# THERMOGRAVIMETRIC DESORPTION AND DE NOVO TESTS
# I. METHOD DEVELOPMENT AND CALIBRATION

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**Abstract**
Thermogravimetric analysis TGA has been combined with evolved gas analysis EGA with the purpose of characterising the thermal behaviour of filter dust samples under inert (desorption, and thermal decomposition) and *de novo* test oxidising conditions. Emphasis is on studying *de novo* formation of dioxins, surrogates and precursors from filter dust, arising in thermal processes, such as Municipal Solid Waste Incineration and Metallurgy. A new method is tested for sampling and analysing the number of dioxin surrogates and precursors in the TGA effluent, which is collected on sampling tubes; the absorbed compounds are eventually desorbed and quantified by TD-GC/MS. The major sources of error and losses are considered, including potential sorbent artefacts, possible breakthrough of volatiles through sampling tubes, or possible losses of semi-volatiles due to their incomplete desorption or re-condensation inside the TG Analyser. As a result the method is optimised and validated for determining di- to hexa-chlorinated benzenes in a range of 10-1000 ppb with average recovery of 85%.

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**Introduction**
Several research groups studied the *de novo* route of dioxin formation, using a laboratory set-up, featuring a fixed bed of fly ash. The evolving chlorinated compounds were collected e.g. on XAD-resin or in toluene and analysed, as were these remaining on the dust. Addink and Olie[1] presented a survey of prior research and of the parameters studied. Due to the trace amounts involved, typically 5-10 g of sample is required for an efficient analysis of dioxins. The procedure implies extraction and several pre-treatment steps and is quite laborious and time-consuming.
In this study a Thermal Gravimetric Analyser (TGA) is used as a reactor for supplying appropriate thermal treatment / oxidative conditions for *de novo* testing of the sample, while the evolving vapours are trapped on-line in a sampling tube. Sample size is limited to 50-250 mg, reducing the chances for re-adsorption and conversion of evolving reaction products, yet at the same time raising the detection limits of the technique to the ng/g or ppb level.. For the purpose of the study selected dioxin surrogate and precursor compounds, i.e. polychlorinated benzenes (CBz), phenols (CPh), naphthalenes (PCN), biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH), are used as indicators for *de novo* activity[2-4].

**Materials and Methods**
The introduced experimental sequence consists of following steps (a) TGA blank run; (b) TGA sampling run with a selected temperature program under inert (desorption) or oxidative (de novo test) conditions, or a combination of both (i.e. desorption followed by de novo), while the evolved vapours are continuously sampled onto a sorbent matrix. A fly ash sample (50-70mg) is placed into the sampling cup of a 951 Thermogravimetric Analyser (DuPont Instruments); (c) TD-GC/MS analysis of exposed sampling tubes; (d) if required, solvent rinsing of TGA tube and collecting these rinses for further GC/MS analysis in order to check for possible analytes losses on the walls.
The sorbent is packed inside glass tubes (4mm I.D., 8.8cm in length), specially designed for a Markes Unity TD-GC/MS instrument. Tubes either filled with Tenax TA or dual-bed sorbent (50mg of Tenax TA + 100mg polydimethylsiloxane, PDMS) are used and both evaluated for the purposes of this study.
For optimising and validating the analytical procedure synthetic samples are prepared from thermally pre-treated (4h, 500°C in air) analytical sand (Merck, GR, 0.1-0.3mm) and spiked with known amounts of the compounds of interest.
Sampling tubes are thermally desorbed using a Markes Unity thermal desorption system with cryofocusing trap and equipped with an autosampler (Ultra TD, Markes), connected to a Finnigan Trace GC Ultra (Thermo Electron Corporation) coupled to a Finnigan Trace DSQ mass-spectroscopic detector (Thermo Electron Corporation). Conditions of analysis and instrumental settings are given in table 1.

