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Ms. Suzanne Rudzinski, Chief
Chemical Regulation Branch
U.S. Environmental Protection Agency
Washington, DC 20460

Dear Ms. Rudzinski:

Thank you for the opportunity to review the package of documents relating to the control of halogenated dioxins and furans that may be produced inadvertently in the manufacture of chemicals. I will address the questions as you have listed them, below.

1. The rationale for developing the list of chemicals seems to be reasonable. The application of the rationale in the list of chemicals has led to some apparent inconsistencies, for example: tetrabromophthalic anhydride (632-79-1) is classified under 2a (polybrominated phenols and derivatives) which does not seem appropriate. Tetrachlorophthalic anhydride (117-08-8) appears to be correctly classified as "3." Does the Group # defined in the document, "Development of List...," correspond to the "Priority" classification in Table I? If so, the assignment of Priority number sometimes disagrees with the Group #. For example, there are no chemicals given Priority 2d, but 344-07-0, 392-56-3 (both assigned 2a) fit the description. Finally, unless data exists to the contrary, the inclusion of halogenated aliphatics and titanium dioxide in Group 3 seems inappropriate. On the other hand, mono-halogenated phenols should perhaps be elevated to the list for testing because of the possibility that they may be contaminated with higher halogenated phenols.

2. I can think of no other chemicals that should be tested.

3. I do not see major problems per se in providing only a skeleton of an analytical framework and relying on industry to fill the gap. However, certain necessary guidance is absent from the skeleton. There is no direction as to whether the analytical scheme be devised to determine all PCDFs and PCDDS, only tetra through octa, or only 2,3,7,8- substituted congeners, which are considered to be the structures having the greatest biological activity.

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Is the analysis supposed to be quantitative for unique positional isomers, or only for total tetra, penta, etc., substituted dioxins and furans? The more specific and the more comprehensive the analysis must be, the more development work, especially in terms of labeled and unlabeled standards, the more time-consuming and costly the analyses must be, and greater the probability that incompatible and unusable information will be generated.

- Re the development of analytical standards:
  This is a mammoth job since every individual structure quantitatively analyzed should have both a labeled and unlabeled standard for determination of response factors and recoveries. The introduction of the concern about mixed bromo and chloro structures greatly enlarges the problem. I recommend that this latter concern be dropped, except for the testing of mixed bromo and chloro chemicals. I further recommend that EPA take the lead in synthesizing and making available the required standards.

- Re the development of cleanup methods.
  Each chemical represents an individual case and will require development work. Most will probably be solvable - some may be quite recalcitrant and require special considerations.

- Re reliable data and comparable results.
  This answer depends to a large extent on the availability of analytical standards and on EPA's simplifying and prioritizing the analytical task. Such a prioritization scheme might be to require the quantitative analysis of the most probable furans and dioxins and a sample representative of the biologically active congeners, such as the 2,3,7,8-tetra substituted dioxins and furans. This would greatly simplify the task and improve chances of getting reliable and comparable data.

4. The sensitivity of the mass spectrometer is limited to one picogram ($1x10^{-12}$ gram) for each individual structure to be analyzed. At one ppb ($1x10^{-9}$), the sample could be analyzed by injecting one mg ($1x10^{-3}$), the maximum sample size that can be injected into a GC, into a GC/MS system. At 0.1 ppb, the sample would have to be concentrated tenfold. This question boils down to one of cleanup. It should also be recognized that at the ppt level, background contamination could also be a factor.

5. There are probably 4 or 5 laboratories worldwide that could perform these tests on the simple cases now. The limiting factor is availability of standards.

6. The sampling and QA plans seem adequate.

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7. General Electric has developed methodologies not referenced in the Draft Final Report dated June 3, 1985, by D. Steele and J. Stanley. The objective of our work was to develop quantitative analyses of PCB fluids for the most biologically active tetra, penta, and hexa chlorinated PCDF structures having the 2,3,7,8-substitution backbone. The work involved the synthesis of all tetra through octa unlabeled PCDFs and C-14 labeled samples of those structures to be quantitatively analyzed. The analytical scheme involved GC-GC-MS instrumental analysis, in some cases preceded by cleanup procedures to extract the furans from the PCBs. This work is described in two papers enclosed for your interest (Target Compound Analysis by Two-Dimensional Gas Chromatography-Mass Spectrometry and Isomer Specific Analysis of Selected Chlorodibenzofurans), both by W.V. Ligon and R.J. May. This analytical approach was also applied to 2,3,7,8-TCDD in hexachlorophene (7-30-4; 2,2'-Methylenebis (3,4,6-trichlorophenol), which is on your list, and provided a quick, quantitative result (see also Determination of Chlorodibenzofurans and Chlorodibenzodioxins using Two Dimensional Gas Chromatography-Mass Spectrometry, by the same authors, enclosed).

8. I have no additional information to provide regarding biological testing systems. I am familiar with the work of Gierthy, et al, at New York State and believe that this work shows real promise since it detects the strongest biological activity of these chemicals, i.e., keratinization. I believe that EPA should devote research funds to the area of biological testing since it could lead to more meaningful data about the toxic potency represented by the impurities in the tested chemical.

