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Dioxin analysis : Harmonized Guidelines and Criteria for the Validation and Quality Control

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Introduction

Disaccord problems for the validation and quality control of analytical work related to polychlorinated dibenzo-ρ-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) among the different methods are presented. The intention is that international harmonized guidelines are need to help to ensure the reliability and comparability of results, especially those which may be used as a basis for the establishing the national residue limit for regulations and international trade. Some examples of the disaccord for the validation and quality control work affect quantification are presented in Table 1.

Table 1. Examples of criteria for conformation of identity and acceptance of quantification

	US EPA Method	United Kingdom
Signal-to-noise ratios	-Qualitative Determination; ≥2.5 for each CDD or CDF detected in a sample extract and ≥10 for all CDDs/CDFs in calibration standard.	-Qualitative Determination; > 2 for all relevant standards >20 for internal quantification standard. -Measured response significantly greater than that for blank.
Ion abundance ratios	-The ratio of the integrated areas must be within the ±15% of the theoretical ion abundance ratio. -Or within ±10% of the ratio in the midpoint(CS3) calibration or calibration verification(VER).	-Isotope ratio within ±15% of mean for standards.
Retention times	-The relative tR of the peak for 2,3,7,8-substituted CDD/CDFs must be within the established criteria limit. -The tR of peaks representing non 2,3,7,8--substituted CDD/CDFs must be within the retention time windows established. -The absolute tR of the $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD GCMS internal standards in the verification test shall be within ±15 s of the tR obtaining during calibration.	-Simultaneous (+2/-0s or +2/-0 scans) response for analyte and matching internal standard. -Identical tR (±2s or ±2 scans) for analyte and matching external standard. -For hepta and octa chloro can be increased ±4s or ±4 scans.

	-The relative tR of CDDs/CDFs and labeled compounds in the verification test shall be within the established limit.	
Recovery	-The recovery of each labeled compound must be within the given limit. If the recovery of any compound fall out side of given limits, method performance is unacceptable for that compound in the sample. To overcome such difficulties of the performance must be carried out. -Correction : not mentioned	-Correct use of Internal quantification standards(IQS) provides quantitative results wich are automatically corrected for recovery and sensitivity validation and should be an integral part of the quantification method. -The use of Internal sensitivity standards is not essential, and the recovery of IQSs can alternatively be assessed by an external standard method.
Smoothing	-Not mentioned	Smoothing process must be investigated as part of initial validation, and the parameters described in the method document and applied consistently.
Analytical time limit	-12-hour period of operation is recommended	-Not mentioned.

The purpose of this study is to identify the instrumental stability related to quality control, to find possibility to prolong the analytical time limit focused on ion abundance ratios.

Methods and Materials

Sample Preparation

Prior to analysis, calibration standard solutions with the different concentrations of PCDD/DFs (CSL,CS1, CS2 and CS3, Wellington Laboratories Inc.) were carefully transferred to the sample vials with equivalent volume, respectively.

Quantification and Identification

Identification and quantification of PCDD/DFs were performed by a high-resolution gas chromatograph (Hewlett Packard 6890 series) coupled with high-resolution mass spectrometer (Micromass, Autospec-Ultima). The mass spectrometer was operated in an electron impact mode and in the selected ion monitoring mode at a resolution R>10,000 (10% valley) using Masslynx 4.0 program. Separation was achived using a DB-5MS (J&W scientific; 0.25 mm ID × 0.25 μm film thickness × 60 m length). The column oven temperature was programmed from an initial temperature of 160□ to a final temperature of 310□(total run time 60 min).

Experiment Design

The calibration standards (CSs) of US EPA 1613 method are logarithmic fold-increasing concentration. Experiments were performed for 24 hours after SIR calibration. CSL and CS1 were injected every an hour,

but CS2 and CS3 were injected 3 hour-interval (eg: CS2, nonane, nonane, CS2…) for 24 hours after SIR calibration to prevent the effect of wrong quantitation by high concentration contamination.

Results and Discussion

The wide range differences of labelled CDDs/CDFs's concentration between sample spiking solution and standard solution could make the quantification errors. The concentrations of native CDDs/CDFs for calibration are logarithmic fold-increase, but the labelled compounds are always equal concentration. The changes of ion abundance ratios were checked under pre- and post- 12 hour period of operation, investigating the standard deviation (SD) of ion abundance ratios between the low concentration natives(≤ CS1) and high concentration natives(≥CS2). The groups of ≤CS1 always showed wide ranges of SD but the groups of ≥CS2 showed narrow ranges. And the labelled CDDs/CDFs were always narrow ranges of SD and stable, too. Those results showed the higher possibilities for increasing the uncertainty factor during analysis under the isotope dilution method for dioxins.

