

APPLICATION OF ASE 200 EXTRACTOR FOR EXTRACTION OF PCB FROM SOIL SAMPLES

VEDRANKA HODAK-KOBASIĆ¹, Mladen Picer¹, Nena Picer¹, Tatjana Kovač¹

¹Rudjer Boskovic Institute, Zagreb

Introduction

During the recent war in Croatia, the karstic area of this country has been endangered by hazardous waste.¹ This pollution is especially dangerous because the area of the karst has very porous ground and existed the possibility of jeopardize the sources of water. Thus, the determination of toxicant levels of PCB concentration in environmental samples is of a great importance. Our group for the determining of the organic pollutants, which is for many years active in problem of pollution environment with PCBs in Croatia, has started analyzes the PCBs in the warfare-polluted area. Results of the analysis of the polychlorinated biphenyls in the soil from E.T.S. Zadar (110/35 kV) indicate significant contamination.^{2,3,4}

Until recently for extraction of PCBs and chlorinated insecticides from soil and sediment samples we have mostly used Soxhlet extraction.^{5,6}

Recently we have possibilities to use Accelerated solvent extraction (ASE) for extraction of PCBs from dry soil samples collected in vicinity of ETS Zadar. It has been described using the accelerated solvent extraction for the extraction various organic pollutants from solid samples. This method is significantly faster and in same time with significantly less solvent consumption in comparison with other methods of organic pollutants extraction.³

Dionex corporation also stressed the potential concerns about possibilities of carryover and cross-contamination for high contaminated soil.⁷

In this work, we have studied the extraction efficiency of the PCBs from soil samples and problem of « cross contamination » during using ASE apparatus for extraction PCBs of soil samples contaminated with PCBs in extremely variable levels. It has to be stressed that these soil samples were «naturally » contaminated before 12 years during rocket attack on ETS Zadar.

Methodology of Analysis

Soil samples were collected next to the transformer station Zadar – TS 110/35 kV, manually (soil 1 in depth of 0,5m, soil 2 in depth of 0,025m, soil 3 and soil 4 from surface layer) and filled into stainless steel containers. The materials to be used for the extraction studies were further dried at room temperature. The dried soils were sieved through sifter quantities of 2 mm particle size. Samples were extracted by ASE 200 extractor (Dionex, USA). A 10 g of soil was weighed in an 11 ml extraction cell. Extraction of PCB was operated at 2000 psi (14 MPa) and the oven was heated to 100 °C. When the oven reaches the set point, the vial and cell were loaded and a preheat period of 1 minute has started. At the end of preheat period, the pump was filled the cell with a mixture of hexane and acetone (1:1). Oven heat-up time was 5 minute and static step was performed in one cycle for 5 minute. After that the extract was transferred from the heated cell to a standard collection vial for cleanup and analysis. This procedure was followed with flushed of 60 % of extraction cell volume of fresh solvent. The remaining solvent was displaced with purge gas for 60 sec. Some samples were extracted three times and some no less than seven times into separate vials. We were analyzed all of the vials for target analytes. ASE 200 was extracted a 10 g sample in about 10 min with a total solvent consumption of approximately 15 ml for one extraction.

The analytical method used for the clean up of raw extracts of samples included filtration through a column of Na₂SO₄ anh. cleaning on an alumina column and the separation of the PCBs from the organochlorine insecticides on a miniature silica gel column. After concentration from 0.3 to 1 cc, elutes were analyzed by gas chromatography with ECD. During all the analytical procedures, the Mirex standard was used as the internal standard. More details of the methods have been described in numerous published papers.^{2, 8, 9}

Results and discussion

Four real samples from the area of the 110/35 kV Electro Transformer Station Zadar were used in this study (taken on different depth). The experiments were performed including the extraction of low (Soil 1) and high (Soil 2) level

contaminated soils, followed by the determination of target analytes in both extracts. After the first extraction, a second extraction was performed on the same sample and collected in separate vial; third extraction was performed on the same way. This process was repeated with all samples. As can be seen in Fig.1 to achieve good recovery it is enough the every sample extracts thrice. For the purpose of achieving the completeness of the recoveries some remained analytes in soil 3 and soil 4 were extracted for more than three times.

Based on the results of the analysis it can be claimed that more than three extractions of the same sample did not result in significantly higher recovery (only 1 to 2%). ASE is an exhaustive extraction technique, and when quantitative extraction occurs, no analytes are left in the sample for subsequent extractions.