I hope these comments will prove useful, and I stand ready to assist further if desired.

Very truly yours,

S. B. Hamilton, Manager-
Environmental Science & Technology

SBH:cas
Enclosures

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ISOMER SPECIFIC ANALYSIS OF SELECTED CHLORODIBENZOFURANS

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(First received December 13th, 1983; revised manuscript received February 16th, 1984)

SUMMARY

Two-dimensional gas chromatography has been used to provide full chromatographic resolution of three chlorodibenzofuran isomers. The materials studied were: 2,3,7,8-tetrachlorodibenzofuran, 2,3,4,7,8-pentachlorodibenzofuran and 1,2,3,7,8,9-hexachlorodibenzofuran. The materials were detected using medium resolution mass spectrometry.

INTRODUCTION

Chlorination of dibenzofuran can potentially yield a total of 135 unique products. These products vary both in degree of chlorination and in the positional substitution of chlorine atoms on the basic ring structure. Certain members of this group which have a 2,3,7,8 substitution pattern are known to have measurable physiological effects in a number of animal species. Other members of the group show little biological activity. For this reason, any attempted evaluation of the potential physiological activity of a given chlorination mixture which is based solely on chemical analysis must utilize techniques which allow quantification of the active components.

Analyses of these mixtures by gas chromatography–mass spectrometry (GC–MS) is the method of choice because of the ability of this technique to deal with complex mixtures and small amounts. Such analyses have been reported by a number of workers[1,2]. Such work has failed, however, to provide unambiguous chromatographic resolution of the most interesting species. Without effective separations, it is not possible to ensure that the observed signals accurately reflect the amounts present. If reliable quantification cannot be ensured correlations of analytical data with clinical or epidemiological data are meaningless.

In this paper, we report the chromatographic resolution of three important components of the set: 2,3,7,8-tetrachlorodibenzofuran, (2378-TCDF); 2,3,4,7,8-pentachlorodibenzofuran, (23478-PenCDF); and 1,2,3,7,8,9-hexachlorodibenzofuran, (123789-HexCDF). Two-dimensional GC methods were used to obtain the separations. Analysis was by mass spectrometry.

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TARGET COMPOUND ANALYSIS BY TWO-DIMENSIONAL GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

The use of two-dimensional gas chromatography* for the analysis of specific target compounds in complex matrices in combination with mass spectrometry has been investigated. The combination of a high capacity, high polarity packed first gas chromatography column followed with a low capacity, low polarity, high resolution second column has been found useful. A component of interest is switched from the first column into a cold trap and then flash-evaporated into the second column. This combination allows part per billion analyses in complex mixtures such as soil extracts, crude oils, and biological extracts without any prior sample cleanup whatever. Two important advantages arise naturally therefore from this approach: a significant reduction in analysis time and a major improvement in the specificity of the analysis. The method offers a relatively inexpensive yet powerful alternative to mass spectrometry–mass spectrometry.

INTRODUCTION

In recent years considerable interest has been focused on the development of analytical methods for part per billion (10^9) and even part per trillion (10^{12}) analyses of selected organic species. Quantification of such materials in unusually complex matrices such as soil and biological extracts has been especially widely studied. The analyses which have been devised for 2,3,7,8-tetrachlorodibenzodioxin in environmental samples are representative of the current analytical approach to such problems[1,2]. Typically a method will involve an arduous multistep purification procedure, including, for example, liquid chromatography and gel permeation chromatography. These preliminary isolation steps are then usually followed by mass spectrometry or gas chromatography–mass spectrometry (GC–MS) for detection and quantification. In the present paper, we show that two-dimensional GC can eliminate much and in many cases all requirements for sample cleanup even in very complex matrices.

* Note by the Editor: The authors insisted on calling this "two dimensional" against the recommendations of our referees (see also I. M. Hais, *J. Chromatogr.*, 187 (1980) 466) and against the judgement of the Editor.

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Determination of Chlorodibenzofurans and Chlorodibenzodioxins Using Two-Dimensional Gas Chromatography-Mass Spectrometry.

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ABSTRACT

Polychlorinated biphenyl fluids, flyash extract, and hexachlorophene have been successfully analyzed for 2,3,7,8-tetrachlorodibenzofuran and 2,3,7,8-tetrachlorodibenzodioxin at part per billion levels by two dimensional gas chromatography-mass spectrometry without resort to preliminary isolation procedures. Detailed experimental procedures are provided. Systematic errors, fundamental limitations and interferences are documented.

INTRODUCTION

Chlorodibenzofurans and chlorodibenzodioxins are known to occur in the environment and in certain industrial materials at low levels. Techniques for the determination of these materials have generally involved multi-step isolation procedures followed by gas chromatography-mass spectrometry (GC-MS). The work of Harless et al is typical (1). A review of various methods has been published (2). We wish to report that for certain classes of sample, important congeners of each of these materials can be determined at part per billion (ppb) levels by two-dimensional-GCMS (GC-GC-MS) without the use of