Gas Chromatography–Triple Quadrupole Mass Spectrometry Analysis of Dioxins in Soil

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The applicability of gas chromatography–triple quadrupole mass spectrometry (GC–MS/MS) for determination of dioxins in soil was investigated. The analytical method was validated based on US Environmental Protection Agency (EPA) Method 1613 and European Union (EU) Regulation No. 709/2014 for selectivity, linearity of sensitivity, and instrumental limits of quantification (iLOQs). Method development commenced with determination of retention times for 17 native polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and selection of characteristic ions from GC–MS/MS spectra. The linearity was measured using 1613 standard solutions (CS1–CS5) containing 0.5 to 200 ng/mL tetrachlorodibenzo-p-dioxin/furan (TCDD/F) congeners, 2.5 to 1000 ng/mL pentachlorodibenzo-p-dioxin/furan (PeCDD/F) congeners, and 20 to 2000 ng/mL octachlorodibenzo-p-dioxin/furan (OCDD/F) congeners. The correlation coefficient ($R^2$) values ranged between 0.9990 and 0.9999, and the iLOQ values ranged from 0.052 to 0.350 pg/μL for TCDD/F congeners, with a relative standard deviation of 2.7–9.6%. The entire analytical method was verified by analysis of certified reference materials (BCR-529 and BCR-530), and the recoveries were 71.79–103.87% and 81.50–103.12%, respectively. Thus, the GC–MS/MS system provides an alternative to GC–high-resolution MS for the simultaneous determination of TCDD/F congeners in soil.

Keywords: dioxins, GC–MS/MS, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, soil analysis

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are important environmental pollutants (also known as dioxins) that are classified as persistent organic pollutants (POPs) and lead to a broad range of toxic effects in humans and natural environments [1–3]. PCDD/PCDFs are unintentionally formed as by-products during a variety of industrial, manufacturing, and combustion processes [4–8]. Dioxins are chemically highly stable and persist in environmental ecosystems for many years due to a halflife in soil of 10–12 years [9]. For this reason, analytical methods for the determination of dioxins in natural environments are being actively developed.

For instrumental determination, exhaustive extraction, extensive clean-up and sensitive detection procedures are required to determine dioxins in complex matrices. High-resolution gas chromatography coupled to high-resolution mass spectrometry (HRGC/HRMS) is a powerful tool for dioxin research, which has been used successfully for analysis of PCDD/F congeners, and designated as an international reference method [10–15]. HRGC/HRMS has advantages and disadvantages in terms of the analysis process and equipment. Advantages include its high sensitivity, high selectivity, and robustness in terms of MS [16–17]. Disadvantages include its relatively high cost and difficult usage [18]. For these reasons, the development of alternative methods that are more reliable than HRMS but with similar or better reliability is ongoing.

As an alternative to HRGC/HRMS, gas chromatography–triple quadrupole mass spectrometry (GC–MS/MS) should in theory be able to determine dioxin congeners at very low concentrations, potentially providing unambiguous evidence to confirm measurements derived from HRGC/HRMS. Accuracy and sensitivity have both been recently improved due to technological and developmental advances in mass spectrometry (MS). These improvements are in accordance with the analytical criteria of HRGC/HRMS and represent enhanced selectivity. In recent years, analysis of dioxins from matrices including food, feed, fats, sewage sludge, and fly ash samples using GC–MS/MS have revealed sensitivity and accuracy comparable with HRGC/HRMS [15, 18–23]. Therefore, GC–MS/MS could, in principle, be employed for analysis of POPs, such as dioxins, and for analysis of harmful and toxic substances in various fields.

To the best of our knowledge, determination of dioxin congeners in soil using GC–MS/MS instead of HRGC/HRMS has not been reported previously. In the present study, we demonstrate the applicability of the GC–MS/MS system for analysis of PCDD/F congeners in soil containing low levels of these compounds.

Experimental

Reagents, Standards, and Materials. All reagents and solvents for dioxin analysis were of analytical grade or HPLC-grade. Toluene and nonane of dioxin analysis grade were provided by Wako Pure Chemical Industries (Tokyo, Japan), and other solvents including dichloromethane, hexane, and methanol (MeOH) were obtained from Burdick & Jackson (Muskegon, MI, USA). A multilayer silica gel column (10% silver nitrate silica gel, 44% sulfuric silica gel,

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22% sulfuric silica gel, and 2% potassium hydroxide silica gel) and activated carbon solid phase extraction (SPE) cartridges were obtained from GL Science Inc. (Tokyo, Japan) and Sigma-Aldrich (St. Louis, MO, USA). Native and 13C12-isotope-labelled standard mixtures of PCDD/Fs (EPA 1613 CS1 to CS5, LCS, and ISS) were certified purchases from Wellington Laboratories Inc. (Guelph, Ontario, Canada) and were used for the development of the analytical methodology. Certified reference material (CRM) samples including BCR 529 (sandy soil) and 530 (clay soil) were obtained from the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) for method validation.

