

## WATER IN SUBCRITICAL CONDITION - AN EFFECTIVE SOLVENT FOR THE EXTRACTION OF DIOXINS FROM SOILS.

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### Introduction

The majority of non-thermal methods of dioxin detoxication require preliminary extraction of dioxins from natural matrices, soil in particular, using organic solvents, which significantly contributes to the cost of analysis. While making an expedient detoxication of soils from dioxins, the most economically favourable approach would be using water as a solvent. Dioxins are believed not to migrate in soil [1] because of their low solubility in water (19,3 ng/l at 22°C for 2,3,7,8-TCDD [2]). However, examinations carried out for Vietnam in cooperation with our laboratory have shown that for past 30 years after the end of the war dioxins have penetrated into 3-5 meters, and in amounts considerably exceeding these that could be dissolved in rain water.

An increase of dioxin solubility in water can be achieved by intermolecular complexation, formation of stable pseudosolutions, or by a change in the properties of the solution due to an increase temperature.

Under normal conditions, water is too polar to dissolve most of the organic pollutants. On the other hand, solubility of polycyclic aromatic hydrocarbons at 250°C is increased by 4-5 orders [3]. At this temperature, polarity and surface tension of water is similar to that of acetonitrile or methanol at room temperature, while its viscosity is threefold lower than in these solvents [4].

This work is directed toward the study of water in subcritical conditions as a possible solvent for extraction of dioxins from the contaminated soil. Other factors that favour solubility in water and transfer of dioxins in soil are investigated.

### Aqueous Extraction of Dioxins from Different Solid Matrices at Subcritical Conditions.

The materials selected for the study (sand, red clay, and black earth) contained PCDD and PCDF below detectable levels. A concentration of 0,5 - 0,8 ng/g of PCDD's was introduced to the samples. Soil samples from the contaminated regions of Vietnam with a known content of PCDD were also used. All the samples were powdered to 250 µm particles.

A special apparatus was constructed for the experiments (see Scheme 1).

A sample (20 g) is extracted with approximately 70 ml of water by required temperature. Then mixture of <sup>13</sup>C-labeled internal standards was added to the resulting water solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was purified and analysed using GC-HR-MS.

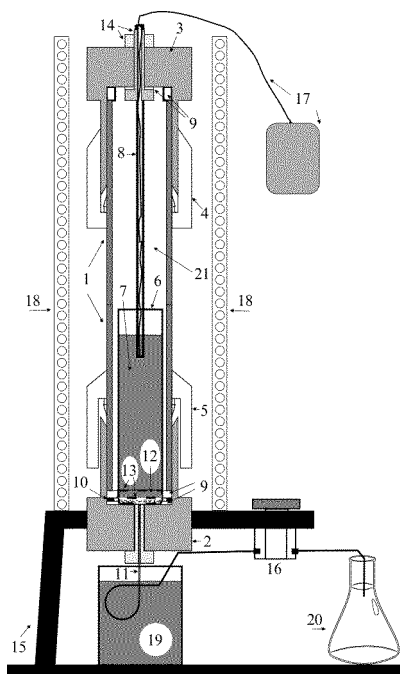


Fig. 1. Apparatus for subcritical extraction.

- 1 - Stainless column
- 2 - Bottom cap
- 3 - Upper cap
- 4 - Upper screw box
- 5 - Bottom screw box
- 6 - Cartridge for a sample
- 7 - Sample
- 8 - Tube for the thermocouple
- 9 - Teflon ring
- 10 - Metal ring
- 11 - Cooling capillary
- 12 - Quartz cotton filter
- 13 - Grid
- 14 - Device of fixing and hermeting of tube for thermocouple
- 15 - Holder
- 16 - Valve
- 17 - Thermocouple
- 18 - Furnace
- 19 - Glass with water with ice
- 20 - Flask
- 21 - Solvent (water)

## Interaction of 2,3,7,8-TCDD with Water-Soluble Compounds.

Desorption of 2,3,7,8-TCDD from the inert matrices – SiO<sub>2</sub> and highly contaminated Vietnamese soil – was studied by shaking and eluting of the solutions through an stationary phase. The following types of compounds were studied:

- Phthalocyanines, able to form strong  $\pi$ - $\pi$  bonds with different polycyclic aromatic compounds with three and more aromatic rings in their structure [5];
- Inorganic salts abundant in natural samples and potentially capable of complexation;
- Surfactants that can assist extraction PCB from soil [6].

The description of the experimental procedure is beyond the frames of this paper.

## Results and Discussion

Experimental data are presented in Table 1 and Fig. 2 and 3. The data shows that the recovery at 250°C from artificially contaminated soils was between 30-100%. For Vietnam soil samples, extraction with water was even more efficient than the extraction with hexane-methylenchlorid (1:1). It leads to the detection of the congeners with concentrations below the limit of detection for common methods of extraction.

