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## Determination of acrolein and other carbonyls in cigarette smoke using coupled silica cartridges impregnated with hydroquinone and 2,4-dinitrophenylhydrazine

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### ABSTRACT

A new method for the determination of acrolein and other carbonyls in cigarette smoke using a dual cartridge system has been developed. Each cartridge consists of reagent-impregnated silica particles. The first contains hydroquinone (HQ) for the inhibition of acrolein polymerization, while the second contains 2,4-dinitrophenylhydrazine (DNPH) for the derivatization of carbonyls. Smoke samples were firstly drawn through the cartridge containing HQ-impregnated silica (HQ-silica) and then through the DNPH-impregnated silica (DNPH-silica). Acrolein in the sample was completely trapped in the first HQ-silica cartridge. Some other airborne carbonyls were also trapped by the HQ-silica, and those that pass through were trapped in the second DNPH-silica cartridge. Extraction was performed in the reverse direction to air sampling. When solvent was eluted through the dual-cartridges, excess DNPH was washed into the HQ bed where it reacted with acrolein and other trapped carbonyls to form the corresponding hydrazone derivatives. All of the hydrazones derived from airborne carbonyls were completely separated and measured using high-performance liquid chromatography. This HQ-DNPH-method can be applied for the determination of acrolein and other  $\alpha,\beta$ -unsaturated aldehydes, such as crotonaldehyde, in cigarette smoke.

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### 1. Introduction

Cigarette smoking causes 30% of all cancer deaths: the smoke contains more than 3500 chemicals and at least 50 of these are carcinogens [1,2]. Carbonyls, including acrolein (propenal), are among the compounds present at high levels. Long-term exposure to carbonyl compounds, such as formaldehyde and acetaldehyde, is known to increase the risk of asthma [3] and cancer [4]. Accurate carbonyl measurements are therefore important both for determining the formation mechanism of carbonyls and for evaluating their implication in human health. Acrolein, is not currently a suspected human carcinogen as, to date, no studies have been conducted to observe its carcinogenic effects on human cells. However, studies in rats have shown an increase in cancerous tumors from ingestion but not inhalation, and Feng et al. [5] have recently suggested a connection between acrolein in cigarette smoke and an increased risk of lung cancer. This emerging evidence suggests a need for an efficient technique for acrolein measurement.

For the analysis of carbonyl compounds including acrolein, their specific reaction with 2,4-dinitrophenylhydrazine (DNPH), forming

the corresponding 2,4-dinitrophenylhydrazones, is one of the most important qualitative and quantitative methods in organic analysis. This was published by both Allen [6] and Brady [7] in the 1930s. The main advantage of the DNPH-method is the ability to analyze various aldehydes and ketones simultaneously in a complex mixture. Sampling can be performed using acidic solutions of DNPH in impingers [8–10] or with acidic solid sorbents using a DNPH-coated cartridge.

A number of cartridge devices containing solid sorbents coated with DNPH have previously been introduced for sampling aldehydes in air. The solid sorbents include XAD-2 [11,12], silica gel [13,14], glass beads [15], octadecylsilane bonded silica gel [16], Florisil [17], and glass fiber filters [18]. More recently, DNPH-coated silica gel has been widely used for a standard procedure by several national standardization bodies [19]. 2,4-Dinitrophenylhydrazone derivatives extracted from solid sorbent are usually separated by means of high-performance liquid chromatography (HPLC) and detected using UV spectrophotometry at 360 nm (depending on the absorption maximum of the hydrazones). However, for the analysis of  $\alpha,\beta$ -unsaturated aldehydes such as acrolein and crotonaldehyde, numerous problems inherent in the methodology have been reported, including the instability of the acrolein DNPhydrazone (ACR-D) during collection and storage [20–23]. Contradictory data for the technique are found in the literature [20,24–27] and

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severe problems have been observed in inter-laboratory comparisons [21].

Tejada was the first to describe the occurrence of chemical interference in the determination of acrolein using the DNPH-method [20]. During storage of samplers coated with acidified DNPH, the ACR-D peak disappeared and was replaced by an unknown reaction product in such a manner that the sum of the peak areas appeared to be invariant with time. Possanzini and DiPalo [24,25] identified two peaks for both acrolein and crotonaldehyde as syn- and anti-isomers. Risner and Martin [26], as well as Risner [27], traced the poor recovery observed during the determination of acrolein back to the formation of a dimer between two acrolein molecules (2-formyl-3,4-dihydro-2H-pyran) before derivatization. Progress has been made in resolving these limitations, such as using mass spectrometry instead of UV detection, but the instability of the ACR-D under the conditions necessary for collection from air had not yet been overcome.

