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Short Communication

Solid-phase trapping of polychlorinated biphenyls in supercritical fluid extraction

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Abstract

A method for the interference-free analysis determination of polychlorinated biphenyl (PCB) congeners in sewage sludge in less than 2 h with quantification limits down to 10–20 ppb (w/w) is presented. Evaluations were made of four different trapping materials for the supercritical fluid extraction of PCBs from sewage sludge. The influence of modifiers at different concentrations and temperatures was studied for different trapping materials with respect to their trapping efficiency with spiked samples.

1. Introduction

The improper use and disposal of commercial materials containing polychlorinated biphenyls (PCBs) has resulted in the contamination of the environment with these compounds. The monitoring of PCBs in environmental, technical and biological samples is incorporated in the legislation of all developed countries. The determination of PCBs at trace levels requires efficient extraction methods and extensive clean-up procedures to remove interferences contributed by the matrix.

Recent studies have demonstrated that the use of supercritical fluids in analytical extraction provides a powerful alternative to traditional liquid extraction methods (reviewed by King [1] and Hawthorne [2]). Apart from the concern that PCBs must be extractable from their matrix, the system being used to trap the PCBs after the supercritical fluid extraction (SFE) must perform efficiently. Until recently, the most popular trapping technique was liquid collection. Most SFE experiments have been carried out at high concentration levels (ppm), mainly with artificially fortified samples, which allowed the direct analysis of the extract without clean-up [1–4]. Real samples contaminated at trace levels require a high degree of extract concentration before analysis. Although SFE can be carried out with some selectivity, real samples produce extracts with residues of matrix components that inevitably end up in the concentrated extracts after liquid collection unless clean-up is performed.

More recently, SFE extracts have been collected on sorbents such as silica gel or bonded-phase packings and then eluted with liquid solvents for subsequent analysis [5–10]. The packing material provides two trapping mecha-

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nisms (cryogenic trapping caused by the cooling of the expanding supercritical fluid and absorption) and a clean-up mechanism (liquid chromatography in the elution phase). Solid-phase trapping is more complex than liquid collection and requires a high degree of optimization of the experimental conditions (choice of trapping material, supercritical fluid modifier, trapping temperature and elution solvent). However, it potentially allows the simultaneous extraction, clean-up and concentration of the extract.

The aim of this study was the evaluation of the selective extraction of PCBs from sewage sludge. The impact of added modifiers was investigated with respect to the efficiency of trapping PCBs on different trapping materials.

2. Experimental

2.1. Chemicals

PCBs and certified sewage sludge (CRM 392) were obtained from the Community Bureau of Reference (BCR) (Brussels, Belgium). PCBs (IUPAC Nos. 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170 and 180), received as neat crystals, were mixed in a spiking solution at concentrations from 5.0 to 17.2 ng/μl. The solvents used were all of pesticide grade (Merck, Darmstadt, Germany). The CO_2- and methanol (MeOH)-modified extraction fluids were all obtained as SFE/SFC grade from SIAD (Milan, Italy). The ethanol (EtOH)-modified extractions were performed by adding absolute ethanol directly to the extraction cells.

2.2. Supercritical fluid extraction

A Hewlett-Packard Model 7680A supercritical fluid extractor was used for all the work presented.

For spike extractions, 50 μl of the spiking solution were added to 10 g of anhydrous Na_2SO_4, giving concentrations of the single PCB congeners from 25 to 86 ppb. Extractions were performed with a number of different modifier concentrations (CO_2, CO_2 + 2% MeOH, CO_2 + 5% MeOH and CO_2 + 2% EtOH) and trap temperatures (20, 65 and 78°C) at a density of 0.75 g/ml and a flow-rate of 1 ml/min liquid CO_2 for 30 min at 60°C. The nozzle temperature was kept at 45°C. The traps were filled with *ca.* 1 ml of trapping material, *i.e.*, 100-μm stainless-steel beads, 30-μm octadecyl-functionalized silica gel (ODS, Hypersil), silica gel 60 (230–400 US mesh) or Florisil (60–100 US mesh, 0.16–0.25 mm). They were eluted with 2 × 1.5 ml of *n*-heptane and 50 μl of internal standard solution (PCBs 35 and 169 at 21.6 and 4.3 ng/μl, respectively) were added and the final volume adjusted to 1.8 ml with *n*-heptane, giving internal standard concentrations of *ca.* 600 pg/μl for PCB 35 and *ca.* 120 pg/μl for PCB 169.

