

Determination of Carbonyl Compounds in Workplace Air

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Key Words

DNPH-Derivatized Compounds, Aldehyde and Ketone Compounds Analysis, Environmental Analysis, Air Quality, HPLC, Acclaim Carbonyl RSLC Column

Goal

To develop an efficient high-performance liquid chromatography (HPLC) method for the sensitive determination of 2,4-dinitrophenylhydrazine (DNPH)-derivatized carbonyl compounds in workplace indoor air samples using a Thermo Scientific™ Acclaim™ Carbonyl RSLC column with an ammonium acetate/acetonitrile mobile phase. The 13 target analytes are those specified in California Air Resources Board (CARB) Method 1004, International Organization for Standardization (ISO) 16000-3:2011, U.S. Environmental Protection Agency (EPA) Compendium Method TO-11A, and the Chinese HJ/T 400-2007.

Introduction

Carbonyl compounds are known to cause adverse effects on human health and many of these compounds are listed by the U. S. EPA in the Health Effects Notebook for Hazardous Air Pollutants.¹ Therefore, it is important to establish effective methods for the determination of these compounds. Because HPLC is a frequently used technique, some standard HPLC methods have been created, including EPA Methods 554,² 1667,³ 8315A,⁴ TO-5,⁵ and TO-11A,⁶ CARB Method 1004,⁷ the Chinese HJ/T 400-2007;⁸ and ISO 16000-3:2011.⁹ Due to the volatility of carbonyl compounds, it is preferable to derivatize them to a nonvolatile stable form, which reduces the possibility of analyte loss and allows the sample to be analyzed later. DNPH is extensively used as a derivatization reagent for such analyses due to its high reactivity, selectivity, and stability of the derivatization products. The reaction yields a chromophore with an absorption maximum of 360 nm, which is suitable for HPLC with UV detection.



CARB Method 1004 reports an HPLC-UV method for the determination of 13 carbonyl compounds generated by automobiles: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, methyl ethyl ketone, methacrolein, hexanaldehyde, butyraldehyde, benzaldehyde, valeraldehyde, and *m*-tolualdehyde.⁷ This method requires a primary separation using a C18 column and a secondary separation using a similar column under different conditions because the DNPH derivatives of methyl ethyl ketone and butyraldehyde do not completely resolve with the primary separation. The secondary separation focuses solely on resolving methyl ethyl ketone and butyraldehyde.

In HJ/T 400-2007, DNPH derivatives of acetone and acrolein are difficult to differentiate on conventional C18 columns using acetonitrile/water mobile phases.⁸ The addition of tetrahydrofuran (THF) to the mobile phase may resolve the problem in CARB Method 1004 and HJ/T 400-2007¹⁰ because the 13 DNPH-derivatized carbonyl compounds are separated using a CH₃CN/THF/H₂O mobile phase.¹¹ However, the use of THF in the mobile phase has some limitations for this application, including longer column re-equilibration time following a gradient run, incompatibility with PEEK tubing and seal rings, peroxide formation, and general toxicity.

Acclaim Carbonyl RSLC columns are silica-based, reversed-phase columns designed specifically for superior resolution and high-throughput separation of DNPH derivatives of the aldehydes and ketones regulated in the EPA and CARB 1004 methods. These columns enable faster analysis with simpler separation conditions when compared to the existing methods (i.e., no THF is needed in the mobile phase).¹²

Equipment

- Thermo Scientific™ Dionex™ UltiMate™ 3000 RSLC system, including:
 - LPG-3400RS Quaternary Pump with SRD-3400 Integrated Solvent and Degasser Rack
 - WPS-3000TRS Well Plate Autosampler, Thermostatted, with 25 μ L sample loop
 - TCC-3000RS Thermostatted Column Compartment
 - DAD-3000RS Diode Array Detector with 13 μ L flow cell
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System software 6.80, SR9 or higher

Reagents and Standards

- Deionized water, 18.2 M Ω -cm resistivity
- Acetonitrile (CH_3CN), HPLC Grade 99.9% (Fisher Scientific P/N AC610010040)
- Ammonium Acetate, Crystalline, Certified ACS (Fisher Scientific P/N A637-500)
- Aldehyde/Ketone-DNPH Stock Standard-13, 13 Components in Acetonitrile for CARB Method 1004, 3 μ g/mL of each component (Cerilliant® P/N ERA-013K)

Preparation of Solutions and Reagents

Working Standard Solutions for Calibration

Prepare six working standard solutions for the calibration with 0.03, 0.075, 0.10, 0.75, 1.0, and 3.0 μ g/mL concentrations by adding the proper amount of aldehyde/ketone-DNPH stock standard-13 and diluting with acetonitrile.

