



## Short communication

## Ozone removal in the collection of carbonyl compounds in air

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## ABSTRACT

The most widely used method for measuring carbonyl compounds in air is 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by high-performance liquid chromatography (HPLC). However, substantial negative interference caused by the presence of ozone in air has been reported. To avoid the influences of ozone, a potassium iodide scrubber (KI-scrubber) is commonly used. However, when air sampling using a DNPH-cartridge and a KI-scrubber is performed under conditions of high humidity, moist potassium iodide in the KI-scrubber traps carbonyls before they reach the DNPH-cartridge. Moreover, wet KI reacts with I<sub>2</sub> to form KI<sub>3</sub> and this oxidative reagent moves to the DNPH-cartridge and destroys the DNPH and DNPhydrazone derivatives. In order to alleviate these problems, new ozone scrubbers (BPE-scrubber, HQ-scrubber) have been developed. BPE-scrubber and HQ-scrubber consist of silica gel particles impregnated with *trans*-1,2-bis-(2-pyridyl) ethylene (BPE) and hydroquinone (HQ), respectively. BPE reacts with ozone to form pyridine aldehyde and HQ reacts with ozone to form benzoquinone. The amounts of reducing agent in silica gel (130 mg) for ozone scrubber are 1% (w/w) for BPE-cartridge; 0.2% (w/w) for HQ-scrubber. These scrubbers can be used in air containing 140 µg/m<sup>3</sup> of ozone for 24 h at a flow rate of 200 mL/min. When the relative humidity exceeded 80%, KI in the KI-scrubber was gradually moistened and changed to yellow in color. Peak abundance of formaldehyde, acetaldehyde and acetone DNPhydrzones was diminished to 25%, 15%, and 2%, respectively, compared with the BPE-scrubber or HQ-scrubber. When using a BPE-scrubber or HQ-scrubber, decomposition of DNPH and DNPhydrzones was not observed at a wide range of relative humidities (3–97%).

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## 1. Introduction

Formaldehyde, acetaldehyde and other carbonyl compounds are ubiquitous pollutants that are formed through oxidation of hydrocarbons by ozone in the troposphere [1–3] and by the reaction between ozone and terpenoid in indoor air [4–6]. Long-term exposure to relatively high levels of carbonyl compounds such as formaldehyde and acetaldehyde is known to increase the risk of asthma [7] and cancer [8]. Accurate aldehyde measurements are therefore important both for determining the formation mechanism of aldehydes and for evaluating the implications for human health.

The most widely used method for qualitative and quantitative analyses of carbonyl compounds is 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by high-performance liquid chromatography (HPLC). Sampling can be performed using acidic solutions of DNPH in impingers or with acidic DNPH-coated solid sorbents in a cartridge. At the present time, a number of cartridge devices packed with DNPH-coated silica gel particles are

commercially available for sampling aldehydes in air. Due to the importance of the method, it has been introduced as a standard procedure by several national and international standardization bodies.

While the derivatization reaction at first glance appears straightforward, substantial negative interference caused by the presence of ozone in the air sample has been reported [9–11]. Ozone decomposes DNPH and DNPhydrazone derivatives to form 2,4-dinitrophenol, 2,4-dinitroaniline and 1,3-dinitrobenzene [12]. Additionally, Rodier and Birks reported that sampling atmospheres containing isoprene and ozone lead to the formation of artifact carbonyl peaks in a system using DNPH or dansylhydrazine-coated C18 cartridges [13]. The peaks were purportedly due to a reaction of isoprene with ozone on the cartridge surface, which led to positive artifacts for a number of compounds including formaldehyde.

To avoid the influences of ozone, a potassium iodide scrubber (KI-scrubber) can be used to destroy ozone before sampling the carbonyl compounds. In this case the air sample is first drawn over a surface on which solid KI is adsorbed. Ozone reacts with KI to form iodine and potassium hydroxide (Fig. 1). At the present time, KI-scrubbers are commercially available from many suppliers and are widely used. However, KI-scrubbers have two disadvantages. When air sampling using a DNPH-cartridge with a KI-scrubber is performed at high humidity, moist potassium iodide in the

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 (S. Uchiyama).