Sewage sludge extractions were made as follows: 1-g portions of sewage sludge were mixed with 9 g of anhydrous Na_2SO_4 and packed into 7-ml extraction cells. Extractions were performed as for the spiked samples using pure CO_2 and a trap temperature of 20°C. The traps were eluted with 2 × 1.5 ml of *n*-heptane, then 1 × 1.5 ml of methanol, followed by 2 × 1.5 ml of *n*-heptane. After extraction, the final volume was adjusted to 1.8 ml with *n*-heptane.

2.3. Dual-column gas chromatography

The extracts were analysed using a pressure-controlled Hewlett-Packard (HP) Model 5890 II gas chromatograph equipped with two ^{63}Ni electron-capture detectors and an HP Model 7673A autosampler. Aliquots (1 μl) of the extracts were injected on-column into two parallel-coupled columns, a 60 m × 0.25 mm I.D. 50% diphenyl–dimethylsiloxane DB-17 (0.25 μm) column (J&W Scientific) and a series combination of a 25 m × 0.25 mm I.D. 5% diphenyl–dimethylsiloxane SIL-8 column (0.25 μm) (Chrompack) and a 25 m × 0.22 mm I.D. 1,7-dicarba-*closo*-dodecarborane dimethylpolysiloxane HT-5 (0.10 μm) column (Scientific Glass Engineering). The columns were installed in the GC oven together with a 2 m × 0.53 mm I.D. fused-silica retention gap using a quick-seal glass T. The GC column oven programme was as follows: initial temperature 90°C, held for 2 min,

then increased at 20°C/min to 170°C, held for 7.5 min, then increased at 3°C/min to 280°C, which was held for 10 min. The hydrogen flow-rate was 43.5 cm/s, held constant by the pressure-controlled inlet throughout the whole temperature programme. This choice of columns and GC conditions has been shown to give optimum separations of PCB congeners [11,12].

2.4. Soxhlet extraction

Aliquots of 1 g of certified sewage sludge were mixed with 9 g of anhydrous Na_2SO_4 and extracted with *n*-hexane–acetone (1:1) for 18 h. The extracts were loaded on a 15 cm × 6 mm I.D. column with activated silica impregnated with 40% (w/w) concentrated sulphuric acid and eluted with 50 ml of *n*-hexane. The extracts were evaporated to dryness and the residues were dissolved in 1.8 ml of iso-octane.

3. Results and discussion

3.1. Performance of the different trap sorbents with various modifier concentrations and trapping temperatures

The importance of the trapping temperature in relation to the modifier concentration has been studied recently by Mulcahey and co-workers [5,7]. Using a broad range of chemical compounds representing various degrees of volatility and polarity, they came to the conclusion that with pure CO_2 as the supercritical fluid, the trapping efficiency is almost unaffected by the trapping temperature. However, with increasing concentrations of methanol as modifier in the supercritical fluid CO_2, the trapping needs to be optimized for a sufficient trapping efficiency. For PCBs, little work has been published on the trapping efficiency as a function of the trapping conditions [5,8,10]. It was therefore decided to investigate the performance of different trap sorbents with various modifier concentrations and trap temperatures. To focus on the trapping mechanism, this study was undertaken with spiked Na_2SO_4, which does not pose any difficulties in the extraction of PCBs [10]. The trapping was carried out below or at the boiling point of the modifier. The results are given for the different trap sorbents in Tables 1–4.

It is evident that with pure CO_2 as the supercritical fluid all trapping materials provide quantitative trapping efficiencies.