Sample Preparation

The preparation for workplace air samples (including pretreatment, sampling, and elution) was performed by a third-party inspection institution located in Shanghai, China and followed the standard methods enacted by the Chinese government.^{13,14}

Chromatographic Conditions

| | |
|---------------|---|
| Column: | Acclaim Carbonyl RSLC Analytical, 2.2 μ m, 2.1 \times 150 mm (P/N 077973) |
| Mobile Phase: | A. 2 mM Ammonium acetate B. Acetonitrile |
| Gradient: | B. -2.5–0 min, 48%; 2.0–7.0 min, 53%; 12.5–14 min, 100% |
| Flow Rate: | 0.4 mL/min |
| Inj. Volume: | 2 μ L |
| Temperature: | 30 °C |
| Detection: | UV, 360 nm |

Results and Discussion

Separation of DNPH-Derivatized Carbonyl Compounds Using the Acclaim Carbonyl RSLC Column

Figure 1 shows the separation of 13 DNPH-derivatized carbonyl compounds specified in CARB Method 1004 using the Acclaim Carbonyl RSLC column and an ammonium acetate/acetonitrile mobile phase. The separation problem of the DNPH derivatives of acetone (Peak 3) and acrolein (Peak 4) found in HJ/T 400-2007 is resolved by the Acclaim Carbonyl RSLC column with a calculated peak resolution (R_s) for those two peaks of 1.67. The Acclaim Carbonyl RSLC column also resolves DNPH-derivatized methyl ethyl ketone (Peak 7) and butyraldehyde (Peak 8) with a R_s of 1.55 for those peaks, which coelute with the primary separation of CARB Method 1004. Complete resolution of the 13 compounds is realized without addition of THF to the mobile phase.

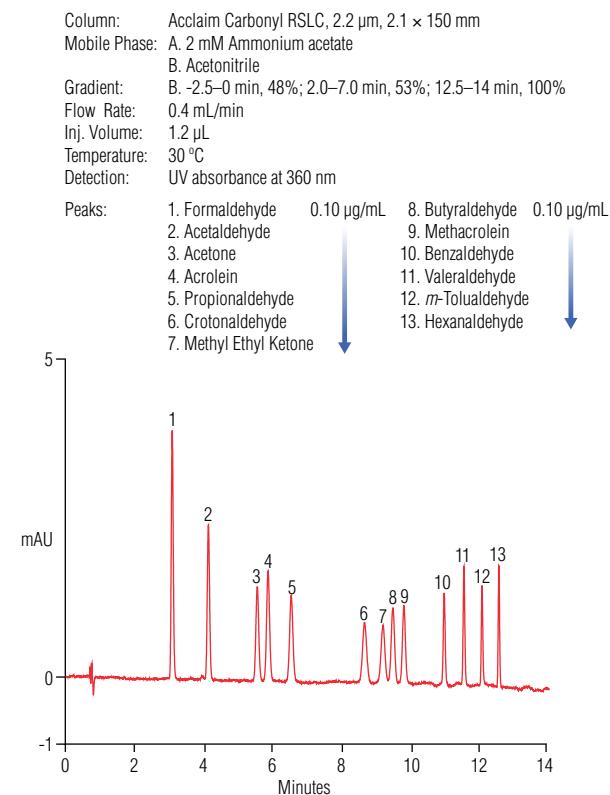


Figure 1. Separation of DNPH-derivatized carbonyl compound standards (0.1 μ g/mL each) using the Acclaim Carbonyl RSLC column.

Reproducibility, Linearity, and Detection Limits

Method precision was estimated by making seven consecutive injections of a calibration standard with a concentration of 0.75 µg/mL for each compound. The retention time and peak area reproducibilities are summarized in Table 1.

Table 1. Reproducibility for retention time and peak area (n = 7).

| Analyte (DNPH Derivative) | Retention Time RSD | Peak Area RSD |
|---------------------------|--------------------|---------------|
| Formaldehyde | 0.063 | 0.49 |
| Acetaldehyde | 0.056 | 0.91 |
| Acetone | 0.053 | 1.14 |
| Acrolein | 0.033 | 1.20 |
| Propionaldehyde | 0.057 | 0.82 |
| Crotonaldehyde | 0.055 | 0.86 |
| Methyl Ethyl Ketone | 0.034 | 0.72 |
| Butyraldehyde | 0.041 | 0.40 |
| Methacrolein | 0.036 | 0.38 |
| Benzaldehyde | 0.022 | 1.20 |
| Valeraldehyde | 0.017 | 0.84 |
| <i>m</i> -Tolualdehyde | 0.014 | 1.71 |
| Hexanaldehyde | 0.012 | 0.56 |

Calibration linearity of the DNPH derivatives of carbonyl compounds was investigated by making three consecutive injections of a mixed standard prepared at six different concentrations (i.e., 18 total injections). The external standard method was used to establish the calibration curve and quantify these DNPH derivatives of carbonyl compounds in the workplace air samples. Linearity was observed from 0.03 to 3.0 µg/mL when plotting the concentration versus peak area, and the coefficients of determination were ≥ 0.9996 for all 13 compounds (Table 2).

