

Classic organic reaction as the powerful tool in the PCDD/Fs and PCBs analysis.

Andrey A. Shelepchikov¹, Vladimir S. Soyfer¹, Efim S. Brodsky¹, Sergey K. Gorogankin¹

¹Institute of Ecology and Evolution RAS

Introduction

Analysis of PCDD/Fs and related compound in the environmental and biological samples is very complex and expensive. The amount of samples and their variety annually increases. Main modern clean-up methods in dioxin and PCBs analysis are based on fractionating on carbon, alumina or florisil column and on chemical reaction caused by sulphuric acid and basic treatment^{1,2}. Unfortunately, in practices it is happened that some foreign substance practically did not destroyed at acid-basic treatment, and under fractionating getting to the PCDD/Fs or ortho-PCB fractions. Their presence can result on coloration or turbidity of final extract and could leads the temporary or constant fall of chromatographic resolution and to deterioration of GC column. Repeat of separate clean-up stages or whole procedure or application of such powerful method as a hot multilayered column³ not always allows completely solve a problem.

Rather high molecular weights (>300 a.m.u.) and absence of obvious functional groups complicate structure elucidation of those substances, but low resolution mass spectra show presence in their structure benzene rings and aliphatic chains. Really, such molecules are poorly subject to effect of a sulphuric acid, and the branched molecule complicate fractionating at chromatographic column. From other hand it is known, that in many cases addition of nitro group occurs easier, than sulfonate group, and that nitrocompounds are well are trapped by alkaline sorbents or unstable.

Previously we found that passing hexane through the column with nitrating mixture on silica gel and alumina allows prepare in laboratory scale price-effectively UV-pure hexane with ideal zero line from raw hexane completely not suitable for use in UV area. At the same time a multilayer column and alumina column did not give practically any effect.

In the given work we have studied acceptability of nitro reaction in the PCDD/Fs and PCBs analysis.

Experimental

In work was used silica gel (Kieselgel 60, 0.063-0.200 mm, Merck) impregnated by HNO₃ (10 mass percent) and H₂SO₄ (20 mass percent) by same procedure. Other consumables and methods were typical for the carried out analysis¹. Overview analysis was performed by low-resolution GC-MS system – Finnigan PolarisQ; isomer specific analysis of PCDD/Fs and dioxin-like PCBs was done on Finnigan MAT 95XP at resolution about 10000.

Results and Discussion

Efficiency of nitration method can be illustrated by technical grade ethylene glycol dimethyl ether (EGDE) GC-MS analysis. 100 ml of EGDE was rotary evaporated to 1 ml and then to 10 µl of added tridecane in the micro turbo evaporating system. 1 µl of extract was analyzed on GC-MS system at full scan mode (m/z 41-550) - top chromatogram on fig. 1. Then extract was cleared by common for dioxin analysis multilayer column and alumina column³, and analyzed at the same condition as raw sample - middle chromatogram on fig. 1. Finally extract was dissolved in 5 ml of hexane and passed through Pasteur pipette filled silica impregnated by nitro mixture - bottom chromatogram on fig. 1. All three chromatograms have been recorded consistently on same instrument without change in analysis program; the volume of extracts before the analysis was 10 µl and injection volume 1 µl.

We could not unequivocally characterize nature of the basic impurity of the solvent, but according with the mass spectra, most probably they containing aromatic (benzyl), cycloalkyl (alkenyl or cycloalkenyl) groups and alkyl chains.

Chromatograms testify that usual clean-up procedure allows to get rid only light fraction of impurity; in heavier part of chromatogram only some improvements of GC separation was observed, but as a whole quantitative or qualitative changes are not significant. While, nitro-column has completely removed remained two clusters of peaks and only peaks of saturated hydrocarbons are observed. Ion chromatograms (m/z 77 and 91) on fig.2 are shown efficiency of removing compound contained of phenyl and benzyl group.

