Detection of Mercuric Bromide in a Gas Phase Flow Cell by Laser Photofragment Fluorescence Spectroscopy

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Photofragment fluorescence (PFF) spectroscopy offers real-time monitoring capability with high-analytical sensitivity and selectivity for volatile mercury compounds found in process gas streams, such as incinerator stacks. In this work, low concentrations (6 ppb to 30 ppm) of mercuric bromide (HgBr$_2$) vapor were introduced into an atmospheric pressure flow cell. The PFF technique used 222 nm laser radiation to photolyze HgBr$_2$ and excite fluorescence from the resulting Hg atoms at 253.7 nm. The fluorescence intensity was linear with laser fluence over the range of 45−180 mJ/cm^2. Extrapolated detection limits by this method below 1 ppb of HgBr$_2$ in the absence of air are estimated. A linear dynamic detection range up to 0.7 ppm (11 mg/m^3) is reported.

Introduction

Mercury compounds are often both volatile and air-stable; therefore, they pose a health threat in the environments in which they are used or produced. They are chemically inert to oxygen and are inert or slow toward hydrolysis. Mercuric oxide (HgO) and mercuric halides (e.g., HgCl$_2$) have been identified in off-gases from waste incinerators. These and other mercury compounds have toxic effects associated with central nervous system disorders, particularly the organo-mercurials, such as methylmercury chloride [Hg(CH$_3$)Cl].

Current technologies for detection of mercury compounds in stack off-gases use a collection/concentration step followed by off-line analysis using atomic absorption spectrometry, gas chromatography, or inductively coupled plasma emission spectroscopy (*1*). None of these three detection methods in their commercially available configurations are suitable for real-time monitoring. In situ stack monitoring for multimetals can be done using laser spark emission spectroscopy (*2,3*). However, no speciation (compound) information is obtained as all parent mercury compounds are converted to excited metal atoms in the intense plasma. It is consequently of interest to develop techniques for online, real-time spectroscopic analysis of mercury compounds that can be used

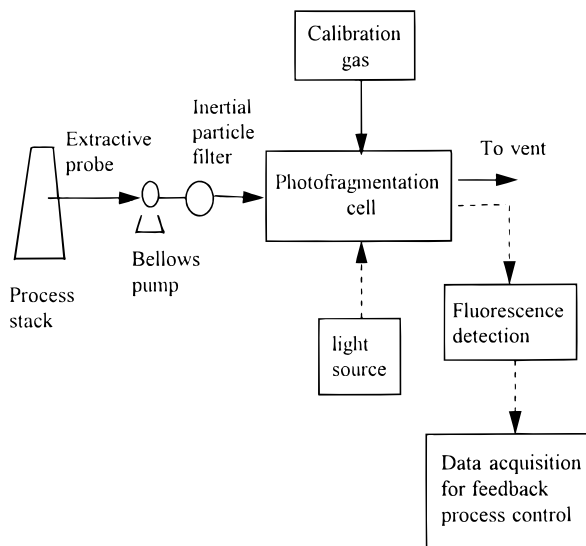* Corresponding author: phone: (973)596-5605; fax: (973)802-1946; e-mail: barat@admin.njit.edu.

FIGURE 1. Continuous mercury species monitor system diagram.

to rapidly monitor industrial stack off-gases and other environments.

Mercury compounds are generally nonfluorescent, and their absorption spectra are too broad and deep-seated in the ultraviolet (UV) to provide useful information. However, the fluorescence of atomic Hg and certain diatomic mercury species fragments opens the possibility of real-time detection through photofragment fluorescence (PFF) spectroscopy.

In PFF spectroscopy, a photolyzing UV light beam is used to dissociate the target molecule A−B into fragments, some of which are imparted with excess energy (step 1). The energy might then be lost by fluorescence (step 2) or by collision (quench) with other molecules Q (step 3).

$$A-B + h\nu \rightarrow A + B^* \tag{1}$$

$$B^* \rightarrow B + h\nu' \tag{2}$$

$$B^* + Q \rightarrow B + Q \text{ (KE)} \tag{3}$$

where A and B can be atoms or polyatomic species and KE represents kinetic energy. Examination of the fragment identities and distributions, as revealed in the PFF spectrum, permits identification of the target mercury compound, in analogy to mass spectrometry.

