NEW APPROACH TO DIOXINS' ANALYSIS: THE SUPPLEMENT OF NMR (MEASUREMENTS AND CALCULATIONS) TO CHROMATOGRAPHY

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It's well known that the analysis of dioxin-like compounds is restricted with their structural diversity. Just for chromatographic determination of polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) it became necessary to synthesize more than 400 individual compounds, including 20 acute toxic ones. The analysis of brominated similar compounds (PBB, PBDD and PBDF) is more difficult but yet realizable.

Some events had sharply limited the chromatographic potency to dioxin-like pollutant's recognition:

- the discovery of mixed Cl,Br-containing dibenzo-p-dioxins and dibenzofurans in the MSW incinerators emissions;
- the discovery in those of dibenzofurans S-analogues;
- the discovery in effluents and in products of different technologies (MSW combustion, pulp and paper industry, pesticides production etc.) the other classes of dioxin-like compounds - polyhalogenated xanthenes, xanthones, biphenylenes and polychlorinated azo- and azoxybenzenes.

Thus it is necessary now to take into account the new tens thousands of compounds with hundreds of extremely toxic ones, moreover the synthesis all of them for chromatographic references evidently cann't be fulfiled.

From the other hand the carbon NMR had already shown its undoubted advantage over others physical-chemistry methods in structural determination of unknown compounds. Earlier it was shown[1] that even in polysubstituted compounds NMR ^{13}C shifts are connected with the molecular structures with a limited number of parameters, and this allows to reconstruct NMR spectra of all species under studying. Using an optimal experimental volume we obtained the reliable calculations of ^{13}C NMR spectra for all homosubstituted benzenes, polyoxybenzenes, related polychlorinated oxybenzenes and PCDD.

The NMR spectroscopy (^{13}C [2,3], ^{1}H [4,5]) have some experience in the dioxin field. Now we suggest the new approach to the solving analytical problem under consideration with an intensification of NMR part. It is necessary to creat new

chromatographic procedures arranged with NMR ^{13}C for an identification of thousands compounds of dioxin-like classes when the synthesis of references is not beneficial. The new approach must include the extraction of the most of compounds from real mixtures and their structure determination with NMR ^{13}C, in order to obtain the chromatographic characteristics without the references synthesis.

It may be two-stage correlating procedure of the molecular structure and chromatographical signal for ever compound:

- the synthesis of some basic compounds for the creating an empirical increment scheme for calculating NMR chemical shifts predictive enough for reliable NMR spectra reconstruction for all compounds of interesting class;
- the extraction the rest compounds from real mixtures with help of preparative chromatography and following NMR measurements with using theoretical spectra for structure identification. The difficulties caused with different sensitive levels of NMR and chromatography may be overcome with modern technique.

It is important that such identification procedure only once will be carried out to every compound, thus one can to complete the chromatographic catalogue. It must be noted that the powerful NMR technique for structure investigations require a lot of time for every compound and similiarly to the special synthesis don't capable to overlape the whole volume of compounds. For these purposes it is necessary to develope the calculating methods for obtaining spectra NMR ^{13}C for all dioxin-like compounds and to create the catalogue of theoretical spectra.

That's why it is necessary to modify the analytical procedure of new classes of dioxin like compounds: the chromatography must be accompanied with modern NMR and we propose the next plan of steps to the cooperation:

1. The creating of the method for theoretical NMR ^{13}C spectra calculations for aromatic compounds of the most important classes: polysubstituted benzenes with homogeneous substituents [1], differently substituted benzenes, biphenyls (PCB and PBB), naphthalenes etc., using literature data.
2. The NMR investigation of compounds with one type of substituents except an oxygen:
   - the application of polychlorinated oxybenzenes results for PCDD spectra calculations [6];
   - the measurement of NMR ^{13}C spectra of an optimal set of PCDD [3] and calculation of theoretical spectra for all 75 PCDD [7];
   - the measurement of NMR ^{13}C of an optimal set of PCDF and theoretical spectra calculating for all 135 PCDF;
   - the same for all 75 PBDD and 135 PBDF.
3. The NMR investigation of compounds with different substituents except oxygen:
   - the creating of calculating method for NMR ^{13}C spectra of polysubstituted benzenes with O, Cl and Br, and than spectra of mixed P(Cl,Br)DD, polyhalogenated dioxins with

other substituents (Me, CF_3, etc.).

4. The NMR investigation of dioxin-like compounds containing sulfur instead of oxygen.
5. The spreading of carbon NMR spectra calculation's method on other types of compounds - polyhalogenic xanthenes, xanthones, biphenylenes, azobenzenic and azoxybenzenic compounds.
6. The creation of the special PC programs for the prediction of ^{13}C NMR theoretical spectra of dioxin-like compounds and for the comparison of each spectrum ^{13}C NMR with the set of theoretical ones.
7. The peparation of the catalogue of theoretical spectra ^{13}C NMR for all classes of dioxin-like compounds.
8. The combination of chromatographic and NMR investigations: the NMR structural elucidation of any dioxin-like compounds, extracted from mixture with help of preparative chromatography.

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