Table 1. Conditions of analysis and instrumental settings (TD-GC/MS)

| | |
|---|---|
| Markes TD | 300°C × 30 min, split 1:20, He |
| Cryo-trap | General purpose cold trap, graphitised carbon (Markes Int. Ltd.), -10°C → 345°C ×15 min |
| GC | CPsil8MS, 5% phenyl-groups column (30m × 0.25mm I.D., 0,5µm); temp. programme: 35°C (5 min)→ (8°C/min) → 100 (0 min)→ (12°C/min) → 280°C (10min), total 38 min; He, constant pressure 85kPa |
| MSD | Electron impact, 70 eV, full scan 50-450 amu |

Table 2. Conditions of analysis and instrumental settings (liquid injection-GC/MS)

| | |
|---|---|
| GC | Trace GC 2000 series (ThermoQuest CE Instruments), CPsil8MS, 5% phenyl-groups column (30m × 0.25mm I.D., 0,25µm); temp. programme: 35°C (0 min)→ (15°C/min) → 320°C (10min); 1µL splitless; He, constant flow 1mL/min |
| MSD | Voyager (ThermoQuest, Finnigan), electron impact, 70 eV, full scan 50-450 amu |

In order to check for analyte losses the TGA tube is soaked in dichloromethane, spiked with a D10-Anthracene recovery standard and extracted in an ultrasonic bath. Then, the extract is concentrated in a stream of nitrogen and GC/MS analysed. GC/MS specifications and operational conditions used for this analysis are summarised in Table 2. Both external standard calibration and internal standard (I.S.) addition methods are used for GC-MS quantification. Decafluorobiphenyl and 4,4'-dibromobiphenyl are chosen as I.S. in TD-GC/MS and in liquid injection GC/MS analysis respectively. Quantification is based on a relative response factor (RRF) using peak area values of the most abundant ion in the spectra for each target compound. Instrumental blanks (blank sampling tube) and TGA blanks (sampling tube from the test with empty TGA cup) are routinely prepared and evaluated.

**Results and Discussion**

Several steps are undertaken in order to test, validate and optimise the procedure:

**TGA blanks**. Blank TGA runs, simulating a complete experiment without introducing a sample, are performed for each series of 4-5 samples. Desorption blanks are usually less than 1 ng, consisting mainly of low chlorinated CBs and naphthalene, while oxidation blanks are even lower. Major artefacts from Tenax TA and PDMS decomposition are identified as phenol, benzaldehyde, acetophenone, in agreement with other researchers[5]. During sample analysis the target analytes are usually corrected for these TGA blank values.

**Oxidation tests.** Applying a de novo test (oxidative conditions) after desorption (inert gas) allows not only to follow a possible carry-over of analyte, but also to evaluate the thermal stability of tenax and PDMS (both used for collecting evolved vapours) under oxidative conditions and at increased temperatures.

**Tenax tube vs tenax + PDMS sampling tube.** Both Tenax and dual-bed (Tenax + PDMS) tubes were tested under identical conditions for sampling evolved vapours. Several target compounds, i.e. DiCBz to HxCBz, TrCB to HpCB, naphthalene, and selected PAH (acenaphthene, acenaphthylene, fluorene, anthracene, phenantrene, fluoranthene, pyrene) are spiked on analytical sand at an average level of 1 µg/g of each analyte. TGA desorption proceeds for 20 min × 350°C ($N_2$, 50 mL/min), followed by oxidation at 200°C-550°C (air, 50 mL/min). Separate sampling tubes are used for desorption and for the oxidation part of this test. In both tests using either Tenax or Tenax + PDMS recoveries on sampling tubes are in general low (<60%), yet variable for different analytes and slightly better for low-chlorinated CBz in the Tenax-PDMS combination. High losses (90-99%) arise for di- to tetra-chlorinated CBz, breaking through the sampling tube. Other losses occur due to incomplete desorption and/or subsequent condensation inside the TGA tube, causing carry-over to the following test. Significant losses (15-70%) take place in the thermobalance and the connecting line for tri- to hexachlorinated CB (due to their low volatility) and carry-over occurs (>50%) for heavier PAH, from fluorene to pyrene. Mass balances are established and the major sources of losses identified.

