

**RECENT ADVANCES IN SAMPLING AND ANALYSIS  
OF COAL-FIRED POWER PLANT EMISSIONS  
FOR AIR TOXIC COMPOUNDS**

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**Keywords:** Emissions, Toxics, Advances

## INTRODUCTION

The new Clean Air Act amendments (CAAs) require the evaluation of potential health effects due to emission of hazardous air pollutants (HAPs) from coal-fired power plant (CFPPs). The amendments also specifically require evaluation of mercury (Hg) emissions from CFPP. Although the CAAs specify these measurements be made, standard reference methods for testing all of the HAP emissions from CFPPs are not available and some of the methods currently being used have not been validated.

Previous studies have shown fly ash from coal combustion may be a potential source of HAPs. Samples for these previous studies, however, were collected using conventional methods which do not allow for the normal dilution and cooling that takes place in a plume. Organic compounds, for example, are typically in the vapor phase at stack temperatures and with conventional methods are collected separately from the particles by condensation and adsorption traps. There is evidence, however, that some polycyclic aromatic hydrocarbons (PAHs) can undergo chemical reactions and/or rearrangements when adsorbed on coal fly ash particles. As a result, samples collected with conventional methods may not be representative of CFPP emissions as they exist in the ambient environment. In addition, there are over a dozen different sampling and analysis methods required to measure HAPs from CFPPs each requiring separate probes and sampling teams. This negates to a great extent the possibility of simultaneous sample collection, greatly increases the cost of sampling and introduces the potential for greater uncertainties in the measurements.

Emission measurements of hazardous air pollutants requires an optimization of sampling and analysis methods. Recent advances in emissions measurements have resulted in major strides towards this optimization process. Two recent advances include the development of a plume simulating dilution sampling system using zero background dilutant for simultaneous measurement of the complete set of hazardous air pollutants and a new hazardous element sampling train.

## PLUME SIMULATING DILUTION SAMPLER

Chester Environmental's plume simulating dilution sampler is illustrated in Figure 1. The configuration illustrated is but one configuration that has been used for the simultaneous collection of both gas and particle phase HAPs. An isokinetic sample is drawn into the system through a cyclone preseparator and a heated stainless steel transfer tube. The hot stack gas is drawn from

the transfer tube (similar to a standard Method 5 transfer tube) into the instrument and blending module where it is surrounded by cooled dilution gas.

The dilution gas used for this sampling is nitrogen ( $N_2$ ) derived from evaporated liquid nitrogen but other mixtures such as an 80/20  $N_2/O_2$  mixture could be used. This provides a cool, bone-dry dilution gas with zero background for both particulate and vapor phase species. Keystone/NEA has been using evaporated liquid  $N_2$  for dilution gas with its PSDS for air toxic emission testing since 1988. This type of dilution gas is considered essential because of the need to minimize sulfate artifact formation and an oxygen mixture of dilutant gas is considered important to simulate the  $O_2$  concentration in a plume so as not to inhibit the formation of oxygenated compounds.

After blending and mixing, the diluted gas stream passes through an aging chamber. After exiting the aging chamber and before sample collection, the diluted gas stream passes through a section for determining the pressure, temperature, velocity, and relative humidity. The particle and gas phase samples are sampled downstream of this section.

The sample entering the inlet nozzle will pass through the transfer tube and the dilution chamber for dilution, aging, and collection. The transfer tube is maintained at stack temperature to prevent premature condensation. An S-type pitot tube and a thermocouple are installed on the transfer tube to monitor stack gas velocity and temperature. The flow rate through the transfer tube is established by the difference between the total stack pressure at the inlet nozzle and the static pressure in the dilution chamber. This pressure difference, monitored with a magnehelic gauge installed between the upstream port of the pitot and the dilution chamber, is referred to as chamber pressure. The chamber pressure/flow relationship is established by calibration of the nozzle/transfer tube assembly as an integrated unit. The operating chamber pressure will be determined on site using this calibration with the appropriate temperature and pressure corrections for the actual stack conditions encountered.

The dilution chamber facilitates mixing of the flue gas with dilution gas, cooling and aging of this mixture to simulate the dilution processes occurring in a plume, and distribution of the aged mixture to the various sampling devices. The chamber sections can be configured to affect a variety of dilution, aging, and sampling schemes. The chamber flows are balanced by throttling the dilution gas (supplied under pressure) as required to establish the operating chamber pressure (for the specified flue gas flow rate through the transfer tube) while maintaining the necessary sampling device flow rates (withdrawn under vacuum).

A wide range of sampling methods can be used with the PSDS. Particle loading, for example, can be determined by direct filtration and gravimetry. Both the 8 x 10-inch quartz fiber high-volume and teflon filters can be used to provide independent determination of the particle loading. Particle and gas phase elemental compositions are determined using a combination of sampling and analysis methods. The teflon filters are analyzed by x-ray fluorescence and neutron activation analysis for particle phase trace elements and charcoal traps are analyzed by the same methods for gas phase elements. This ultra-sensitive trace element procedure provides low detection limits (down to  $0.05 \mu\text{g}/\text{m}^3$ ) for a wide range of elements. The particulate phase elements measured by this method include Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Cd, Sb, Ba, Hg, Pb, U, and Th. Of the four elements expected to have a significant gas phase component at plume-simulated conditions (As, B, Hg, and Se), three (As, Hg, and Se) can be sampled and measured by the charcoal trap method.

