Analysis of Polyhalogenated Dioxins and Furans (Hal_xDD/Hal_xDF; Hal = Br, Cl;) Routine and Unsolved Problems

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The public discussion of the "dioxin problem" has recently become more rational than it was years ago. Emotions and hard facts are nearly in a balance now. Two reasons are responsible for this:

It has become obvious that there is a detectable environmental baseline pollution of dioxins about everywhere which has to be assigned to various chemical and technical sources. Finding of "dioxins" in soil, leaves, fish or mother milk mainly demonstrates the professional skill of the laboratory involved and is no longer a headline in the evening news.

There are PCDD/PCDF emissions not only from municipal waste incinerators - at least in Germany this will be in the near future a historical source - but also from automobiles and metal reclaiming plants among others. Particularly dioxin emissions from automobiles are much less dramatic than those from waste incinerators.

Dioxins like the PCBs and other organochlorines are part of the emissions of modern technical civilization. Whether we like it or not. As part of the chemistry of uncomplete combustion dioxins have been around since wood is used for heating (1). The mean levels of dioxins in the various matrices from air to mother milk are known meanwhile and standard procedures are reported for many specific applications (2). Reference standards are commercially available though at high prices. Even dioxin analysis dedicated GC-MS units are on the market. Does the occurrence of dioxins in the environment justify all these efforts? At least for those who invested in this market.

Only very recently did the concept of considering the whole group of the "2,3,7,8" congeners for both the dioxins and the furans as the most relevant compounds of a complex dioxin pollution find its way into legislative measures. This group of compounds defines both the routine and the unsolved problems in analytical chemistry of the dioxins and furans.

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The steps of any organic trace analysis are well known and are to be applied to the analysis of polyhalogenated dioxins and furans. First of all one has to define the problem that has to be solved. This will lead to the definition of the analytical approach which starts with the selection of the objects to sample. In almost all cases the analytical problem is nowadays given by the determination of the seventeen congeners of the 2,3,7,8 group that are reported as a weighted sum in 2,3,7,8-Cl_4DD equivalents. This pragmatic approach does not estimate the toxicological impact of an existing dioxin pollution but it approximates and generalizes otherwise uncomparable concentrations of varying mixtures of dioxins and furans.

Sampling strategy, time and location of sampling lead to the samples. Special care has to be given for the sampling in flue gas of incinerators and similar gas stream. Basically, adsorption or condensation can be used for an effective sampling of semivolatiles in air. The modified EPA method 5 train for sampling of organics in air (3) and the Ames vapour sampling system with its impinger effect (3) have led us to develop a shock freezing technique for probing gases and small particulates at 800 ^{o}C and above (4). High volume sampling of air is mostly done using low blank polyurethane foam (5). Sampling in water includes the use of adsorbents on the basis of polystyrenes or graphite types like e.g. Carbopack C.

In most cases sample treatment in organic trace analysis requires time, man power, know how, carefulness and the right equipment. Standard procedures have evolved including the LC separation on silica, superactive alumina and finally a graphite phase. Pioneering work has been done in this field by Lamparski and Nestrik (6) and Patterson jr and his group (7). Sample treatment or clean-up is a part of the chemical analysis as is the sampling step where unreparable sytematic errors can completely adulterate the results. Controlling the recovery by using appropriate internal standards is a must for this part of the analytical procedure. It is an unspectacular and often non esteemed part of work in the laboratory but of enormous importance (8).