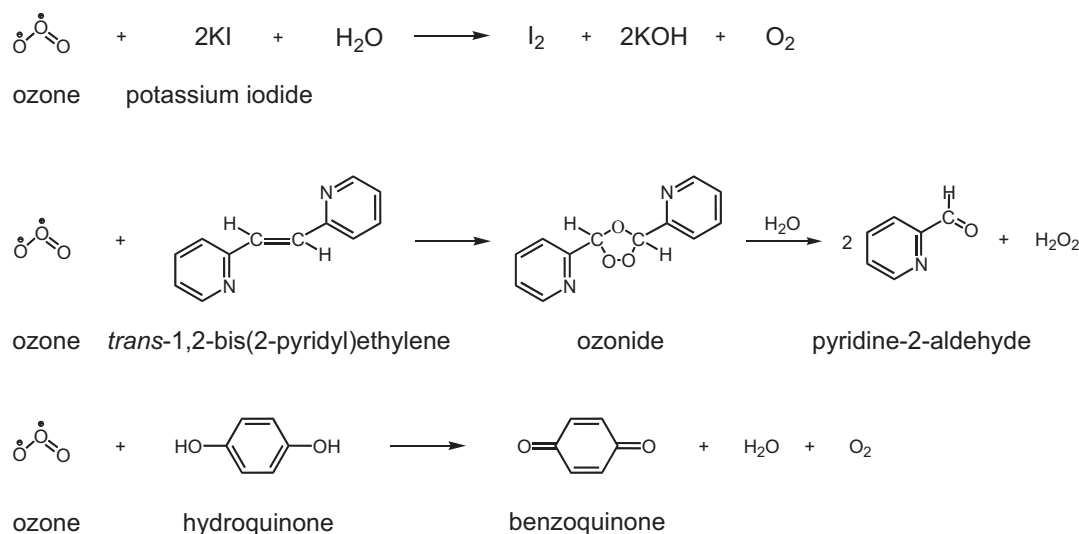


Fig. 1. Reactions of ozone with reducing agents.

KI-scrubber traps carbonyl compounds before they can reach the DNPH-cartridge. Moreover, wet KI reacts with  $\text{I}_2$  to form  $\text{KI}_3$  and this oxidative reagent moves to the DNPH-cartridge and destroys the DNPH and DNPhydrazone derivatives.

We have previously developed a method for the simultaneous determination of ozone and carbonyls in air using a two-bed cartridge system [14,15]. Each bed consists of reagent-impregnated silica particles. The first contains *trans*-1,2-bis(2-pyridyl)ethylene (BPE), while the second contains 2,4-dinitrophenylhydrazine (DNPH). Air samples are drawn through the cartridge first through the BPE and then through the DNPH. Ozone in the air sample is trapped in the first bed by the BPE-coated silica particles and produce pyridine aldehyde (Fig. 1). In this method, BPE acts as an ozone scrubber. We have also developed a method for the determination of acrolein and other carbonyls in cigarette smoke using a dual cartridge system [16]. Each cartridge consists of reagent-impregnated silica particles. The first contains hydroquinone (HQ) for the inhibition of acrolein polymerization, while the second contains DNPH for the derivatization of carbonyls. HQ is a radical and ozone-trapping reagent and is used to inhibit acrolein radical polymerization and to remove ozone. Ozone reacts with HQ to form benzoquinone (Fig. 1). Thus, both BPE and HQ can function as ozone scrubbers. In this study, the effectiveness of KI-scrubber, BPE-scrubber and HQ-scrubber as ozone removers was investigated.

## 2. Experimental

### 2.1. Apparatus and reagents

The HPLC system (Shimadzu, Kyoto, Japan) used included two LC-20AD pumps, an SIL-20AC autosampler and an SPD M20A photodiode array detector. The analytical column was an Ascentis Express RP-Amide, 2.7  $\mu\text{m}$  particle size, 150 mm  $\times$  4.6 mm i.d. column (Supelco Inc, Bellefonte, PA, USA). Solution A of the mobile phase mixture was acetonitrile/water (45/55, v/v) containing 5 mmol/L ammonium acetate and solution B was acetonitrile/water (75/25, v/v). HPLC elution was carried out with 100% A for 5 min, followed by a linear gradient from 100% A to 100% B in 50 min and then held for 10 min. The flow rate of the mobile phase was 0.7 mL/min. The column temperature was 40  $^\circ\text{C}$ , the autosampler temperature was 25  $^\circ\text{C}$  and the injection volume was 10  $\mu\text{L}$ .

The environmental test chamber, supplied by Ohnishi Netsugaku Co., Ltd., Tokyo, Japan, was used for the sampler exposure tests.

