess of the carbonyl) [20]. The peak area of the hydrazone was plotted against an equivalent ppbv air sample, determined by assuming 100% collection and reaction efficiency of the cartridge, and taking into account the fraction of the sample injected.

2.6. Ozone generator

A simple UV ozone generator was constructed (Fig. 2) for the purpose of evaluating the effect of ozone on TCPH and the hydrazones. It is based on a model constructed previously in our lab [11] and consists of a Pen-Ray low-pressure mercury lamp attached along the length of a 0.635 cm O.D. quartz tube through which air or oxygen is passed. The system employs a secondary mercury emission line at 185 nm which photolyzes oxygen to form ozone. A small fraction of light at this wavelength is able to pass through the quartz tube. The effluent from the ozone generator was passed through 0.635 cm O.D. PTFE tubing into a glass sampling port and was diluted with ~3 l/min air from a compressed air tank or from the diffusion apparatus described in Section 2.4, if carbonyls were desired in the sampling stream. Variation of the flow of compressed air or oxygen through the ozone generator changes the amount of time it is exposed to the ultraviolet radiation and changes the ozone concentration resulting in the sampling port. Ozone mixing ratios were monitored during sample collection using a Thermo Environmental Instruments, Model 49, UV photometric O_3 analyzer (Franklin, MA, USA) and could be easily controlled from 0 to 400±5 ppbv using compressed air for low ozone concentrations, and oxygen for high ozone concentrations.

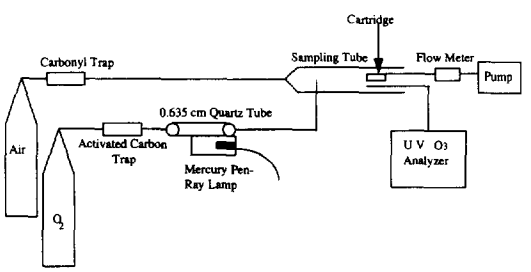


Fig. 2. Schematic diagram of the apparatus used for studying the effect of ozone on the hydrazone formation. The ozone concentration in the sampling tube (0–400 ppbv) was controlled by adjusting the flow of compressed air through the quartz tube adjacent to the UV light source.

2.7. Materials

The acetonitrile solvent was Burdick and Jackson HPLC grade and was distilled once from an acidic DNPH solution to remove trace amounts of carbonyls. 2,4,6-Trichlorophenylhydrazine (99%) was obtained from Aldrich and was purified by recrystallization in CH_3CN. Paraformaldehyde and other aldehydes and ketones were obtained in their pure form from Aldrich and used without further purification. Sodium thiosulfate was obtained from Fisher Scientific.

3. Results and discussion

3.1. Reaction time

The formation of the hydrazones involves a dynamic equilibrium; therefore, an excess of the derivatizing agent is necessary to force the equilibrium toward hydrazone formation. Generally, a 20–40-

fold excess of the derivatizing agent is needed on the cartridge to complete the reaction, depending on the concentration of the carbonyls sampled. Unlike DNPH and other derivatizing agents, the TCPH reaction does not require an added acid catalyst if C_{18} cartridges are used to collect the sample. Using no acid eliminates a source of possible contamination and is an advantage for field studies where transport of concentrated acids may be difficult. Also, the column stationary phase can undergo acid-catalyzed decomposition, so column life can be extended significantly by avoiding acidic injections.

It was found that heating the cartridge at 100°C for 6 min was long enough to give 100% reaction completion of all the lower molecular weight aldehydes and ketones studied. Fig. 3 is a plot of propionaldehyde hydrazone peak vs. reaction time at 100°C. Within an experimental deviation between cartridge samples of ±8%, propionaldehyde was completely reacted after approximately 6 min. Heating at higher temperatures was prohibited by softening of the PTFE ferrules, which caused the cartridges to leak.