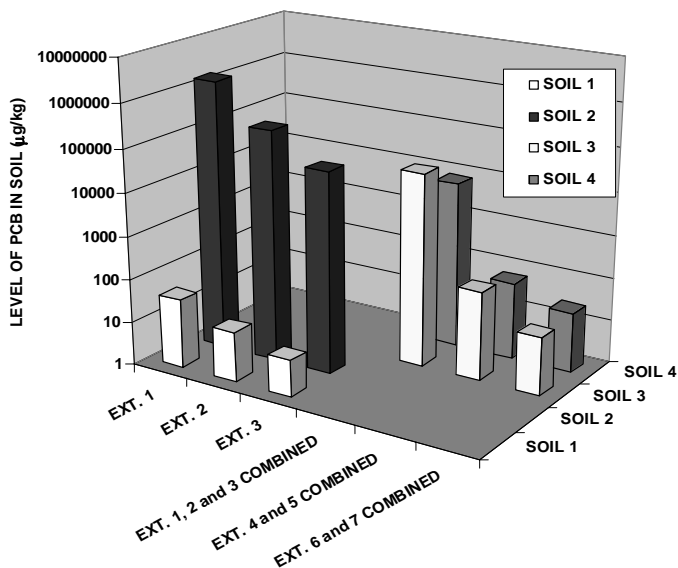


Figure 1. PCB recoveries in soils by ASE

Efficiency of extractions of soil samples using ASE 200 extractor is shown in Table 1. In these experiments the total PCB counts of the first extract were compared to those of the second and third. Also three extracts of the soil 3 and the

soil 4 were combined and compared with the 4th and 5th combined extracts and 6th and 7th combined extracts of the same sample.

Table 1. Efficiency of extractions of soil samples using ASE 200 extractor

ASE EXTRACTIONS	SOIL 1 (%)	SOIL 2 (%)	SOIL 3 (%)	SOIL 4 (%)
EXT. 1	65,11	86,26		
EXT. 2	23,63	11,41		
EXT. 3	11,26	2,33		
EXT. 1, 2 and 3 COMBINED			99,53	98,82
EXT. 4 and 5 COMBINED			0,39	0,84
EXT. 6 and 7 COMBINED			0,07	0,34

This table shows the percentages of efficiency of every single extraction for PCB congener content of these matrices. In according to results were showed that a significant level of target analytes existed in first extract (recoveries were 65 to 85%) in the comparison of second (obtained recoveries were 10 to 20%) extract. Residual amount of PCB found in a third extract of the same sample was generally less than 10%.

The experiments on the high contaminated soils were performed to determine if any material remained and was not completely flushed from the extraction cell. ASE 200 extracted two samples of soil. The concentration of one sample in the cell 4 was about 52 000 ppm and the concentration of other sample in the cell 7 was about 131 584 ppm expressed as the equivalents of Aroclor 1254. After the extraction, the samples were removed and cells were cleaned. Cell bodies were cleaned on the high temperature, but the caps cannot be cleaned by high temperature heating. Thus the end caps were disassembled, soaked in solvents (hexane and acetone) and sonicated. After this were made blank of these cells by ASE 200.

Extractions were performed on the empty cells using the same conditions. Extract of the blank was concentrated to 1 ml and analyzed by GC with ECD. The results of blank extraction in cells 4 and 7 are illustrated in Fig. 2. by the assumption that their was 10 g of the sample. Concentration of the analytes ranged from 8 ppm to 0.1 ppm for cell 4 and 17.5 ppm to 0.5 ppm for cell 7.

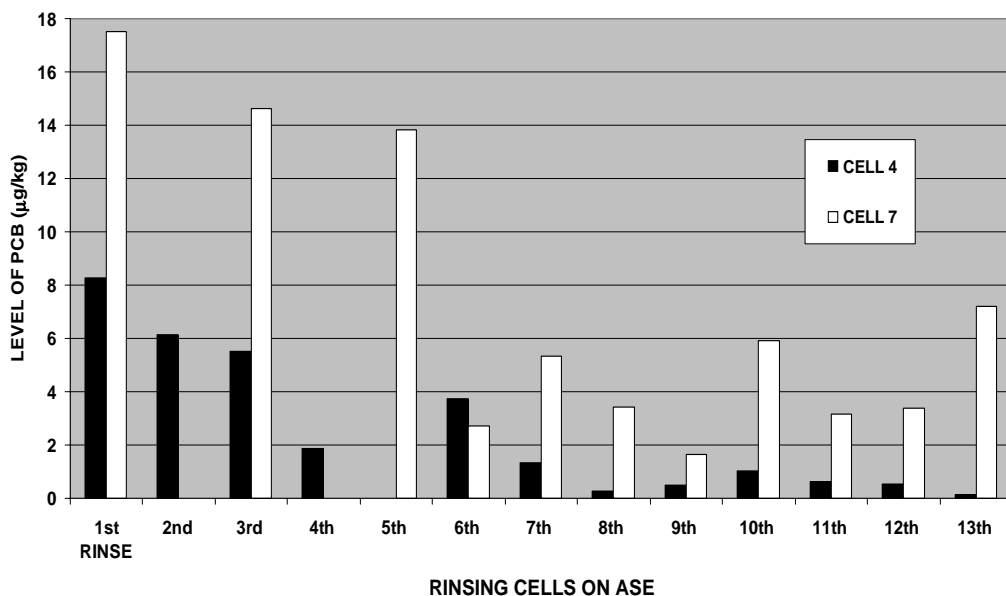


Figure 2. Testing of purities of contaminated cells on ASE 200 extractor

Results of the analysis of residual PCB in other ten cells indicated lower contamination than blank extraction in cells 4 and 7. Even through the levels of PCB in this investigated cells were not so alarming for all cells, accept for cells 5, 9 and 10 (concentration of the analytes ranged from 4 ppm to 1,5 ppm), they should not be ignored considering the acceptable blank. The results of blank extraction in other cells are shown in Fig.3.

