

SIMPLIFIED GEL PERMEATION METHOD FOR THE ANALYSIS OF PCDD/FS IN STACK EMISSION AND WASTE SOLID SAMPLES FROM VARIOUS THERMAL INDUSTRIAL PROCESSES

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Introduction

Common methods for analyses of dioxins and dioxin-like PCBs are expensive and slow. Therefore low-cost and fast methods have to be developed allowing to analyse in routinely manner a great number of samples and to provide quick, cheap, and reliable results on the presence of those compounds in the environment, feed and food, as stated in the Community Strategy for dioxins, furans and polychlorinated biphenyls¹ and in method EPA 1613². The analysis of dioxins can be carried out on different kind of samples. Sample preparation of dioxin extracts is one of the most challenging in analytical chemistry. Many coextractable and potentially interfering compounds present in the raw extract must be removed in order to achieve the enrichment of PCDD/Fs in the extracts, considering the small amount of analytes to be determined. Reference methods^{2,3} for the quantitative analysis of PCDD/Fs involve successive clean-up steps on various chromatographic adsorbents (multi-layer silica, Florisil, alumina, activated carbon) which considerably increase the time needed for analysis. The clean-up step can be modified to overcome interferences or lower the cost of measurements, provided that all method equivalency and performance criteria are met.

In order to simplify the clean-up step the use of two columns have been chosen: gel permeation and alumina.

In this work, an assessment of a new automated clean-up system based on gel permeation chromatography (AccuPrep MPSTM, J2 Scientific) combined with an in-line concentration system (AccuVapTM, J2 Scientific) was performed. Gel-permeation chromatography (GPC) is a size exclusion clean-up procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules. The removal of this high molecular weight, high boiling material may reduce contamination of GC injection ports and column heads, prolong column life, stabilize the instrument, and reduce column reactivity. The automated concentration system⁴ combines heat and vacuum with precise level sensing technology to perform fast, accurate concentration of GPC collect fractions as they elute off the column.

The objectives of this study were:

- i) to evaluate the chromatographic pattern of combined purification on size exclusion gel and alumina columns in samples with low organic content as ambient air, fly ashes and industrial emissions;
- ii) to verify the recovery of each ¹³C 2,3,7,8-chlorine substituted congeners added before the extraction;
- iii) to apply the combined clean-up (GPC/alumina) to different matrices to evaluate the general applicability of this method and the possibility to extend it to more complex samples, such as biological samples and soils.

Materials and methods

Samples

In order to evaluate the suitability of the method for real sample analysis a comparison between a well established manual clean-up procedure and the new automated system was made in several different environmental matrices for a total of about 200 samples, as summarized in table 1. Appropriate extraction techniques and standards were applied depending on the sample nature.

Clean-up

The manual clean-up process was based on the sequential use of open chromatographic multilayer silica and basic alumina columns. The multilayer silica column was composed of sequential layers (from bottom to top) silica, SiO₂ – AgNO₃, silica, SiO₂ - H₂SO₄, silica and Na₂SO₄. The extract applied to the top of the silica column was eluted with 150 ml of n-hexane and then concentrated prior to basic alumina column. PCBs were eluted

from this column with a n-hexane:dichloromethane (98:2) solvent mixture. The PCDD /PCDF were recovered with a n-hexane:dichloromethane (1:1) solvent mixture.

The automated clean-up system configuration consists of a 2.5 cm x 50 cm glass column packed with BioBeads SX-3 resin in 100% methylene chloride, a pump, an auto sampler and the evaporating chamber. The whole system is computer controlled and can be programmed as required (i.e. volume, flow-rates, direction of solvent flow, etc.). The system used a 5-mL sample loop and a flow rate of 5 mL/min with methylene chloride as the mobile phase. The GPC column was calibrated using the method outlined in USEPA Method 3640A⁵. The autosampler loads the 5 ml sample on the GPC column. The eluate is collected between 34 and 38 minutes, concentrated by AccuVap and taken through 3 consecutive washes with methylene chloride up to a final volume of 1.5 ml. The extract is concentrated by a gentle stream of nitrogen prior to alumina column.