In solution, the reaction proceeds very slowly, even with an acid catalyst, unless a large excess of the carbonyl is present. Reaction times longer than 24 h were needed to complete the reaction in most cases. The hydrazine and hydrazones were stable in solution at room temperature for longer than a week, with no change in the chromatogram evident.

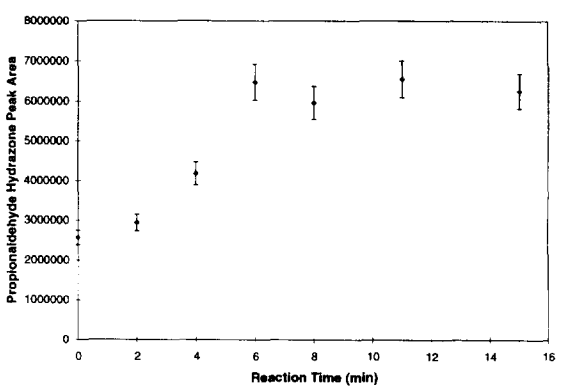


Fig. 3. Peak area of the propionaldehyde hydrazone as a function of reaction time in the cartridge at 100°C. Error bars represent ±8% variability of peak area from sample to sample using the cartridges.

3.2. Cartridge collection efficiency

To test the collection efficiency of the cartridges, two sampling cartridges were connected in series at the outlet of the chamber used to generate gas phase carbonyls, as described in Section 2.4. Ten injections of a 1–3 ppbv equivalent solution of various aldehydes and ketones were injected over a 10-min time period at a He flow-rate of 100 ml/min. Carbonyl compounds tested include C_1–C_7 aldehydes, benzaldehyde and acetone. Collection efficiencies were greater than 99% for all aldehydes and ketones tested, except for acetaldehyde and propionaldehyde, which had collection efficiencies of 80 and 94%, respectively. The C_{18} packing material of the cartridge should retain higher-molecular-mass carbonyls more efficiently than the lower-molecular-mass, more polar, carbonyls, so it is interesting that formaldehyde had >99% collection efficiency while acetaldehyde and propionaldehyde did not. One explanation is that formaldehyde reacts more rapidly than the other carbonyls and is derivatized during sampling and thus becomes much less volatile. Acetaldehyde and propionaldehyde do not react as quickly and have a chance to pass through the cartridge before reacting with the TCPH. Compounds of higher molecular mass than propionaldehyde are retained by the C_{18} and react during heating of the cartridge.

3.3. Retention times for standards

Dilute solutions of various aldehydes and ketones were prepared (10–20 mM) and 5 μl of each injected onto the cartridge and analyzed to obtain retention data. Table 1 summarizes the retention factors for various standards. Methane was injected to determine the hold-up time (t_0) of the system used in calculating k' values. The Kovats retention indices (listed in Table 1) were obtained from a plot of the natural logarithm of the adjusted retention time versus the retention index for normal alkanes. The plot was not linear due to the temperature program, but linearity was assumed between consecutive points in order to obtain the retention indices for the hydrazones [21].

There was some difficulty in obtaining good resolution between TCPH and the hydrazone of

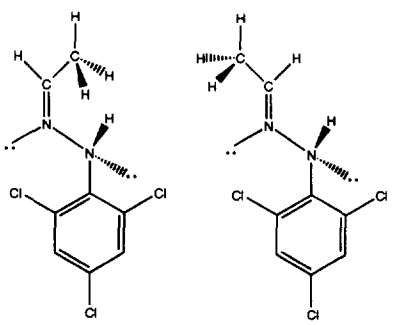
Table 1
Retention factors for various aldehydes and ketones