**Sample Extraction and Clean-up.** Extraction procedures for determination of dioxins in soil were performed as described previously [24] with a slight modification, as shown in Figure 1. Briefly, 10 g soil was spiked with 13C-labelled compounds (EPA 1613 LCS) as internal (surrogate) standards, and extraction was performed using an ASE 300 system ( Dionex, Sunnyvale, CA, USA) with instrument settings as follows: 170 °C, 1500 psi, 70% flush volume, 2 static cycles of 6 min, and toluene as an extraction solvent. The aliquots were evaporated by rotary evaporation, solvent was replaced with n-hexane, and samples were injected into a multilayer silica gel column pre-equilibrated with 25 mL n-hexane. After elution of 100 mL n-hexane and evaporation to dryness, the samples were redissolved in 3 mL n-hexane and transferred to auto-sampling vials and analyzed by GC–MS/MS.

**Instrumental Analysis (GC–MS/MS).** For determination of PCDD/F congeners, we used a Bruker Scion TQ triple quadruple mass spectrometer (Bruker, Fremont, CA, USA) coupled to a Bruker 451 GC and CP 8400 auto sampler, with a DB-5MS UI capillary column (60 m × 0.25 mm × 0.25 μm; J&W Scientific, Folsom, CA, USA) operated in the selected ion monitoring (SIM) mode and the electron ionization (EI) positive mode at 70 eV. The temperatures of the transfer line, injector, and ion source were 280 °C and 230 °C, respectively. For analysis, a 2-μL sample was injected in the pulse splitless mode. Helium at a constant flow rate of 1 mL/min was used as the carrier gas. The program temperature was 140 °C for 1 min, increased to 220 °C at 20 °C/min (held for 1 min) and then to 320 °C at 5 °C/min (held for 14 min) for a total runtime of 35 min. Details of the GC–MS/MS operational parameters, as well as the multiple reaction monitoring (MRM) conditions for PCDD/Fs determination, are provided in Tables 1 and 2.

**Results and Discussion**

**Analytical Validation of the GC–MS/MS Method.** Analytical performance was assessed in terms of selectivity, linearity of sensitivity, and instrumental limits of quantification (iLOQs) according to the validation parameters for GC–MS/MS method development. EPA-1613 CS3 calibration standard solutions were selected to evaluate the chromatographic separation of PCDD/Fs, and the separation was acceptable for all PCDD/F congeners (Figure 2). Optimization of operational parameters was performed by selecting the two most abundant precursor ions for each target compound from full scan spectra of PCDD/Fs. Tables 2 summarizes the MRM transitions and optimum collision energy (CE) voltages for each congener and transition.
Table 1. Experimental conditions for gas chromatography–triple quadrupole mass spectrometry (GC–MS/MS) analysis of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).

| GC conditions |  
|----------------|---------------------------------------------------------------|
| Column         | DB-5MS UI                                                     |
| Injection volume (μL) | 2.0, splitless                                                |
| Inlet temp. (°C) | 280 Pulsed splitless, 50 psi (1 min)                         |
| Carrier gas    | Helium                                                       |
| Column flow (mL/min) | 1.0                                                           |
| Oven program   | 140 °C (1 min)                                                |

| MS conditions |  
|----------------|---------------------------------------------------------------|
| Operation mode | Electron ionisation (EI), multiple reaction monitoring (MRM) |
| MS system      | MS WS 8.0 SPI                                                |
| Transfer line  | 280 °C                                                       |
| temperature    | 230 °C                                                       |
| Ion source     | 20 °C/min to 220 °C (1 min)                                  |
| Oven temperature | 5 °C/min to 320 °C (14 min)                                 |
| Electron energy | −70 eV                                                      |
| Collision gas  | 1.5 mTorr                                                    |

Table 2. Multiple reaction monitoring (MRM) conditions for detection of the PCDF/D congeners.