The gas concentration in the PSDS is typically reduced by about 30 fold from the stack concentration by dilution. To compensate for this lower concentration, larger volumes are sampled and more sensitive analytical methods used to provide improved detection limits.

#### HAZARDOUS ELEMENT SAMPLING TRAIN

Current EPA sampling and analysis methods for hazardous elements rely on method 101A for mercury and tentative method 29 for multiple metals testing. Both methods are based on EPA method 5 stack sampling probes and impinger trains. Method 101A uses potassium permanganate in sulfuric acid impingers to extract mercury from a gas stream. Tentative method 29 adds hydrogen peroxide-nitric acid impingers in front of the permanganate impingers to remove other metals. These impinger trains are difficult to run, somewhat dangerous, require complex sample recovery and analysis procedures and are costly. In addition, concerns for the validity of these methods have also been raised and extended sampling periods are required to achieve adequate detection levels.

A method has recently been developed to measure hazardous element emissions that combines activated charcoal impregnated filters (CIFs) and XRF analysis. This method is applicable to all of the elements on the EPA hazardous air pollutants (HAPs) list except beryllium which must be analyzed by inductively coupled argon plasma (ICAP) methods but can be done with the same hazardous element sampling train (HEST). This new, innovative method not only has the ability to measure mercury in CFPP emissions with sampling intervals as short as 10 minutes, but has the potential to achieve order of magnitude better detection limits for mercury and the other HAP elements that are now measured with tentative method 29. ◦

Chester Environmental's HEST is schematically illustrated in Figure 2 to collect both particulate and gas phase samples, and XRF and ICAP to determine elemental concentrations as illustrated with the flow diagram shown in Figure 3.

The sampling train uses a standard in-stack filter probe which draws in an isokinetic sample that passes through a filter pack. The filter pack holds three 47 mm diameter filters. Arranged as illustrated in Figure 2. A stainless steel washer at the filter pack entrance and a stainless steel washer/screen at the exit, hold the three stacked filters in place and prevent sticking to the filter holder O-rings. The first filter collects the particulate phase. Only quartz fiber filters have been used to date but optimum detection limits will be obtained with teflon filters. The second filter is a CIF used to collect gas phase elements. The second CIF is a backup which can be analyzed if there is concern for breakthrough. (To date, in-stack measurements have demonstrated CIF collection efficiencies in excess of 99.7% for total mercury).

The stack gas passes through the filter pack and to a series of impactors to remove water vapor before the flow and volume are monitored.

The filter pack, including the inlet nozzle, are separated from the probe at the end of a sampling period, capped and returned to the laboratory for analysis. In-field sample train rinsing and sample recovery steps are not required by this method. If repeated field tests are required, the filter may be transferred to petri slides and fresh filters loaded in the filter pack. Special filter treatment is not required after sample collection. (Mercury, for example, is not lost from the CIF even after 15 hours exposure to a vacuum of 150 microns of mercury at room temperature).

Upon receipt in the laboratory, the probe inlet is separated from the filter pack, the filters removed, placed in petri slides and archived. (This method does not require total filter deposit mass to be determined). The filters are removed from storage and analyzed first by nondestructive XRF analysis using a high powered modified Ortec Tefa III analyzer. The complete analysis which requires two excitation conditions (Mo anode and Mo x-ray filter at 50 KV, tungsten anode with Cu filter at 35 KV). The front particulate catch filter is then cut in half after nondestructive XRF. One half of the filter is archived and one half is analyzed for ICAP for Be by ICAP. The entire filter may be analyzed by ICAP if lower detection limits are required. Elemental detection limits of the HEST will range from about 10 to 100 ng/m<sup>3</sup>.