Decomposition of ACR-D may be prevented by collecting acrolein away from the DNPH. In this study, an improved method which enables the determination of acrolein in addition to previously measurable carbonyls in air, and therefore cigarette smoke, using a dual cartridge system has been developed.

## 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 photo-diode array detector. The analytical column was an Ascen-tis Express RP-Amide, 2.7  $\mu\text{m}$  particle size, 150 mm  $\times$  4.6 mm i.d. (Supelco Inc, Bellefonte, PA, USA). The column temperature was 40 °C and the injection volume was 10  $\mu\text{L}$ . Two analytical conditions were adopted. The first was used in isocratic mode for rapid C<sub>1</sub>–C<sub>3</sub> aldehyde derivative analysis and the mobile phase mixture was acetonitrile/water (60/40, v/v) containing 5 mmol/L ammonium acetate. The flow rate of the mobile phase was 0.6 mL/min. The second was used in gradient mode for C<sub>1</sub>–C<sub>10</sub> aldehyde derivative analysis. Solution A of the mobile phase mixture was acetonitrile/water (40/60, 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 8 min, followed by a linear gradient from 100% A to 100% B in 37 min and then held for 15 min. The flow rate of the mobile phase was 0.7 mL/min.

The smoking machine model LM1/PLUS (Borgwaldt Technik GmbH, Hamburg, Germany) was used for collection of cigarette smoke. Air pump (SP-100 Dual GL Sciences Inc., Saitama, Japan) and wet gas meter (WS D-1A; Shinagawa Co., Tokyo, Japan) were used for the collection of air samples.

The 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). The 2,4-dinitrophenylhydrazine hydrochloride (>98%) was obtained from Tokyo Kasei Co., Ltd., (Tokyo, Japan). The acetonitrile (HPLC grade, >99.9%), ethanol (>99.5%), hydroquinone (>99%), phosphoric acid (85% solution in water), and ammonium acetate (99.999%) were from Sigma–Aldrich Inc., (St. Louis, MO, USA). Silica gel (spherical, 60/80 mesh, 120 Å mean pore size) was from AGC Si-Tech. Co., Ltd. (Fukuoka, Japan).

### 2.2. Preparation of a DNPH-impregnated silica cartridge (DNPH-cartridge) and a hydroquinone impregnated silica cartridge (HQ-cartridge)

Two types of DNPH-silica particles, for sampling low and high levels of carbonyls, were prepared. DNPH-silica: silica gel (50 g) was

washed with water (3  $\times$  500 mL), methanol (2  $\times$  500 mL), and lastly acetonitrile (2  $\times$  500 mL). 2,4-Dinitrophenylhydrazine hydrochloride (0.25 g for low-level carbonyls and 1 g for high-level carbonyls) and phosphoric acid (0.5 mL for low-level carbonyls and 1 mL for high-level carbonyls) were dissolved in 200 mL acetonitrile. This solution was added to the washed silica gel (50 g), the mixture was stirred and the solvent was evaporated to dryness at 40 °C under vacuum on a rotary evaporator.

Hydroquinone (HQ)-silica: silica gel (50 g) was washed with water (3  $\times$  500 mL), methanol (2  $\times$  500 mL), and lastly acetonitrile (2  $\times$  500 mL). Then the solvent was completely evaporated to dryness at 100 °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. HQ (0.05 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 °C under vacuum on a rotary evaporator.

DNPH-silica (270 mg) and HQ-silica (270 mg) were packed into separate polyethylene cartridges (Rezorian tube, 1 mL, Supelco Inc., Bellefonte, PA) and stored in a refrigerator at 4 °C.

### 2.3. Collection and analysis of cigarette smoke and air sample

Before collecting a sample, an HQ-cartridge and a DNPH-cartridge were connected.

In the case of analyzing mainstream cigarette smoke, test cigarettes were prepared at 22 °C temperature and 60% humidity. Mainstream smoke constituents were collected under the conditions of 35 mL puff volume, 2-s puff duration, and 60-s puff interval according to ISO machine-smoking conditions [28]. A coupled cartridge was connected to the back of the filter, and cigarette smoke was drawn through the coupled cartridge from the HQ-cartridge to the DNPH-cartridge.

