

A Novel Low-Cost Air Sampling Device (AmbStack Sampler) and Detection System (CALUX Bioassay) for Measuring Air Emissions of Dioxin, Furan, and PCB on a TEQ Basis Tested With a Model Industrial Boiler

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Introduction

The analysis of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) in gaseous samples is very labor intensive, and expensive. Regulatory reporting usually requires a sampling team and several days collect multiple samples. Shipping too is complicated by the use of organic solvent rinses and numerous subsamples that require complex and expensive shipping. Sample analysis, after collection, is also expensive. Multiple clean up steps are needed, and expensive instrumentation is used, such as high resolution gas chromatography (HRGC) coupled to high resolution mass spectrometry (HRMS).

A low cost unitized sampling system, the "AmbStack Sampler" was designed by our group, and combined with a reporter gene bioassay system, the "CALUX" method, to give accurate PCDD/PCDF analyses with much simpler techniques than are currently in use. The AmbStack/CALUX system provides reliable air emission data at a fractional cost of conventional emission methods.

This system has been demonstrated for ambient sampling, low temperature stack emissions, and simulated industrial boiler discharges. The sampling unit, called the "AmbStack Sampler", is commercially available, and uses a polyurethane plug (PUF) insert in a glass sampling cartridge for ambient and stack sampling. AmbStack samples can be directly analyzed for PCDD, PCDF, PCB or polycyclic aromatic hydrocarbons (PAH). The AmbStack Sampler contains a glass probe-cartridge unit, and Teflon® connections a dry gas meter and air pump. After sampling, the probe-cartridge unit is sealed with Teflon®-lined end caps, and shipped directly to the laboratory for analysis. Sample extraction is done by *in situ* solvent extraction and clean up, followed by CALUX reporter gene bioassay.

Xenobiotic Detection Systems, Inc. (XDS) has a genetically engineered cell line which contains the firefly luciferase gene under trans-activational control of the aryl hydrocarbon receptor. This cell line can be used for the detection and quantification of AhR agonists. Exposure of this patented cell line to AmbStack sample extracts yields a direct measure of total TEQ since response of these cells is based on the mechanistic basis by which biologically active PCDD, PCDF, and PCB express their toxicity (1,2).

In the current experiments we demonstrate the sensitivity and performance of the AmbStack Sampler for PCDD/PCDF quantification on a TEQ basis, using the CALUX bioassay and a simulated industrial boiler discharge.

Materials and Methods

Incinerator Conditions

The combustion system used to perform this test was a North American Package Boiler (NAPB), which is capable of firing natural gas or #2 through #6 fuel oils. The boiler is a three pass firetube "Scotch" marine-type design fitted with a North American burner rated at 2.5×10^6 Btu/hr. A dopant (a mixture of 1,2 dichlorobenzene and copper naphthenate) was injected through a separate injection system to the main fuel injection system prior to the burner. The dopant flow rate was adjusted to yield a HCl concentration at the stack of approximately 500 ppm at 7% O₂. A Method 23 sampling train and the AmbStack sampler were placed at the same location in the stack. The flue gas stream for this experiment was stable at a temperature of about 140 °C with a moisture level of about 11 %. Prior to testing the Boiler unit experienced a thermal decontamination process of about 400 hours.

AmbStack sampling and CALUX bioassay

The PUF insert was removed from the cartridge, and the flow direction noted. The forward or "front end" section of the PUF cartridge was separated from the remaining PUF and analyzed separately with the probe rinse, to determine an Apparent Collection Efficiency, ACE. The front 2/3 of the PUF insert was extracted using toluene, and combined with the toluene rinsate from the probe and the cartridge holder. The remaining back 1/3 section of the PUF insert was extracted separately. The front and back extracts were analyzed separately to determine if any sample breakthrough had occurred.

