QUALITY ASSURANCE CONCERNS IN DIOXIN/FURANS ANALYSES IN THE PULP AND PAPER INDUSTRY

John J. Tice IV, Georgia-Pacific Corporation
Washington D.C. 20006

ABSTRACT

Pulp and Paper dioxin/furan analyses in the United States, particulary compliance testing, could be improved by implementing further methods development, consistent and standardized methods, statistically sound data criteria, and a better understanding of inter-laboratory variability. Efforts to achieve many or these improvements are underway.

INTRODUCTION

The pulp and paper industry in the United States has committed considerable resources to characterize and decrease the concentrations of dioxins and furans in its pulp and paper products, plant effluents and sludges. Numerous analytical challenges have been encountered in characterizing these complex sample matrices and in determining the sub-trace concentrations, frequently at the low parts per trillion and low parts per quadrillion level. These analytical challenges underscore quality assurance concerns which must be addressed to provide accurate, precise, cost effective and timely results. Some of these concerns are presented in this paper.

METHOD STANDARDIZATION

Consistent analytical methodology is essential to characterize products, to make process improvement changes, and to perform analyses to determine compliance relative to various regulatory standards. The only officially issued method for compliance monitoring is RCRA 8280, an EPA low resolution, full congener GC/MS method which has insufficient sensitivity for determining dioxins and furans in most paper industry samples. Methods ITD 1613A, RCRA 8290 and 513, all EPA high resolution, full congener, GC/MS methods are presently still in draft form. Consequently, it is difficult to perform dioxin and furan compliance testing without officially approved and issued methods. The National Council of Air and Stream Improvement For the

Paper Industry (NCASI) has issued NCASI Method 551, a high resolution, tetras only screening method. It would be beneficial to the regulated community and the regulating agency to have approved methods before any regulatory standards are established. In addition, it is desirable to have the fewest number of methods possible for similar applications.

METHOD CAPABILITY

Once the standardized dioxin/furan analytical approach is established, it is necessary to determine if the method is capable for the type of samples intended, and at the concentration anticipated or where the regulatory standard is set. A number of quality assurance considerations must be taken into account to ensure reliable results:

1) At the outset it must be determined if the analysis is intended for screening, as in process optimization studies, product development or characterization, or for dioxin/furan compliance testing. With screening studies, turn around time is usually critical and quality assurance restrictions are often relaxed. With dioxin/furan compliance testing, very rigid quality assurance requirements must be followed because of the critical implications of the results and the very low concentrations encountered: low parts per trillion for pulp, paper and sludge, and low parts per quadrillion for effluents.

2) The method must be sufficiently sensitive, so that any reported dioxin/furan results are statistically significant. The limit of detection (LOD) for the sought for isomer must be determined experimentally for a given sample matrix. From the detection limit, a limit of quantitation (LOQ) is calculated and is typically 3.3 times the LOD. Any isomer result greater than its corresponding LOQ is considered statistically significant (with approximately 99.9% confidence). The use of the LOQ as a lower quantitation limit, minimizes the possibility of committing Type I and II errors in reporting of results. ITD 1613A employs the minimum level concept and RCRA 8290 the minimum calibration limit, both based upon the lowest calibration point, rather than from experimentally derived parameters.

3) The method must be proven and reliable for the sample matrix intended. Sample preparation and extraction steps should provide reproducible extraction of the sought for isomer. Considerable disagreement exists within the industry as to whether to air-dry pulp samples prior to extraction. Air-drying the pulp aids in

taking a more representative laboratory sample, but 5 days are required and ethanol must be employed as the extractant to adequately penetrate the partially closed cellulosic structure. Although not yet widely accepted in the pulp and paper industry, the Soxlet Dean Stark approach affords the advantage of much faster pulp sample preparation because the water is removed azeotropically during the extraction step. Labeled internal standards are added prior to extraction to assess the efficiency of the extraction step. Here it is assumed that equilibrium between the labeled internal standard and the sought for native analyte is achieved during the extraction step, but insufficient data exists to corroborate this. The cleanup procedure is tailored to minimize interfering species and the actual cleanup scheme can only be devised experimentally. In the pulp and paper industry, sludge samples are considered to be the most difficult to analyze for dioxins and furans and although the sample cleanup procedure has been much improved, not enough is understood about its mechanism to determine the cause of occasional, unexplained low internal standard recoveries.

LABORATORY CAPABILITY

Currently, four paper companies have internal dioxin laboratories, which are used primarily for screening studies. Fewer than ten commercial laboratories are available in the United States to provide the pulp and paper industry with dioxin/furan analyses. A number of quality assurance steps could be taken to improve the dioxin/furan analyses at and among these laboratories through a better understanding of inter-laboratory variability. Some of these improvements are as follows:

1) Uniform methodology, as mentioned earlier, needs to be established at all laboratories serving the pulp and paper industry.

2) Method LOQs should be determined and published at each laboratory for actual samples of the type and expected concentration to be analyzed.

3) Laboratory certification programs should be established, where not available, by any regulatory agency requiring compliance testing.

4) Practical Quantitation Limits (PQL), which are similar to the LOQ but are established through round-robin testing with the various laboratories, should be determined for dioxin/furan analyses. These round-robin samples should be well composited and homogeneous for the laboratories participating in the study, and representative of the types of samples to be analyzed. The PQL should be the

benchmark in determining whether a dioxin/furan isomer is present or absent.

SAMPLING CONSIDERATIONS

As stated earlier, pulp and paper industry samples are complex matrices, are not homogeneous, can consist of two phases, and often represent many tons of product or material. While the development of any sampling protocol involves many steps, a few key points should be considered.

1) Seven day composites for high throughput processes, such as pulp manufacturing, should be taken and statistically composited. This provides a realistic view of the process capability, rather than that of a one sample "snap-shot" which is easily affected by short-term process upsets.

2) Large enough portions of multi-phasic samples, such as effluents, should be taken to ensure that the sample is representative of that taken at the site. Vigorous agitation should be employed when sampling, both at the site and when partitioning the sample in the laboratory for the dioxin/furan analysis.

3) Many samples taken hot stratify when cooled to room temperature. Proper instructions need to be given to the laboratory in reheating the sample to ensure that a representative aliquote is taken.

4) Plant samples are often taken by maintenance personnel and they need to be properly trained in all quality assurance aspects of sampling.

CONCLUSIONS

The successful implementation of these suggested improvements will greatly assist the pulp and paper industry as well as the regulatory agencies in developing high quality dioxin/furan results. Such an implementation should be a joint effort with industry, the contract laboratories and the agencies.

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