Separation of the wanted congeners by high resolution gas chromatography combined with mass spectrometric detection is the next step. Isomer specific separation of the dioxins started with the pioneering work of Buser and Rappe laid down in many papers. The problem has fascinated many researches afterwards. Ryan and Masuda have recently summarized the gas chromatographic separation of all 49 + 87 tetra- to octa-polychlorinated dibenzo-p-dioxins and dibenzofurans on nine different stationary phases (9). Their work includes the polysiloxanes from bonded dimethyl to wallcoated biscyanopropyl(90%)phenylcyanopropyl(10%) (SP-2331) and biscyanopropyl(100%) (CP-Sil 88). More recently Bacher and Ballschmiter reported about the complete assignment of the above 135 dibenzodioxins and -furans on the new polar polysiloxane phase DB Dioxin. This mixed stationary phase gives several advanced separations of critical pairs of isomers (10). Capillary column coupling has also been of help to resolve the overlapping of specific isomers (11). This problem can come up when the origin of an environmental pattern has to be assigned to a specific source. Particularly when

chemometric methods like the principal component analysis (PCA) are applied, the analytical data should have an optimum in accuracy.

A major problem are losses of the 2,3,7,8-congeners due to their pronounced adsorptivity in the chromatographic system and/or on the capillaries of the SP 2331 and SP Sil 88 type. The problem is often overlooked. Our routine includes the on-column injection in any case of dioxin analysis and in addition the separation on a SE 54 capillary for the quantitation of the hepta- and octachloro congeners. The respective bromo congeners are detectable only when 10 m SE 54 capillary columns are used. Such short columns are also very useful for screening purposes.

Detection of the dioxins by mass spectrometry adds selectivity and sensitivity to the quantitation of the seventeen "2,3,7,8" congeners. We believe that high resolution mass spectrometry is no must in dioxin analysis though it may help to repair an uneffective sample pre-treatment. Striving for an optimum in separation in the sample pre-treatment step and in the capillary gas chromatography optimizes any mass spectrometric detection. The advantage of increased sensitivity of detection of the high resolution MS instruments due to an improved signal to noise ratio is slowly getting lost to the new generation of quadrupol and ion trap instruments.

New analytical approaches have to be developed if the concept of the toxicity equivalency factors (TEF) is extended from the seventeen "2,3,7,8" chloro congeners towards all bromo-chloro and bromo-congeners. The determination of the two 2,3,7,8-tetrachloro congeners will extend to two bromo and thirteen bromo-chloro tetrasubstituted congeners. 91 pentahalogenated congeners are added to the three pentachloro congeners of the 2,3,7,8 group. Donelly, Sovocol and coworkers reported about an combined approach using gas chromatographic retention indices and mass spectrometric charecteristics to forward the isomer specific identification of the 1700 bromo- chloro- and bromochloro- dibenzodixons (12). High resolution gas chromatography is surely at its end to solve this separation problem in terms of a single component approach as the pattern analysis of soot from a wood burning chimney and of automobile exhausts reveals (1,13). Both sources emit the mixed bromochloro congeners. Structure specific separations of the 2,3,7,8 group of congeners as given by the smectic polysiloxanes developed by Lee and Karasek and their groups are one step to bring defined structures and not single compounds to the mass spectrometric detection. Similar structure specific interactions have been observed in LC separations on highly active Al_2O_3 (14) and on a polyphenol phase (15).

The molar response of polychlorinated dibenzodioxins and dibenzofurans by the mass spectrometric detector after electron impact ionization (16) is a further step to advance from a single compound determination to a quantiation of structure specific groups. The need of structure identical ^{13}C-isotope marked internal standards is not necessary any more.

Based on capillary gas chromatography and mass selective detection the seventeen "2,3,7,8" congeners are analyzed by numerous laboratories. In spite of the enormous political and economic impact of the analytical work in the midst eighties dealing with dioxins, only minor efforts have been made by the authorities to the question of quality control of the reported results. Only in 1993 the first true reference materials have become available by the BCR of the EC for broad qualitiy control purposes. Quality control exercises under the participation of the leading laboratories in Europe, Canada and the United States are defining the state of the art. Quality control of the day by day work of the laboratories selling dioxin analysis to the customers is equally or even more important. Chemical analysis is a chain of processes and a chain is only as strong as its weakest link.

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