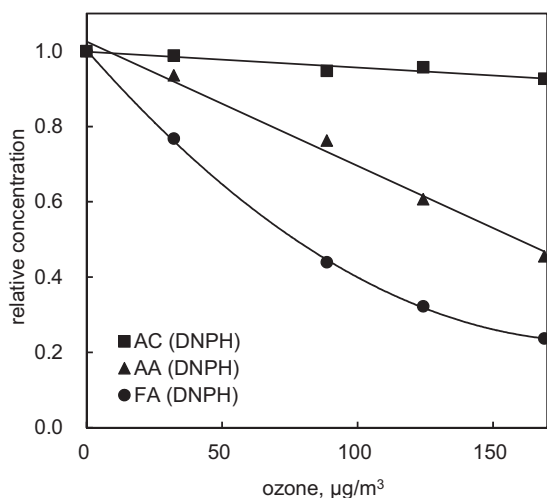
The test chamber had a volume of 34.8  $\text{m}^3$  (4.2 m  $\times$  3.6 m  $\times$  2.3 m) and was equipped with an adjustable constant temperature and humidity controller. Ozone gas was generated using an Ozone Generator (TGO-1, Funatech Ltd., Tokyo, Japan). Air pumps (MP- $\Sigma$ 30N, Shibata Scientific Technology Ltd., Tokyo, Japan) and wet gas meters (WS D-1A; Shinagawa Co., Tokyo, Japan) were used for air sample collection. The humidity and temperature of standard ozone gas were recorded using a TR-72U data logger (T&D Corporation, Japan).

Water used for HPLC and sample preparation was deionized and purified using a Milli-Q Water System equipped with a UV lamp (Millipore, Bedford, MA, USA). 2,4-Dinitrophenylhydrazine hydrochloride (>98%) and *trans*-1,2-bis(2-pyridyl)ethylene (BPE, >97%) were purchased from Tokyo Kasei Co. Ltd. (Tokyo, Japan). Acetonitrile (HPLC grade, >99.9%), hydroquinone (HQ, >99%), 2-pyridinecarboxaldehyde (pyridine-2-aldehyde, 99%), phosphoric acid (85% solution in water), hydrochloric acid (37%), and ammonium acetate (99.999%) were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). Rezorian Ozone Scrubbers and LpDNPH Rezorian cartridges were obtained from Supelco Inc. Silica gel (spherical, 60/80 mesh, 120  $\text{\AA}$  mean pore size) was obtained from AGC Si-Tech. Co., Ltd. (Fukuoka, Japan). Pyridine-2-aldehyde 2,4-DNPhydrazone was synthesized according to previously reported methods [15].

### 2.2. Preparation of a *trans*-1,2-bis(2-pyridyl)ethylene-impregnated silica cartridge (BPE-scrubber) and a hydroquinone-impregnated silica cartridge (HQ-scrubber)

Silica gel (50 g) was washed with water (3  $\times$  500 mL), methanol (2  $\times$  500 mL), and lastly acetonitrile (2  $\times$  500 mL). The solvent was then completely evaporated to dryness at 100  $^\circ\text{C}$  for 30 min under vacuum on a rotary evaporator. After cooling to room temperature, acetonitrile (200 mL) was added to the washed silica gel. BPE (0.5 g) or HQ (0.1 g) was dissolved in 50 mL acetonitrile. This solution was added to the washed silica gel, the mixture was stirred and the solvent was evaporated to dryness at 40  $^\circ\text{C}$  under vacuum on a rotary evaporator. BPE-impregnated silica (130 mg) or HQ-impregnated silica (130 mg) was packed into polyethylene cartridges (Rezorian tube, 1 mL, Supelco Inc, Bellefonte, PA) and stored in a refrigerator at 4  $^\circ\text{C}$ .

The commercially available ozone scrubbers used in this study contained 1.5 g of potassium iodide.



**Fig. 2.** Changes in measured carbonyl concentrations with the coexistent ozone concentration. DNPH-cartridges were used without an ozone scrubber. FA: formaldehyde; AA: acetaldehyde; AC: acetone.