Compound	k'	Kovats retention index
TCPH-ox	1.65	1270
TCPH	6.56	1654
Formaldehyde	6.89	1673
Acetaldehyde	8.10, 8.83	1751, 1797
Acetone	8.67	1840
Propionaldehyde	9.55, 10.35	1846, 1895
2-Butanone	10.85	1926
Butyraldehyde	11.05, 11.99	1938, 1993
Methacrolein	11.27	1950
Isovaleraldehyde	11.93, 12.80	1989, 2040
2-Methylbutyraldehyde	11.94	1990
Crotonaldehyde	12.56	2026
Valeraldehyde	12.70, 13.57	2034, 2083
Methyl vinyl ketone	12.98	1819
Hexanal	14.35	2126
4-Heptanone	14.50	2133
trans-2-Hexenal	15.25, 15.89	2174, 2207
Heptanal	15.89	2208
Cinnamonaldehyde	16.91	2261
Octanal	17.71	2301
Benzaldehyde	19.47	2389

Entries with two values are for the *trans* and *cis* isomers, respectively.

formaldehyde without having very long analysis times and poor peak shape. The temperature program used provides adequate resolution of these two peaks, provided TCPH is not in too large an excess. A 40-fold excess will still allow the two peaks to be adequately resolved, but baseline resolution was not achievable under these conditions. Acetone, methacrolein and propionaldehyde were all baseline resolved, as were methyl vinyl ketone and butyraldehyde.

Asymmetric aldehydes and ketones show two different peaks which are a result of the formation of the *cis* and *trans* isomers of the derivatization reaction. For the hydrazone of acetaldehyde, for example, the two isomers are:



The *trans* isomer is expected to be the favored reaction product because it is less sterically hindered than the *cis* isomer, which is in agreement with the observed *trans*/*cis* ratio greater than three for all aldehydes we have analyzed. In work using DNSH derivatization and HPLC separation, the *trans* product eluted after the *cis* isomer because its elongated form permits more interaction with the C_{18} stationary phase [11]. In this work, the *trans* derivative of TCPH elutes prior to the *cis* isomer. It has a smaller dipole moment than the *cis* isomer, somewhat lowering its boiling point. As a result, the *trans* isomer has a shorter retention time.

3.4. Standard curves

Using the solutions made with excess aldehydes and ketones (see Section 2.5), a standard calibration curve for formaldehyde was obtained. The curve was linear over at least three orders of magnitude up to $3 \cdot 10^{-9}$ g of the formaldehyde hydrazone injected, and a plot of $\log_{10}$ of the ECD detector signal vs. $\log_{10}$ of the concentration gave a slope of 1.02 ± 0.01. The instrumental detection limit was determined to be $\sim 3 \cdot 10^{-12}$ g injected for a 5:1 split ratio; thus, the ECD limit is approximately 0.6 pg on-column. The actual detection limit of the method using sampling cartridges was determined by the blank. Formaldehyde is the major contaminant which, unfortunately, could not be eliminated from the blank, resulting in a detection limit of 0.1 ppbv (signal equal to blank value) based on a 10-l sample. Limits of detection for other aldehydes and ketones are much lower, due to much lower blank values of typically 0.02–0.03 ppbv.

3.5. Atmospheric examples

An example chromatogram of a 2-l sample of air obtained on February 13, 1995 at the University of Colorado campus in Boulder, CO, USA, and its blank are provided in Fig. 4a,b. The measured concentrations of formaldehyde and acetaldehyde are 3.2 and 2.2 ppbv, respectively, after correcting for the blank. The concentration of acetaldehyde was determined by adding together the peak areas for both isomers. The peak labeled TCPH-ox is believed to be an oxidation product of the derivatizing agent. It is always present and increases in area with

