PREPARATION AND QUALITY CONTROL OF POLYHALOGENATED DIBENZO-P-DIOXIN AND DIBENZOFURAN ANALYTICAL STANDARDS

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Abstract

Polyhalogenated dibenzo-p-dioxins and dibenzofurans have been synthesized and standard solutions have been prepared to be used as analytical reference standards. Rigorous quality control procedures have been developed and followed to ensure accuracy and reliability of these analytical standards.

Introduction

Analytical reference standards have a variety of uses such as isomer identification, quantitation, and as spiking solutions in the analysis of dibenzo-p-dioxins (dioxins) and dibenzofurans. The accuracy of an analysis is dependent upon the reliability and accuracy of the reference standard. Since 1983, Cambridge Isotope Laboratories, Inc. (CIL) and Radian Corporation have provided analytical standards to government, industrial, and research laboratories. It has been our goal to provide standards of the highest quality through a strict QA/QC process.

Consensus values of 2,3,7,8-substituted isomers of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from CIL/Radian were determined through an interlaboratory testing study.[1] The results of that study illustrated that consensus average values agreed closely with CIL/Radian standards (15 out of 17 were within 4% of the target value). The accuracy of these and many other standard solutions was achieved using standard preparation methods and quality control procedures developed by CIL/Radian. Presently, we wish to describe these procedures in greater detail.

Methods

Each dioxin and dibenzofuran isomer is synthesized from well characterized intermediates using well documented isomer-specific procedures. High chemical purity is achieved through multiple crystallizations and/or chromatographic methods and confirmed by GC (FID) and HPLC. Isotopic purity for ^{13}C materials is confirmed by GC/MS. Structure confirmation is accomplished by GC, GC/MS, and NMR. Standard solutions of purified compounds are then prepared through a multistep process.

A microanalytical balance is first calibrated internally and then externally using a class "S" National Bureau of Standards (NBS) traceable weight. Three technicians each independently weigh the crystalline material into screw cap vials. Each technician then transfers the contents of each vial into volumetric flasks. The vials are rinsed and sonicated with the appropriate solvent three times each to ensure complete transfer of crystalline material. The solutions are then diluted to volume. The three solutions are sonicated for 30 minutes to ensure complete dissolution of solid material. A standard dilution of an aliquot from each solution is made for analysis by GC using an electron capture detector (ECD). Each of the three solutions is injected in triplicate. Three injections of a single solution must be within 3% relative standard deviation (RSD) of peak areas. Overall comparison of peak areas of the three solutions must be within 5% RSD. When these criteria are met the three solutions are combined and flame sealed in ampules. Random analysis of ampules from early, middle, and late portions of the sealing process is then performed. This is carried out as described above for the three solutions with the overall RSD of peak areas falling within three percent.

Due to limited amounts of ^{13}C labeled crystalline material, the procedure is altered slightly. A single weighing each of labeled material and unlabeled material is performed, and a stock ampule of the appropriate unlabeled material are used for comparison analysis by the GC/ECD method.

The interlaboratory testing study mentioned above provided consensus values for seven PCDDs and ten PCDFs, and these isomers can be termed "certified" reference standards. All new batches of these unlabeled and ^{13}C labeled

isomers are compared to the "certified" standards using the GC/ECD method as a further assurance of the accuracy of the solutions.

Results and Discussion

By using three technicians for independent weighing and solution preparation, the risk of human error is minimized. The multi-injection process then assures agreement of the three solutions. Any minor errors are averaged out by combining the three independent solutions. Any changes to the combined solutions during the ampuling process would be indicated by the random ampule analysis.

By using the above methods, over 100 analytical reference standards have been prepared including ^{13}C labeled and unlabeled polychlorinated dibenzo-p-dioxins and dibenzofurans, ^{13}C labeled and unlabeled polybrominated dibenzo-p-dioxins and dibenzofurans, and mixed bromo/chloro dibenzo-p-dioxins and dibenzofurans. Based on results from the interlaboratory testing study, the methods described above yield highly accurate solutions and provide the quality assurance necessary to ensure reliable analytical reference standards.

REFERENCE

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