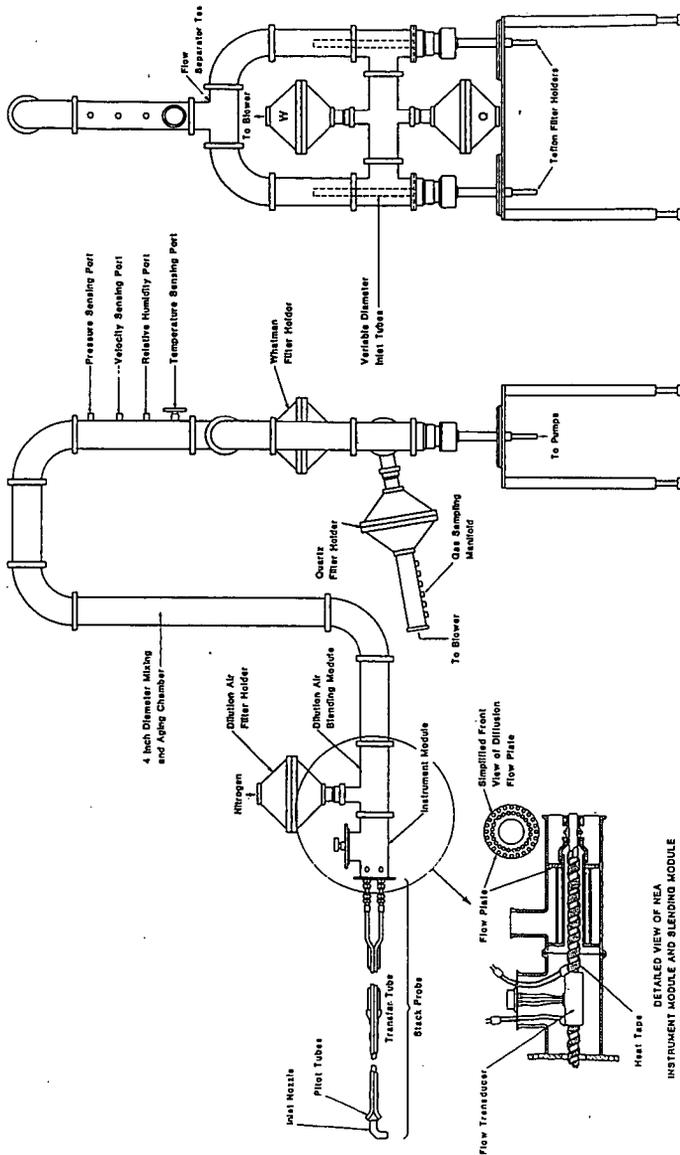
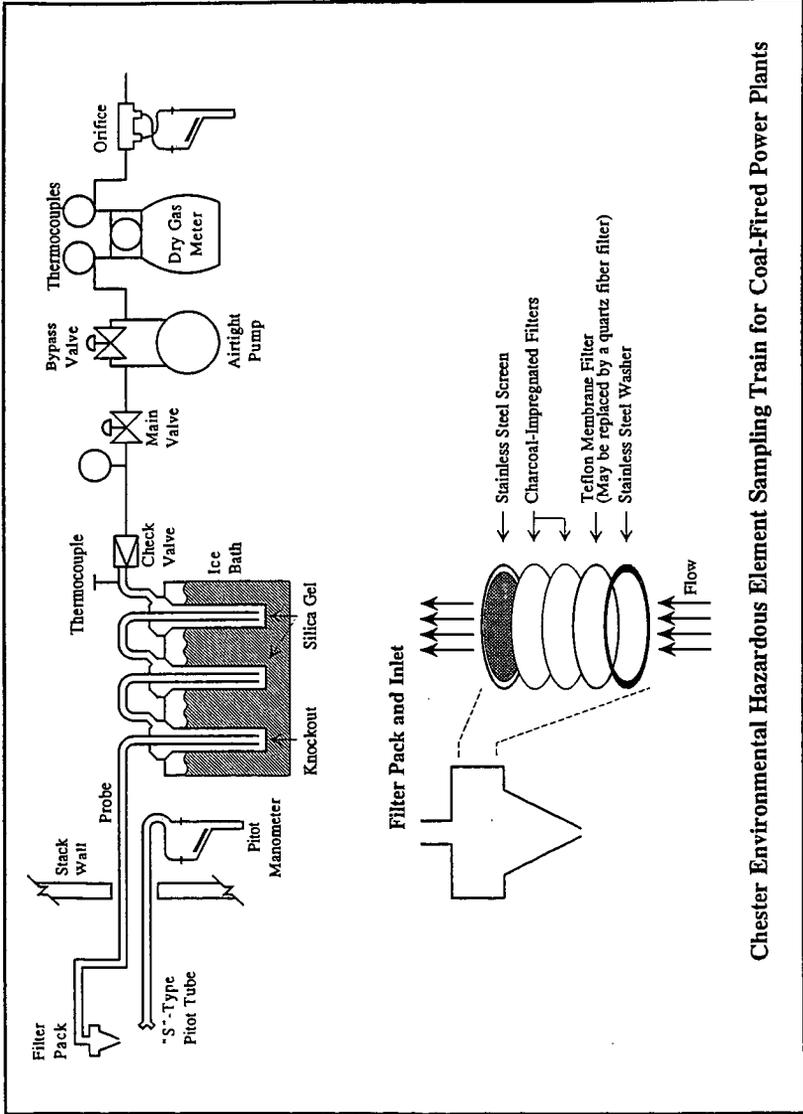


Figure 1. Schematic Representation of the Plume-Simulating Dilution Sampler (PSDS) for Simultaneous Collection of Particle and Gas Phase Hazardous Air Pollutants.



Chester Environmental Hazardous Element Sampling Train for Coal-Fired Power Plants

Figure 2.