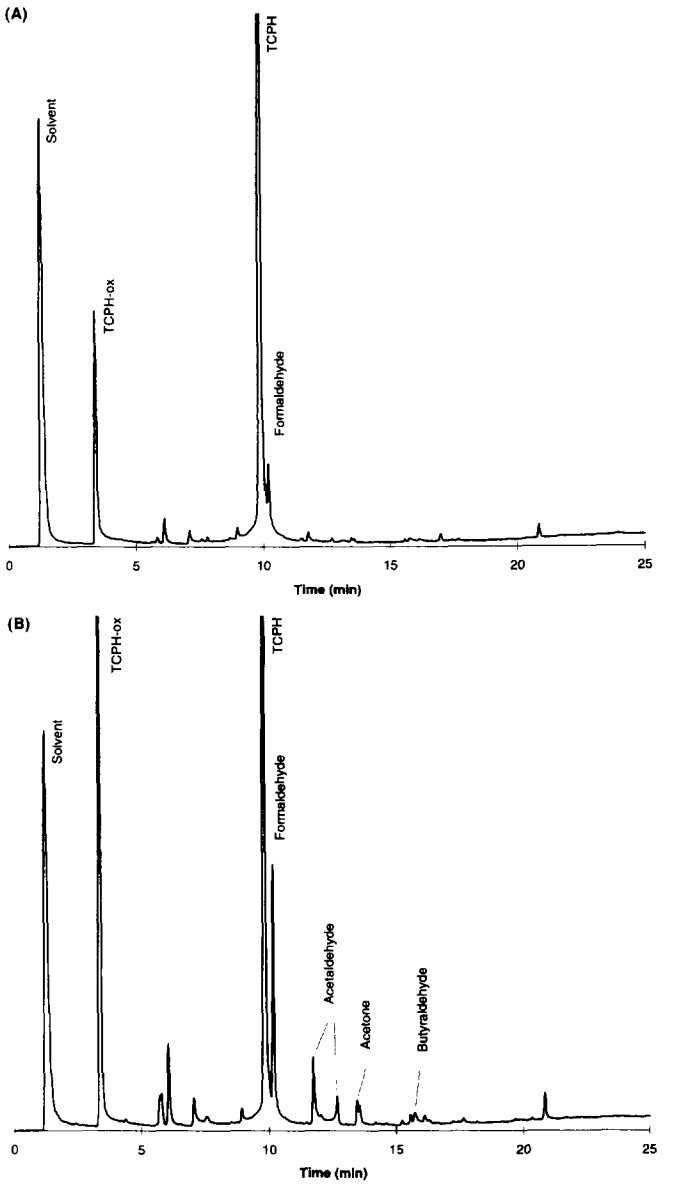


Fig. 4. (a) Blank chromatogram using 2,4,6-trichlorophenylhydrazine. Labeled peaks are the hydrazone products of the TCPH reaction. (b) Chromatogram resulting from a 2-l sample of air obtained on the University of Colorado campus.

increasing sampling time. The addition of O_3 to a sampling stream greatly increases the area of this peak, while the addition of an antioxidant decreases its area (see Section 3.7). Other peaks eluting prior to the derivatization reagent are possibly polar multifunctional carbonyl compounds, including a product resulting from reaction of TCPH with NO_2 to form 2,4,6-trichlorophenylazide, which has been demonstrated in an analogous reaction with DNPH [22]. The sample was taken in the early afternoon, and automobile traffic was probably the largest contributor to the levels of carbonyls seen.

The technique also works well for concentrated samples. Fig. 5 is a 5-min sample (500 ml) taken 12.5 cm away from the tailpipe of an automobile burning unleaded gasoline. Large amounts of form-