Table 2. Method linearity data.

| Analyte (DNPH Derivative) | Regression Equation | r^2 |
|---------------------------|----------------------|--------|
| Formaldehyde | A = 1.0345c + 0.0927 | 0.9996 |
| Acetaldehyde | A = 0.8946c + 0.0618 | 0.9997 |
| Acetone | A = 0.7249c + 0.0545 | 0.9997 |
| Acrolein | A = 0.8396c + 0.0682 | 0.9996 |
| Propionaldehyde | A = 0.7196c + 0.0471 | 0.9998 |
| Crotonaldehyde | A = 0.6266c + 0.0452 | 0.9997 |
| Methyl Ethyl Ketone | A = 0.5317c + 0.0377 | 0.9997 |
| Butyraldehyde | A = 0.6869c + 0.0536 | 0.9998 |
| Methacrolein | A = 0.6245c + 0.0385 | 0.9997 |
| Benzaldehyde | A = 0.4458c + 0.0349 | 0.9996 |
| Valeraldehyde | A = 0.5219c + 0.0208 | 0.9997 |
| <i>m</i> -Tolualdehyde | A = 0.3672c + 0.0201 | 0.9996 |
| Hexanaldehyde | A = 0.4510c + 0.0326 | 0.9996 |

To estimate method detection limits (MDLs), Figure 2 shows a carbonyl compound calibration standard with a concentration of 0.03 µg/mL for each DNPH derivative separated on the Acclaim Carbonyl RSLC column. These MDLs were estimated using a signal-to-noise ratio (S/N) = 3. The calculated S/Ns and MDLs are summarized in Table 3.

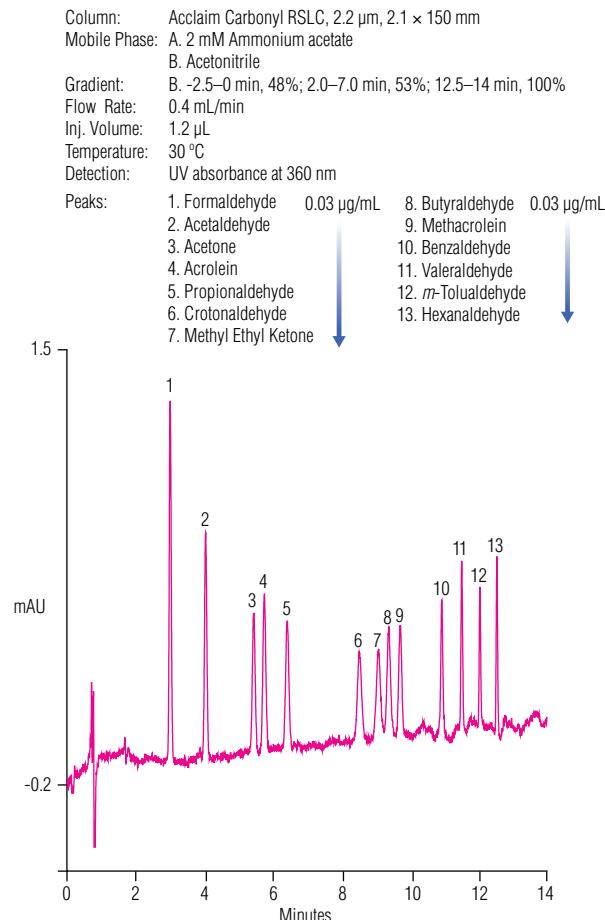


Figure 2. Separation of DNPH-derivatized carbonyl compound standards (0.03 µg/mL each) using the Acclaim Carbonyl RSLC column.

