SCREENING METHOD OF PCBS DETECTION IN ENVIRONMENT BY REACTION WITH *IN SITU* GENERATED BMC PERCHLORINATING AGENT

Nikolay À. Kluyev, Denis B. Feshin, Efim S. Brodsky, Galina A. Kalinkevich, Vladimir S. Soyfer

Institute of Ecology and Evolution RAS, Leninsky prosp. 33, 117701 Moscow, Russia. tel./fax: +7 (095) 135-13-80; e-mail: kluyv@online.ru

Introduction

Polychlorinated biphenyls (PCBs) are chemical substances which are persistent, bioaccumulate, and pose a risk of causing adverse effects to human health and the environment. Accordingly, UNEP´s Governing Council included PCBs in the Stockholm Convention among the 12 persistent organic pollutants (POPs) identified for international action.

Most of the PCBs pollutions are because of using of industrial PCBs containing mixtures which compositions are well known and constant. Hence, for exposure of adequate real pollutions it's sufficient to conduct a lot of express analysis for total PCBs content with periodical control by standard analytical methods. Consequently, a simple and cheap method for operative control is needed.

One of these methods is immunoassay[1]. It's very convenient and quite simple. However, in any cases this method gives overestimated results because of matrix influence and interferences. Moreover, using optical spectrophotometer as analyzer constricts the dynamic range of PCBs content in sample under analysis. It is also impossible to use internal standard method. In addition, it should be pointed out that necessity in company own materials makes immunoassay method application difficult for use in economically undeveloped countries.

So it is advisable to have an express-method that will allow PCBs determination in wide range of concentration with internal standards control by simple instrumentation. The method based on perchlorination of PCBs considerably simplifies detection of PCB congeners as compared to other techniques. In this practice all polychlorinated derivatives are converted into decachlorobiphenyl (DCB). This is followed by gas chromatography with electron capture detector (GC-ECD), which is highly sensitive for substances of interest. Currently EPA procedure #508a (1989) is the only official screening method for detection of PCBs using perchlorination. It uses $SbCl_5$ and powdered Fe mixture as reagent at 270°C. No using of internal standards is noticed.

We reported about using a powerful perchlorination reagent **BMC** (a mixture of SO_2Cl_2, $AlCl_3$ and S_2Cl_2 1000:1:2)[2] for converting dibenzo-p-dioxin and dibenzofuran into octachloroderivatives with high yields and purity[3]. However, this method is inefficient with ultra-trace amounts of dioxins. We modified the procedure by producing **BMC** *in situ*. Powdered alloy of duralumin and sulfur were introduced into the reaction mixture to yield $AlCl_3$ and S_2Cl_2 by interaction with SO_2Cl_2. This allowed us to conduct the perchlorination of PCDD/DF extracts with 70 % yield under mild conditions – 70 °C, 4 hours[4]. In presented work we extended our experience of perchlorination by modified **BMC** reagent to detection of PCBs.

Methods and Materials

GC-ECD measurements were conducted on gas chromatograph Hewlett-Packard 5890A equipped with ECD (^{63}Ni, b-particles ionization), carrier gas – nitrogen, 25 ml/min; HP-1column 20 m, 0.32 mm

i.d., 0.52 mm film thickness; constant flow of carrier gas (nitrogen) 2.0 ml/min. The injector temperature, 240 °C; the detector temperature, 300 °C. The GC was programmed as followed: 150 °C isothermal for 2 min, heating to 300 °C at the ramp of 10 °C/min, isothermal for 4 min. 1ml of the sample was injected in splitless mode with 0.1 min delaying of injector gas washing.

LR-GCMS measurements were conducted on ion trap Finnigan MAT ITD 700 with gas chromatograph Varian 2400; DB-5ms 30 m column, 0.25 mm i.d., 0.25 mm film thickness; constant flow of carrier gas (helium) 1 ml/min. Ionization by 70 ev electron impact, scan velocity – 1 spectra/sec, M/Z range – 41-450. The GC injector temperature, 240°; transfer line temperature, 200 °C. The GC was programmed as followed: 100 °C isothermal for 2 min, heating to 220 °C at the ramp of 10°C/min, then to 280 °C at the ramp 5 °C/min. 1ml of the sample was injected in splitless mode with 0.1 min delaying of injector gas washing.