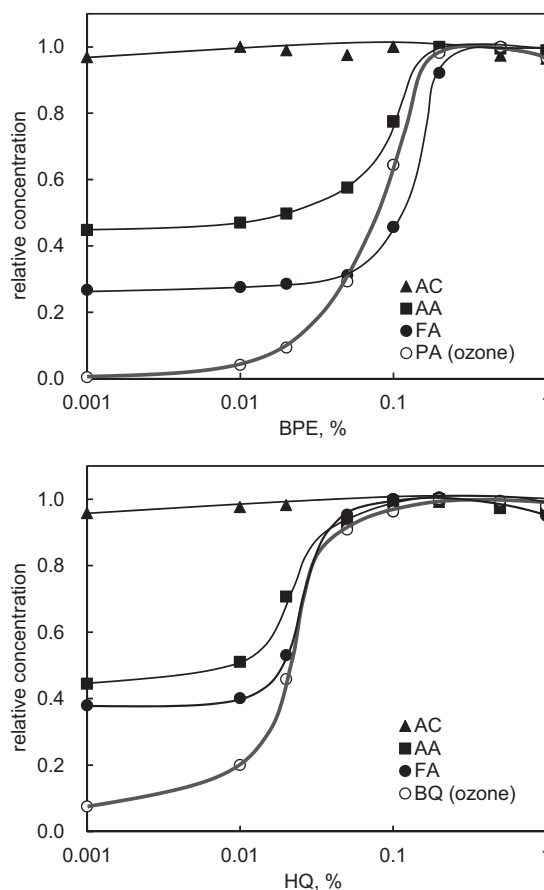
### 2.3. Air sampling and analysis

Prior to air sample collection, each KI-scrubber, BPE-scrubber or HQ-scrubber was connected to a DNPH-cartridge to construct a dual-cartridge sampling train (KI-DNPH, BPE-DNPH and HQ-DNPH). Air was drawn through a coupled cartridge pair from the ozone scrubber to the DNPH-cartridge at a flow rate of 200 mL/min. After collection, the coupled cartridges were extracted. In the case of KI-DNPH, the KI-cartridge was discarded and the DNPH-cartridge was eluted with acetonitrile to a final volume of 5 mL. With BPE-DNPH, elution was performed in the reverse direction to air sampling. An intact, coupled cartridge pair was eluted with 30% dimethyl sulfoxide in acetonitrile solution containing 0.085% (v/v) phosphoric acid to a final volume of 5 mL. The HQ-DNPH cartridge pair was also eluted intact and in the reverse direction to air sampling. Acetonitrile was used as the elution solvent to a final volume of 5 mL. After 30 min of elution, the eluates were analyzed by HPLC.

## 3. Results and discussion

### 3.1. Decomposition of DNPhydrozones by ozone

An ozone generator was operated in the environmental test chamber set at a temperature of 25 °C and a relative humidity of 50%. The concentrations of formaldehyde, acetaldehyde and acetone in the environmental test chamber were 14, 15 and 8.0 µg/m<sup>3</sup>, respectively. Air sampling was performed by using a DNPH-cartridge without an ozone scrubber for 24 h at a flow rate of 200 mL/min. After collection, DNPH-cartridges were eluted with acetonitrile and analyzed by HPLC. Fig. 2 shows changes in the concentrations of carbonyl compounds with changes in ozone concentration. Carbonyl concentrations are expressed as relative concentrations in Fig. 2. Concentrations of formaldehyde and acetaldehyde decreased dramatically with increased ozone concentration. When the concentration of ozone is 170 µg/m<sup>3</sup>, the measured concentrations of formaldehyde and acetaldehyde are 20% and 45%, respectively, of the concentrations measured when no ozone is present. Alternatively, the measured concentration of acetone remained within 5% of the concentration when no ozone was present.

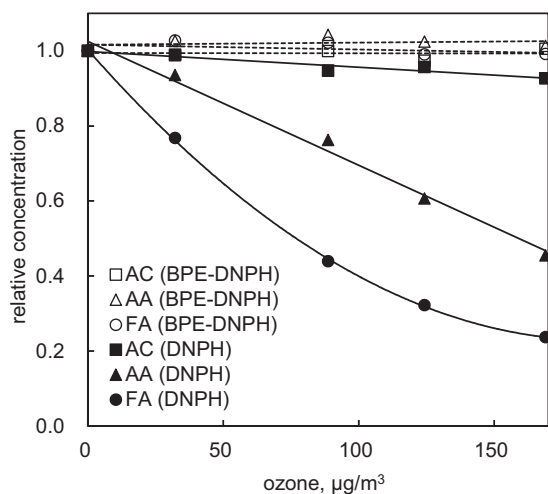


**Fig. 3.** Changes in the concentrations of carbonyl compounds with the contents of BPE (upper panel) and HQ (lower panel) in the ozone scrubber at a temperature of 25 °C and a relative humidity of 50%. FA: formaldehyde; AA: acetaldehyde; AC: acetone; PA: pyridine-2-aldehyde; BQ: benzoquinone.