| Congeners | RT (min) | Precursor ion | Product ion | CE (V) | Precursor ion | Product ion | CE (V) |
|-----------|----------|---------------|-------------|--------|---------------|-------------|--------|
| 1,2,3,7,8-TCDD | 15.40    | 316           | 252         | 30     | 318           | 254         | 30     |
| 2,3,7,8-TCDD | 15.41    | 304           | 241         | 30     | 306           | 243         | 30     |
| 1,2,3,4,7,8-TCDD | 15.46   | 332           | 268         | 22     | 334           | 270         | 22     |
| 2,3,7,8-TCDD | 15.71    | 332           | 268         | 22     | 334           | 270         | 22     |
| 1,2,3,7,8-PeCDF | 17.62   | 350           | 286         | 32     | 352           | 288         | 32     |
| 1,2,3,4,7,8-PeCDF | 17.63   | 338           | 275         | 30     | 340           | 277         | 30     |
| 2,3,4,7,8-PeCDF | 18.18    | 338           | 275         | 30     | 340           | 277         | 30     |
| 1,2,3,7,8-PeCDF | 18.36    | 368           | 304         | 22     | 370           | 306         | 22     |
| 1,2,3,7,8-PeCDF | 18.38    | 354           | 291         | 25     | 356           | 293         | 25     |
| 1,2,3,4,7,8-HxCDF | 20.22   | 386           | 322         | 32     | 388           | 324         | 32     |
| 1,2,3,4,7,8-HxCDF | 20.24    | 374           | 311         | 30     | 376           | 313         | 30     |
| 1,2,3,4,6,7,8-HxCDF | 20.33   | 386           | 322         | 32     | 388           | 324         | 32     |
| 1,2,3,4,7,8-HxCDF | 20.34    | 374           | 311         | 30     | 376           | 313         | 30     |
| 1,2,3,4,6,7,8-HxCDF | 20.76   | 386           | 322         | 32     | 388           | 324         | 32     |
| 2,3,4,6,7,8-HxCDF | 20.77   | 374           | 311         | 30     | 376           | 313         | 30     |
| 1,2,3,4,7,8-HxCDF | 20.90    | 402           | 338         | 22     | 404           | 340         | 22     |
| 1,2,3,4,7,8-HxCDF | 20.85    | 388           | 262         | 40     | 390           | 327         | 25     |
| 1,2,3,4,6,7,8-HxCDF | 21.14   | 402           | 338         | 22     | 404           | 340         | 22     |
| 1,2,3,4,7,8-HxCDF | 21.16    | 388           | 262         | 40     | 390           | 327         | 25     |
| 1,2,3,4,7,8-HxCDF | 21.48    | 386           | 322         | 32     | 388           | 324         | 32     |
| 1,2,3,7,8-HxCDF | 21.48    | 374           | 311         | 30     | 376           | 313         | 30     |
| 1,2,3,4,6,7,8-HpCDF | 22.61   | 420           | 356         | 35     | 420           | 358         | 35     |
| 1,2,3,4,6,7,8-HpCDF | 22.60    | 408           | 345         | 35     | 410           | 347         | 35     |
| 1,2,3,4,7,8-HpCDF | 23.46    | 436           | 372         | 22     | 438           | 374         | 22     |
| 1,2,3,4,6,7,8-HpCDF | 23.48    | 424           | 361         | 25     | 426           | 363         | 25     |
| 1,2,3,4,7,8-HpCDF | 23.94    | 420           | 356         | 35     | 422           | 358         | 35     |
| 1,2,3,4,6,7,8-HpCDF | 23.96    | 408           | 345         | 35     | 410           | 347         | 35     |
| 1,2,3,4,6,7,8-CDFD | 25.87    | 470           | 406         | 25     | 472           | 408         | 25     |
| OCDF | 26.07 | 442           | 379         | 30     | 444           | 381         | 30     |

*aISS, internal standards (EPA-1613ISS).*

Linearity is an important factor determining the accuracy of the analytical validation process. Linearity tests were optimized and applied to five calibration standard solutions (EPA1613 CS1 to CS5) including native and 13C12-labelled tetrachlorodibenzo-p-dioxin/furan (TCDD/F) congeners at concentrations ranging from 0.5 to 2000 pg/μL and 100 pg/μL, respectively, except for 13C12-octachlorodibenzo-p-dioxin (OCDD), which was 200 pg/μL. Determination coefficient (R2) values higher than 0.999 indicated good linearity, and the relative response factor (RRF) and relative standard deviation (RSD) values were in good agreement (RSD <15%) for PCDD/F congeners (Table 3). These excellent linearity results confirmed that method was in accordance with the criteria established earlier by the EPA 1613 method.

