Evolution of dioxin analytical techniques

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Dioxins—more accurately termed polychlorinated dibenzo-*p*-dioxins (PCDDs)—and the corresponding polychlorinated dibenzofurans (PCDFs) represent two classes of highly stable, planar aromatic molecules found in the environment as contaminants of soil, water, and organic matrices such as wood and pulp. The degree of substitution of the aromatic rings in these substances can range from one to eight, resulting in monochloro to octachloro isomers. Thus there are 75 isomers of PCDD and 75 of PCDF. Some of the isomers, particularly those with chlorine in the lateral 2,3,7, and 8 positions, are among the more toxic substances known. The most toxic of all such compounds is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The chemistry of these species has been extensively studied in many laboratories (*1*).

The analysis of polychlorinated aromatics in different matrices requires three principal operations.

1. Separation of organic compounds from the matrix, which is sometimes insoluble
2. Purification of the residue to remove low-molecular-weight and nonchlorinated materials
3. Identification of the product(s), either qualitatively or quantitatively.

The separation and purification stages have often encompassed a combination of extraction processes, especially Soxhlet extractions and chromatographic techniques (*2*). The latter are frequently accomplished using silica, alumina, or analogous chemically modified supports or by carbon-absorption chromatography. The identification step relies almost exclusively on GC/MS (gas chromatography/mass spectrometry) analysis (*3*), which is capable of detecting concentrations as low as parts per trillion (ppt).

The detection and analysis of PCDDs and PCDFs in chlorinated paper pulp has been of prime importance to the paper industry, since these materials constitute two of the more toxic pollutants from the processing of wood. Although analysis of samples is routinely accomplished by existing protocols, exploration of other techniques may lead to elimination of three problems with current methods.

1. Extraction and purification of PCDDs and PCDFs frequently require substantial amounts of solvents and adsorbents. These materials require disposal themselves, adding to waste-removal problems.
2. Some pulp samples contain substances that interfere with the mass spectra. In such cases, the original sample must be reextracted, or the analyte must be purified further, resulting in loss of material.
3. The techniques devised for isolating the analytes from pulp were adapted from procedures used for other matrices in which the interfering constituents were known. Such techniques are not necessarily applicable to extraction of PCDDs from pulp, for example, or for the separation of PCDDs from other compounds.

The objective of our work has been to devise new methods for extracting and purifying PCDDs and PCDFs from chlorinated pulp and to compare these new procedures with existing methodologies. In particular, we are exploring the dissolution of pulp in solutions with a high sulfuric acid content in order to remove the matrix that may absorb the aromatic analytes.

Materials and methods

Materials

All reagents were obtained from commercial sources and were of the highest purity. All glassware, solid chemicals, and other equipment were washed with hexane prior to use.

Analysis

The GC/MS analytical techniques were carried out as described in the literature (*4*).

General procedures

Method A. Chlorinated wet pulp (150 g, ca. 25 g dry weight) was placed in a flask cooled in an ice bath, and an internal standard was added. A 400-mL solution of cold, 75% sulfuric acid was added, and the solution was

allowed to stand in the ice bath with occasional swirling for 60 min. After warming to room temperature, the solution of pulp was treated with 800 mL of water. The mixture was then subjected to steam distillation, in which the distillate percolated through a layer of isooctane to extract the organic material. After 45–90 min at reflux, the solution was allowed to cool, and the isooctane extract was removed and dried. Purification of the extract followed standard methods (extraction with base, chromatography on silica, alumina, and/or carbon).

Method B. Chlorinated wet pulp (150 g) was placed in a flask cooled in an ice bath and treated with an internal standard. A 360-mL solution of cold, concentrated sulfuric acid was added, and the solution was allowed to stand in the ice bath with occasional swirling for 60 min. After warming to room temperature, the solution was extracted with two 100-mL portions of hexane, which in turn were washed with 200 mL of water, two 100-mL portions of 10% potassium hydroxide solution, and 200 mL of water. The organic layer was dried with sodium sulfate and purified by a combination of chromatographic techniques.

Results

The dissolution of pulp in a high concentration of aqueous sulfuric acid is an established procedure (*5*) that effectively removes the matrix. At that juncture, either steam distillation or extraction with hexane separates the organic materials from the aqueous medium. **Table I** summarizes the results of the steam-distillation experiment vs. extraction methods for the analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF. The results are comparable.

I. Concentrations of 2,3,7,8-TCDD, 2,3,7,8-TCDF, total TCDD, and total TCDF in wet pulp. Concentrations determined using various extraction methods.

	2,3,7,8-TCDD, ppt	*2,3,7,8-TCDF, ppt*	*Total TCDD, ppt*	*Total TCDF, ppt*
Soxhlet (toluene)	39.9	293	78.5	869
Soxhlet (ethanol)	57.7	335	96.0	1240
SDS (toluene)*	37.9	419	89.6	1200
Steam distillation	33.3	427	36.3	902

*SDS = Soxhlet with Dean-Stark trap to remove water

The steam-distillation method is not effective for the recovery of the higher congeners, especially the octachloro isomers, OCDD and OCDF. On the other hand, this method uses very little solvent (only 4 mL of isooctane) and is therefore perhaps preferable for analysis of TCDD and TCDF.

Conclusion

Sulfuric acid digestion of pulp destroys the matrix and allows efficient separation of organic materials from the pulp, specifically by using the techniques of steam distillation. As the industry works to eliminate PCDDs and PCDFs from bleached pulp, it is expected that a more efficient analytical protocol will be developed.□

Literature cited

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