SAND2007-7309C

DEVELOPMENT OF A FIELDABLE REAL-TIME MERCURIC CHLORIDE MONITOR USING LASER PHOTOFRAGMENT EMISSION

Thomas A. Reichardt, Jeffrey M. Headrick, Alexandra A. Hoops, Jude A. Kelley[a], Jeffrey P. Koplow, Sean W. Moore, and Dahv A. V. Kliner

Sensing and Energetic Materials Department
Sandia National Laboratories
P. O. Box 969, MS 9056
Livermore, CA 94551

Introduction

In the United States, coal-fired power plants are the dominant anthropogenic source of mercury to the environment, and impending regulations will place strict limits on these emissions. Existing continuous emissions monitors are adequate for current regulatory monitoring, but compliance with anticipated regulations requires development of a new generation of mercury sensors with high sensitivity (~0.1 part per billion, ppb), high specificity, and fast time response. A further challenge arises from the fact that power plants emit gaseous mercury in both elemental (Hg^0) and oxidized ($HgCl_2$) forms, which have different clean-up strategies, atmospheric lifetimes, and environmental and biological effects. Mercury sensors should therefore be able to speciate the vapor-phase mercury. Finally, current mercury sensors require extractive sampling from the exhaust stack, an invasive and expensive process. Non-extractive, stand-off detection of the various forms of mercury would be an attractive alternative to sampling-based approaches.

Towards the development of such a mercury monitor, we have constructed a breadboard instrument capable of detecting ppb levels of $HgCl_2$ by photofragment emission (PFE). The PFE technique, in which photodissociation generates an excited daughter species that subsequently emits a photon, has been shown to be effective for detection of fugitive airborne metal compounds at low concentrations.[1,2] The dissociation wavelength selected for the PFE approach depends in part on the absorption spectrum of the parent species. $HgCl_2$ has three broad, structureless absorption features arising from excitation of the ground state, $1^1\Sigma_g^+$, to valence states $1^1\Pi_u$, $1^1\Sigma_u^+$, and $2^1\Sigma_u^+$.[3,4] We have previously demonstrated that excitation of the lowest-lying absorption band of $HgCl_2$ at 209.8 nm yields PFE from the Hg $6^3P_1 \rightarrow 6^1S_0$ transition at 253.7 nm.[5]

Detection of $HgCl_2$ PFE has typically been demonstrated in laboratory environments using either Nd:YAG-pumped dye lasers frequency converted into the UV[5,6] or ArF and KrF excimer lasers[7,8]. However, the physical characteristics of conventional laboratory laser systems hamper an extension of this technique to the field. We note that excimer laser sources have been previously used in fieldable sensing devices; for example, an excimer-laser-based PFE instrument developed at the University of Heidelberg[9] has been deployed in measurement campaigns of alkali species in the flue gas of semitechnical scale and pilot scale coal-combustion and gasification systems. Nevertheless, these lasers are not ideal because of their hazardous gas consumables; all-solid-state laser sources are preferred for routine emission monitoring. Moreover, the fieldable laser should be compact and rugged, while maintaining high average and peak powers with the requisite spatial beam quality for a stand-off approach. Frequency conversion of pulsed, rare-earth-doped fiber-based lasers has the potential to meet these requirements for a practical laser source[10]. Pulsed fiber amplifiers operate in the low-energy, high-repetition-rate regime. Consequently, the per-pulse signal levels of $HgCl_2$ PFE produced by a fiber laser source will be substantially less than those generated by a high-energy Nd:YAG-pumped dye laser. This apparent drawback can be overcome by incorporating a photon-counting detection approach, which is appropriate for low-light measurements involving the acquisition of less than one photon per count cycle. Photon counting has the added advantage of eliminating noise attributable to pulse height fluctuations from the detector, which increases the precision of low-signal-level data compared with analog detection. Furthermore, the high repetition rates of pulsed fiber lasers make possible the acquisition of sufficient count levels within measurement times that are reasonable for a fieldable device.

We have previously characterized and quantified the $HgCl_2$ PFE method by evaluating the potential impact of interference gases, determining the dependence of the PFE signal on laser irradiance, and examining the effects of collisional quenching by major flue-gas constituents N_2, O_2, and CO_2.[5] In this paper we describe the system architecture of this instrument, including the compact laser source, beam-formatting optics, photodetector, signal-conditioning electronics, and on-board system performance diagnostics. Initial testing of the instrument is also summarized.

Experimental

Laser Source. UV light is generated with the frequency-converted fiber amplifier source described by Hoops *et al.*[11]. A Sandia-built fiber amplifier[3] is seeded with a passively Q-switched Nd:YAG microchip laser (Poly-Scientific) operating at a repetition rate of ~6 kHz and a wavelength of 1064 nm. Half-wave plates are used to adjust the polarization of both the seed beam and the output of the fiber amplifier in order to provide linearly polarized light that is correctly oriented for the nonlinear crystals.