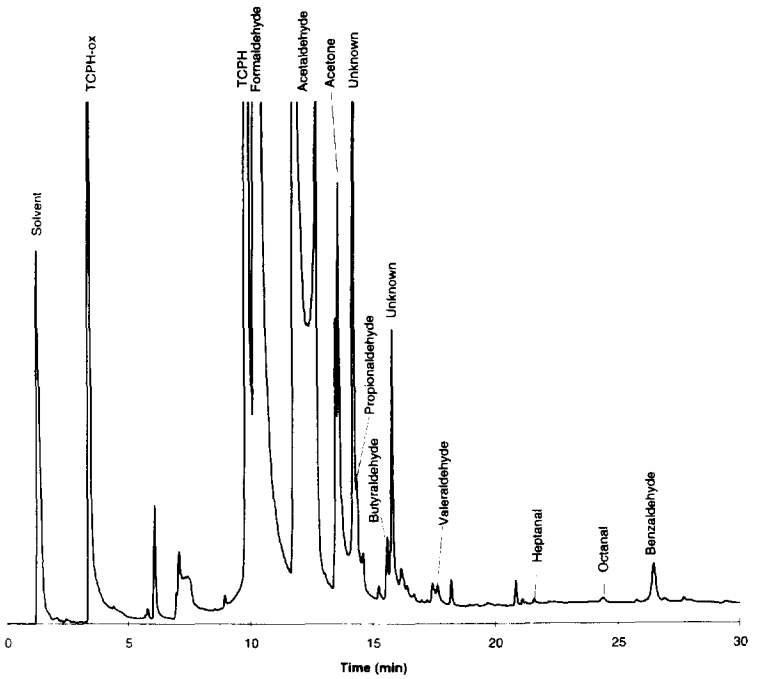


Fig. 5. Chromatogram resulting from a 5-min sample of air obtained 12.5 cm from the tailpipe of an automobile burning unleaded gasoline. Labeled peaks are the hydrazone products of the TCPH reaction.

aldehyde, acetaldehyde and some acetone are present in addition to C_3–C_8 aldehydes and benzaldehyde. Benzaldehyde is thought to be emitted only by fossil fuel burning and as such could be a good indicator of anthropogenic sources of air pollution [23].

3.6. FID capability

In addition to ECD, the use of FID is also possible for detecting atmospheric carbonyls derivatized with TCPH. There are a couple of disadvantages of this method of detection, however. One disadvantage is that the response of the detector is dependent on the length of the hydrocarbon chain in the analyte and, as a result, separate calibration curves or response factors are required for each carbonyl compound. A second disadvantage is that FID is not as sensitive or selective as ECD, so that larger sampling volumes are required. The relative sensitivity of the two detectors was determined for the formaldehyde hydrazone by comparing their instrumental detection limits. Dodecane was first injected to insure the FID detector was operating at optimal sensitivity. The instrumental detection limit for dodecane using FID was 80 pg injected with the 5:1 split ratio, or 16 pg on column. The detection limit for TCPH was 1.8 ng on column and for the formaldehyde hydrazone was 1.5 ng on column. Compared to the 0.6 pg on column detection limit for the formaldehyde hydrazone in ECD, FID is approximately 2500-times less sensitive toward the formaldehyde hydrazone of TCPH.

3.7. Elimination of the ozone interference

One important aspect of cartridge sampling is the interference that can result from ozone since hydrazines and the corresponding hydrazones are both susceptible to oxidation [24]. Sirju and Shepson found significant negative interference for the formaldehyde hydrazone of DNPH at ozone concentrations as low as 42 ppbv [7], while Arnts and Tejada found no significant interference below 120 ppbv [25]. The explanation offered by Sirju and Shepson for this discrepancy is that the magnitude of the O_3 interference may depend on both the amount of O_3

sampled and on the carbonyl concentrations. The potassium-iodide-based ozone traps used by both groups are prone to producing organic iodine artifacts which, unfortunately, would be highly detectable with ECD [26].

A negative interference was also noted for DNSH derivatives, but it was shown to be insignificant for ozone mixing ratios up to 300 ppbv as long as an excess of the hydrazine is present [11]. Water vapor was a more significant interference, but could be almost eliminated through the use of octadecyl silica as the sorbent. Heterogeneous oxidation of isoprene within the cartridge was found to result in a large positive interference for formaldehyde, methacrolein, methyl vinyl ketone and several larger carbonyl compounds using both DNSH and DNPH [12]. A substantial reduction in the ozone interference was reported in both of these studies by using N,N,N′,N′-tetramethyl-1,4-phenylenediamine dihydrochloride as an ozone "scavenger". Unfortunately, however, it interfered in the chromatography by producing a broad peak that co-eluted with some of the analyte hydrazones.