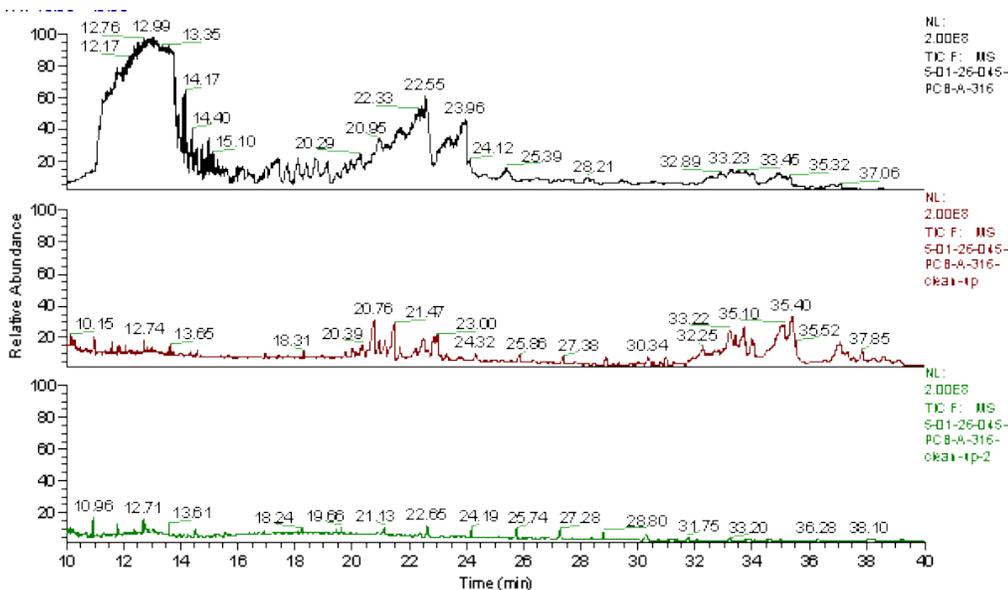


Fig. 1. Total ion current mass chromatogram (m/z 41-550) of impurities in the technical grade ethylene glycol dimethyl ether:

*top - raw sample;
middle - after multilayer and alumina column;
bottom - after micro column with (10% HNO₃ + 20% H₂SO₄)/SiO₂.*

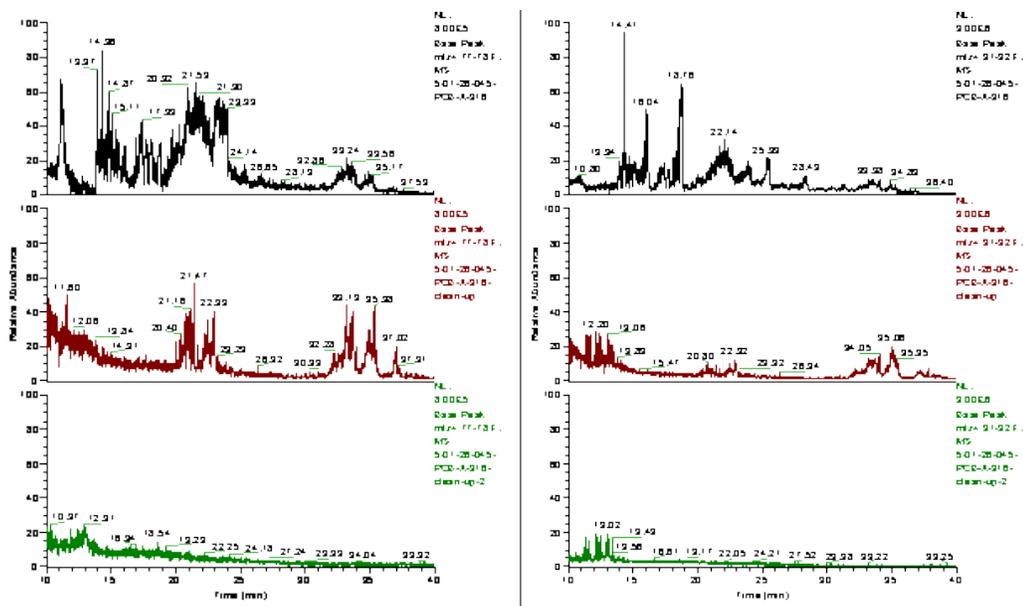


Fig. 2. Chromatograms from fig.1, constructed by $m/z=77$ (left column) and $m/z=91$ (right column).

Total ion current chromatograms in fig. 3 and 4 show stability of PCBs at passing through a nitro column. Raw technical PCB solution in hexane and the same solution after nitro column were analyzed. The presented data shows that application of nitro column does not caused changes in the congener profile, i.e. PCBs are stable on that condition. While side pick (RT 13.42) was almost completely removed.

