Consideration of Alternative Ion Abundance Ratio Criteria for the Identification of PCDDs and PCDFs by High Resolution GC/MS

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The natural occurrence and abundance of stable isotopes of various elements have been important aspects of mass spectrometry since its inception. The high relative proportions of the heavy isotopes of carbon, oxygen, nitrogen, sulfur, and chlorine have been useful in the identification of specific compounds and the elucidation of their structures. In the field of environmental chemistry, the presence of m/z's due to the ^{37}Cl isotope is often crucial to the identification of an environmental contaminant.

The study of polychlorinated dioxins and furans (PCDDs/PCDFs) relies on the presence of mass spectrometric peaks representing the ^{37}Cl contribution. The ratio of the abundances or intensities of the peaks representing the $[M]^+$ and $[M+2]^+$ ions or the $[M+2]^+$ and $[M+4]^+$ ions have been recognized as an essential aspect of the qualitative identification of these compounds since the early 1970's. Baughman and Meselson[1] specified the use of the ratio of m/z 320 and 322 as early as 1973. Other early investigators in the field also specified the ratio of these ions as an important means of confirming the presence of TCDD.

While these investigators used the ion abundance ratio as part of their requirements for identifying a chromatographic peak as a PCDD or PCDF, their discussions of its use most often simply refer to a comparison to the theoretical isotopic ratio. From the work of Benyon[2], one can derive the theoretical relationship between the $[M]^+$ and $[M+2]^+$ or $[M+2]^+$ and $[M+4]^+$ ions for the tetra- through octachlorinated dioxins and furans. The more difficult problem is to specify the degree to which an observed ion abundance ratio must match the theoretical ratio.

The U. S. Environmental Protection Agency has been actively working on dioxin-related problems since the mid-1970's, and has developed and published a variety of methods for the determination of TCDD or PCDDs/PCDFs (see the table below for examples). Each of these methods has relied on some assessment of the ion abundance ratio in identifying the compounds of interest. Unfortunately, these methods have used a variety of specific limits on the ion abundance ratio, and the rationales behind the choice of those limits has never been explicit. Examples of these EPA methods and their respective limits are shown in the table that follows.

EPA Method	Date	Ion Abundance Ratio Specification
Harless et al. (TCDD only)[3]	1980	0.75 - 0.98 (observed)
Harless et al. (TCDD only)[4]	1982	0.79 ± 10%
EPA CLP (TCDD only)[5]	1983	0.67 - 0.87 (± 13%)
EPA Method 613 (TCDD only)[6]	1984	± 10% of ratio in calibration standard
EPA Region 7[7]	1985	± 15%
EPA CLP (TCDD only)[8]	1986	0.67 - 0.90 (-13% to +17%)
EPA SW 846 Method 8280[9]	1986	approx. ± 15%, slight variation by level of chlorination
EPA SW 846 Method 8290[10]	1987	± 15%, except pentas, at ± 20%
EPA Method 1613[11]	1990	± 15%

Based on extensive reviews of EPA documents and discussions with Agency personnel, it is apparent that the ion abundance ratio limits have typically been derived from a consensus of acknowledged experts in this field. Literature reports on the analysis of PCDDs and PCDFs have often followed the lead of the EPA methods. In recent years, the limits have typically comprised a ± 15% window around the theoretical ion abundance.

The need for some limits on the degree of agreement between the observed ion abundance ratio and the theoretical ratio is obvious. The difficulty comes from the use of a single set of limits. Once a limit is established, any peak that has an ion ratio outside that limit cannot be unequivocally identified as a PCDD or PCDF. The use of data from peaks that do not meet ratio then becomes subject to professional judgement and specific policies within an EPA Program Office. For instance, the reporting requirements for Methods 8280 and 8290 from the EPA Office of Solid Waste and Emergency Response require that a laboratory calculate a worst-case estimate of the concentration represented by a peak that does not meet the ion abundance ratio limits. The estimate, termed an "Estimated Maximum Possible Concentration" or EMPC, may be useful in calculating the worst-case risk that might result from exposure to soil, water, or solid waste.