For perchlorination studies the following solutions were prepared:

- calibrating solutions of PCBs mixture Sovol (analog of Arochlor-1254 in Russia[5]) in hexane with C=820, 82, 8.2 mg/ml, 820, 82 ng/ml;
- working solution of unsubstituted biphenyl in hexane with C=5 mg/ml;
- working solution of "surrogate" internal standard 4,4'-difluorobiphenyl (4,4'-DFB) in acetone:hexane mixture 1:1 with C=250 mg/ml;
- working solution of recovery external standard for GC-ECD analysis of 2-fluoro-3-bromo-6,7,8,9-tetrachlorodibenzo-*p*-dioxin (FBrTClDD) with C=1 mg/ml.

All reactions were conducted in Fishers 4 ml rubber caped screw-top vials, provided with self-made Teflon lining.

All solvents and consumes used were PCB grade. Sulfur and SO_2Cl_2 by Fluka.

Industrial duralumin alloy D18ä brand (Russia) was used in all reactions.

Water, soils and sediments extract preparation

Soils and sediments 10 g samples non-containing PCBs were spiked by 1.64 mg of "Sovol". 50 mg of 4,4'-DFB was added to each sample before extraction on contentious-flow extractor[6] by 200 ml aceton:hexane 1:1 mixture at 65 °C.

1 l of water non-containing PCBs was spiked by 1.64 mg of "Sovol". 50 mg of 4,4'-DFB was added before extraction by 2 x 80 ml of methylenechloride. Organic layer was separated and dried over $MgSO_4$.

All extracts were rotary evaporated with isooctane to 2 ml and treated at small multilayer column filled down-up with $MgSO_4$, Na_2SiO_3, $MgSO_4$, H_2SO_4/SiO_2 (44%), then eluted with 30 ml of hexane:methylenechloride 1:1 mixture and rotary evaporated to ~2 ml.

Perchlorination procedure

Calibrating PCBs solutions (or biphenyl solution), 50 mg of 4,4'-DFB in 200 ml of solvent, 10 ml of tridecane as kipper were put and evaporated in reaction vial in air flow at 45 °C (sample extracts were evaporated the same way, but no additional 4,4'-DFB was added). 40 mg of powdered duralumin, 9 mg of sulfur and 150 ml of SO_2Cl_2 were added; vial was filled with dry gas (nitrogen, argon), thoroughly closed up and heated at 105 °C for 2 h. Then SO_2Cl_2 was evaporated in air flow at 50°C. Reaction mixture was extracted by 5 x 2 ml of hexane. Extract was passed through small multilayer column filled down-up with $MgSO_4$, Na_2SiO_3, $MgSO_4$, H_2SO_4/SiO_2 (44 %), then eluted with 30 ml of hexane, evaporated in the air flow at 45 °C with adding of 10 ml tridecane as kipper. 10 mg of FBrTClDD, 0.5 ml of hexane were added to the sample before GC-ECD analysis.

