

LABORATORY STUDY ON THE EFFECTS OF MOLECULAR CHLORINE ON EPA METHOD 23 FOR PCDD/PCDF SAMPLING AND ANALYSIS

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Introduction

Stack gases from a primary magnesium production facility located near Grantsville, Utah, have reportedly contained as much as 56 g/dscm (19,000 ppm,) molecular chlorine (Cl₂) (1.9% by volume), as well as over 100 ppm, of hydrogen chloride (HCl). Citizen have expressed concerns as to the potential for dioxin formation from this facility, and federal and state environmental officials have investigated this situation. Analysis of water, soil, and sediment samples collected in and near a contained drainage ditch from the facility has indicated elevated levels (up to 130 ppb) of polychlorinated dibenzodioxin and dibenzofuran (PCDD/PCDF)¹. The need for stack gas testing for PCDD/PCDF has been established, but the reliability of standard test methods when sampling from streams with high chlorine levels was previously unknown.

The U.S. Environmental Protection Agency (EPA) contracted with Midwest Research Institute (MRI) to investigate the accuracy and precision of EPA Reference Method 23² sampling and analysis procedures for measuring PCDD/PCDF levels in this high-chlorine environment. The study was performed under an EPA-sponsored Community Based Environmental Protection (CBEP) project for the Grantsville, Utah area. Grantsville is located close to several other potential pollution sources, including a copper smelter, a commercial hazardous waste incinerator, U.S. Army chemical weapons demilitarization facilities, and a hazardous waste landfill.

The primary objective of the MRI study was to systematically examine the reliability of Method 23 when measuring PCDD/PCDF in gas streams with high chlorine concentrations. A series of laboratory tests was conducted to evaluate method precision, accuracy, bias, and overall suitability under high-chlorine, simulated process gas conditions. In these tests, a gas stream was generated which should be the most likely to affect method operation due to expected or potential "worst-case" stack gas conditions at the magnesium production facility. A mixture of PCDD/PCDF components was dynamically spiked into the gases sampled by a Method 23 train. The dynamic spiking system was designed and used by MRI in a previous study for EPA's Office of Air Quality Planning and Standards^{3,4}. Spiking was conducted while approximating the source stack characteristics for temperature, moisture, particulate matter (PM), chlorine (Cl₂), and hydrochloric acid (HCl) concentrations in accordance with an experimental test design.

Methods and Materials

Twelve (12) test runs were completed to assess the method performance in an environment of high Cl_2 , along with maximum HCl and PM levels encountered at the magnesium production facility. Method 23 was followed, with minor modifications to the XAD preparation and sample extract cleanup procedures. All samples were analyzed using a VG70-250 high resolution mass spectrometer at a resolution exceeding 10,000, following chromatographic separation with a DB-5MS column. Confirmation analysis for 2,3,7,8-TCDF (using a DB-Dioxin 60 column) was not performed since the DB-5MS column has been shown to have equivalent performance to the DB-Dioxin column^{7,8}.

As part of these 12 test runs, 4 "baseline" tests were performed to indicate the effects of changing each individual variable (clean system "zero baseline," HCl only, high Cl_2 only, and PM only). Next, a set of 4 replicate tests was performed to assess the combined effects of HCl and PM on the recoveries of dynamically spiked PCDD/PCDF compounds ("no-chlorine"). Finally, a set of 4 replicate tests was performed in which high Cl_2 was combined with the same HCl and PM levels ("high chlorine"). The no-chlorine and high-chlorine tests provided the two primary data sets used for statistical evaluation as to potential method bias and method precision.

The target and actual test conditions are presented in Table 1. The "high chlorine" condition is a composite worst case of stack gas conditions that may be present at the facility. The "no chlorine" condition is identical except for the absence of chlorine. Each test involved approximately 2 hr of actual sample collection and PCDD/PCDF spiking. The experimental test conditions measured in the laboratory came very close to the target levels for all test runs, and acceptable run-to-run precision was achieved.

TABLE 1. TEST MATRIX AND EXPERIMENTAL CONDITIONS

Parameter	Target	Test Condition					
		Zero Baseline	HCl Baseline	Cl_2 Baseline	PM Baseline	No Cl_2 (4 tests)	High Cl_2 (4 tests)
HCl, ppm	120	-	144	-	-	136-146	143-151
Cl_2 , %	2.0	-	-	1.9	-	-	1.9
PM ^a	Present	-	-	-	Present	Present	Present
Moisture, %	22.0	18.7-21.5				19.0-19.4	18.8-21.1
CO_2 , %	110	10.6-11.0				10.8-11.0	10.6-10.8
O_2 , %	11.4	11.9-12.2				12.1	11.8-12.2
Gas temp., °C	-	69				69	69

- Not applicable

^a Approximately 1,650 mg total mass of particulate matter (PM) placed on sampling train filter, to represent anticipated amount that would be deposited on the filter during stack gas sampling.

Figure 1 shows the experimental apparatus, including the process gas generation system and the dynamic spiking system. Further details on the experimental equipment, the process gas generation procedures, and the dynamic spiking procedures have been reported elsewhere^{5,6}.

A commercially available standards mixture was diluted to achieve spike levels near 1 ng for the tetra- components, 5 ng for the penta- through hepta- components, and 10 ng for the octa- components. Labeled PCDD/PCDF compounds were not used since native compounds were not expected to be present. To simulate typical stack gas particulate matter (PM) at the industrial source, a mixture of 95% magnesium chloride (MgCl_2), 2.5% ferric chloride (FeCl_3) and 2.5% ferrous chloride (FeCl_2) was applied to pre-cleaned quartz filters used in the sampling train, based upon information supplied by the facility to EPA.