In the case of analyzing an air sample, air was drawn through a coupled cartridge from the HQ-cartridge to the DNPH-cartridge at flow rates of 0.1–1000 mL/min. After collection, the coupled cartridges were extracted with acetonitrile (containing 1% phosphoric acid) in the reverse direction to air sampling until the total volume of solution was 4.5 mL. After 10 min, the eluate solution was added with ethanol (0.5 mL) and was analyzed by HPLC. If the extraction was not performed immediately, the HQ-DNPH-cartridge set was decoupled and the individual cartridges were capped with stoppers.

## 3. Results and discussion

### 3.1. Decomposition of acrolein in the DNPH-cartridge

Acrolein standard gas (20 ppm) was drawn through DNPH-cartridges at a flow rate of 100 mL/min for 10 min. The DNPH-cartridges were then stored at 35 °C. At various times, the DNPH-cartridges were eluted with acetonitrile until the total volume of solution was 5 mL. The eluates were then immediately analyzed in isocratic mode using an HPLC instrument equipped with an autosampler set to 4 °C. Acrolein in air reacts with DNPH in the cartridge to form ACR-D. As DNPH-cartridge storage time increased, the peak of ACR-D decreased and unknown peaks appeared. Fig. 1 shows the chromatogram of the sample following 2.4 h storage at 35 °C.

ACR-D ( $\lambda_{\text{max}} = 372 \text{ nm}$ ) and four unknown peaks, a, b, c and d, were detected in the chromatogram. The maximum wavelengths of ACR-D, a, b, c and d were 373, 356, 350, 353 and 350 nm, respectively. Other unknown products may not have been extracted from the DNPH-cartridge. During the collection of acrolein, the intake side of DNPH-silica (about 1 mm thickness) changed color from yellow

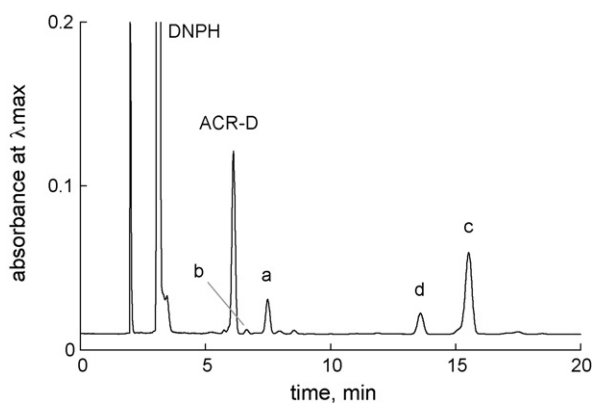


Fig. 1. Chromatographic profile of ACR-D and unknown peaks in the eluate of the DNPH-cartridge 2.4 h following acrolein standard gas sampling.

low to red. The red color remained after extraction. Unknowns a and b, and c and d are double peaks. It has been suggested that a and b, and c and d are geometric isomers [29–32], assigned AD1' and AD1, and AD2' and AD2 respectively, about the C=N double bond, because the peak area ratios of AD1':AD1 and AD2':AD2 are constant in this experiment. Schulte-Ladbeck et al. [22] reported that the unstable hydrazones react with excess reagent to form adducts (AD1, AD2 and their isomers). Fig. 2 illustrates the reaction of ACR-D with DNPH. ACR-D reacts with excess DNPH generating adduct (AD1). Further reaction between AD1 and ACR-D results in formation of AD2.

The decomposition reactions are observed both in the DNPH-cartridge and in the eluate with acetonitrile; however, faster decomposition is observed in the DNPH-cartridge. Fig. 3 shows the changes in HPLC peak areas of ACR-D and its adducts as the DNPH-cartridge is allowed to stand at 35 °C.

ACR-D concentration decreased rapidly on standing to 86% after 10 min, 29% after 2.4 h and 12% after 10 h. AD1 increased rapidly at first, dropped slightly after 1 h, then maintained a constant level. The major decomposition product is AD2, which increased in concentration while the ACR-D concentration decreased.