When methanol or ethanol is added at a level of 2%, only Florisil and ODS give *ca.* 100% recoveries at the two trapping temperatures for all twelve PCB congeners. Silica has problems with the lower chlorinated PCBs. Stainless-steel works unsatisfactorily below the boiling point of the modifier for all twelve PCB congeners and has problems with lower chlorinated PCBs when the trapping is carried out at the boiling point of the modifier.

When the modifier concentration is increased to 5%, none of the trap sorbents produce satisfactory results at temperatures below the boiling point of the modifier. The mean recoveries are in the range 18–34% and for lower chlorinated PCBs as low as 2%. At this combination of high modifier concentration and low trapping temperature, liquid methanol is formed in the trap during the expansion of the supercritical CO_2, which mechanically rinses (elutes) the trapped PCBs into the waste bottle [5,7]. Residues of liquid methanol are even seen in the final extract after elution with *n*-heptane. The formation of liquid methanol is avoided when the trapping temperature is raised to the boiling point of the modifier. However, this may lead to the loss of the lower chlorinated PCBs, which are more volatile, as is clearly seen for silica and stainless steel. Only ODS and florisil produce quantitative trapping efficiencies at a 5% modifier concentration. Whether this is attributable to chemical interactions between the Florisil and ODS sorbents and the PCBs or to the mechanical properties of the sorbent surface remains unclear.

3.2. Performance of the different trap sorbents in SFE of sewage sludge

For the realistic evaluation of the solid-phase trapping of PCBs in SFE, a complicated matrix, contaminated at trace levels, was chosen. BCR

Table 1
SFE recovery of spiked samples on an ODS trap

PCB	CO_2 (20°C)		CO_2 + 2% MeOH				CO_2 + 5% MeOH				CO_2 + 2% EtOH			
			20°C		65°C		20°C		65°C		20°C		78°C	
	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)
28	103	3	81	2	100	1	10	4	94	1	96	5	94	2
52	101	1	86	4	102	2	15	5	99	1	91	4	99	3
101	100	1	91	4	100	1	19	5	100	2	94	3	100	4
105	100	1	94	4	103	1	16	5	100	1	95	1	96	3
118	99	1	93	4	100	1	19	5	99	1	97	1	97	2
128	98	1	92	5	100	1	18	5	100	1	89	6	99	2
138	100	1	91	5	101	1	19	5	101	2	94	2	100	3
149	100	1	92	5	101	2	20	5	100	1	91	5	100	3
153	99	1	92	5	100	1	22	5	100	1	96	2	101	4
156	99	1	94	5	102	1	20	5	99	1	101	2	99	4
170	98	1	93	5	100	1	21	5	99	1	96	2	100	3
180	98	1	92	6	101	1	22	4	100	1	101	1	101	4
Mean	100	1	91	5	101	1	18	5	99	1	95	3	99	3

S.D. = standard deviation ($n = 4$).

Table 2
SFE recovery of spiked samples on a Florisil trap

PCB	CO_2 (20°C)[a]		CO_2 + 2% MeOH				CO_2 + 5% MeOH				CO_2 + 2% EtOH			
			20°C[a]		65°C[a]		20°C[a]		65°C		20°C		78°C	
	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)
28	98	3	108	3	115	4	31	13	106	2	100	30	93	5
52	96	5	103	3	111	3	34	13	102	1	100	25	96	4
101	96	6	101	3	109	3	35	12	101	3	95	14	97	3
105	97	4	104	3	112	4	33	12	104	3	94	9	94	3
118	97	5	100	3	107	3	34	12	101	4	93	9	96	4
128	96	5	107	4	116	4	34	13	100	5	92	8	92	4
138	96	5	100	3	108	4	34	11	101	3	93	6	98	4
149	96	6	101	3	107	3	35	12	101	4	94	8	97	3
153	97	5	100	3	107	3	36	11	101	3	93	8	98	4
156	97	4	99	3	108	4	34	11	101	3	92	7	96	4
170	96	6	102	3	111	4	36	11	101	5	92	7	98	5
180	97	5	100	3	108	4	35	11	100	4	92	7	97	3
Mean	97	5	102	3	110	4	34	12	102	3	94	12	96	4

S.D. = standard deviation ($n = 4$).
[a] Calculated without the use of internal standard.