Because of its high sensitivity and selectivity for numerous trace gases, much work has been done on application of the PFF technique in real industrial environments. Measurement of alkali traces in coal combustion off-gases has been reported (*4*−*7*). Trace toxic metal species, such as lead, manganese, nickel, and chromium, in post-flame gases also has been tested using the PFF technique (*8*). We envision PFF as an online detection method to analyze continuously extracted samples as shown in Figure 1.

Considerable work has been done recently on PFF of mercury compounds of interest for off-gas monitoring. Poulos and Barat (1998) observed PFF on Hg(CH$_3$)Cl, mercuric chloride (HgCl$_2$), and mercuric iodide (HgI$_2$) in a static cell (*9*). Measured spectra revealed Hg* fluorescence as well as fluorescence from diatomic fragments (HgCl*, CH*).

In our work, we used mercuric bromide (HgBr$_2$) vapor, which can be present in incinerator stack gases due to the nature of the original waste; for example, Hg-containing
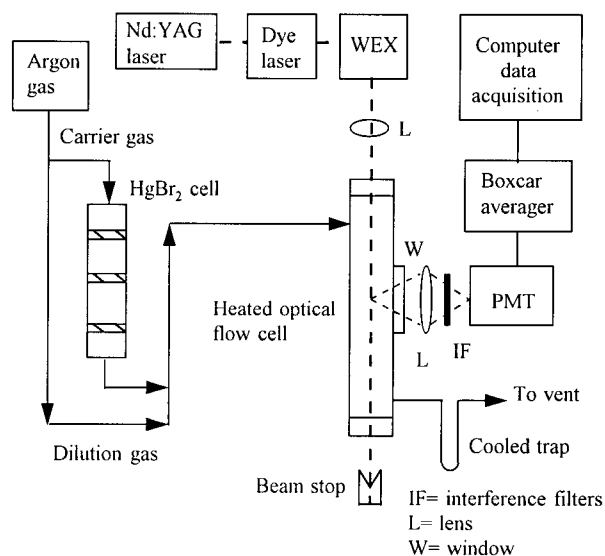
FIGURE 2. Research apparatus for PFF studies.

batteries and Br-based flame retardents. We examine PFF of $HgBr_2$ in an atmospheric pressure flow cell in this paper. The dependence of the electronically excited Hg atomic fluorescence on $HgBr_2$ vapor pressure and dissociation laser energy is reported. Limits-of-detection and dynamic range are also addressed.

Experimental Section

The apparatus consists of a pulsed dye laser system and optical guides, PFF spectroscopy flow cell, optical sampling system, detection system, and data acquisition system. An overview schematic of the apparatus is shown in Figure 2. Each subsystem is described separately below.

Ultraviolet Laser System. A Spectra-Physics PDL-3 dye laser is pumped by the second harmonic (532 nm) of a Spectra-Physics Model GCR-3 pulsed Nd-YAG laser (Q-switched, 10 Hz, pulse width 6 ns). A given dye laser wavelength in the visible portion of the spectrum is converted into a UV line using nonlinear optics in the Spectra-Physics WEX-1. For the present experiments, doubled Rhodamine 590 is mixed with residual fundamental YAG radiation (1064 nm) in the WEX to produce output in the range 219–227 nm. Typically, the wavelength chosen for the PFF studies of $HgBr_2$ is 222 nm.

The UV laser power was monitored intermittently using a Scientech Model 372 power meter. Typical average laser power in this study at 222 nm is 30 mW. Energy per pulse is 3 mJ, and the laser is generally run at 10 Hz. The laser beam passes through a focusing lens (25 mm diam × 28 cm focal length) prior to entering the PFF cell. The laser beam is focused to a spot size of 1 × 2 mm, which yields an average laser fluence of 150 mJ/cm² per pulse.

PFF Spectroscopy Optical Flow Cell. Designed for flow conditions, the cross-shaped quartz photolysis cell contains four Suprasil windows and two ports at opposite ends for connection to the gas flow system. The laser beam is introduced through the "windowed" long axis (37 cm). Fluorescence is collected along the "windowed" short axis (8.5 cm). The laser windows are set at Brewster's angle (56 degree), while the collection windows are normal to the short axis.

