APPLICATION OF "ALTERNATIVE" METHODS FOR DIOXIN MONITORING—SHIFTING THE PARADIGM

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Introduction

Many times we have seen environmental practices and procedures develop based more upon circumstances and immediate needs, than upon the best use of resources to address public health issues. At present, the dioxin analysis industry represents more a continuation of the *status quo* than a means to deal with real world human health and ecological issues. Although complete speciation of polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDFs) is very important to understand their generation and disposition, for routine monitoring of environmental media, alternative methods that provide an indication of toxicity at reasonably low detection limits and at low cost should be brought into mainstream use where appropriate.

Background

Although chlorinated dioxins were first synthesized in Germany in 1872, and studies of dioxin were reported in the chemical literature in the 1950's, dioxin was not heavily studied as an environmental contaminant until the late 1960's and the 1970's. As toxicological studies of specific congeners indicated the widely varying toxicity according to the degree of chlorination and orientation of the chlorine atoms on the dioxin or furan structure, it quickly became apparent that analysis of complex mixtures would be very challenging. Around the same period of time, the advent of routine use of gas chromatography coupled with mass spectrometry (GC/MS) seemed to provide the much sought after solution to how monitoring for dioxin and related compounds could be performed in a variety of matrices.

In one combined technique, GC/MS was able to separate the numerous congeners, accurately identify those present, and quantify with reasonable accuracy and precision each individual congener. Continued development of the method brought improvements in resolution from use of capillary column GC and high-resolution mass spectrometry (HRMS). Detection limits continued to decrease, and sample cleanup procedures were refined, so that GC/HRMS has become the "gold standard" for dioxin analysis.

The underlying premise was that complete characterization according to chemical species was critical to fully assessing dioxin contamination occurrences. Of course, as toxicity data became available and some degree of consensus was established on how toxic equivalence factors (TEF) could be derived, it was possible to use the speciated results to calculate a total toxic equivalents (TEQ) by summing the products of the concentration of each congener and its respective TEF. Speciated data, though, have also provided numerous insights into the formation and fate of PCDDs and PCDFs.

Speciation, i.e., congener distribution patterns have been widely used to compare varying sources of PCDD/PCDF and to determine whether the same mechanisms are in place, and this type of information has historically been very useful. However, for routine monitoring over time from a given source, or monitoring over a wide area to determine the extent of transport or contamination, such congener distribution patterns are infrequently used. And yet, we have continued to rely upon GC/MS as the means to obtain an estimate of total toxicity, regardless of the specific use of the data. This would appear to be based more upon convention, than upon the lack of suitable alternatives.

There is certainly nothing inherently wrong with continuing to rely upon GC/MS for accurate quantitation of the species of interest, whether for compliance purposes or for environmental studies and assessments. However, there is now available a plethora of alternative methods[1] that offer several advantages over GC/MS in certain situations. These methods, primarily bioassays, are generally much less costly than GC/MS. In many cases the turnaround time is much shorter, and in some cases the methods lend themselves to field use, where turnaround time can be reduced even further. These methods provide an indication of dioxin-like toxicity or potential toxicity by measuring one "link" in the biochemical chain of events that begins with the Ah receptor responding to dioxin and related substances.

Due to the current heavy demand for high-qualify, speciated GC/MS analysis for PCDD/PCDF, typical costs are US$500 to US$1500 per sample, with a turnaround time of 3 weeks (minimum) to 6 weeks (common) or more. Unfortunately, it is the time spent waiting for laboratory results that can often be the most costly aspect of a project. In many cases, ironically, only rough information is needed as to the extent of contamination of a site, or as to the effectiveness of control equipment at different operating conditions, but there are no options available from the laboratory to provide an appropriate grade of data for an appropriate cost.

Global Needs

Global concern over dioxin is continuing to increase due to several factors. Most nations have agreed to curtail the use or production of persistent organic pollutants (POPs) under the United Nations Environmental Programme (UNEP)[2], while evidence mounts on the long-range transport of dioxin into pristine arctic regions[3]. Human health studies of exposures occurring in the 1970s are just beginning to have sufficient time to observe long-term effects. Meanwhile, incidents of contamination of food and milk erupt here and there, and suddenly in a particular region of the world, there is not nearly enough capacity to keep up with the demand for analysis.

There are many nations with an active interest in performing monitoring of food and dairy products, as well as measuring emissions from industrial sources and addressing contaminated soil characterization and cleanup. However, many developing nations do not yet have HRMS equipment available, nor do they have appropriately trained staff to perform this analysis. They do, nevertheless, have immediate needs to determine whether public health or occupational exposure threats are present.

For many of the needs for dioxin assessment throughout the world, quick, inexpensive screening methods would be much more useful than sophisticated speciation approaches. Financial resources are often very limited, regardless of what party is footing the bill. Inexpensive screening

methods offer the opportunity to obtain much more *useful* information, collected from more locations or at more frequent time intervals, than could be done within the same project budget using more traditional GC/MS methods.

Current Problem

The real dilemma is that regulatory agencies and the regulated community are very accustomed to a particular method. The current paradigm is one where isolating a certain seventeen 2,3,7,8-substituted PCDD/PCDF congeners, quantitating all of them individually, then applying TEFs that at best are only correct to an order of magnitude, and summing up seventeen multiplication products, is preferable to using a bioassay where TEQ can be approximated in one direct analysis, the cost is much less, the turnaround time much faster, and method training is much less involved than with GC/MS.

There is much interest in use of alternative techniques, such as the Ah-IMMUNOASSAY® or the CALUX™ methods, but potential users are cautious until government bodies have more to say about these methods. Even so, these methods can easily provide a large amount of useful information, which can complement analysis of selected samples via GC/MS.

Possible Solutions

A major refereed evaluation program is needed, whereby the merits as well as the drawbacks of alternative dioxin analysis methods can be documented via peer review from independent, authoritative bodies. One outcome of such a program would be a rating of each method according to criteria agreed to by both method developers and users, broken down by various sample matrices and applications. As this paper is being prepared, steps are underway to initiate, if possible, such a program through the American Society of Mechanical Engineers (ASME) Research Committee on Industrial and Municipal Waste (RCIMW). Collaboration with existing verification programs and various professional and government bodies is encouraged.

Recommendations

It is recommended that rapid, low cost alternative methods for analysis of dioxin and dioxin-like compounds, including those that provide a single measure of toxicity or potential toxicity according to a biochemical reaction, be considered for routine monitoring programs, and that appropriate sample preparation methods be developed. A multi-lab or multi-vendor evaluation program, refereed by independent bod(ies), is recommended to provide a well-established basis for understanding the capabilities and limitations of each method.

References

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