Table 3
SFE recovery of spiked samples on a silica trap

PCB	CO_2 (20°C)		CO_2 + 2% MeOH				CO_2 + 5% MeOH				CO_2 + 2% EtOH			
			20°C		65°C		20°C		65°C		20°C		78°C	
	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)
28	104	1	83	6	76	3	7	5	21	9	73	8	77	1
52	103	1	82	5	83	3	9	7	35	6	82	5	91	2
101	101	1	93	3	92	2	14	9	63	3	90	2	97	1
105	101	1	100	1	98	1	14	9	64	6	92	5	93	3
118	102	1	100	1	96	1	18	11	67	5	91	3	94	1
128	101	1	96	1	95	1	14	9	68	6	93	3	100	1
138	101	2	96	2	93	2	18	11	70	5	94	3	101	1
149	101	1	93	3	91	2	16	10	72	6	94	1	103	1
153	101	1	97	1	93	1	24	13	72	4	94	1	102	1
156	101	2	102	2	98	1	25	13	71	4	96	5	98	1
170	101	1	99	1	94	1	27	12	72	5	95	2	103	1
180	102	1	100	2	94	1	32	14	74	3	97	3	103	1
Mean	102	1	95	2	92	2	18	10	62	5	91	3	97	1

S.D. = standard deviation ($n = 4$).

Table 4
SFE recovery of spiked samples on stainless steel trap

PCB	CO_2 (20°C)		CO_2 + 2% MeOH				CO_2 + 5% MeOH				CO_2 + 2% EtOH			
			20°C		65°C		20°C		65°C		20°C		78°C	
	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)
28	101	4	35	8	28	4	2	3	7	2	68	25	38	8
52	99	2	40	7	60	5	7	4	29	6	77	23	66	12
101	97	3	40	7	92	1	20	14	80	18	77	23	82	14
105	94	5	38	8	98	2	24	17	91	9	70	24	79	14
118	95	4	40	8	98	3	26	18	92	12	74	24	81	15
128	95	4	38	8	93	3	26	18	95	8	75	24	87	14
138	94	4	38	8	91	2	27	18	94	8	76	23	87	15
149	96	3	40	7	90	1	28	18	92	10	78	21	88	14
153	95	3	40	7	92	2	28	18	94	9	77	22	87	14
156	96	4	40	8	98	1	27	17	97	8	74	25	88	16
170	94	3	39	7	92	2	30	16	97	7	78	23	91	13
180	94	3	39	8	93	1	29	17	96	6	77	23	91	14
Mean	96	4	39	8	85	2	23	15	80	9	75	23	80	14

S.D. = standard deviation ($n = 4$).

certified sewage sludge (CRM 392) has previously been demonstrated to pose problems in the extraction phase [14]. This material contains PCBs at ppb levels (Table 5) and a broad range of interfering compounds such as lipids, surfactants and mineral oil.

David *et al.* [15] have recently demonstrated the potential of SFE (under mild conditions) for the simultaneous extraction and clean-up of PCBs in sewage sludge using ODS traps. In order to extend the scope of this anlysis, extractions were performed on all four sorbents used above. Chromatograms (SIL-8–HT-5) for eluates after SFE of sewage sludge with trapping on (A) silica and (B) Florisil are compared with (C) the cleaned-up Soxhlet extract in Fig. 1. All possible interfering compounds are marked with asterisks. It is evident that Florisil produces eluates (extracts) with less interference from matrix components in the sludge than silica. The stainless-steel traps produced eluates comparable to silica (data not shown), and it can be concluded that these two trapping materials are unsuitable for the direct analysis of sewage sludge SFE eluates. Compared with the cleaned-up Soxhlet extract, the Florisil eluate still contains some non-PCB components. However, any potential interference is separated by dual-column GC from the target PCBs. The ODS eluates were comparable to those with Florisil (data not shown).