ORGANOHALOGEN COMPOUNDS

Results and Discussion

The Method 23 sampling train was found to be quite robust in the harsh, simulated process gas environment produced in the laboratory. Absorbed gases from the high chlorine condition did chemically burn the cellulose thimble used to extract the Method 23 samples, yet the recovery of QC spiked samples generally still met the method quality assurance objectives.

Potential bias was examined for each of seventeen 2,3,7,8-substituted congeners by comparing tests performed with high chlorine present to tests performed without chlorine added (Figures 2 and 3). Results for the homolog groups were also evaluated to look for any evidence of conversion reactions (Figure 4). Figures 2 through 4 show the mean recoveries of each quadruplicate data set and the error bars indicate the standard deviation.

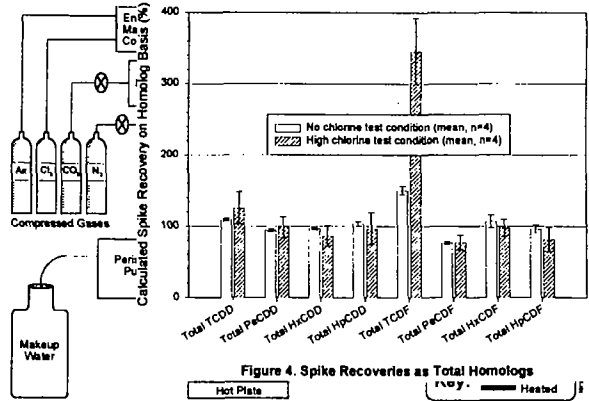


Figure 1. Schematic of Experimental Equipment

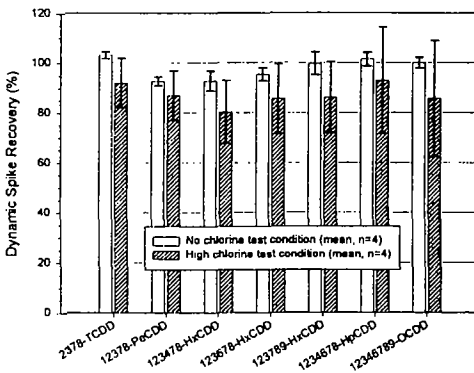


Figure 2. Dynamic Spike Recoveries—PCDDs

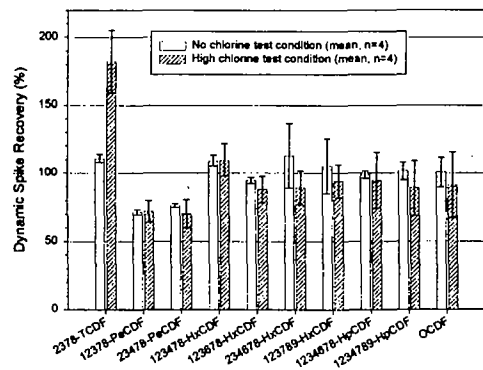


Figure 3. Dynamic spike recoveries—PCDFs

The only statistically significant differences (at the 95% confidence level) found in the dynamic spike recoveries were for 2,3,7,8-TCDF and for total TCDF, with observed positive biases under the high chlorine condition of 71% and 196%, respectively. There was a statistically significant deterioration in precision (at the 95% confidence level) with the high chlorine present, for most cases of the individual congeners and for total homologs (refer to error bars in figures). The lower precision may be due to Cl_2 effects on Method 23, or possibly due to difficulties in maintaining experimental conditions with high Cl_2 .

The high chlorine baseline run showed an elevated recovery of 205% for 2,3,7,8-TCDF (vs. an average of 109% for the other baseline runs) and a recovery of 325% on a total TCDF basis (vs. 179%), providing further evidence that the chlorine was the cause for the method bias observed for the TCDFs.

Except for the high spike recoveries for the 2,3,7,8-TCDF in the high chlorine condition and for some low recoveries experienced in a single high chlorine run, the dynamic spike recoveries were in the range of 70% to 130%, meeting data quality objectives for

the combination of experimental technique, sampling technique, and analytical technique. The cause of the limited (TCDF only) method bias is not clear and further testing is needed to better understand the nature of the observed bias or to see if it would be repeated in actual field conditions, where PCDD/PCDF precursors may be present. It is possible that in the high chlorine test environment, higher chlorinated congeners could have been converted to various TCDFs (including 2,3,7,8-TCDF), but since these congeners were spiked at levels 5 to 10 times higher than the 2,3,7,8-TCDF, it would be difficult to detect a reduction in their recoveries. It is also possible that organic contaminants within the experimental system reacted with the Cl_2 to form TCDF.

To fully address this issue, a field study is recommended using actual process conditions, with spiking (ideally, dynamic spiking) of labeled PCDD/PCDF congeners, including, if feasible, labeled mono- through trichlorinated congeners and unchlorinated dioxin and furan. (Some of the labeled analogs used as field surrogates by Method 23 could be switched from static spikes to dynamic spikes as needed.) For any testing under high chlorine conditions, it is recommended that in the sample extraction, glass wool be placed over the Soxhlet siphon tubes to hold the XAD in place instead of using cellulose thimbles to contain the XAD, since cellulose is subject to chemical burning and degradation from the released gases.

Acknowledgements

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