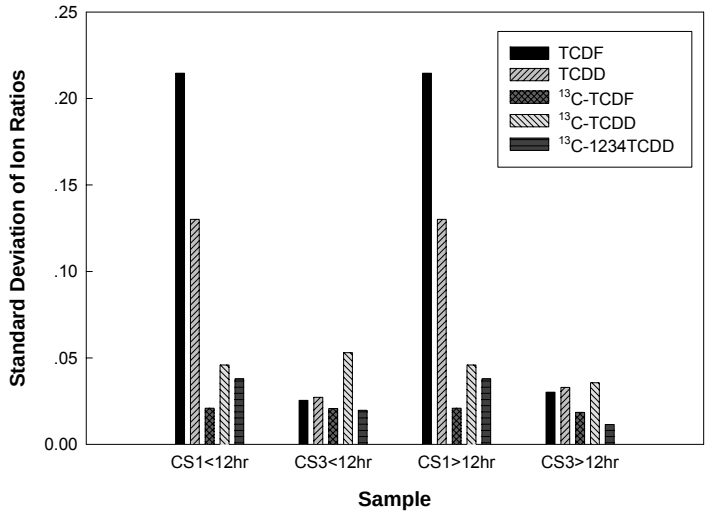

Fig. 1. The changes of ion abundance ratios between CS1 and CS3 TCDD/Fs under the pre- and post- 12 hour period of operation.

During the 24-hour period of operation, the native group of ≤CS1 always showed outer-range ion abundance ratios at the 15% control limits until the 10-hour period of operation, but the native group of ≥ CS2 and the labelled CDD/Fs were within the 15% control limit every time(Fig. 2). These results have no relationship to the numbers of chlorination. In conclusion, to determinate the higher concentration of dioxin contaminated sample, 24-hour period of operation can not affect the determination of dioxin levels which are nearly at the CS2 levels of concentration, and the analysis time can be prolonged within 24 hours. But to determinate the low concentration of dioxin contaminated sample, instrumental stability focused on ion abundance ratios must be kept on eye on for the isotope dilution method within 12- hour period of

operation. Besides, the concentrations of VER standard in US EPA method are not proper for method verification at the low level quality control.

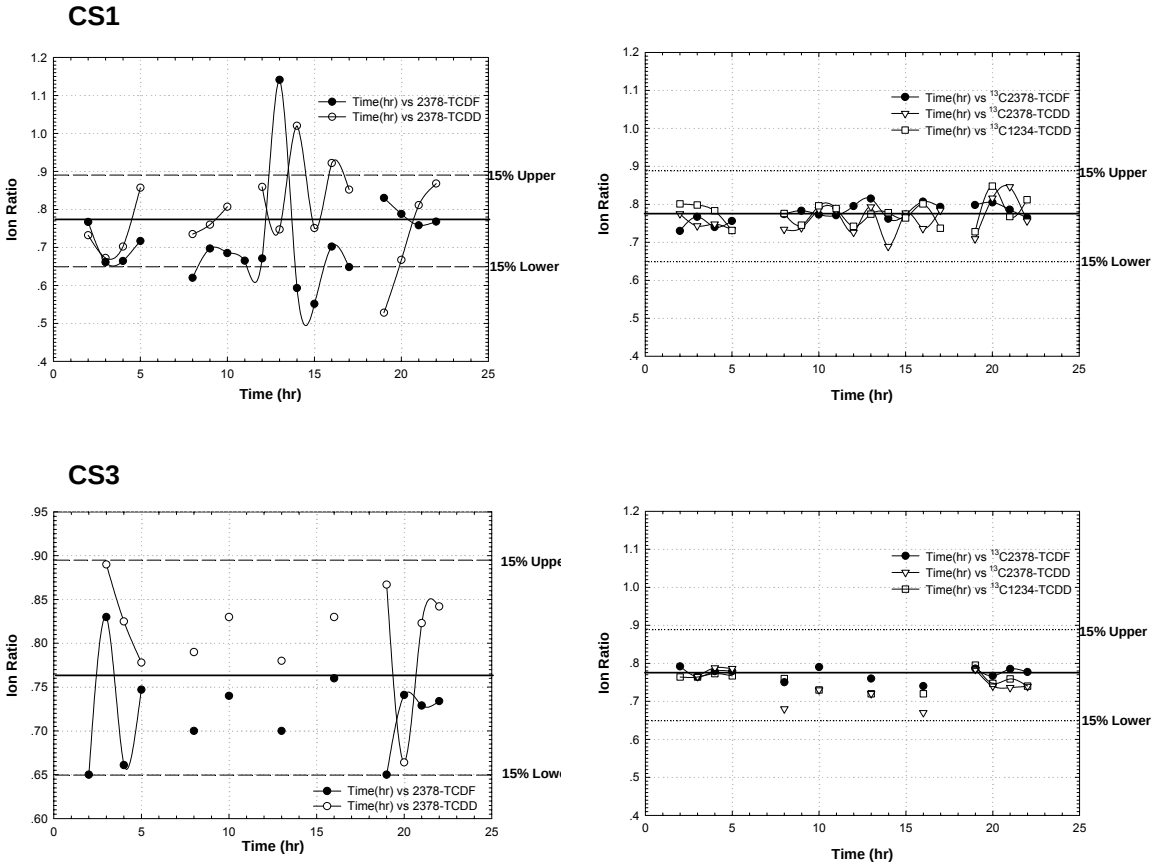

Fig. 2. The changes of ion abundance ratios during the 24-hour operation.

4. References

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