One of the major differences between HRGC/HRMS and GC–MS/MS is the ability to set the iLOQ value; although HRGC/HRMS is measured by the signal-to-noise (S/N) ratio for raw signals, GC–MS/MS does not allow calculation of the S/N ratio due to filtering of ions by the quadrupoles [25]. For these reasons, iLOQ values for the GC–MS/MS system were measured using a 10-fold dilution of the EPA-1613CS1 standard solution following 10 repeated injections, which were considered to be 10 times the RSD of the replicates. The iLOQ values ranged from 0.052 to 0.350 pg/μL for TCDD/F congeners. All %RSD values were below 9.6% (Table 4), suggesting that the proposed GC–MS/MS analytical method was sufficiently sensitive to easily detect low-level dioxin congeners.

**Determination of Dioxins in CRMs.** To assess the accuracy of the validation tests used to assess the analytical method, we evaluated the analytical efficiency using two CRMs, BCR 529 and 530, which are the same matrices as the real samples. The accuracy values obtained as recovery factors for dioxin congeners were used as reference values for quality assurance with the GC–MS/MS instrument. CRM and accuracy results are shown in Table 5. The measured total dioxin values for BCR 529 (16,865.53 pg. g−1) and BCR 530 (1495.69 pg. g−1) were in good agreement with the certified values for BCR 529 (20,025 ± 2981 pg/g) and BCR 530 (1575 ± 174 pg/g). The range of accuracy values for dioxin congeners compared with certified values for BCR 529 and BCR 530 were 71.79–103.87% (average = 84%) and 81.50–
103.12% (average = 95%), respectively, which was satisfactory (>90% for most congeners) according to US Environmental Protection Agency (EPA) 1613 [14] and European Union (EU) Regulation 709/2014 [26]. These results indicate that GC–MS/MS approaches were suitable for the monitoring of dioxins in soil and comparable in terms of sensitivity to HRGC/HRMS.

**Conclusion**

Analysis of dioxins in environmental samples is generally performed by HRGC coupled to HRMS. However, we demonstrate that a GC–MS/MS analysis could be used as an alternative method, thanks to the recent technical advances in MS. In this study, a GC–MS/MS-based analytical method was developed to detect low concentrations of dioxins in soil. The method was validated according to the US EPA Method 1613 and EU Regulations 709/2014 guidelines using EPA-1613 standard solution. The results were satisfactory in terms of

**Table 3. Linearity of calibration curves and relative response factors (RRFs) of PCDD/F congeners**

| Congeners       | Concentration range (pg/μL) | $R^2$  | Average RRF | RRF%  |
|-----------------|----------------------------|--------|-------------|-------|
| 2,3,7,8-TCDF    | 0.5–40                     | 0.9994 | 1.23        | 8.2   |
| 2,3,7,8-TCDD    | 0.5–40                     | 0.9997 | 1.16        | 3.8   |
| 1,2,3,7,8-PeCDF | 2.5–1000                   | 0.9999 | 1.28        | 2.9   |
| 2,3,4,7,8-PeCDF | 2.5–1000                   | 0.9990 | 1.52        | 1.5   |
| 1,2,3,7,8-PeCDF | 2.5–1000                   | 0.9999 | 0.81        | 9.4   |
| 1,2,3,4,7,8-HxCDF | 2.5–1000        | 0.9991 | 1.38        | 8.5   |
| 1,2,3,6,7,8-HxCDF | 2.5–1000        | 0.9999 | 1.22        | 3.6   |
| 2,3,4,6,7,8-HxCDF | 2.5–1000        | 0.9996 | 1.03        | 5.2   |
| 1,2,3,4,7,8-HxCDF | 2.5–1000        | 0.9994 | 1.27        | 5.8   |
| 1,2,3,6,7,8-HxCDF | 2.5–1000        | 0.9999 | 0.95        | 4.7   |
| 1,2,3,7,8,9-HxCDD | 2.5–1000        | 0.9992 | 1.14        | 10.2  |
| 1,2,3,7,8,9-HxCDF | 2.5–1000        | 0.9999 | 1.09        | 9.4   |
| 1,2,3,4,6,7,8-HpCDF | 2.5–1000        | 0.9995 | 0.91        | 2.5   |
| 1,2,3,4,6,7,8-HpCDD | 2.5–1000        | 0.9999 | 1.22        | 4.8   |
| 1,2,3,4,7,8,9-HpCDF | 2.5–1000        | 0.9991 | 1.05        | 3.8   |
| OCDD            | 5.0–2000                  | 0.9999 | 1.34        | 2.4   |
| OCFD            | 5.0–2000                  | 0.9999 | 1.25        | 7.2   |