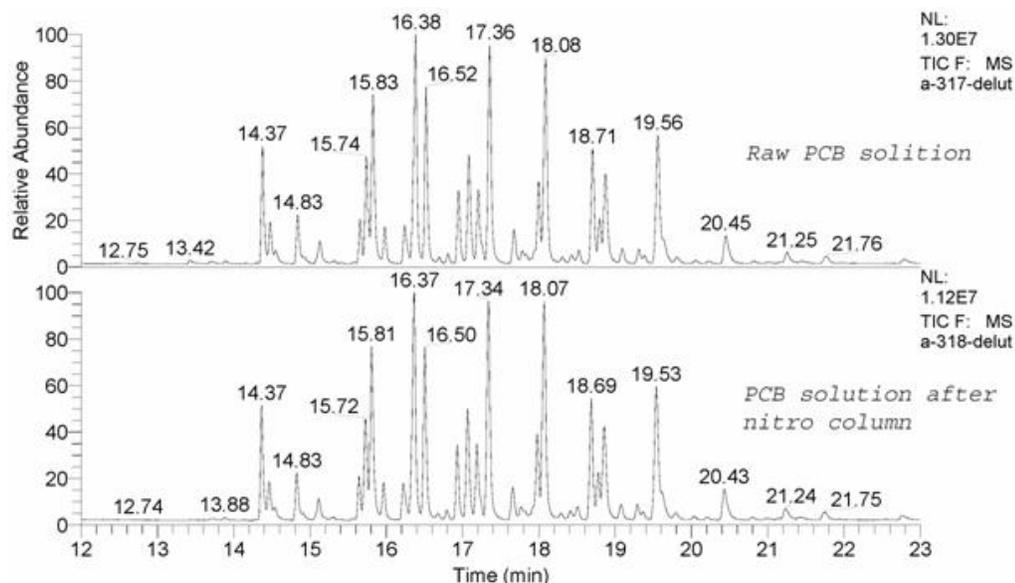


Fig. 3. Total ion current mass chromatogram (m/z 41-550) of Russian PCB mixture Sovtol:

top - raw solution;

bottom - after micro column with $(10\%HNO_3 + 20\%H_2SO_4)/SiO_2$.

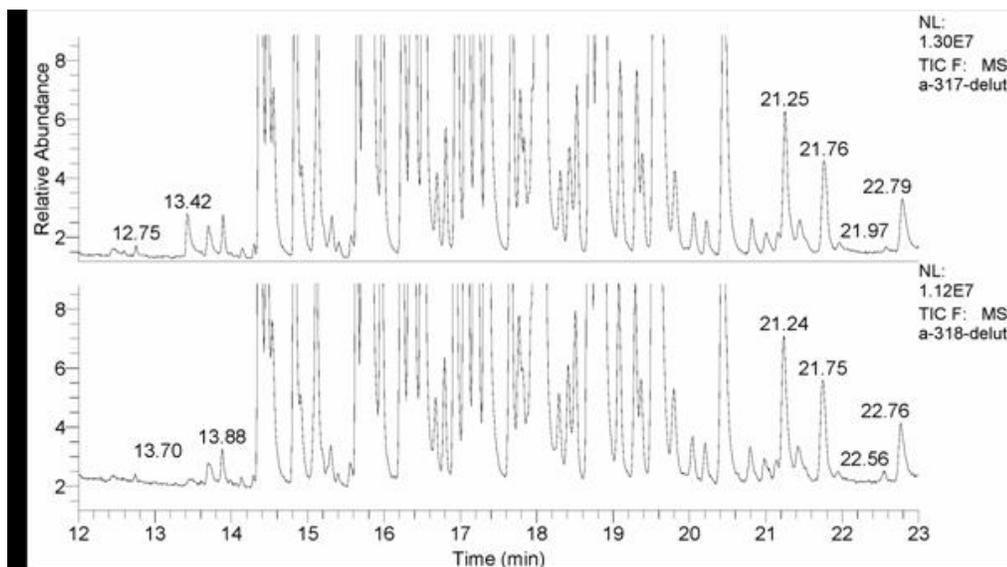


Fig. 4. The same chromatograms as in fig.3 with zoomed Y axis.

The further researches have shown:

- Polychlorinated dibenzo-p-dioxins, furans and are stable on nitro silica (at least from TrCDD/Fs to OCDD/F) independently of molecular structure.

ANA - Advances in Sample Preparation

- Application of nitro-treatment does not lead to changes in recoveries of PCDD/Fs and WHO-PCBs from real environmental and biological samples.
- There was no deterioration chromatographic separation or other undesirable effects (for more than 50 analysed real samples of HRGC-MS).
- Micro column with silica gel impregnated with nitrating mixture and potassium silicate can be used as an independent final stage of clean-up procedure; or nitrating layer could be added to the common multilayer column before potassium silicate; products of nitrating were not detected in the total ion chromatograms.
- Usual solvents and mixtures can be used; presence in the extract of traces of toluene does not cause poisoning of nitrating layer.
- The method is cheap, safe in use, allows avoiding repeated cleaning up.

Acknowledgments

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