### 3.2. Decomposition of acrolein derivative in the acetonitrile eluate

An unused DNPH-cartridge was eluted with acetonitrile until the total volume of solution was 4.95 mL. ACR-D acetonitrile solution (50 μL, 1 mmol/L) was then added to the eluate. The sample was analyzed immediately and re-analyzed every 1.7 h for a total

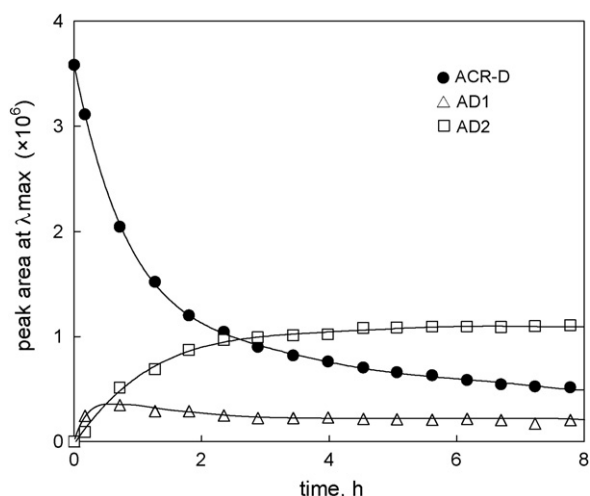


Fig. 3. The decomposition of ACR-D and the formation of adducts (AD1, AD2) in a DNPH-cartridge at 35 °C over time.

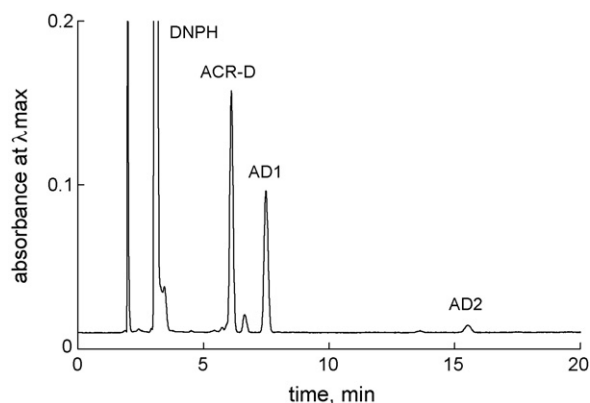


Fig. 4. Chromatographic profile of the DNPH-cartridge eluate of the acetonitrile solution after 60 h at 25 °C.

of 60 h by HPLC in isocratic mode using an instrument equipped with an autosampler set to 25 °C. Fig. 4 shows the chromatogram of the sample following standing for 60 h.

ACR-D and its adducts (AD1 and AD2) were detected in the chromatogram. The decomposition of ACR-D in the eluate is accelerated with the addition of acid. Fig. 5 shows the changes in the levels of ACR-D and AD1 in the eluate at various concentrations of phosphoric acid.

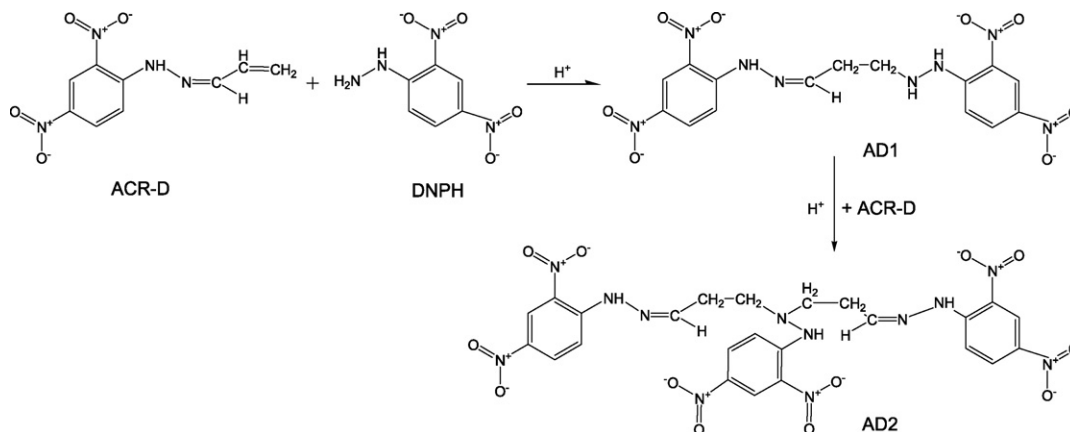


Fig. 2. Decomposition of ACR-D with DNPH.

In the case of the reaction in the DNPH-cartridge, the major decomposition product was AD2 and the minor decomposition product was AD1. By contrast, AD1 is the predominant decomposition product in the acetonitrile eluent solution; AD1 concentration increased in direct proportion to the decrease in ACR-D concentration. ACR-D concentration decreased gradually with time to 89% after 10 h and 64% after 60 h when no acid was added to the eluate. Adding phosphoric acid accelerated the decomposition of ACR-D to the extent that a 50% concentration decrease was measured following 12 h in the presence of 1% phosphoric acid.