Table 1. Results of the extraction using water at subcritical conditions

Object	t, °C	Congener	Injected <sup>1</sup> , ng	Found, ng	Recovery, %
Sand	250-260	2,3,7,8-TCDD	11,6	11,1	95,6
		1,2,3,7,8-PeCDD	11,3	9,5	83,8
		1,2,3,6,7,8-HxCDD	16,0	11,9	74,1
		OCDD	11,1	8,2	73,3
Red clay	245-265	2,3,7,8-TCDD	11,6	7,2	62,2
		1,2,3,7,8-PeCDD	11,3	8,2	72,9
		1,2,3,6,7,8-HxCDD	16,0	4,6	28,7
		OCDD	11,1	3,05	27,4
Black earth	250-270	2,3,7,8-TCDD	11,6	8,6	73,9
		1,2,3,7,8-PeCDD	11,3	12,8	113,7
		1,2,3,6,7,8-HxCDD	16,0	13,1	81,8
		OCDD	11,1	8,4	75,8
Vietnamese soil	255-295	2,3,7,8-TCDD	15,5	21,7	139,9
		1,2,3,7,8-PeCDD	0,6	1,3	212,4
		1,2,3,6,7,8-HxCDD	2,7	7,8	287,4
		OCDD	10,2	74,4	729,5

<sup>1</sup> For the Vietnamese soil it - value obtained at usual extraction by hexane-methylenchlorid (1:1).

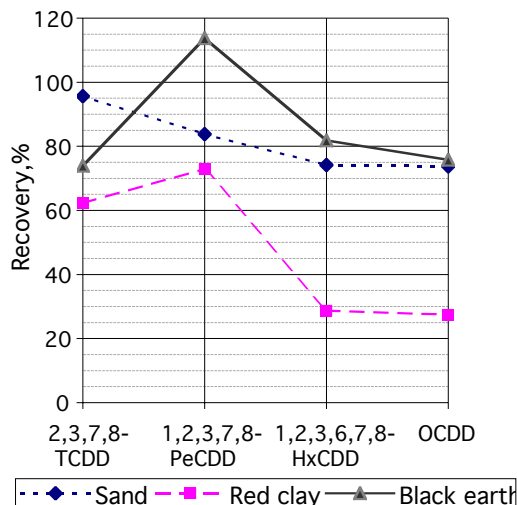


Fig. 2. PCDD's recovery by water from the spiked contaminated soils at 250°C.

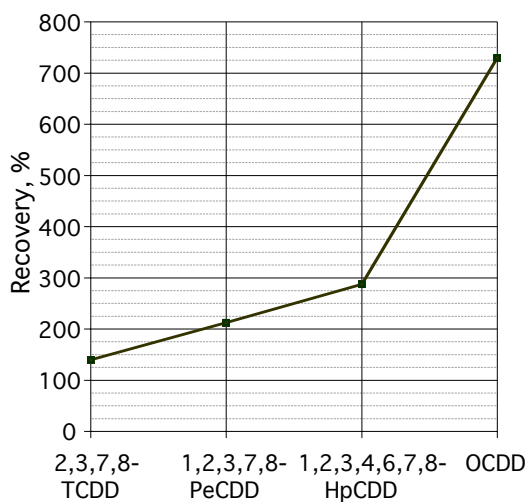


Fig. 3. PCDD's recovery by water at 250°C from contaminated Vietnam soil.

Additional experiments were carried out at low temperatures. A decrease in the temperature caused only a small decrease in the recovery. The recovery practically does not depend on the degree of chlorination. The differences in the extraction of different congeners from various soils for organic solvent extraction can be explained by the interaction with the matrix and the effect of organic impurities. In our case, the presence of organic impurities may aid in the extraction due to co-extraction.

Studying possible interactions of 2,3,7,8-TCDD with different compounds in the aqueous phase did not lead to a significant increase in the solubility (the maximal effect for the phthalocyanines is a 10-fold increase and 20-fold for metal salts; cationic, anionic, and nonionic

surfactants did not cause any detectable change). However, we found the ability of 2,3,7,8-TCDD to form stable colloidal-type solutions. This was not described before. The colloidal nature of these solutions made it possible to filter such a solution through quartz cotton filters. Quartz itself does not absorb dioxins, and only mechanical trapping of the particles is possible. The total solubility for 2,3,7,8-TCDD in distilled water was equal to 20 ng/ml, which is 3 orders higher than its true solubility. All modifications of the solution also affect the colloidal solubility.

### Conclusions

The data showed that water at subcritical conditions can be used for extraction of dioxins from different soils, and aqueous extraction was more efficient than a common extraction procedure with hexane-methylenchlorid (1:1). The maximum increase in the solubility at 250°C is 33000-fold for OCDD. This effect can be applied both for analysis and for decontamination of contaminated territories. Besides this, the increase in the solubility due to such additives can be a possible pathway of dioxin transport by thermal water.

We discovered that 2,3,7,8-TCDD formed stable colloidal solutions. Colloidal solubility in the experimental conditions exceeded the true solubility by 3 orders. Addition of different water-soluble compounds (phthalocyanines or metal salts) increased both true and colloidal solubility of dioxins. This feature may provide their mass transfer in nature. As a whole, small mobility of dioxins in soils is maximally affected by the interaction with matrix rather than by low solubility; and dioxins are capable for intermolecular interactions with organic molecules as well as with inorganic ions. Surfactants apparently cannot be used for the extraction because of their insignificant influence on the solubility of dioxins. In general, interaction of dioxins with the matrix can have a greater influence on their mobility in soil than the solubility.

The ability of 2,3,7,8-TCDD to increase its solubility by forming complexes and colloidal solutions might lead to a revision of the accepted system of estimation of the effect of dioxin-like compounds to the human organism, because, the toxicity of isomers containing the fragment of 2,3,7,8-TCDD increases with an increase in their true solubility in water [7].

### References

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