Sample extracts were split into equal aliquots, the first aliquot was prepared by our Method 1 cleanup procedure to measure TEQ activity of chlorinated species (PCDD, PCDF, and PCB). The second aliquot was prepared using our Method 2 Procedure which provides separate extracts to estimate TEQ for PCB and PCDD/PCDF individually. These proprietary clean up processes involve differential chromatography. All extracts were solvent exchanged into DMSO before analysis.

Sample extracts were suspended in cell culture medium. This media was applied to H1.1C2 mouse hepatoma cells (Patent # 5,854,010) grown in 96 well culture plates. In addition to sample dilutions a standard curve of 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD) was assayed. All assays of standards and unknowns were run in duplicate. Plates were incubated for 4 hours in a humidified CO₂ incubator. Following incubation media was removed and cells observed microscopically for viability. Luciferase response, the induction of luciferase activity, was measured optically as total light emission using a BMG Luminometer.

Results

Cell viability: Microscopic examination of the cells following exposure to sample extracts did not reveal any indication of toxicity. Samples were analyzed and compared to a clean PUF blank.

Results of CALUX measurements of TEQ activity from the simulated industrial boiler extracts are presented in Table I.

TABLE I. CALUX RESULTS (NANOGRAM TEQ ACTIVITY PER SAMPLE)

<u>Method 1</u>		<u>Total TEQ(PCDD/PCDF/PCB)^A</u>	
Front End (2/3 PUF/Rinsate)		13.7 ± 3.6	
Back End (1/3 PUF)		2.8 ± 0.6	
<u>Method 2</u>	PCDD/PCDF ^B <u>TEQ</u>	PCB ^C <u>TEQ</u>	Sum ^D <u>Total TEQs</u>
Front End	12.1 ± 2.07	2.01 ± 0.44	14.1
Back End	2.2 ± 0.47	0.91 ± 0.11	3.1

- A. Data are Mean ± Standard Deviation of 5 independent determinations in the CALUX assay for total TEQ activity.
- B. Data are Mean ± Standard Deviation of 3 independent determinations in the CALUX assay for TEQ activity in a sample fraction purified for dioxins and furans.
- C. Data are Mean ± Standard Deviation of 3 independent determinations in the CALUX assay for TEQ activity purified for planar PCB.
- D. Data are the sum of TEQ determinations from PCDD/PCDF and PCB fractions.

Relative emission levels found in collected PUF samples are presented in Table II based on 3.58 M³ air sampled during the 3 hour test period.

TABLE II. ANALYSIS OF AIR SAMPLES (NANOGRAM /METER³ TEQ ACTIVITY)

<u>Method 1</u>		<u>Total TEQs</u>	
Front End		3.8	
Back End		0.78	
Apparent Collection Efficiency		83%	
<u>Method 2</u>	PCDD/PCDF <u>TEQ</u>	PCB <u>TEQ</u>	Sum <u>Total TEQ</u>
Front End	3.4	0.56	3.9

A comparison HRMS analysis was performed by collecting a parallel U.S. Environmental Protection Agency, Method 23 sample. The results of that analysis were 2.75 ng/dscm (7% O₂)

versus 1.9 ng/dscm (7% O₂) by AmbStack and CALUX. The comparison analysis of AmbStack/CALUX showed excellent agreement with HRMS.

Discussion

The comparison analysis of AmbStack/CALUX showed excellent agreement with HRMS. The AmbStack Sampler, combined with CALUX TEQ quantification, gives a rapid and cost effective method to measure PCDD/PCDF emissions. The method was sensitive at concentrations found in a simulated industrial boiler emission. The CALUX screen proved to be rugged in analyzing this complex sample type. The clean up procedure was rapid and data reports were generated in two working days after sampling was complete.

Performance in this study suggests that the AmbStack/CALUX system, using PUF, is suitable for many ambient and industrial applications, such as post control emissions testing. This technique is especially useful as a low cost diagnostic tool to quickly measure dioxin emissions from thermal combustion systems.

References

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