The entire flow cell is suspended within an insulated box, which is heated with an internal strip heater. The heater is part of feedback temperature control loop that also includes a type K thermocouple located inside the box and a

proportional controller. The cell is maintained at 90 °C, which is 10 degree higher than the highest temperature of the vapor saturator. The system is first evacuated and then purged with argon gas, while heating prior to introduction of $HgBr_2$ vapor.

Detection System. Fluorescent light emerging from the test cell is collected and focused by a lens (50 mm diam × 30 mm focal length) through two stacked 253.7 nm interference filters (each ±5 nm bandwidth). The transmitted light is detected by an end-on Thorn-EMI Model 9558QB photomultiplier tube (PMT). The output signal voltage is input to an SR250 gated integrator module of a Stanford Research Systems Model 280 boxcar averager. The boxcar is interfaced to a laboratory computer equipped with dedicated software for boxcar control and digital data transfer and collection.

Vapor System. Mercuric bromide vapor is generated in a heated, stainless steel tube containing $HgBr_2$ powder on three porous steel disks. A metered, downward flow of argon carrier gas entrains the vapor. The tube is suspended inside a heated cylinder. The temperature is feed-back controlled. The flow rate of argon gas through the tube is regulated at less than 70 cm³/s (standard conditions) to ensure the saturation of $HgBr_2$ vapor. A separate, metered argon flow bypasses the heated source and serves as a diluent to generate lower $HgBr_2$ concentrations.

Mercuric bromide vapor concentrations in the source outlet are determined based on published (*10*) vapor pressure/temperature data in the form of the Claussius–Clapyeron equation:

$$\log P^v = a - b/T \qquad (4)$$

where P^v = vapor pressure (Torr), T = absolute temperature (K) and a, b = species-specific constants (for $HgBr_2$, a = 10.181 and b = 4168).

As an independent means to verify the $HgBr_2$ concentration, vapor leaving the cell was passed through a cold trap (0 °C). Condensed vapor collected over a measured time period (3 h, no laser) was washed from the trap with an aqueous hydrochloric acid (HCl) solution. This wash was analyzed for Hg by independently calibrated flame atomic absorption (AA). The $HgBr_2$ vapor concentrations calculated from temperature data in this work were correct to within 8% as compared to the independent AA analysis.

Final $HgBr_2$ concentrations at the optical cell are based on both gas flows and one atmosphere (absolute) total operating pressure. Low $HgBr_2$ concentrations are achieved by increasing the fraction of diluent and/or operating the source at lower temperatures. In the experiment, the temperature of the $HgBr_2$ source was regulated at a specific temperature in the range of 20–80 °C, corresponding to vapor pressures of 90 ppb to 30 ppm. Temperature control was maintained to within ±2 °C, with a typical source temperature of 32 °C. This corresponds to a typical precision of ±80 ppb in the corresponding calculated vapor concentration of 430 ppb.

To prevent any condensation and subsequent loss of $HgBr_2$ concentration, all transfer lines downstream of the source, like the optical cell, are kept at an elevated temperature (typically 90 °C) that is always higher than the source temperature.

Results and Discussion

Response of $HgBr_2$ Photofragment Emission to Laser Pulse Energy. In this work, the chosen excitation wavelength is at 222 nm, the shortest wavelength at reasonable power available from the on-site Spectra-Physics Laser system in the mercury halide absorption region of interest. Photofragment fluorescence is monitored at 253.7 nm, which is the strongest atomic emission line ($^3P_1 \rightarrow {}^1S_0$) of mercury. The
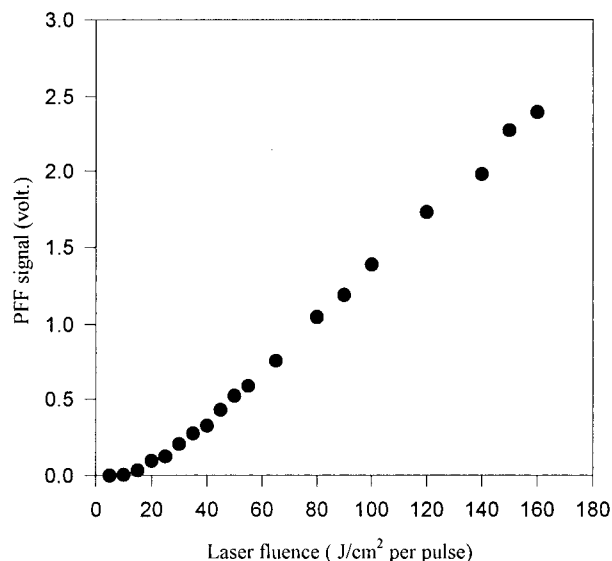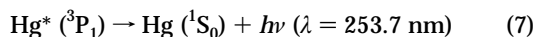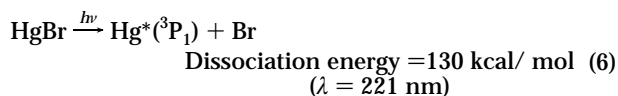
FIGURE 3. HgBr$_2$ PFF signal dependence upon laser fluence.