Analysis

Purified extracts were analysed by HRGC-HRMS on a GC 8000 series gas chromatograph (Fisons Instruments) coupled to an Autospec mass spectrometer (Micromass, Manchester, UK), using a positive electron ionization (EI) source and operating in the SIM mode at 10 000 resolving power (10% valley definition). Verification of the resolution in the working mass range was obtained by measuring perfluorokerosene (PFK) reference peaks. Chromatographic separation was achieved with a RTX-5 (Restek) fused-silica capillary column (60 m x 0.25 mm ID, 0.25 mm film thickness) with helium as carrier gas in the splitless injection mode.

| SAMPLE SOURCE | SAMPLE TYPE | SAMPLES |
|--|---|----------------|
| Kiln for the production of clay expanded | 25 emissions + 3 Fly ashes | 28 |
| Cement plant | 30 emissions + 5 Fly ashes + 6 bottom ashes | 41 |
| Cement plant (co-burning) | 36 emissions + 2 Fly ashes | 38 |
| Tyre incinerator | 15 emissions + 8 Fly ashes | 23 |
| Sintering plant | 24 emissions + 6 Fly ashes | 30 |
| Ambient air | Particulate matter and vapour phase | 15 |
| Medical waste incinerator | 6 emissions | 6 |
| RDF incinerator | 10 emissions + 1 bottom ash | 11 |
| Kiln for the production of aluminium | emissions | 2 |
| Refinery (boilers) | 3 emissions + 1 bottom ash | 4 |
| Pharmaceutical incinerator | 4 emissions | 4 |
| Biomass incinerator | 8 emissions | 8 |
| MSW incinerator | 4 emissions + 1 Fly ash | 5 |
| TOTAL | | 198 |

Table 1. Samples analysed by manual and automated clean-up

Results and Discussion

The suitability of the new automated system in the analysis of real samples was evaluated against a well established manual cleanup procedure. Different environmental matrices such as flue gas emissions, fly- ashes, ambient air, sludges and soils were considered for this study.

In order to evaluate the quantitative performance of the semi-automatic system, the mean recoveries and standard deviations (%) of the labeled PCDD/PCDF congeners (EN-1948 ES, Wellington Laboratories) obtained

on 24 iron ore sintering plant emission samples are shown in Table 2. The values are all in good agreement with the minimum requirements of well accepted reference methods.

| CONGENER | RECOVERIES [%] | |
|---------------------|--------------------|-----------------------|
| | MANUAL CLEAN-UP | AUTOMATED CLEAN-UP |
| 2,3,7,8-TCDD | 88 ± 4 | 80 ± 6 |
| 1,2,3,7,8-PeCDD | 90 ± 3 | 81 ± 5 |
| 1,2,3,4,7,8-HxCDD | 99 ± 3 | 85 ± 7 |
| 1,2,3,6,7,8-HxCDD | 95 ± 3 | 85 ± 8 |
| 1,2,3,4,6,7,8-HpCDD | 87 ± 6 | 70 ± 5 |
| OCDD | 67 ± 9 | 58 ± 11 |
| 2,3,7,8-TCDF | 88 ± 6 | 75 ± 8 |
| 2,3,4,7,8-PeCDF | 86 ± 4 | 70 ± 6 |
| 1,2,3,4,7,8-HxCDF | 98 ± 3 | 91 ± 5 |
| 1,2,3,6,7,8-HxCDF | 93 ± 4 | 91 ± 6 |
| 2,3,4,6,7,8-HxCDF | 100 ± 3 | 90 ± 6 |
| 1,2,3,4,6,7,8-HpCDF | 93 ± 6 | 71 ± 8 |
| OCDF | 68 ± 9 | 62 ± 9 |

Table 2. Mean recoveries and relative standard deviation of EN-1948 ES in 24 iron ore sintering plant samples

Similar results were obtained with all the other matrices analysed: ambient air, industrial emissions and fly-ashes.