### 3.3. Inhibition method for the decomposition of acrolein derivative in the DNPH-cartridge

The decomposition of ACR-D can be prevented by collecting acrolein using an alternative medium, followed by derivatization with DNPH just before analysis. The use of a dual sampling cartridge system comprised of silica gel and DNPH-silica results in the acrolein vapor being trapped by the silica. Acrolein is degraded by a reaction with hydroxyl radicals [33,34], and it has been shown in previous work that free radicals are generated in mainstream cigarette smoke [35]. Therefore, hydroquinone (HQ), a radical-trapping reagent, was used to inhibit acrolein decomposition. Several coupled HQ-DNPH-cartridge sets were prepared. Acrolein standard gas (20 ppm) was drawn through the coupled cartridges from the HQ-cartridge to the DNPH-cartridge at a flow rate of 100 mL/min for 10 min. After collection, the coupled cartridges were separated and were capped with stoppers. The HQ-cartridges and the DNPH-cartridges were stored at 35 °C. At various times, an HQ-cartridge and a DNPH-cartridge were reconnected. Elution was performed from the DNPH-cartridge to the HQ-cartridge with acetonitrile (containing 1% phosphoric acid) until the total volume of solution was 4.5 mL. After 10 min, ethanol (0.5 mL) was added to the eluate solution. This was analyzed by HPLC using an autosampler set to 4 °C. In contrast to the decomposition seen in Fig. 3, products such as AD1 and AD2 were not detected and the level of ACR-D stayed relatively constant over 8 h (Fig. 6).

In the case of separate storage of the HQ-silica and DNPH-silica cartridges, decrease of the ACR-D was not observed. The separated HQ-cartridge was stable for at least 2 weeks. However, in the case of coupled-cartridge storage, ACR-D concentration decreased gradually with time during storage at 35 °C. It was found that acrolein trapped in HQ-silica migrated into the DNPH-cartridge of the dual sampling cartridge causing decomposition. Therefore, it is neces-

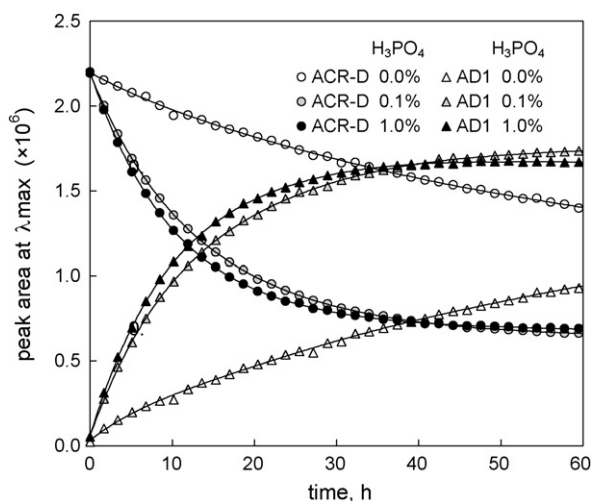


Fig. 5. Decrease of ACR-D and increase of AD1 with time in the acetonitrile eluate at various concentrations of phosphoric acid.

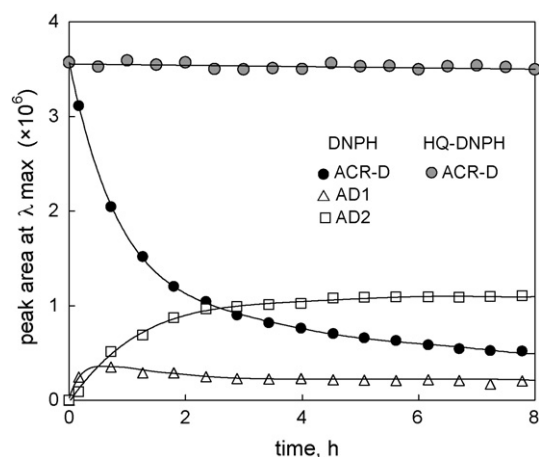


Fig. 6. Changes in ACR-D in a HQ/DNPH dual cartridge method and a DNPH-cartridge method with time at 35 °C over time.

sary to separate the cartridges when analysis is not carried out immediately after sample collection.

