

On-line GPC/carbon clean-up method for determination of PCDD/F in sediment and sewage sludge samples.

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Introduction

Gel permeation chromatography (GPC) combined with silica gel column chromatography is a widely used clean-up method for multi residue analysis of food stuff¹. GPC followed by either alumina and Florisil² or activated charcoal³ is also used for the clean-up of marine fat samples for PCDD/F determination.

GPC is not only able to remove high molecular compounds but also sulphur from the PCDD/F, PCB and pesticide fraction¹. Therefore, the combination of GPC and carbon column should be very suitable for the clean-up of sulphur containing sediment and sewage sludge samples.

The sample matrix in sewage sludge samples is normally difficult to remove with conventional multi column chromatography⁴ (MCC) based on a modified version according to Smith et. al.⁵. For such samples it is often necessary to treat the raw extracts with two extra steps using sulphuric acid and metallic mercury to remove oxidizable organic compounds and sulphur. Despite this additional clean-up which makes the MCC procedure work intensive, satisfactory results are not always obtained.

Therefore an on-line GPC/carbon system was applied to such samples. The results are compared to those of the conventional MCC method and the benefits of the alternative method are discussed.

Experimental

The sediment or sewage sludge sample was dried at 50° C for about 24 h. A ¹³C internal standard mixture is added to 25 g of sample. After soxhlet extraction with toluene for about 24 h the sample was divided into two aliquots and treated with one of the methods described below.

The on-line GPC/carbon clean-up system is shown in Figure 1. It consists of a HPLC pump (Constametric-III) and an injector system with a 10 ml loop (Omnifit) connected to a glass column (Omnifit) filled with 50g Bio Beads S-X3 (GPC column). The outlet of the GPC column is either connected to "waste" or to a small glass column filled

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with 50 mg activated charcoal (Andersen Development Comp. AX21) suspended on glass fibres (carbon column). The fittings, tubing and valves (Omnifit) are made from Teflon or Tefzal.

5 ml raw extract dissolved in cyclohexane/ethylacetate (CH/EA) is injected and transferred to the GPC column (solvent flow 5 ml/min). The first fraction of 100 ml of CH/EA containing the high molecular sample fraction is discarded. Then, the GPC column is connected to the carbon column for 15 min (= 75 ml eluent) to transfer the PCDD/F, PCB and pesticide fraction. Afterwards the GPC column is disconnected again, and sulphur or other late eluting compounds are washed out with 250 ml of CH/EA.

The carbon column is first washed with 75 ml of CH/EA and 50 ml of dichloromethane/methanol/benzene 75+20+5 (solvent B in Figure 1). This fraction contains the chlorinated pesticides and most of the PCB. PCDD/F and nonortho PCB are eluted in reversed flow direction with 50 ml of toluene. The carbon column is rinsed with 100 ml of toluene, dichloromethane and methanol in reversed flow direction. The whole system is equilibrated with 200 ml of CH/EA before the next sample is injected.

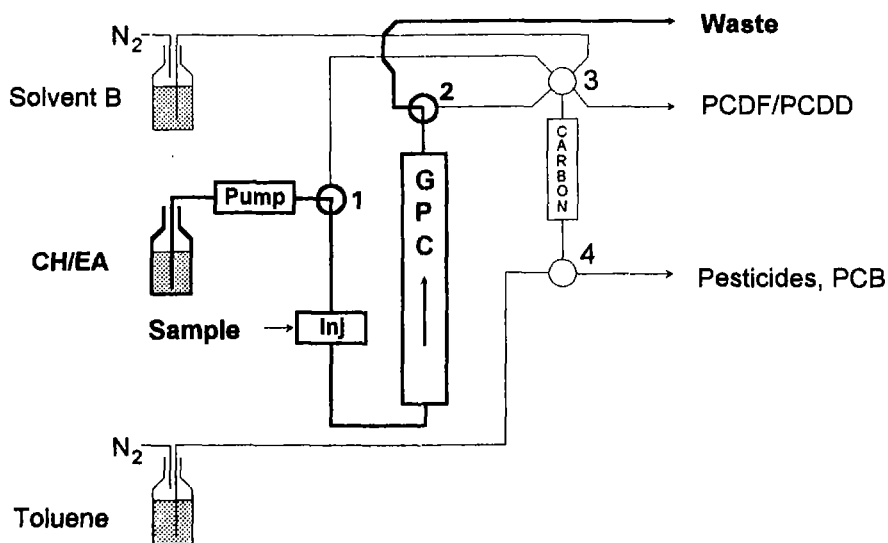


Figure 1
On-line GPC/carbon clean-up system.

The multi column chromatography method described earlier⁴ (MCC) consists of chromatography on first silica and potassium silica, second silica and potassium

silica and third activated charcoal. For sediment and sewage sludge samples this method requires a preceding treatment of the raw extract with sulphuric acid and a sulphur removal step with metallic mercury.