FIGURE 4. PFF signal sensitivity vs HgBr$_2$ concentration.

energies and corresponding wavelengths are (*11*):

$$HgBr_2 \xrightarrow{h\nu} HgBr + Br$$

Dissociation energy = 72 kcal/mol (5)
(λ = 398 nm)

$$HgBr \xrightarrow{h\nu} Hg^*(^3P_1) + Br$$

Dissociation energy =130 kcal/ mol (6)
(λ = 221 nm)

$$Hg^* (^3P_1) \rightarrow Hg (^1S_0) + h\nu \ (\lambda = 253.7 \ nm) \qquad (7)$$
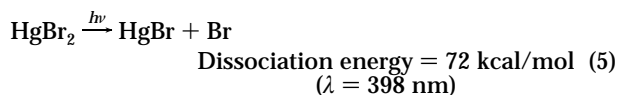
Therefore, absorption of a single photon at 222 nm is sufficiently energetic to dissociate HgBr$_2$. Absorption of one or two additional photons by HgBr will produce excited atomic Hg*($^3P_1$) photoproduct, which emits at 253.7 nm.

Experimental PFF signal dependence upon laser fluence is shown in Figure 3 where the HgBr$_2$ concentration is 124 ppb. The curve can be separated into two parts by using data regression analysis. The quadratic portion for laser fluence less than 45 mJ/cm^2 per pulse suggests two-photon absorption with second-order regression coefficient R = 0.998. For laser fluence greater than 45 mJ/cm^2 per pulse, the PFF signal is linear with first-order regression coefficient R = 0.999. A similar phenomenon was also observed by Schendel in his work of laser PFF spectrometric determination of Nitromethane (*12*). It is likely that the higher laser pulse energy fluences used here led to saturation of one of the two steps of photon absorption necessary for production of Hg* from HgBr$_2$. For analytical purposes, the laser energy in this work is set in the linear response range.

Limit of Detection. To estimate the detection limit, we use inert gas dilution methods to simulate low-level concentrations. By keeping the total flow rate through the PFF cell constant, changing the ratio of flow through the saturated vapor source to the bypass argon flow, the concentration of HgBr$_2$ can be made as low as 6 ppb (96 μg/m^3) at room temperature.

Figure 4 gives the plot of sensitivity of HgBr$_2$ photofragment fluorescence signal using the PMT as the detector. Experimental parameters are: laser energy = 3.5 mJ/ pulse; boxcar averaged 30 pulses. This corresponds to a duty cycle of 3 s. By extrapolating, the concentration back to a S/N = 2, the limit of detection is estimated to be 0.8 ppb, corresponding to 13 μg/m^3. Further enhancement of the detection sensitivity might be obtained by averaging the

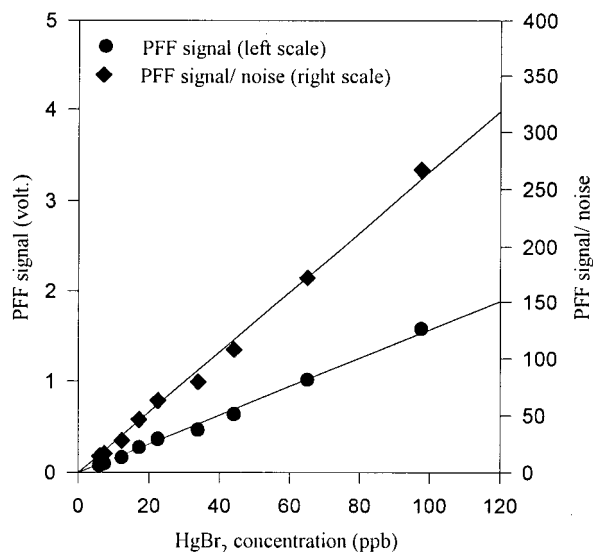fluorescence signal over more laser pulses (i.e., increasing the duty cycle).