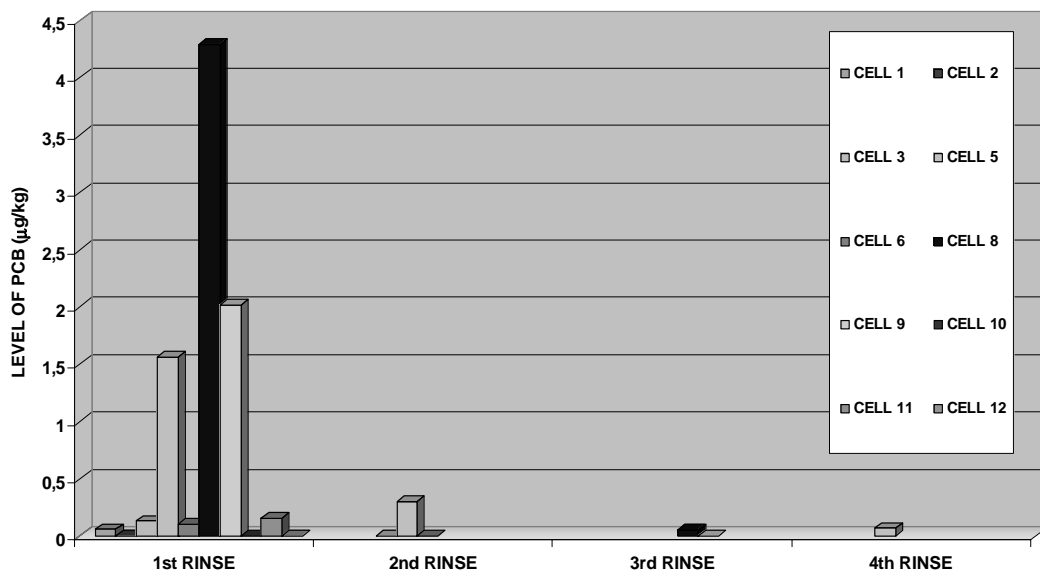


Figure 3. Testing of purities of contaminated cells on ASE 200 extractor

An obtained result shows that a significant level of carryover exists and therefore was the problem of interoperating between the sample and parts of cells. The impurity levels of these cells were exceeding an acceptable blank, and the need for additional clean-up must be done. Determined amount of PCBs were detected in all rinsed extracts. This indicates that the lines of cells are not cleaned out well after extraction. Previous described way for cleaning the cell is not adequate. Thereupon cells were multiple rinsed with mix of acetone and hexane on ASE 200 extractor to the complete purity. In order to achieve acceptable blank cells 4 and 7 were rinsed even 13 times and more.

Conclusion

Recoveries using ASE extraction were in all soil samples satisfactory. It is enough three extraction of every sample for getting a high recovery. ASE produced recoveries over 90%. Some advantages of ASE are saving in the time, solvent

usage and labors. The obtained results show that a significant level of carryover exists and therefore was the problem of interoperating among the samples and parts of cells. The impurity levels of these cells were exceeding an acceptable blank, and the need for additional clean-up must be done.

Acknowledgements

The authors express their gratitude to the Ministry for Science and technology of Republic Croatia for financial support. This work has been carried out as part of the Contract ICA2- CT-2002-10007 (APOPSBAL) between the European Commission and Rudjer Boskovic Institute, Zagreb, Croatia

References

1. Picer, M., Picer, N., (1998) Croatian Water Management 7, No. 73, 10.
2. Picer, M., (2000) Croatica Chemica Acta 73, 123.
3. Richter, B., Ezzell, J., Felix, D., (1994) Document 101124, Dionex Corporation.
4. Picer, M., Picer, N., (2003) Periodicum Biologorum 105, No 3, 345-354.
5. Picer, M., Picer, N., (1991) Bull. Environ. Contam. Toxicol., 47, 864-873.
6. Picer, N., Picer, M., (1992). Wat. Res. 26, 899-909.
7. Tehnical note 207, (1996). Dionex Corporation
8. Picer, M., Ahel M., (1978), J. Chromatogr. 150, 119.
9. Picer, M., Picer, N.,(1993): Water, Air and Soil Pollut., 68, 435.