In Table 5, the SFE recovery of endogenous PCBs from sewage sludge is compared with that given by Soxhlet extraction. The results were obtained by comparing peak heights on SIL-8–HT-5 and controlled by comparing peak heights on DB-17. The recoveries by Soxhlet extraction were normalized to 100%. It appears from Table 5 that SFE produces PCB recoveries as high as Soxhlet extraction. No significant difference is observed between the mean results and the mean standard deviation is of the order of 3–5%. No

Table 5
SFE Recovery of PCBs from sewage sludge compared with Soxhlet extraction

PCB	Florisil[a]		ODS[a]		Soxhlet[b]		Certified value[c]	
	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Recovery (%)	S.D. (%)	Concentration (ng/g)	S.D. (ng/g)
28	120	26	100	4	100	5	100	20
52	112	12	105	2	100	4	78	16
101	98	3	100	3	100	3	134	21
105	100	4	101	4	100	3	–	–
118	97	2	100	4	100	4	97	21
128	101	2	106	2	100	5	–	–
138	100	2	104	3	100	4	[d]	–
149	100	2	102	1	100	3	–	–
153	99	1	103	3	100	5	288	36
156	100	3	103	3	100	2	–	–
170	106	2	108	2	100	5	–	–
174	101	3	103	2	100	3	–	–
180	101	1	104	4	100	4	313	49
194	112	5	109	3	100	4	–	–
199	105	3	107	3	100	3	–	–
Mean	103	5	104	3	100	4		

Samples extracted for 18 h in hexane–acetone (1:1). All mean values in Soxhlet set to 100%.
[a] Mean values of 3 replicates.
[b] Standard deviation of mean values of 3 replicates.
[c] Values not indicated are in the range 10–300 ng/g.
[d] Certified value for PCB 138 withdrawn because of a *ca.* 30% interference from PCB 163 [13].