Figure 2. Chromatographic and mass spectrometric separation of 17 polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) using gas chromatography–triple quadrupole mass spectrometry (GC–MS/MS)
Table 4. Calibration curve data and instrumental limits of quantitation (iLOQ) values

| Congeners | Retention time (min) | Lowest calibration point (pg/µL) | Highest calibration point (pg/µL) | Lowest calibration point RSD (%) | $R^2$ correlation coefficient | Difference RF (low-RF) (All %) | Average RF (iLOQ) (pg/µL) |
|-----------|---------------------|----------------------------------|----------------------------------|---------------------------------|-------------------------------|--------------------------------|-----------------------------|
| PCDDs     |                     |                                  |                                  |                                 |                               |                                |                             |
| 2,3,7,8-TCDD | 15.961              | 0.078                            | 3.957                            | 6.7                             | 0.999                         | -0.411                         | 2.799, 0.052                |
| 1,2,3,7,8-PeCDF | 18.638              | 0.421                            | 20.213                           | 4.1                             | 0.999                         | -0.242                         | 1.450, 0.173                |
| 1,2,3,4,7,8-HxCDF | 21.418              | 0.414                            | 20.204                           | 8.5                             | 0.999                         | 2.170                          | 1.436, 0.350                |
| 1,2,3,6,7,8-HxCDF | 21.425              | 0.394                            | 20.067                           | 5.7                             | 0.999                         | 0.994                          | 1.507, 0.226                |
| 1,2,3,7,8,9-HxCDF | 21.427              | 0.361                            | 20.093                           | 6.6                             | 0.999                         | 1.498                          | 1.546, 0.239                |
| 1,2,3,4,6,7,8-HpCDF | 23.750              | 0.391                            | 19.985                           | 5.1                             | 0.999                         | 1.008                          | 1.408, 0.199                |
| OCDF      | 26.165              | 0.850                            | 40.142                           | 3.7                             | 0.999                         | 0.492                          | 0.945, 0.315                |

PCDFs

| Congeners | Retention time (min) | Lowest calibration point (pg/µL) | Highest calibration point (pg/µL) | Lowest calibration point RSD (%) | $R^2$ correlation coefficient | Difference RF (low-RF) (All %) | Average RF (iLOQ) (pg/µL) |
|-----------|---------------------|----------------------------------|----------------------------------|---------------------------------|-------------------------------|--------------------------------|-----------------------------|
| 2,3,7,8-TCDF | 15.652              | 0.090                            | 3.957                            | 9.6                             | 0.999                         | -16.286                        | 5.554, 0.086                |
| 1,2,3,7,8-PeCDF | 17.879              | 0.427                            | 19.929                           | 3.2                             | 0.999                         | -0.392                         | 2.799, 0.137                |
| 2,3,4,7,8-PeCDF | 18.482              | 0.394                            | 19.957                           | 3.9                             | 0.999                         | -0.503                         | 3.151, 0.154                |
| 1,2,3,4,7,8-HxCDF | 20.511              | 0.421                            | 19.855                           | 7.5                             | 0.999                         | 0.869                          | 2.926, 0.317                |
| 1,2,3,6,7,8-HxCDF | 20.596              | 0.423                            | 20.086                           | 6.1                             | 0.999                         | 0.518                          | 3.230, 0.255                |
| 2,3,4,6,7,8-HxCDF | 21.037              | 0.384                            | 20.275                           | 2.7                             | 0.999                         | 1.283                          | 3.166, 0.114                |
| 1,2,3,7,8,9-HxCDF | 21.736              | 0.405                            | 20.179                           | 6.4                             | 0.999                         | 2.137                          | 2.505, 0.261                |
| 1,2,3,4,6,7,8-HpCDF | 22.864              | 0.419                            | 19.909                           | 3.2                             | 0.999                         | -0.127                         | 1.987, 0.136                |
| OCDD      | 24.220              | 0.425                            | 19.857                           | 3.6                             | 0.999                         | -0.243                         | 1.484, 0.153                |
| OCDF      | 26.349              | 0.849                            | 40.157                           | 3.7                             | 0.999                         | 0.624                          | 1.290, 0.315                |

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selectivity, linearity of sensitivity, and iLOQ. Furthermore, the accuracy of the analytical method was confirmed using CRM BCR 529 and BCR 530, and the accuracy was successfully optimized. Thus, GC–MS/MS provides an alternative method for routine screening and quantification of dioxins in soil.

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240 GC–MS/MS Analysis of Dioxins in Soil

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