### 3.2. Preferable contents of BPE and HQ in silica gel

An ozone generator was operated in the environmental test chamber set at a temperature of 25 °C and a relative humidity of 50%. The ozone concentration reached a constant value of 140 µg/m<sup>3</sup> after 24 h. The concentrations of formaldehyde, acetaldehyde and acetone in the environmental test chamber were 13, 11 and 8.0 µg/m<sup>3</sup>, respectively. BPE-scrubbers containing 0–1% (0–7.1 µmol) of BPE and HQ-scrubbers containing 0–1% (0–12 µmol) of HQ were connected to DNPH-cartridges. Air sampling was performed for 24 h at a flow rate of 200 mL/min. After collection, BPE-DNPH-cartridges were eluted with 25% dimethyl sulfoxide in acetonitrile solution containing 0.085% (v/v) phosphoric acid and HQ-DNPH-cartridges were eluted with acetonitrile. After 30 min following elution, the eluate was analyzed by HPLC. Fig. 3 shows changes in the relative concentrations of carbonyl compounds with the loading of BPE (upper panel) and loading of HQ (lower panel) in the ozone scrubber.

In the case of BPE-DNPH cartridge, concentrations of formaldehyde, acetaldehyde, acetone, and pyridine-2-aldehyde increased with increasing BPE concentration, and reached a maximum value when the BPE concentration exceeded 0.5% (3.6 µmol). HQ-DNPH cartridges exhibited similar behavior. Measured concentrations of carbonyls reached a plateau when the HQ concentration exceeded 0.1% (1.2 µmol). HQ may react more efficiently with ozone than BPE. Based on the data presented in Fig. 3, appropriate ozone scrubbers with 130 mg silica support packing should contain 1% BPE-cartridge and 0.2% HQ-cartridge.

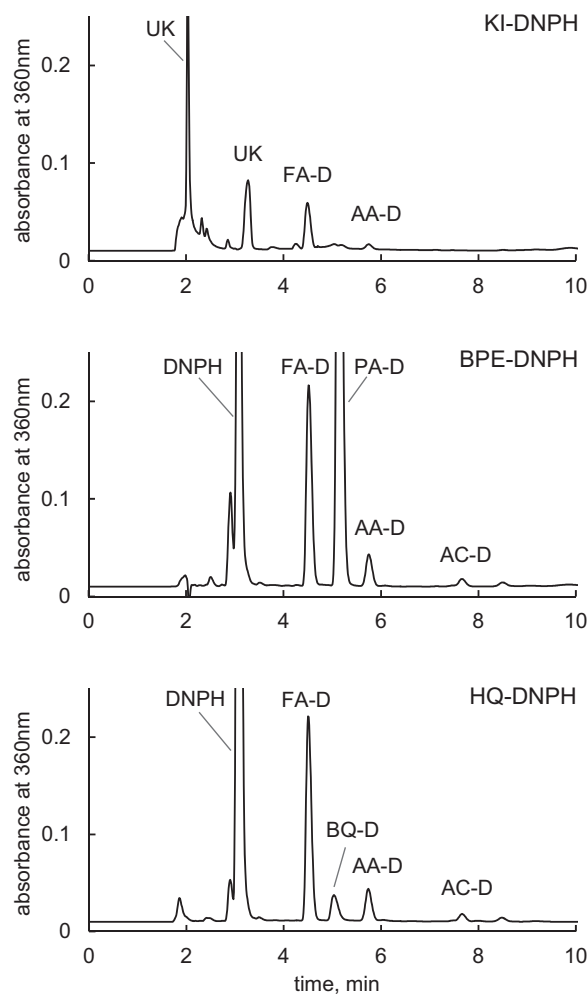


**Fig. 4.** Changes in measured carbonyl concentrations with the coexistent ozone concentration. DNPH-cartridges were used with BPE-scrubber and without an ozone scrubber. FA: formaldehyde; AA: acetaldehyde; AC: acetone.

Under the same conditions described in Fig. 2, KI-DNPH, BPE-DNPH and HQ-DNPH methods showed good performance in ozone removal and analysis of carbonyls. Broken lines of Fig. 4 show changes in measured carbonyl concentrations with the coexistent ozone concentration by using BPE-DNPH. Decreases of formaldehyde, acetaldehyde and acetone were not observed at a wide range of ozone concentrations (0–170  $\mu\text{g}/\text{m}^3$ ). HQ-DNPH and KI-DNPH exhibited similar behavior to BPE-DNPH.

