VALIDATION METHOD FOR DETERMINATION OF PCB CONGENERS IN SOIL USING GC-MS

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Abstract
Polychlorinated biphenyls (PCBs) are the most highly toxic species of POPs. More than 200 PCB congeners exist in nature. [1] PCBs are highly toxic for humans. They enter the human body *via* inhalation, ingestion or sorption through the skin and the bloodstream transports them to the organs, muscles and adipose tissues, where they are accumulated. This study presents the validation of analytical method for determination of 7 PCBs congeners in soil: PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, and PCB 180. The method is based on solid-liquid extraction with cyclohexane and the analysis by gas chromatography with mass spectrometric detection (GC-MS). [2] Samples were analyzed in SIM mode, and the analytes qualitative confirmation was performed comparing the mass spectra of analytical standards of PCB congeners with the NIST data base. The method developed can be applied in range from 0,005 to 10 mg/kg with the appropriate parameters of precision, accuracy, repeatability and linearity and can be used for simultaneous determination of low PCBs concentrations in different types of soil (agricultural, contaminated soil, etc.).

Introduction
For the first time, PCBs were synthesized in 1881. Their production in 20th century raised from 1000 tons/year in early 30s up to 200,000 tons/year in 1975 (Abraham et al, 2002). In the beginning of the 80s, the production and the use of PCBs were stopped due to their toxicity. They were classified as POPs – Persistent Organic Pollutants and covered by the Stockholm Convention on Persistent Organic Pollutants. PCBs consist of a skeleton with two benzene rings linked through a carbon atom. The aromatic structure can be substituted with one to ten chlorine atoms. PCBs are chemically inert compaunds, remarkably resistant to elimination, addition, electrophilic substitution, oxidation and reduction. They are soluble in most organic solvents, oils and fats. PCBs penetrete through the soil surrounding places they were produced and used. [3] The concentration of PCBs on these sites is between 10 and 104 mg/kg, which is extremely higher then limits established by numerous national regulatory agencies (range of 0.01 to 50 mg/kg). The aim of presented study is validation of GC-MS method for determination of 7 PCB congeners in soil. Samples were prepared by liquid-solid extraction with cyclohexane and were analyzed in SIM mode. The validation parameters are: selectivity, linearity, repetability, accuracy, precision, limit of detection (LOD), and limit of quantification (LOQ).

Experimental
The following chemicals were used: cyclohexane, HPLC grade (Fisher chemical), PCB standards mix 3, Dr Ehrenstorfer, sodium sulphate anhydrous (Centrohem), acetone p.a. (Fisher Chemical). Chromatographic analyses were carried out on the gas chromatograph coupled with mass detector Agilent Technologies 7890B GC System, Agilent Technologies 5977MSD. The gass chromatograph was equiped with a capilar column HP-5 MS Inert ((5% phenyl)-methylpolysiloxane, 30m x 0,25 mm, film thickness 0,25 μm. Agilent technologies).

The oven temperature was raised from 125°C to 200°C at a heating rate 25°C per minute. Then 200°C to 260°C at a heating rate 4°C per minute and isothermaly holded 10 min. As a carrier gas, helium at of flowrate 0,7 ml min-1 was used. Injection volume was 1 µl and injected in a splitless mode. Calibration range was from 0,005 to 0,5 mg/l. Working standard solution was prepared by dilluted working standard with concentration 10 ppm. For determination of accuracy, soil samples were spiked in 3 concentration levels, with 0,01 mg/l, 1,0 mg/l and 10,0 mg/l. Samples were prepared by measuring 10 g of dry soil samples in conical flasks and adding 50 ml cyclohexane, 50 ml acetone and specific volume of standard solution for spike. Then samples were shaked 30 min in orbital shaker. After time elapsed, cyclohexan aliquots were filtered throught filter 0,22 µm into separation funnels and extraction was repeated with new aliquots of cyclohexane 50 ml and 30 min shaking. After that, aliquots were filtered into a separation funnels and shaked two times with 400 ml water. The extracts were filtered throught a layer of anhydrous sodium sulphate and evaporeted in vacuum evaporeator to a volume of about 2 ml and then in stream of nitrogen to a finale volume of 1 ml. Then samples were injected in GC-MS.

Results and discussion

Results of validation showed that the method for determination of low PCBs concentrations in soil was developed. Performed linearity test showed excellent linearity with correlation coefficient R>0,999. Obtained low limits of detection (LOD of 0,002 mg/kg) and quantification (LOQ of 0,005 mg/kg) confirmed the method can be applied for determination of PCB congeners in traces. The precision criterion (<5%) was fulfilled for all analyzed congeners. Analysis results of samples spiked in 3 concentration levels showed the recovery was in range 92 – 110%, which fulfilled the accuracy criterion (Table 1) [4,5].

Table 1: Required criterion for accuracy

	Accuracy (recovery %)
I spike level	60-115
II spike level	80-110
III spike level	80-110

Table 2: Summary of results

Analytes	Regression equation	R	LOD (mg/kg)	LOQ (mg/kg)	Precision (%)
PCB 28	y=565089x-2935	0,999	0,002	0,005	4,01
PCB 52	y=405060x-2118	0,998	0,002	0,005	3,42
PCB 101	y=354554x-2829	0,999	0,002	0,005	4,90
PCB 118	y=425740x-4459	0,999	0,002	0,005	3,42
PCB 138	y=296806x-3203	0,999	0,002	0,005	4,61
PCB 153	y=255957x-2929	0,999	0,002	0,005	3,68
PCB 180	y=185581x-2695	0,998	0,002	0,005	4,12

Table 3: Recovery and repetability results

Analytes	Spike 0,1 mg/kg Recovery (%)	Spike 1,0 mg/kg Recovery (%)	Spike 10,0 mg/kg Recovery (%)	Repetability (%)
PCB 28	110	98	105	4,25
PCB 52	92	97	102	3,28
PCB 101	98	108	108	2,98
PCB 118	110	110	110	3,53
PCB 138	105	109	110	4,88
PCB 153	107	109	110	4,70
PCB 180	103	106	110	3,91

Conclusion

The method for the identification and quantification of the PCB congeners in soil by using gas chromatographic method with mass spectrometric detection analytical technique was developed and validated in presented study. Based on precision, accuracy, repeatability and linearity, it can be concluded that the measuring range of developed method is from 0.005 to 10,0 mg/kg. The method will be used for testing PCBs congeners in contaminated sites and another soil samples.

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