6-17-91 RF

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

JUN 17 1991

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

**MEMORANDUM**

Subject: Protocol for the Determination of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in Chlorothalonil. Chemical 081901. I. D. 1812-268. DP Barcode D158701. CBRS No. 7363.

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Background

Griffin Corporation previously submitted manufacturing data for technical 97.5% chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) in response to a DCI. The purpose of the DCI was to evaluate certain manufacturing processes for the potential to form polyhalogenated dibenzo-p-dioxins and/or dibenzofurans. The data were reviewed and it was concluded that the potential existed for the formation of halogenated dibenzo-p-dioxins and dibenzofurans under the manufacturing conditions described by Griffin Corporation (DEB Memorandum 02/23/90, S. Funk, DEB No. 6121). The registrant was requested to supply the results of the analyses of seven lots of technical chlorothalonil for polyhalogenated dibenzo-p-dioxins and dibenzofurans. The registrant has responded (11/02/90; received 11/09/90) with a document entitled "Determination of Polychlorinated Dibenzo-p-Dioxins nd Dibenzofurans in Chlorothalonil."

Discussion

The document supplied is not an analytical protocol. Rather it is a general outline of objectives and of a method development program. The overall objective is to develop an isotope dilution high resolution gc/high resolution ms method modeled on EPA methods 8290 and 1613. The registrant repeats the mandatory limits of quantitation (LOQ's), precision, and accuracy requirements stated in the dioxin/dibenzofuran DCI of 06/87 as data quality objectives. The outline notes that a technique must be developed for separating the dioxin/dibenzofuran impurities from the chlorothalonil matrix. Suggested techniques include liquid/liquid extraction, fractionation by chromatography columns, size exclusion chromatography, and supercritical fluid chromatography. Residual interferences in the dioxin/dibenzofuran extracts will be removed by standard micro-column chromatography. No additional details are provided.

The majority of the submission deals with the deliverables. Some of the more pertinent sections are:

1. Discussion of sampling, and details of any deviations from protocol.
2. Discussion of the sample preparation, specifically which options were utilized, any deviations from protocol, and problems encountered.
3. Summary of all initial and continuing calibration results, including average response factors, percent relative standard deviation, and relative percent difference. Any outliers will be discussed.
4. Tabular summary of sample analysis results, including internal standard recovery statistics.
5. Quality control results, including limit of quantitation determination, matrix spike, and labeled internal standard recovery (blanks, samples, and fortified samples).
6. All raw data and chromatograms (appendix, optional).

The registrant notes that sufficient detail will be provided to permit verification of all calculations.

Conclusions

The document submitted is a general statement of objectives and a very general outline of the procedures contemplated to achieve the objectives. It is not a detailed analysis protocol. The objectives and course of action outlined are acceptable to CBRS. The registrant should consult the Guidelines for the Determination of Polyhalogenated Dibenzo-p-Dioxins and Dibenzofurans in Commercial Products (EPA-5609/5-87/007) and EPA methods 8290 and 1613 for direction on specific details of the analysis. The registrant is reminded of the following (not inclusive) requirements:

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1. At least one labeled internal standard is required for each level of 2,3,7,8-chlordibenzodioxin and dibenzofuran chlorination (8 internal standards minimum).
2. Internal standards must be present at or below the EPA-required limit of quantitation (LOQ) for the corresponding unlabeled dioxin/dibenzofuran series, e.g., 0.1 ng/g for TCDD and 2.5 ng/g (or less) for HxCDD.
3. One or more recovery standards must be added to the final extract before analysis to determine the internal standard recoveries in every sample and control.
4. At least one sample must be analyzed in duplicate. The RPD for any target analytes and for the internal standards must be $\leq$ 20%.
5. At least one sample must be spiked (MS) with the target analytes at concentrations in the calibration range, about 1X to 10X the LOQ's. Recoveries (accuracy) of each analyte must be 50% - 150% with no correction for internal standard recovery.
6. The initial calibration must include the LOQ concentration of each analyte and at least 3 additional points. An average relative response factor for an analyte may be used only if the relative standard deviation is $\leq$ 20%.
7. The response factor for an analyte in a continuing calibration check may not differ from the initial mean relative response factor by more than 30%
8. A method blank must be processed with each group of samples (10 or less prepared at the same time). The blank must contain all internal standards, surrogates, etc. No target analyte may be present in the blank at or above the analyte's LOQ.
9. The actual ratio observed for each pair of monitor masses (both natural abundance and radiolabeled) must be within 20% of theoretical. Theoretical values are given in the Guidelines....
10. Retention time windows must be established for each target analyte. Observed retention times (targets and internals) must be summarized for each standard, control, and sample.
11. Confirmatory analyses (second column) are required if there is any question as to the presence/absence of a target analyte at or above that analyte's LOQ. For example, a second column confirmation would be required if 2,3,7,8-TCDF appeared to be in a sample at a concentration of $\geq$ 1 ng/g and the analytical column were a DB-5.
12. Proper tune of the mass spectrometer and adequate resolution must be demonstrated.
13. The signal-to-noise ratio for each internal standard (at or below the LOQ) and each calibration analyte (at or below the LOQ) must be $\geq$ 10 to 1.
14. Chromatograms and raw data should be provided and

arranged in logical, labeled fashion. The registrant listed this as optional; it is required.

The registrant is advised to validate the final analytical method before the analysis of actual sample lots of chlorothalonil. Four or more samples of the technical product should be spiked with the target analytes (at or near the LOQ) and analyzed. Precision and accuracy should be established. The registrant may want to consider the use of control charts for monitoring internal standard recoveries.

A detailed analytical methodology is required with the final report.

The registrant is also reminded that the seven samples must be be chosen in random fashion from all available lots. A detailed sampling protocol is required with the final report.

Recommendation

The registrant is advised to proceed with the collection and analysis of seven lots of technical chlorothalonil for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans after developing a sampling protocol that provides for the random selection of seven lots and after developing adequate analytical methods that follow the outline of the current submission and that meet the requirements (nos. 1 - 14) stated in the Conclusions. The sampling protocol and analytical method(s) may be submitted with the final report. Failure to meet the requirements of the dioxin analytical chemistry DCI and Guidelines may necessitate resampling and reanalysis. The registrant is advised to consult CBRS or submit complete protocols if questions/concerns arise.

cc: RF, Dioxin SF, Chlorothalonil Reg. Standard File, Circ., S. Funk, C. Furlow (PIB, FOD).

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