TRACE CHLORINATED ORGANICS ANALYSIS IN HIGHLY RADIOACTIVE SAMPLES – PROBLEMS AND SOLUTIONS

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ABSTRACT

This paper discusses some of the problems that are associated with the analysis of highly radioactive samples for chlorinated organic compounds at the part per trillion level. To date, both high fission product activity and transuranic activity have been handle successfully. Communication issues, sample handling, transfer between laboratories and analytical challenges are discussed.

HISTORICAL PERSPECTIVE

The post World War II time period brought about the advanced development of nuclear weapons, nuclear fuel and experiments that produced large amounts of mixed wastes - radioactive materials contaminated with hazardous materials, such as polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF). The accepted waste disposal criteria of the time included underground storage of liquids and sludges in large tanks and the burial of solid materials in waste pits. This created storage areas containing mixed wastes. Regulations involving these wastes were not promulgated until the 1970's which include the Solid Waste Disposal Act as amended by the Resource Recovery Conservation Act of 1976 (RCRA) and the Toxic Substance Control Act (TSCA). Over the same time period, laboratory methodology and the associated instrumentation was being developed to specifically address the need for this type of regulatory analysis.

THE CHALLENGE

The analysis of organic samples for the presence of PCDD, PCDF and PCBs at the part per trillion or part per quadrillion level is a very challenging task. The analysis requires very careful handling in order to remove bulk interferences without losing the analytes of interest, which may be present at picogram amounts. Very few laboratories are equipped with the personnel and equipment to perform this analysis.

When this task is complicated by the presence of high radioactivity in the sample matrix, the difficulty of the job is greatly magnified. A laboratory that is equipped to deal with the high radioactivity is unlikely to be able to handle the analysis for PCDD, PCDF and PCBs and vice versa.

THE SOLUTION

A unique solution to this problem has been to combine the capabilities of two laboratories. A protocol that places the sample receipt, primary bulk sample handling, sample fortification and extraction into the hands of a laboratory that is qualified and licensed to handle highly radioactive samples is the first step in the process. The radioactive components can be separated from the PCDD, PCDF and PCB materials in this primary separation stage. The non-radioactive sample extract is then shipped to a laboratory that is equipped to perform further stages of extract purification and sample analysis for the PCDD, PCDF and PCB contaminants. In this manner, a very difficult and potentially dangerous analytical problem is safely solved.

The first step of the process involves communication with the client to determine the project scope, timelines, budgetary considerations, communication pathways, and special requirements. Communication of the data objectives, the points of contact, backup personnel must be established first with the laboratory that will receive the radioactive samples (NELS). They serve as the primary point of contact to coordinate the project from that point.

The communication that is needed between the client, NELS and the laboratory that performs the PCDD, PCDF, PCB sample analysis (TRI) involves the issues addressed above and also, progress reports, unexpected findings and problem resolution.
The logistics of shipping of radioactive samples to NELS and the plans for eventual waste and sample disposal or return to the client must be addressed in the planning stages of the process. Once received at NELS, the samples must be screened for the levels of radioactivity, the types of radioactive emitters and any special problems that the samples may present. The issuance of a radiation work permit (RWP) may occur if the activity of a sample exceeds 100mRem/hour at one foot. Similarly, the presence of transuranics dictates the use of additional safety procedures. All such extraction and analysis work is carefully planed and monitored by health physics and safety professionals who augment the laboratory staff.

The analysis of materials for PCDD, PCDF and PCBs at the part per trillion level involves 7 steps:

1. Measuring an aliquot of the sample
2. Addition of a known amount of carbon-13 labeled internal standard analogs of the analytes of interest to the sample aliquot.
3. Solvent extraction of the analytes of interest from the bulk sample matrix
4. Concentration of this sample extract
5. Purification of the sample extract to remove interfering materials that are not the analytes of interest – typically done by normal phase column chromatography
6. Analysis of the purified and concentrated extract using high resolution gas chromatography – high resolution mass spectrometry (GCMS)

7. Data analysis, review and reporting

Steps 1 through 4 are performed at NELS. A radioactive screening of samples is performed before extraction to determine any special needs in the process. The carbon-13 labeled internal standard analogs and the protocols for their usage are provided by TRI. The use of carbon-13 labeled internal standards enables the analyses to be more precise and accurate.