The recoveries of the automated clean-up were sometimes lower than the manual clean-up (between 10% to 15%). It could be due to reduced efficiency washing the vial and the evaporation chamber after the sample loading and after the automated concentration step, respectively.

The pattern of TCDD and HxCDF chromatograms of an iron ore sintering plant emission extract cleaned-up by the automated and the manual methods respectively are shown in Fig. 1. Significant differences between the two chromatograms were not found, which indicates the capability of the new automated procedure. The peaks are well resolved and not interferences are present that can disturb the analysis.

Similar results were obtained with all the congeners in the matrix analysed: ambient air, fly ashes, industrial emissions.

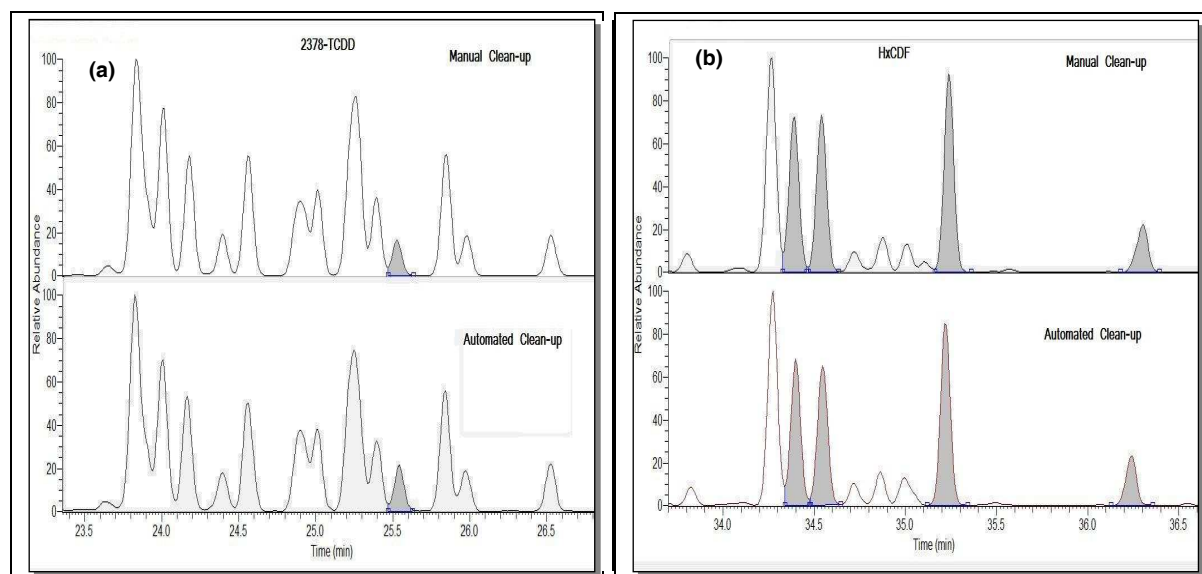


Fig. 1. Comparison of HRGC-HRMS chromatograms of (a) 2378-TCDD (m/z : 321,894) and of (b) HxCDF (m/z : 373,821) of an iron ore sintering plant emission extract cleaned-up by manual method and automated method

J2 Scientific provided the possibility to couple several SPE modules to the Accuprep. Our goal is to obtain a completely automated system for PCDD/Fs purification, able to send the concentrated pre-purified sample directly to the alumina column. Moreover, another SPE tube could be filled with acidic silica in order to process samples with a high organic content before the GPC/alumina combined clean-up.

Conclusions

The GPC/alumina purification is an economic system, as it needs a few consumables: the GPC column is the same for hundreds of samples and the alumina microcolumn is one for each sample. Moreover, the automated evaporation step is on-line: this allows a minor exposure of the operator to toxic solvents. It can be considered a good time-saving clean-up system, able to satisfy the criteria request by the European reference methods.

References

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