### 3.3. Influence of humidity on the ozone scrubbers

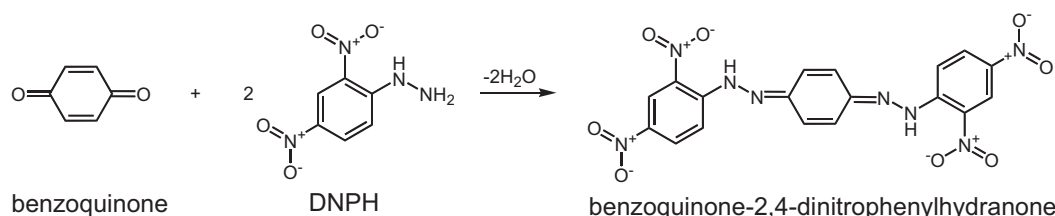
The environmental test chamber was set to a temperature of 25 °C and relative humidity was varied from 3% to 97%. The concentrations of ozone, formaldehyde, acetaldehyde and acetone in the environmental test chamber were 70, 40, 12 and 9.0  $\mu\text{g}/\text{m}^3$ , respectively. Air sampling was performed by using KI-DNPH, BPE-DNPH and HQ-DNPH for 24 h at a flow rate of 200 mL/min. Fig. 5 shows the chromatographic profiles of the eluates eluted from KI-DNPH, BPE-DNPH and HQ-DNPH cartridges. In the case of KI-DNPH, when the relative humidity exceeded 80%, KI in the KI-scrubber was gradually wetted and changed to yellow in color ( $\text{KI}_3$ ). The liquefied, wet KI migrated into the DNPH-cartridge where the DNPH-silica was discolored to brown. DNPH was decomposed by the wet KI and the DNPH peak was not detected in the chromatogram. Peak abundance of FA-D, AA-D and AC-D was diminished to 25%, 15%, 2%, respectively, relative to the same peaks when BPE-DNPH or HQ-DNPH was used. It is suggested that carbonyl compounds dissolve in the wet KI because carbonyl compounds are polar, hydrophilic and water-soluble. In the case of BPE-DNPH and HQ-DNPH, decomposition of DNPH was not observed and large unreacted DNPH peaks were detected. Peak abundance of FA-D, AA-D and AC-D is of the same order of magnitude as



**Fig. 5.** Chromatographic profiles of DNPhydrazone obtained from KI-DNPH (upper panel), BPE-DNPH (middle panel) and HQ-DNPH (lower panel) methods. FA-D: formaldehyde DNPhydrazone; AA-D: acetaldehyde DNPhydrazone; AC-D: acetone DNPhydrazone; PA-D: pyridine-2-aldehyde DNPhydrazone; BQ-D: benzoquinone DNPhydrazone; UK: unknown compound.

those measured by both BPE-DNPH and HQ-DNPH under dry conditions.

The large PA-D peak in the BPE-DNPH chromatogram is the derivative derived from PA and DNPH. PA is formed by the reaction of BPE with ozone [15]. Therefore, it is possible to determine ozone concentration by measuring PA concentration quantitatively [15]. By the same token, BQ-D peak in the HQ-DNPH is the derivative derived from BQ and DNPH (Fig. 6). Ozone reacts with HQ completely to form BQ, however, partial subsequent reaction with DNPH also occurs. Ozone concentration can be determined by summing BQ-D and underivatized BQ concentrations.



**Fig. 6.** Reaction of benzoquinone with DNPH.

#### 4. Conclusions

For measuring carbonyl compounds using DNPH-cartridge, a potassium iodide has been widely used as ozone scrubber. However, when air sampling is performed under conditions of high humidity, moist potassium iodide in the KI-scrubber traps carbonyls before they reach the DNPH-cartridge. Moreover, wet KI reacts with I<sub>2</sub> to form KI<sub>3</sub> and this oxidative reagent moves to the DNPH cartridge and destroys the DNPH and DNPhydrazone derivatives. BPE-DNPH and HQ-DNPH methods have the advantage of air sampling under high humidity conditions without the problems associated with the hygroscopic nature of potassium iodide, and besides, these methods allow the simultaneous measurement of ozone and carbonyl compounds.

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