The increased precision and accuracy is provided because the technique of isotope dilution mass spectrometry is used during the GCMS analysis. In this technique, the response of the analytes are measured relative to that of the carbon-13 labeled internal standards that are added to the sample prior to extraction. Any losses of analyte that occur during the extraction and purification stages are compensated for by the use of the carbon-13 labeled internal standards response.

After sample extraction and concentration, the extract is tested to determine that no residual radioactivity can be measured. After the extracts are determined to be free of radioactivity, they are shipped to TRI for the performance of steps 5 through 7. To date there have been no extracts that the laboratory has been unable to ship because of radioactivity and licensing requirements.

This transfer requires accurate documentation of all of the procedures that occurred in steps 1 through 4.

The sample extracts that are received at TRI are logged into a tracking system, their identities confirmed and they are then scheduled for purification and analysis. The typical process involves a solvent exchange into a non-polar solvent, followed by chromatography on silica and alumina. These chromatographic procedures are designed to remove the components that are not similar in properties to the PCDD, PCDF and PCBs. In some cases, additional steps are required to remove other interfering materials that may be in the extract at high concentrations. Typical of such interfering materials would be polynuclear aromatic hydrocarbons (PAH).

The final purified extract is analyzed on a GCMS system that is capable of achieving a minimum of 10,000 mass resolution. This use of mass resolution enables the analysis to be very specific for compounds of interest. The separation of compounds that differ by as little as 0.030 Dalton at a molecular weight of 300 can be achieved at this mass resolution. Therefore, compounds that are not of the correct mass will not create analytical interferences. This increased specificity, coupled with the extensive extract purification and the basic instrumental sensitivity enables the detection of less than one picogram of a given compound injected onto the GC column. This translates into a part per trillion level detection limit for this technique.

Quality control is demonstrated at several stages of the GCMS analysis. The demonstration of instrument mass resolution is performed every 12 hours. The linearity of the calibration for the analytes of interest (initial calibration) is performed by the

analysis of 6 calibration standard solutions, ranging in concentration from 0.5 pg/ìL to 200 pg/ìL. The specification is less than 20% relative standard deviation of the calculated relative response factor for analytes. On a 12-hour basis, this calibration is demonstrated to be validated by the analysis of a single point from the curve (continuing calibration). The GC column performance is also demonstrated on a 12-hour basis.

After performance of all of the required quality control steps, sample analysis is performed. Each sample is analyzed and the resulting gas chromatogram is analyzed. The data system determines the peak area and retention time of each peak that is greater than the required signal to noise level. For each analyte that is measured, two different ions corresponding to the molecular ion (M) and a ^{37}Cl (M+2) containing isotope are recorded. Software reduces the data set to GC peaks with the appropriate mass ions that have matching retention times. For a given level of chlorination, the expected theoretical ratio of the M to M+2 ion is known. The detected GC peaks are identified as the analyte of interest if they:

1. Have the expected retention time for the two masses
2. Have the expected peak area ratio for the two masses

Each chromatogram is reviewed after GCMS analysis, then reviewed by a separate analyst. This analyst generates a concentration report for the sample based upon the measured peak areas for the analyte and its internal standard, the initial sample size, the amount of the internal standard added and the calibration factors. A final data review chemist then inspects this report. A narrative description of the analysis is prepared, copies of relevant information are added and the report is sent to the client.

After delivery of the report, the customer reviews the data and communicates any problems or points of confusion to the NELS laboratory. If these are minor points of interpretation or explanation, they can be handled by communication directly between the parties. More complex issues may require a plan of action with timelines established and detailed coordination among the groups. In this case, the NELS serves as the point of central contact.

CONCLUSIONS

The part per trillion level analysis for toxic organic compounds in the presence of high fission product activity and transuranic activity has been routinely handled. A variety of sample matrices have been treated by this systemic approach.