Thiosulfate, commonly used to titrate iodine, is one of the few reducing agents that is stable to air oxidation [27]. Thiosulfate is only moderately stable in aqueous solution, and its stability is decreased by metal ions, UV light, low concentration, and sulfur bacteria [28]. Boiling distilled water and keeping the solution in the dark will keep thiosulfate solutions stable for weeks [27], but we preferred to make a fresh solution daily. The reaction between thiosulfate and ozone produces tetrathionate and water as follows:

$$2S_2O_3^{2-} + O_3 + 2H^+ \rightarrow S_4O_6^{2-} + O_2 + H_2O \qquad (1)$$

Table 2 compares the measured concentrations of hydrazones using the formaldehyde calibration curve before and after adding 300 ppbv ozone to a 1-l sample of compressed air, with and without the addition of 35 mg thiosulfate to the cartridge. The derivatizing agent had a 14% decrease in peak area upon addition of ozone in the absence of thiosulfate, perhaps due to oxidation, as well as derivatization of the aldehydes produced from the reactions of ozone with the sorbent or with trace amounts of unsaturated hydrocarbons in the compressed air stream. The addition of ozone to the air stream increased the area of almost all other peaks present, most notably the formaldehyde hydrazone peak, and it lead to the generation of numerous peaks not found in the initial ozone-free sample. After the addition of 35 mg of thiosulfate to the cartridge, the artifacts generated by the addition of ozone were nearly completely eliminated. Virtually all peaks returned to their equivalent mixing ratios found before the addition of ozone or thiosulfate. One exception was the formation of a significant peak at 10.6 min, the identity of which is not known.

Upon addition of thiosulfate, the peak labeled TCPH-ox and the formaldehyde hydrazone peak were both reduced in area to levels below those of ozone-free, thiosulfate-free samples. Compounds eluting prior to TCPH are expected to be more polar, multi-functional compounds, and the TCPH-ox peak is possibly an oxidation product of the TCPH produced by in-cartridge heterogeneous oxidation by both O_2 and O_3. TCPH-ox may be lower in the sample with thiosulfate added if thiosulfate limits the oxidation of TCPH by O_2. The reduction of the formaldehyde hydrazone peak area suggests that thiosulfate reduces formaldehyde itself. Under strongly acidic conditions, thiosulfate is decomposed into sulfite and free sulfur, and the sulfite reacts with formaldehyde to form formaldehyde hydrogen sulfite [29]:

$$S_2O_3^{2-} + 2H^+ \rightarrow H_2SO_3 + S \qquad (2)$$

$$SO_3^{2-} + HCHO + H^+ \rightarrow HCHO \cdot HSO_3^- \qquad (3)$$

As mentioned previously, however, the collection of carbonyls and reaction of TCPH are accomplished with no acid added and there is no reason to believe highly acidic conditions exist on the cartridge, so another explanation is necessary.

A set of experiments was performed in which a formaldehyde spiked air stream was sampled by cartridges with and without the addition of thiosulfate. The results presented in Fig. 6 indicate an average 30% reduction in formaldehyde collection for those cartridges containing thiosulfate, clearly showing that thiosulfate does prevent formaldehyde hydrazone formation. A likely reaction responsible for this negative interference of thiosulfate is the reduction of formaldehyde to methanol:

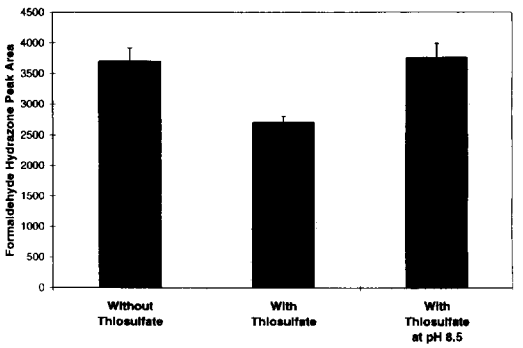


Fig. 6. Formaldehyde collection with and without thiosulfate and with thiosulfate adjusted to pH 8.5. Error bars represent one standard deviation of three trials.

$$HCHO + 2H^- + 2S_2O_3^{2-} \rightarrow CH_3OH + S_4O_6^{2-} \quad (4)$$

In solution, this reaction is spontaneous with an equilibrium constant of $1.3 \cdot 10^8$, calculated from standard reduction potentials found in Bard et al. [30]. The reaction of ozone with thiosulfate (reaction 1) has a solution equilibrium constant of $5.4 \cdot 10^{72}$, calculated in the same manner. Since the two equilibria depend on pH, it was reasoned that it should be possible to adjust the pH such that the reaction of thiosulfate with formaldehyde becomes unfavorable while still allowing for reaction with ozone. Experiments in which the thiosulfate solution was adjusted to pH 8.5 using KOH before addition to the cartridge, resulted in formaldehyde collection equal to collection in cartridges not containing thiosulfate (Fig. 6). A study of the effect of formaldehyde collection as a function of pH in the presence of thiosulfate was performed. At acidic pH, the thiosulfate solution becomes cloudy and smells sulfurous as a result of reaction 2. Variation of pH under more basic conditions showed no change in the collection efficiency of formaldehyde; all basic conditions resulted in no loss of formaldehyde. A pH dependence need not be evident because highly basic conditions can result on the cartridge when even only slightly basic solutions are added and the solvent evaporated.

A repeat of the ozone experiment conducted initially and described in Table 2, but with the pH of the thiosulfate solution adjusted to 8.5, resulted in the ozone effect again being eliminated, but without loss of formaldehyde.

The effect of ozone on the hydrazones of TCPH was studied in another set of experiments. Cartridges were spiked with dilute solutions of C_1–C_4 aldehydes and reacted at 100°C for 6 min; 0.80 l of

Table 2
Effect of adding thiosulfate to the cartridge to reduce the ozone interference by calculating the equivalent mixing ratio for selected peaks in a 1-l sample based on the formaldehyde hydrazone calibration curve

Peak retention time (min)		Measured equivalent in a 10-min sample (ppbv)	Measured equivalent after adding 300 ppbv ozone (ppbv)	Measured equivalent after adding 300 ppbv ozone and 35 mg thiosulfate (ppbv)
3.35	TCPH-ox	112	166	70
5.74		1.8	2.6	1.6
6.01		3.1	3.9	3.9
7.00		3.1	4.9	3.0
7.54		0	3.8	0
9.68	TCPH	550	474	515
10.08	Formaldehyde	28	122	21
10.48		0	0	2.9
11.65	Acetaldehyde	6.3	12.0	6.5
13.46	Propionaldehyde	0	4.0	0
15.65	Butyraldehyde	0	10.0	0
16.05		0	6.4	0
17.52	Valeraldehyde	0	2.4	0
19.54	Hexanal	0	0.9	0
20.62		1.8	2.5	1.3
22.91		0	2.6	1.1

compressed air subsequently was pulled through the cartridge with or without 300 ppbv ozone. No significant differences in the peak areas of the four hydrazones were observed between samples with and without ozone.

The applicability of thiosulfate as an ozone scavenger to the commonly used DNPH technique is questionable, because generally it requires acidic conditions for the derivatization reaction. DNSH, like TCPH, does not require strongly acidic conditions for the derivatization reaction; thus, thiosulfate may eliminate the ozone interference for DNSH as well. Additional work investigating the effectiveness of this antioxidant toward ozone and other interferents using these other derivatization techniques is in progress.

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