### 3.4. Inhibition method for decomposition of acrolein derivative in the eluate

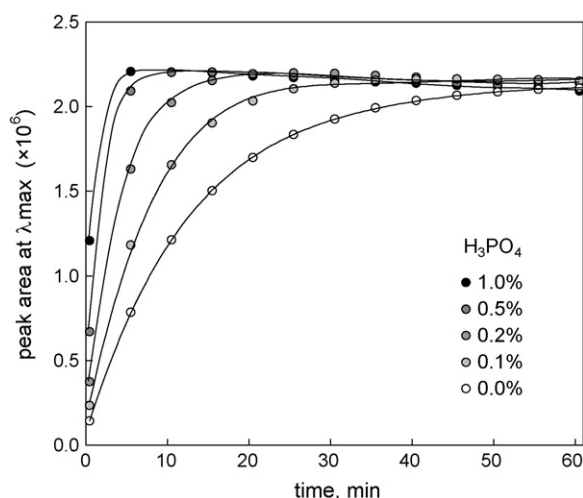
Acrolein adsorbed onto the HQ-cartridge is extracted with acetonitrile through the DNPH-cartridge, meaning acrolein reacts with DNPH in the acetonitrile eluate. The reaction of acrolein and DNPH is relatively slow unless accelerated with catalytic acid. Unused DNPH-cartridges were eluted with acetonitrile containing various concentrations of phosphoric acid until the total volume of solution was 4.95 mL. ACR solution in acetonitrile (50  $\mu$ L, 1 mmol/L) was then added to the eluate. This was immediately analyzed by HPLC in isocratic mode using an instrument equipped with an autosampler set to 25 °C. Fig. 7 shows the reaction rate between acrolein and DNPH in the acetonitrile eluate from DNPH-cartridges.

When the eluent from the DNPH-cartridge contained no acid, the derivatization reaction in the eluate was slow and complete in 60 min at 25 °C. The reaction rate for DNPH derivatization increased with an increase in the concentration of phosphoric acid. The most efficient eluent was acetonitrile containing 1% phosphoric acid and the derivatization reaction could be finished within 5 min. As stated above (Fig. 5), ACR-D was rapidly decomposed when 1% phosphoric acid was used as eluent. Unused DNPH-cartridges were eluted with acetonitrile or ethanol containing 1% phosphoric acid until the total volume of solution was 4 mL. In an attempt to combat the acid effect, ethanol was added to these solutions at 0, 10, 20 and 90% concentration levels. ACR-D acetonitrile solution (50  $\mu$ L, 1 mmol/L) was then added to the eluate. The sample was immediately analyzed and was analyzed every 1.7 h for a total of 60 h by HPLC in isocratic mode using an instrument equipped with an autosampler set to 25 °C. Fig. 8 shows the changes of ACR-D and its adduct (AD1) with time in the eluate containing ethanol.

The decomposition of ACR-D was depressed by adding ethanol to the DNPH eluate. This suggests that the addition reaction of DNPH to ACR-D proceeds readily in polar aprotic solvents such as acetonitrile, but is inhibited in protic solvents such as ethanol.

### 3.5. Limit of detection, limit of quantitation and reproducibility

The limit of detection (LOD) and limit of quantitation (LOQ) of a HQ-DNPH coupled cartridge method was calculated using linear regression theory [36]. 5 mL of carbonyl standard gas (20 ppm, 5 components) was introduced into the HQ-DNPH coupled cartridges and analyzed using the analytical conditions described above. The



**Fig. 7.** Rate of reaction of acrolein and DNPH in the eluate with various concentrations of phosphoric acid.

**Table 1**

LOD, LOQ and reproducibility of HQ-DNPH coupled cartridge method.

Compounds	LOD, $\mu\text{g}$	LOQ, $\mu\text{g}$	RSD, %
Formaldehyde	0.015	0.050	1.9
Acetaldehyde	0.034	0.11	1.8
Acetone	0.020	0.067	2.1
Acrolein	0.074	0.25	1.2
Propionaldehyde	0.059	0.20	2.1

LOD and LOQ were calculated as being three times the standard deviation obtained from the data of 10 replicate measurements (Table 1). The reproducibility of DNPH coupled cartridge-HPLC analysis was estimated from data of 10 samplers spiked with 1000 mL of carbonyl standard gas (20 ppm, 5 components). The relative standard deviation (RSD) is shown in Table 1.