**Cooling the sampling tube.** In order to avoid breakthrough of target compounds sampling tubes (Tenax + PDMS) are cooled to -21°C (NaCl/ice mixture 1:3) during the entire run. Analytical sand, spiked with 1µg/g of each of Di- to HxCBz and PAH compounds (listing see supra), is thermally desorbed in the TG Analyser (25 min × 350°C, $N_2$, 50

mL/min). Cooling markedly (70-83%) improves CBz recovery and also naphthalene, acenaphthene and acenaphthylene show now good recoveries (71-82%); yet, they remain low (3-50%) for PAH, because of higher (> 50%) losses arising in the thermobalance and its connection line to the sampling tubes.

**TD-GC/MS instrument.** Prior to analysis all TD-GC/MS settings are optimised. A desorption temperature is set (300°C as a standard), considering the known decomposition tendencies of sorbents (Tenax TA and PDMS) and relative ease of desorption. Desorption time (30 min as a standard) and cold trap conditions (-10°C → 345°C ×15 min) are those recommended by the manufacturer of the TD-instrument for this type of analytes. The split ratio is based on both GC column properties and estimated levels of the target compounds in the analysed tubes.

The TD-GC/MS ability to detect the analytes of interest has been verified. The same amount of the target compounds is introduced into the GC/MS analyser, either via thermal desorption from a sorbent matrix or by direct injection of a test solution. The MS responses are compared. Differences between two responses average 9% for CBz (mainly for Pe- and Hx-CBz), 7-13% for naphthalene, acenaphthene and acenaphthylene, and are still somewhat acceptable for TrB and TCB (15-17%). Low-volatile compounds, however, such as most PAH, PeCB, HxCB, HpCB, are out of acceptable limits, suggesting high losses in the thermal desorber (as well as in TGA) or incomplete desorption from the matrix.

**Validating the procedure for different concentration levels.** Based on results and interpretations described above, a new experimental scheme, implying a combination of TGA with evolved gas analysis via collection on sampling tubes has been designed: the samples undergo thermal desorption or/and oxidation in a thermobalance, while evolved vapours are sampled on a dual-bed (tenax + PDMS) sampling tube, cooled during sampling by means of a NaCl/ice mixture. The compounds collected on the sampling tubes are analysed by a TD-GC/MS technique. The method is validated for analytes with a vapour pressure > $10^{-2}$ Pa, roughly corresponding to a boiling point < 300°C. This range is estimated by comparison with effectively detected analytes in the tests conducted as described above: volatile dichlorobenzene (b.p. 170°C, v.p. 196Pa at 25°C[6]) to low volatile acenaphthylene (b.p. 280°C, v.p. 0.9Pa at 25°C[7]).

The procedure is tested for four synthetic samples: 0.2g of analytical sand, spiked with different amounts of various CBz isomers (cf. table 3a/b) is tested under replicate experimental conditions (25 min × 350°C, $N_2$, 50 mL/min). Possible losses of analytes in TGA tube are carefully checked after each run (rinsings collected as described above). Both TD-GC/MS and liquid-GC/MS (for analysis of TGA rinses) quantifications are based on four-point calibration lines. Recoveries of extraction procedure, TGA and laboratory blanks are checked for quality of the results.

Results are presented in tables 3a and 3b. In average, recoveries are acceptable (80-102 %) showing slight decreases for light CBz at low levels (10 ng/g). For a majority of CBz losses are insignificant (0.8-7%). However, HxCBz shows a tendency to condense in thermobalance and line; detected losses vary between 6-32%, the highest loss occurring at the lowest concentration (10 ng/g). The data is statistically treated, showing losses to be independent of the amount spiked, in a range of 10-1000 ng per isomer. The TD-GC/MS method shows excellent linearity: $R^2$ of the regression line for the four-point calibration curve are higher 0.999 for all CBz isomers. Yet, as stated above, low amounts tend to increase variability and potential losses. Recoveries of the extraction procedure range 50-86% (average 70%). ΣCBz mass balances indicate acceptable deviation (average 12%) from the original spiked amounts.