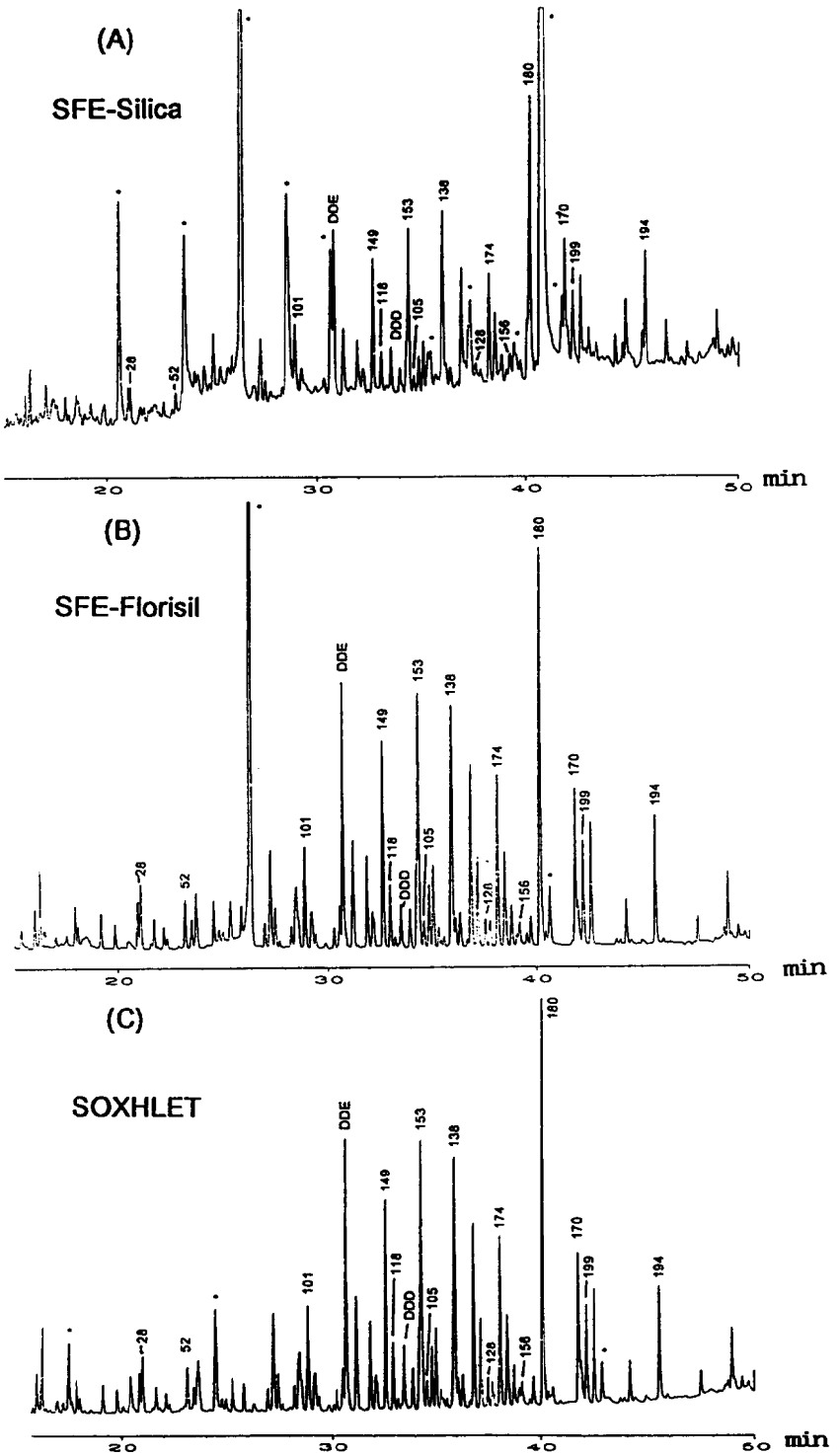

Fig. 1. GC–ECD (SIL-8–HT-5) of (A) raw extract from SFE with silica, (B) raw extract from SFE with Florisil and (C) cleaned-up extract from Soxhlet extraction.

difference is observed for mean recoveries between the two trapping materials Florisil and ODS in SFE. Only PCBs 28 and 52 gave slightly higher results for Florisil (112–120%). This was due to a single high result, probably caused by a dirty GC injection port. If this result is disregarded, the recovery of PCBs 28 and 52 on Florisil is decreased to 100–105%.

Continued extraction of the sewage sludge for longer periods (1 h) or sequential extraction with 2–5% methanol as modifier did not alter the results. In fact, only interfering matrix compounds were found in the later fractions after sequential extraction (data not shown).

4. Conclusions

By choosing the appropriate extraction conditions, trap material, trap temperature and eluent, it is possible on a routine basis to perform interference-free congener-specific analysis of PCBs in sewage sludge by off-line SFE and GC with electron-capture detection (ECD). The total analysis time (from the beginning of the extraction to the end of the GC–ECD run) can be shortened to less than 2 h without any manual sample work-up between extraction and GC analysis.

For the SFE of PCBs in sewage sludge using *n*-heptane as trap eluent, it is only possible to use either Florisil or ODS (of the four sorbents tested) if a clean PCB extract is necessary. Concerning the SFE of PCBs with the help of modified CO_2 (MeOH and EtOH), less than 2% of modified should be used, preferably at a trap temperature above the boiling point of the modifier. Of the four sorbents tested, stainless steel can only be used in special cases (pure CO_2 or extraction of high-boiling PCBs with <2% of modifier). Only Florisil and ODS were able to perform satisfactorily using 5% of methanol as modifier, and then only with a trap temperature at the boiling point of methanol (65°C). Given the purity of the PCB extracts from a real sewage sludge sample, Florisil and ODS must be the sorbents of choice among the four tested, at these permit the reproducible use of modifiers. If the cost of the sorbents is taken into consideration, Florisil is the better choice, as its price is less than 10% of that of ODS.

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