### 3.6. Analysis of cigarette smoke

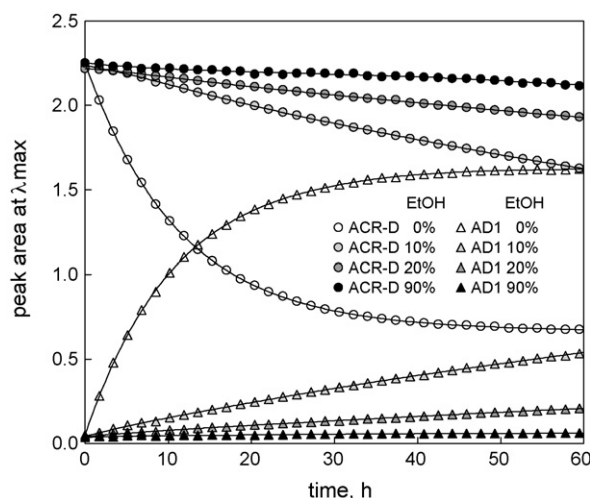
#### 3.6.1. Normal cigarette

The mainstream smoke vapors of three brands of cigarettes (A, tar 6 mg, nicotine 0.5 mg; B, tar 12 mg, nicotine 1.0 mg; C, tar 8 mg, nicotine 0.7 mg) were collected in HQ-DNPH coupled cartridges by a smoking machine in accordance with ISO machine-smoking conditions [28] and then analyzed using the aforementioned HQ-DNPH-method. DNPH-cartridges for high-level carbonyl analysis were used. Table 2 shows the carbonyl compounds generated from cigarettes. Many carbonyls including acrolein were detected

**Table 2**

Amounts of carbonyls in mainstream smoke vapors of cigarettes,  $n = 10 \mu\text{g}/\text{cigarette}$ .

Compounds	A			B			C		
	Puffs: 7.3–8.0			Puffs: 7.5–8.6			Puffs: 6.0–7.0		
	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.
Formaldehyde	2.0	1.4	3.1	2.4	1.4	5.5	3.3	2.4	5.1
Acetaldehyde	270	230	320	520	490	580	380	310	430
Acetone	78	60	97	140	130	150	130	110	150
Acrolein	19	16	22	36	30	44	18	12	24
Propanal	20	16	25	42	39	47	29	24	34
Crotonaldehyde	3.4	2.1	4.3	9.4	7.1	11	7.4	5.9	8.9
Butanal	12	9.2	15	23	21	27	26	20	31
i-Pentanal	4.5	3.0	5.8	11	8.7	12	7.3	6.1	8.6
Pentanal	0.3	0.2	0.4	0.8	0.6	1.3	0.6	0.4	0.8
Glyoxal	0.2	0.0	0.2	0.1	0.0	0.2	0.5	0.4	0.7
Methylglyoxal	0.3	0.1	0.4	0.4	0.3	0.5	0.9	0.5	1.7



**Fig. 8.** Decrease of ACR-D and increase of AD1 with time in the acetonitrile eluate containing various concentrations of ethanol.

in cigarette smoke. For reference, after collection, the collected HQ-cartridge was eluted with an unused DNPH-cartridge and the collected DNPH-cartridge was eluted individually. From this experiment it was found that all carbonyls, except acetaldehyde, were completely (>99%) trapped in the HQ-cartridge and not detected in the DNPH-cartridge. Most of the acetaldehyde (89%) was trapped in HQ-cartridge, with the remainder (11%) trapped in DNPH-cartridge.