Table 3. S/Ns of DNPH derivatives (30 µg/L each) and calculated MDLs for each compound.

| Analyte (DNPH Derivative) | Conc (µg/L) | S/N | MDL (µg/L) |
|---------------------------|-------------|------|------------|
| Formaldehyde | | 30.5 | 3.0 |
| Acetaldehyde | | 18.9 | 4.8 |
| Acetone | | 11.3 | 8.0 |
| Acrolein | | 13.4 | 6.7 |
| Propionaldehyde | | 10.8 | 8.3 |
| Crotonaldehyde | | 7.19 | 12.0 |
| Methyl Ethyl Ketone | | 6.80 | 13.0 |
| Methacrolein | | 9.08 | 10.0 |
| Butyraldehyde | | 9.39 | 9.6 |
| Benzaldehyde | | 11.6 | 7.8 |
| Valeraldehyde | | 14.8 | 6.1 |
| <i>m</i> -Tolualdehyde | | 11.7 | 7.7 |
| Hexanaldehyde | | 15.1 | 6.0 |

Sample Analysis

Figure 3 shows a workplace air sample derivatized with DNPH. Formaldehyde and acetone were found, demonstrating the presence of aldehyde and ketone compounds in workplace air. The analysis results are summarized in Table 4. The detected concentration of acetone in the sample is 250 mg/m³—lower than the permitted amount of 300 mg/m³ in the Standardization Administration of China (SAC) GB/T18883-2002—whereas that of formaldehyde is 76 mg/m³—much higher than the permitted 0.5 mg/m³—indicating that changes are needed to make the air in this workplace safe for workers.¹⁵ Recoveries for the two detected DNPH derivatives of carbonyl compound standards in the sample exceed 90%, demonstrating good accuracy of the HPLC method.

Table 4. Sample analysis results.

| Analyte | Workspace Air | | | | Permitted in GBZ2-2002 ¹⁵ (mg/m ³) |
|--------------|-------------------------------|--------------|--------------|--------------|---|
| | Detected (mg/m ³) | Added (µg/L) | Found (µg/L) | Recovery (%) | |
| Formaldehyde | 76 | 200 | 185 | 93 | 0.5 |
| Acetone | 250 | | 190 | 95 | 300 |

Conclusion

The work shown here describes an efficient HPLC method with UV detection for the determination of DNPH-derivatized carbonyl compounds in workplace air samples. All 13 carbonyl compounds listed in CARB 1004, ISO 16000-3, U.S. EPA Compendium Method TO-11A, and the Chinese HJ/T 400-2007 are well resolved within 15 min on an Acclaim Carbonyl RSLC column using an ammonium acetate/acetonitrile mobile phase.

| | |
|---------------|---|
| Column: | Acclaim Carbonyl RSLC, 2.2 µm, 2.1 × 150 mm |
| Mobile Phase: | A. 2 mM Ammonium acetate B. Acetonitrile |
| Gradient: | B. -2.5–0 min, 48%; 2.0–7.0 min, 53%; 12.5–14 min, 100% |
| Flow Rate: | 0.4 mL/min |
| Inj. Volume: | 1.2 µL |
| Temperature: | 30 °C |
| Detection: | UV absorbance at 360 nm |
| Samples: | A. DNPH-derivatized indoor air sample B. A spiked with a DNPH-derivatized carbonyl compound mixed standard (0.2 µg/mL each) C. DNPH-derivatized carbonyl compound mixed standard (0.075 µg/mL each) |
| Peaks: | 1. Formaldehyde 8. Butyraldehyde 2. Acetaldehyde 9. Methacrolein 3. Acetone 10. Benzaldehyde 4. Acrolein 11. Valeraldehyde 5. Propionaldehyde 12. <i>m</i> -Tolualdehyde 6. Crotonaldehyde 13. Hexanaldehyde 7. Methyl Ethyl Ketone |

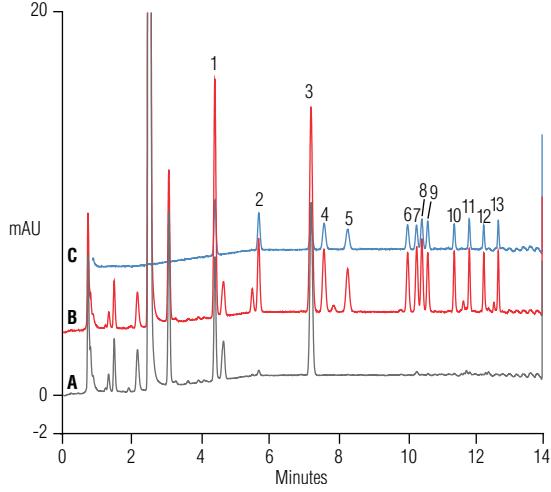


Figure 3. Overlay of chromatograms of a DNPH-derivatized workspace air sample and spiked samples.

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