The final clean-up of the sample is done on two Pasteur pipettes, the first filled with sulphuric acid coated silica gel and the second with alumina⁴.

Before quantification with GC/HRMS the sample is spiked with a ¹³C recovery standard. After splitless injection the sample is separated on a 30m x 0,22mm x 0,12µm Rt_x-2330 GC column and quantified on a VG AutoSpec mass spectrometer at resolution 10000.

Results and Discussion

For comparison of the on-line GPC/carbon system with our well-established multi column chromatographic (MCC) method (controlled frequently with intercalibrations) we analysed identical samples in parallel with both clean-up methods. To avoid deviations resulting from sample inhomogenities or different extraction efficiencies the samples were divided after extraction. Some of the results of this comparison are shown in Table 1.

Table 1: Comparison of the GPC/carbon and the conventional MCC method for selected samples.

Compound	Blank	Sew. sludge 1		Sew. sludge 2		Sew. sludge 3		Sediment	
	GPC pg/g	GPC pg/g	MCC pg/g	GPC pg/g	MCC pg/g	GPC pg/g	MCC pg/g	GPC pg/g	MCC pg/g
2378-TCDD	<0,1	1,05	1,06	1,03	0,96	0,37	0,43	0,19	0,16
12378-PeCDD	<0,1	1,67	1,42	1,54	2,20	0,89	0,99	0,53	0,56
123478-HxCDD	<0,12	2,13	2,69	3,48	3,89	1,60	1,44	0,80	0,75
123678-HxCDD	<0,12	16,0	20,3	21,8	24,3	2,39	2,80	2,88	1,83
123789-HxCDD	<0,12	16,2	11,9	9,12	7,65	2,40	2,93	1,26	1,53
1234678-HpCDD	0,71	413	507	791	923	49,9	50,1	57,6	31,5
OCDD	6,62	4823	5898	6744	6978	332	324	362	189
2378-TCDF	<0,1	17,5	20,6	8,04	6,72	4,24	4,06	1,49	1,11
12378/12348-PeCDF	<0,1	2,19	3,39	4,67	5,17	3,09	3,11	1,20	0,77
23478-PeCDF	<0,1	3,73	4,58	3,73	4,78	2,80	3,14	1,08	1,08
123478/123479-HxCDF	<0,12	4,44	6,59	6,30	7,86	4,26	4,86	1,74	1,81
123678-HxCDF	<0,12	3,12	4,23	3,30	3,39	2,98	3,35	1,25	1,36
123789-HxCDF	<0,12	0,29	0,11	0,44	0,38	0,22	0,38	0,12	<0,4
234678-HxCDF	<0,12	6,37	5,04	4,33	3,97	2,92	4,00	0,89	1,28
1234678-HpCDF	0,29	63,2	n. q.	76,6	87,2	14,2	14,4	13,5	10,2
1234789-HpCDF	<0,14	0,76	n. q.	3,74	5,51	1,68	1,79	1,57	2,22
OCDF	<0,4	293	n. q.	834	996	43,5	42,1	63,0	44,5
i-TE		20,4	23,3	25,7	28,7	5,49	6,07	3,25	2,71

n. q.: not quantified due to adsorption to the GC column, i-TE: Sum of 2378-TCDD-equivalents according to the international model.

The sewage sludge sample no. 1 was still fermenting just before starting the clean-up. With the conventional MCC clean-up HpCDF and OCDF were nearly lost and the

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recovery of the added ^{13}C congeners was also close to zero. For this and a series of similar samples the higher chlorinated dibenzofurans were heavily adsorbed both to the glass liner and glass wool of the GC injector and to the GC column. These problems were caused by not removed sample residues. The GC column was permanently damaged after injection of 5 to 6 of such samples.

The same sample pretreated with the GPC/carbon method showed no adsorption of HpCDF and OCDF. The recovery of ^{13}C congeners was satisfactory (40-95%), and the conformity of the results from both methods was within the documented precision of PCDD/F quantification (about 10-15%).

The two methods were compared further using sludge samples of different origin. As can be seen from Table 1 the agreement was very satisfactory for most congeners including HpCDF and OCDF. Only the material sedimented from the run-off water of a landfill showed some variations for the hexa to octa-chloro dibenzo-p-dioxins. These deviations might have been caused by lower recovery rates due to repeated treatment with sulphuric acid and metallic mercury before the MCC method.

The blank values of the GPC/carbon method are equal to the detection limits of the single congeners with exception of HpCDD, OCDD and 1,2,3,4,6,7,8-HpCDF. For these congeners blanks were at least 25 times below the levels found in real samples. With the described washing routine between each sample no measurable carry over was observed.

Conclusions

The analysis of sewage sludge and sediment with the GPC/carbon and the established multi column method gave comparable results. However, the GPC/carbon method removes the sample matrix more complete. The clean-up takes only 3-4 hours compared to 12-16 hours for the MCC method with the described additional clean-up step. The decreased analysis time and reduced solvent consumption are strong arguments to use the described method.

References

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