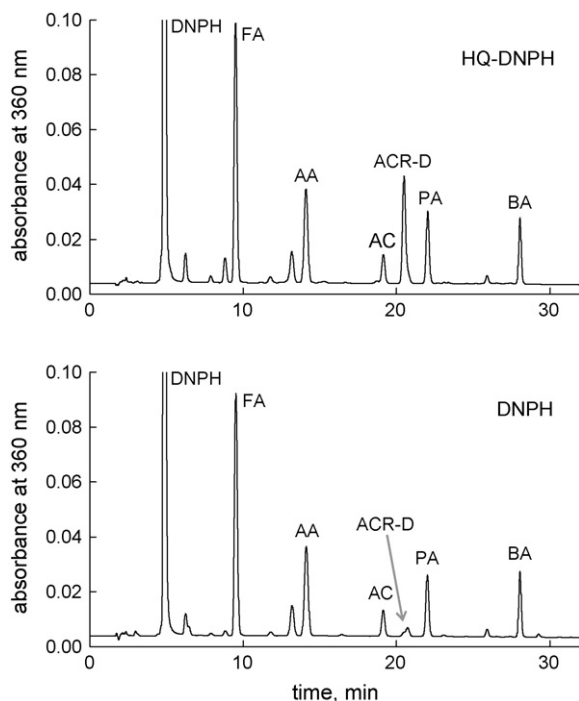
#### 3.6.2. Electronic cigarette

The HQ-DNPH coupled cartridge was connected to the electronic cigarette (The Plemium Smoker, EPI International Co., Ltd., Tokyo Japan) and air was drawn through at a flow rate of 500 mL/min. DNPH-cartridges for low-level carbonyl analysis were used. After collection, the coupled cartridge was kept for 10 min or 16 h at room temperature and was eluted with acetonitrile containing 0.1% phosphoric acid in the reverse direction to air sampling. The eluate was analyzed by HPLC operating in the gradient mode. For comparison, a DNPH-cartridge was used simultaneously for collection. Fig. 9 shows the chromatograms of formaldehyde DNPhydrazone (FA), acetaldehyde DNPhydrazone (AA), acetone DNPhydrazone (AC), acrolein DNPhydrazone (ACR-D), propanal DNPhydrazone (PA), butanal DNPhydrazone (BA), glyoxal DNPhydrazone (GO), and methylglyoxal DNPhydrazone (MG) in the eluate of the HQ-DNPH coupled cartridge and the DNPH-cartridge.

Various kinds of carbonyls, including acrolein, were detected in the electronic cigarette sample. Complete separation of the ACR-D peak and the acetone DNPhydrazone peak was achieved on an RP-

**Table 3**  
Concentrations of carbonyls generated from the electronic cigarette, mg/m<sup>3</sup>.

Compound	HQ-DNPH		DNPH	
	10 min	17 h	10 min	17 h
Formaldehyde	8.3	7.9	8.1	7.6
Acetaldehyde	11	9.2	10	9.3
Acetone	2.9	3.0	2.6	2.4
Acrolein	9.3	9.2	6.4	0.3
Propanal	8.0	7.4	8.3	7.6
Butanal	1.5	1.7	1.7	2.4
Glyoxal	1.3	1.3	1.2	1.6
Methylglyoxal	4.5	4.2	4.3	4.7



**Fig. 9.** Chromatographic profiles of acrolein and other carbonyl DNPhydrazones in the eluate of the HQ-DNPH coupled cartridge and DNPH-cartridge 17 h after sample collection.

Amide column with a mobile phase consisting of acetonitrile/water. In the case of the HQ-DNPH coupled cartridge, a large ACR-D peak was detected. In the case of the DNPH-cartridge, ACR-D was greatly diminished in peak area. Table 3 shows the concentrations of carbonyls generated from the electronic cigarette.

With the exception of the acrolein concentration, the HQ-DNPH-method is in good agreement with the traditional DNPH-method. The acrolein concentration measured by the DNPH-method was about one thirtieth of that measured by the HQ-DNPH-method; therefore, the use of the traditional DNPH-method for analysis of acrolein may lead to erroneous results.

The electronic cigarette, introduced recently to the marketplace, is a battery-powered device that provides inhaled doses of nicotine by heating a nicotine-chemical solution into a vapor. Many legislation and public health investigations are currently pending in many countries due to its relatively recent emergence. High concentrations of hazardous pollutants such as formaldehyde, acetaldehyde and acrolein were detected by using the HQ-DNPH-cartridge.

#### 4. Conclusions

In the analysis of acrolein using a traditional DNPH-cartridge, ACR-D is decomposed rapidly in the DNPH-cartridge and forms

DNPH and ACR-D adducts. Therefore, decomposition of ACR-D is prevented by collecting acrolein in a separate cartridge from DNPH. In this study, a dual cartridge system has been developed. Each cartridge consists of reagent-impregnated silica particles. The first contains hydroquinone (HQ) for the inhibition of acrolein polymerization, while the second contains 2,4-dinitrophenylhydrazine (DNPH) for the derivatization of carbonyls. Air samples are drawn through the cartridge first through the HQ-impregnated silica (HQ-silica) and then through the DNPH-impregnated silica (DNPH-silica). Acrolein in the air sample is completely trapped in the first HQ-silica cartridge without addition of DNPH. ACR-D decomposition also occurs, albeit more slowly, in acidified acetonitrile solution. This process can be inhibited by the addition of a protic solvent such as ethanol. The HQ-DNPH-method can be successfully applied to the determination of 2-alkenals such as acrolein or crotonaldehyde in air and cigarette smoke.

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