In contrast, under the National Pollutant Discharge Elimination System (NPDES), EPA requires that some municipal and industrial wastewater dischargers monitor their effluents for a wide range of pollutants including PCDDs/PCDFs. Many of these pollutants have associated mass discharge limits, and the presence of a pollutant above such a limit constitutes a violation of the Clean Water Act. Substantial penalties may be associated with such violations. In the case of PCDD/PCDF analyses, the presence of a peak that does not meet the established identification criteria is not sufficient evidence of such a violation, and the calculation of an EMPC value is not appropriate. If Method 613 or 1613 is specified for compliance monitoring, peaks that do not meet all of the identification criteria, including the ion abundance ratio, are reported as "not detected". While this approach may lead to an increased risk of false negative results, the difficulties in regulating compliance using a value termed "Estimated Maximum Possible Concentration" are immense.

There are a variety of possible causes for peaks that do not meet the ion abundance ratio limits. Those causes include: co-eluting interferences such as PCBs that produce an m/z in one of the channels being monitored for PCDDs/PCDFs, contaminants in the instrument carried over from previous samples, instrument drift, inadequate tuning of the instrument, misquantitation of oddly shaped peaks, peaks with small shoulders, etc. While the occurrence of peaks just outside the ± 15% limits is more common for sample peaks, it is also occasionally observed for peaks in calibration standards, in spiked reagent water aliquots, and even for peaks representing isotopically labeled standards.

Careful review of all analytical results can detect most co-eluting interferences, misshapen peaks, and common laboratory errors and omissions, especially where problems occur with labeled compounds or calibration standards. However, it is not feasible to rule out interferences extracted from the sample matrix in every instance. Similarly, it is not feasible to reanalyze each affected sample, nor to subject each such extracts to additional cleanup techniques which may not resolve the issue.

While not always readily apparent from the review of the analytical results, slight variations in tuning or the effects of instrument drift during the course of a day may cause some PCDD/PCDF peaks to appear to be outside the specified limits for ion abundance ratio. Instruments in need of routine cleaning and maintenance are also cited by laboratories as potential causes for peaks outside of ion abundance ratio limits.

Because of the need to use PCDD/PCDF measurements for compliance monitoring, the EPA Office of Water is proposing a new approach to using ion abundance ratios as a means of identifying PCDDs and PCDFs determined by EPA Method 1613. First, the ion abundance ratio of each unlabeled and labeled analyte in the calibration standards must meet the ± 15% window around the theoretical value. As in the past, any peak in a field sample that meets all of the identification criteria, including the ± 15% window around the theoretical value is considered identified as a PCDD/PCDF.

However, once the daily performance of the instrument has been established by the analysis of a calibration standard, if a peak meets all the identification criteria except the ion abundance ratio limit, then its ion abundance ratio would be compared to the ion abundance ratio of that calibration standard. A ± 10% window would be established around the observed ion abundance ratio for the standard. If the ion abundance ratio of the sample peak falls within this new window, the peak would be considered identified as a PCDD/PCDF. If the ion abundance ratio of the sample peak falls outside both windows, then the peak would not be reported as a PCDD/PCDF.

For example, if the 1,2,3,7,8-PeCDD in the most recent calibration standard has an ion abundance ratio of 1.40, compared to the theoretical value of 1.55, and a sample peak has a ratio of 1.29, the sample peak would be outside the traditional ± 15% window of (1.32 - 1.78). However, a ± 10% window around the standard would allow values as low as 1.26 to be considered as positively identified.

At worst, if the calibration standard had an ion ratio at the very edge of the existing window, e.g. 1.32 for a PeCDD, the expanded window would range as low as 1.19. This would represent less than a 25% deviation from the theoretical value.

The major advantage of this approach is that it recognizes the potential effects of instrument tuning and drift on ion abundance ratios and qualitative identification. The adjustments to the acceptance criteria are made on a daily basis, and reflect a measure of

daily performance. This is preferable to simply widening the limits beyond ± 15%.

The need to calculate the ± 10% window around the most recent calibration standard may seem cumbersome, and may be viewed as a disadvantage by some. However, it would ultimately lead to fewer reanalyses, and fewer questions raised weeks or months after the analyses have been submitted to the client. Moreover, its places emphasis on monitoring instrument performance and stability back on the operator, rather than relying on the review of various quality control measurements to determine acceptable performance.

EPA plans to include these alternative ion abundance criteria in a future revision of Method 1613, which is expected to become the Agency's sole high resolution GC/MS method for dioxins and furans. In the meantime, EPA is soliciting comments from conference participants and others regarding this proposal.

References

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