In a real combustion environment, extracted stack gas consists of combustion species such as CO$_2$, CO, H$_2$O, O$_2$, and N$_2$. Among them, O$_2$ has the largest quenching cross section for state Hg*($^3P_1$) (*13*). The PFF signal at 253.7 nm would be reduced by a factor (*14*) of 0.05 at an O$_2$ concentration of 8%. In this case, the extrapolated detection limit would rise to approximately 16 ppb from 0.8 ppb. To improve the application of PFF to mercury compound detection in real industrial environments, a shorter wavelength excimer laser could be chosen. The absorption cross-section of HgBr$_2$ at 193 nm is 3× greater than that at 222 nm (*15*). Also, the relatively high laser energy, which can be 50 times greater than the present laser system, make the excimer quite attractive for this application.

Response Time. An important consideration for a future application of this method for real-time monitoring is the response time, which is defined as the time interval between the start of a step change in the concentration of the monitored gas stream and the time when system output reaches 95% of its final value. The response time would represent a time lag.

The response time was investigated by purging the fluorescence cell for a long enough time using bypass argon flow, then turning off this bypass flow and opening the source flow to let only saturated HgBr$_2$ vapor go through the fluorescence cell. Figure 5 shows the dependence of PFF signal with time during flow of 150 ppb HgBr$_2$ vapor to the initially clean fluorescence cell where laser energy was set at 1.3 mJ/pulse. At t = 0, the introduction of HgBr$_2$ vapor into cell begins at a flow rate of 60 cm^3/s. It takes approximately 3 s for the signal to reach half value, and about 45 s for the signal to be maximum.

The response time can be further reduced by increasing the flow rate of carrier gas. The fluorescence cell is held at a higher temperature than the source to prevent surface condensation. However, cold points and persistent adsorption on surfaces apparently lead to an increase in the response time. In the absence of such effects, the minimum response time could be as low as 1.5 s (based on gas residence time). To reduce the response time, the temperature homogeneity of the flow cell could be improved. An alternative material, such as glass or Pyrex, for the transfer line could be evaluated.

Linear Dynamic Range. By heating the source to a high enough temperature (53 °C), and using the inert gas dilution method, we investigated the dynamic range of this detection
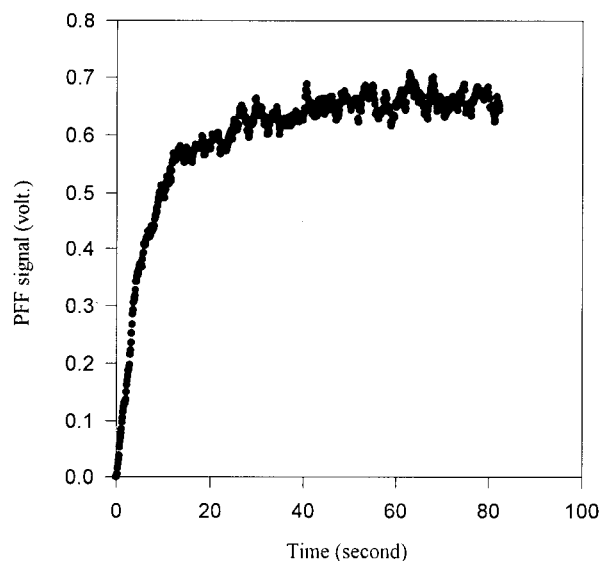
FIGURE 5. Time dependence of PFF signal during flow of 150 ppb HgBr$_2$ vapor.

method. A linear response with the PMT for HgBr$_2$ concentration is observed up to 0.7 ppm (11 mg/ m^3). At higher concentrations, the PFF signal is sufficiently large to cause PMT saturation. This was experimentally verified with neutral density filters.

Total mercury, including elemental and compound, emitted from incinerators ranges from 10 to 2000 μg/m^3, corresponding to 1−200 ppb. This work indicates that the PFF technique has sufficient sensitivity with linear response to measure volatile mercury compounds in most real industry stack gases (i.e., concentrations greater than 16 ppb). Moreover, the low detection limit from this PFF technique shows promise as a near real-time, continuous emissions monitoring method for toxic mercury compound species.

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