**Conclusions**

A novel procedure is developed, tested and validated. It involves a combination of TGA and EGA, implying sorption of evolved volatiles on sampling tubes and their analysis by a TD-GC/MS technique. The method is suitable for reliable detection and quantification of CBz in a range of 10-1000 ppb for each isomer or 110-11000 ppb for ΣCBz. The method can be used for thermal desorption of fly-ash samples or studying thermal desorption or *de novo* formation of dioxins. Still, unexpected matrix effects may occur, as explained in another contribution.

In this work a TG Analyser serves as a reactor for simulating desorption and *de novo* conditions and CBz monitoring is applied for indicating *de novo* activity by monitoring CBz as surrogates.

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Table 3a. Results for levels of 10 and 50 ng/g of each spiked CBz congener (110 and 550 ng/g of ΣCBz)

| compound | **ΣCBz 110 ng/g** | | | **ΣCBz 550 ng/g** | | |
|---|---|---|---|---|---|---|
| | Amount spiked to the matrix, ng/g | Losses in the TGA-volume, % | Absorbed on sampling tube, % | Amount spiked to the matrix, ng/g | Losses in the TGA- volume, % | Absorbed on sampling tube, % |
| 1.3-dichlorobenzene | 10 | ND* | 64 | 50 | 1 | 80 |
| 1.4-dichlorobenzene | 10 | ND | 60 | 50 | 2 | 79 |
| 1.2-dichlorobenzene | 10 | ND | 44 | 50 | 3 | 77 |
| 1.3.5-trichlorobenzene | 10 | ND | 65 | 50 | 1 | 83 |
| 1.2.4-trichlorobenzene | 10 | ND | 96 | 50 | 5 | 120 |
| 1.2.3-trichlorobenzene | 10 | ND | 80 | 50 | 3 | 95 |
| 1.2.4.5-tetrachlorobenzene | 10 | ND | 80 | 50 | 4 | 93 |
| 1.2.3.5- tetrachlorobenzene | 10 | ND | 87 | 50 | 2 | 92 |
| 1.2.3.4-tetrachlorobenzene | 10 | ND | 86 | 50 | 4 | 96 |
| Pentachlorobenzene | 10 | 5 | 91 | 50 | 6 | 96 |
| Hexachlorobenzene | 10 | 32 | 84 | 50 | 7 | 84 |
| ΣCBz ,ng | **110** | **3** | **76** | **550** | **3** | **91** |

*ND – not detected (value (ng/g) is below the detection limit of GC/MS)

Table 3b. Results for levels of 100 and 1000 ng/g of each spiked CBz congener (1100 and 11000 ng/g of ΣCBz)

| compound | **ΣCBz 1100 ng/g** | | | **ΣCBz 11000 ng/g** | | |
|---|---|---|---|---|---|---|
| | Amount spiked to the matrix, ng/g | Losses in the TGA-volume, % | Absorbed on sampling tube, % | Amount spiked to the matrix, ng/g | Losses in the TGA- volume, % | Absorbed on sampling tube, % |
| 1.3-dichlorobenzene | 100 | ND | 89 | 1000 | ND | 92 |
| 1.4-dichlorobenzene | 100 | ND | 90 | 1000 | ND | 93 |
| 1.2-dichlorobenzene | 100 | 0.4 | 90 | 1000 | 0.2 | 90 |
| 1.3.5-trichlorobenzene | 100 | ND | 84 | 1000 | 0.2 | 81 |
| 1.2.4-trichlorobenzene | 100 | 0.1 | 115 | 1000 | 0.4 | 90 |
| 1.2.3-trichlorobenzene | 100 | ND | 93 | 1000 | 0.3 | 82 |
| 1.2.4.5-tetrachlorobenzene | 100 | 0.2 | 93 | 1000 | 0.8 | 85 |
| 1.2.3.5- tetrachlorobenzene | 100 | 0.2 | 92 | 1000 | 2 | 78 |
| 1.2.3.4-tetrachlorobenzene | 100 | 0.3 | 95 | 1000 | 1 | 82 |
| Pentachlorobenzene | 100 | 2 | 102 | 1000 | 2 | 80 |
| Hexachlorobenzene | 100 | 6 | 85 | 1000 | 23 | 37 |
| ΣCBz ,ng | **1100** | **0.8** | **93** | **11000** | **3** | **81** |