ORGANIC TRACE ANALYSIS UNDER GLOBAL ASPECTS - THE GLOBE AS A REACTION FLASK

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Organic trace analysis in environmental science mostly deals with multi-matrix and multi-component problems. In environmental science concentrations of the looked-for components are often in the microgram/Kilogram (ppb) range or may be even go down to the nanogram/Kilogram (ppt) range. Examples in organic trace analysis combining such extremes are the determinations of polyaromatic hydrocarbons (PAH), polychlorinated naphthalenes (PCN, Cl_XN, x=1-8, 75 congeners), polychlorinated biphenyls (PCB, Cl_XB, x=1-10, 209 congeners), polychlorinated dibenzo-p-dioxins (PCDD, Cl_XDD, x=1-8, 75 congeners) and polychlorinated dibenzofurans (PCDF, Cl_XDF, x=1-8, 135 congeners) among others in a variety of sample types. A special task is the determination of the 96 tetrachlorobenzyltoluene (TCBT) isomers in the technical mixture Ugilec.

The lecture will focus on the question, where do such persistent anthropogenic organic pollutants (POPs) go when they apparently disappear in the global environment. It summarizes approaches and results of our studies of the general baseline pollution. These studies combine extreme organic trace analysis and global environmental chemistry.

Any analytical procedure is a chain of operations that can be summarized as follows: definition of the problem, definition of the general analytical approach, definition of the sample in terms of significance under temporal and spatial aspects, sampling, sample transportation and storage, aliquoting of sample, depletion of the matrix compounds (often summarized as sample preparation), separation and detection of the analytes, identification and quantitation, calibration and validation of the results and finally discussion of the obtained results under the aspect of the starting problem.

While the steps "separation" and "detection" are widely considered as an exciting part of science in analytical chemistry if not the only topic at all, the fields "sampling" and "sample preparation" are often left to the motivated technical assistant or so called standard procedures are applied. The chain picture given above names it, any chain is as weak as its weakest link. Poor sampling and/or poor sample pre-treatment makes poor analytical chemistry if one considers accurate results as an important part of the scientific effort.

Sampling in global environmental chemistry requires the consideration of pre-sampling factors (where, what, when, transport, energy supply) as well as an optimizing of the real sampling parameters of time and space. Sampling is the problem oriented cutting out of a selected but representative piece of our environment regarding the factors time and space. Sampling transforms the idea of a scientific problem to a piece of physical reality.

Sample preparation is enrichment of the analytes from the total sample minimizing interfering organics and avoiding any significant losses of the analytes A nanogram per kilogram level of the analyte in the sample has to be transferred into a nanogram per 25 microlitre level in an organic solvent ready for further separation and detection steps. This is an enrichment by the factor of 10^5. The steps extraction/dissolution, removal of interfering matrix components (clean-up), and preseparation by liquid chromatography into groups of related compounds are crucial for reducing the number of organic components to a level which is amenable to separation by high resolution gas chromatography.

During the last decade organic trace analysis has triggered and also has been driven by a development of so called instrumental techniques. The use of a mass-spectrometer as a detection device particularly in true combination with high resolution separation techniques in the gaseous or the liquid phase - GC/MS; LC/MS, CE/MS - has a still lasting impact. HRGC/MS operation give three basic types of analytical information: firstly retention time as a measure of the molecular interaction of the analyte with the stationary phase in the GC part, secondly data regarding the molecular structure as given by the ion pattern, and thirdly a signal that correlates to the amount of the analyte entering the ion source.

Sensitivity in HRGC-MS, besides requiring an optimized functioning of the ion source and the ion separation part, depends primarily on the structural parameters of the analytes. Strong molecular ions or fragments such as they are obtained with many arene compounds clearly give optimum sensitivity. Even with an electron-impact source 0.1 - 1 pg of an arene can be detected in the multiple-ion mode of a sector field instrument. Negative ion chemical ionisation has detection limits well into the femtogram range, if one uses the right compounds.

Quantitation by GC-MS particularly when a multiplicity of analytes has to be determined should always operate on the basis of keeping all operational parameters constant. Only this way the given inherent systematic errors can be regarded as similar in both the calibration and the analytical runs. ^{13}C-isotope labelled analyte identical compounds give an optimum in error compensation right on from the beginning of the analytical process. ^{13}C-isotope dilution analysis (IDA) is typical for the determination of a single or at utmost a few analytes. For the analysis of more than ten and up to 50 or more analytes in a complex mixture the extend and the specifity of the synthetic procedures alone to obtain the necessary ^{13}C-standards is mostly self-prohibiting.

It has been shown by us that the MSD after electron impact ionization (EI-MS) gives a rather strict molar proportionality for the polychlorinated arenes, like the naphthalines, dibenzodioxins and dibenzofurans. For the PAHs and the polychlorinated naphthalenes the normalized signal of the isotope pattern has to be corrected by the ionisation cross-section to obtain a molar proportionality. In contrast to these groups of compounds the relative EI-MS response factors of the PCBs isomers differ quite substantially.

The mass spectrometer detector is an extremely helpful positive identification device in analytical chemistry, whereas most other detectors merely detect an analogy between an unknown and a reference standard. But one should always bear in mind when using a specific detector such as a mass spectrometer that it only answers the questions being asked for.

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