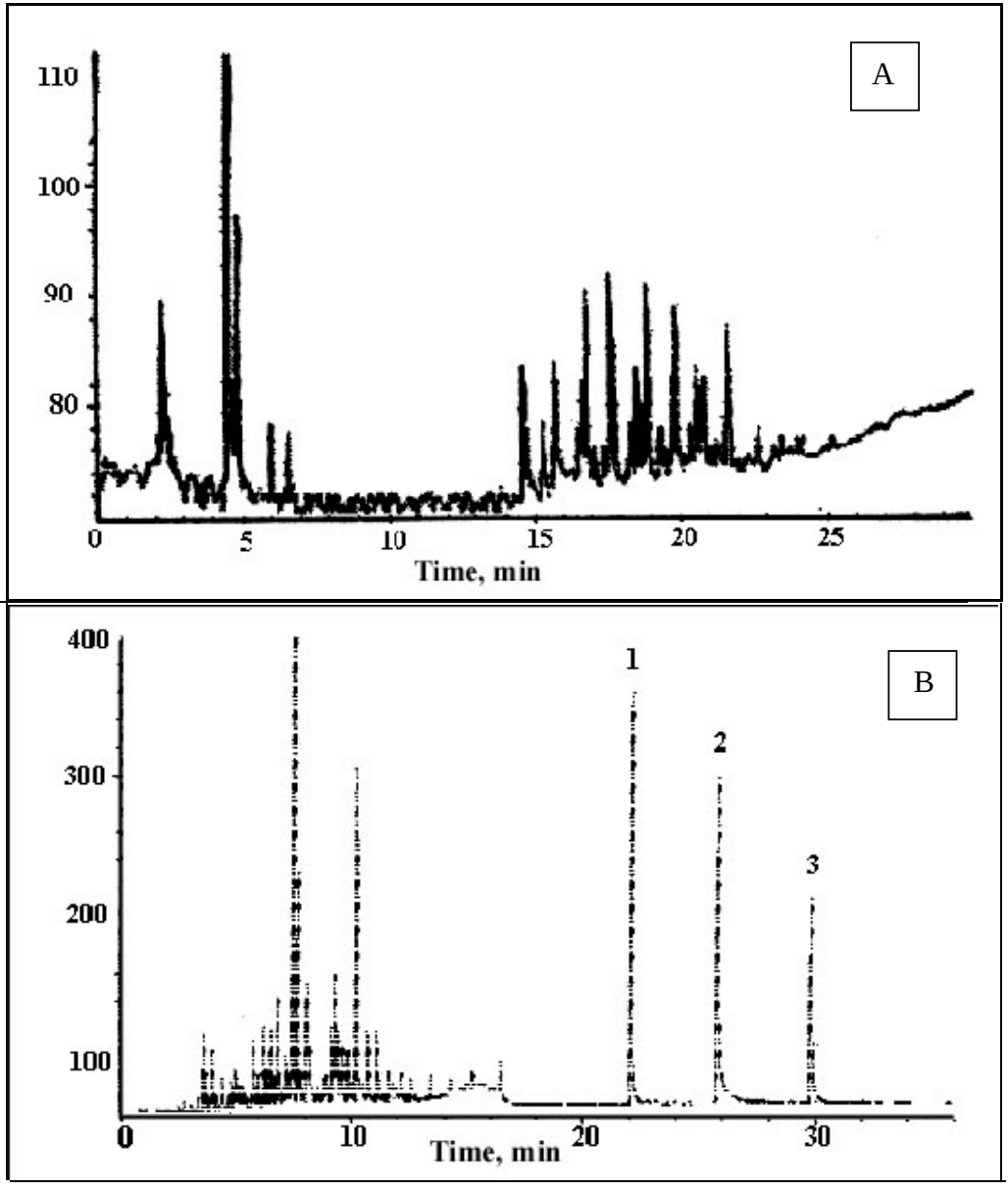

Figure 1. A – chromatogram of initial PCBs mixture "Sovol"; **B** – perchlorinated soil extract chromatogram: **1** – 4,4'-difluorooctachlorobiphenyl,

ANALYSIS II

Results and discussion

Powdered duralumin, sulfur and SO_2Cl_2 were reacted with PCBs mixture "Sovol". Reaction products were analyzed with GC-ECD and identified by LR-CMS. Complete conversion of PCBs into DCB was observed after two-hour heating of the mixture at 105 °C. These results were consistent, independent of the initial substrate amount (16.4 ng - 164 mg). This range is sufficient for PCBs analysis in most of the environmental matrixes.

Unsubstituted biphenyl also gave DCB with 90% yield under these conditions. Further heating for 8 hours did not lead to noticeable decomposition of the decachlorinated product.

Reliability of the results was confirmed by 4,4'-difluorobiphenyl as an internal standard that has the same structure and physicochemical properties with PCBs. Under perchlorination conditions it converted into 4,4'-difluorooctachlorobiphenyl. Conversion into DCB was not observed as a result of electrophylic aromatic substitution by "*ipso*" attack.

Elaborated procedure was successfully examined for PCBs perchlorination in real environmental samples. Water, soils and sediment samples spiked by ~1mg of PCBs were extracted and subjected to perchlorination. GC-ECD analysis of reaction products showed a full conversion of all PCBs into DCB and of the internal standard into 4,4'-difluorooctachlorobiphenyl. As shown at the fig.1 all perchlorination products and recovery standard could be easily identified due to long retention times. No background created by other matrix components is observed in this part of chromatogram.

Elaborated procedure is simple, cheap, doesn't require a sophisticated GC-ECD devise.

Conclusion

- At the model experiments the conditions for PCBs perchlorination by modified **BMC** reagent were found.
- It is shown that this procedure allows detecting of PCBs as DCB by GC-ECD in wide range quantities of former: for 16.4 ng/sample to 164 mg/sample.
- The foolproof stabile internal standard was proposed for the analysis reliability – 4,4'-difluorobiphenyl.
- It is shown that elaborated method allows analyzing of water, soils and sediments samples containing PCBs at the regulations levels.

References

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