The fundamental output of the fiber amplifier at 1064 nm is frequency converted to 213 nm by the three-step process: (1) the 1064-nm light is frequency doubled to 532 nm in KTP using Type II phase-matching, (2) the third harmonic at 355 nm is generated by Type I mixing of the 1064-nm and 532-nm beams in LBO, and (3) the 532-nm and 355-nm beams are used to produce 213-nm light using Type I mixing in BBO. A zero-order wave plate (full-wave at 355 nm, half-wave at 532 nm) is placed between the LBO and BBO crystals to rotate the polarizations of the 532-nm and 355-nm beams to be parallel. In order to provide a rugged and simple frequency-conversion module, no additional optics are placed between the crystals. The nonlinear crystals are positioned near the beam waist and are angle tuned to maximize the 213-nm pulse energy.

Beam-Formatting Optics. We have previously demonstrated that the $HgCl_2$ PFE signal generated following excitation at 213 nm varies as the square of the laser intensity *I*. With the dependence I^2V (where *V* is the probe volume) the signal will vary inversely with the beam spot size. Therefore, we format our beam for relatively tight focusing at the probe volume by expanding the beam (see Fig. 1) with a -100-mm-focal-length (fl) lens (L1) followed by a +500-mm fl lens (L3). In between L1 and L3, a cylindrical lens (L2) corrects for the asymmetrical spatial profile[11] of the 213-nm beam resulting from walk-off in the crystals. The beam is then tightly focused with a +180-mm fl lens (L4) to a 28-µm diameter.

[a] Current address: Chemistry Department, College of Holy Cross (Worcester, MA).

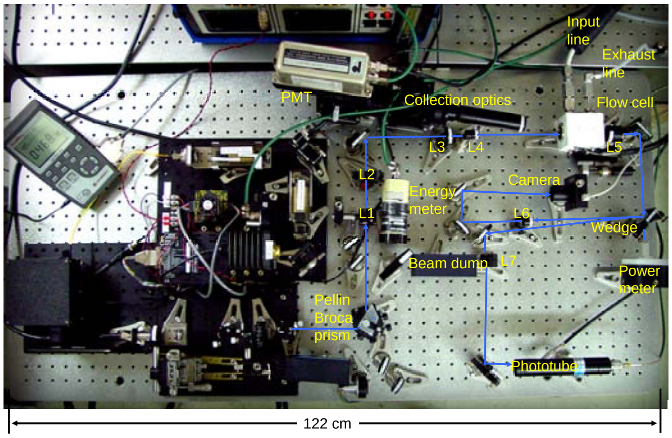

Figure 1. Overhead photograph of the optical layout. For clarity, only the path of the 213-nm beam has been added to the photograph. See text for a further description of the optical components.

<u>Photodetector and Signal-Conditioning Electronics.</u> The $HgCl_2$ PFE signal is collected in the backscattered geometry, wherein emission is captured through the same window as the excitation beam enters. The final version of the instrument will allow non-extractive monitoring of the flue-gas, with the aforementioned window attached directly to the flue gas stack, similar to the PFE system described by Gottwald and Monkhouse.[9] However, in the current configuration of the instrument, the flue gas is extracted into a 2.5-cm diameter, 5-cm long heated cell (CIC Photonics, Scout-EN). The emission is collected with a +100-mm-fl, f#/4 lens and is imaged onto a variable aperture with a +50-mm-fl lens. Light passing through the aperture is collected with a solar-blind photomultiplier tube (PMT), and the signal from the PMT is sent to photon-counting electronics. Spectral filters in the collection channel decrease the noise contribution due to laser scattering. These filters have a nominal transmission of 31% at 254 nm, a 4.6-nm bandwidth full-width-at-half-maximum, and $>10^4$ out-of-band rejection.

<u>On-Board Performance Diagnostics.</u> After passing through the focus in the flow cell, the transmitted beam is directed to on-board, real-time diagnostics which monitor the laser power as well as the spatial and temporal profiles of the laser pulses.

Results and Discussion

The cart-mounted instrument has been used to detect $HgCl_2$ by PFE in the backscattered geometry. A $HgCl_2$ permeation tube is placed in the cell which is stabilized at 40^oC with air as the buffer gas. Figure 2 displays the signal as a function of pulse energy. For these measurements a half-wave plate and polarizer are added before L3 to provide controlled adjustment of the laser pulse energy. As illustrated in Fig. 2, the dependence of the $HgCl_2$ PFE counts on laser energy follows the expected quadratic relationship, which is indicated by the solid line. The current data show more spread than the previous results[9] acquired in a low-pressure (0.4 Torr) bath of N_2 due to Poisson counting statistics. For these previous measurements, the quadratic relationship between the count rate and the pulse energy was well defined for measured counts between 5×10^2 and 5×10^4. The increased spread we observe for counts $<5\times10^2$ is consistent with the photon-counting signal-to-noise ratio (SNR) scaling as the square root of the number of counts.

Our future efforts are focused towards demonstrating the performance of the PFE cart-mounted instrument for detection of $HgCl_2$ in a multi-fuel combustor[12] burning pulverized coal. In addition, we are also developing a filtered fluorescence approach[13] for the detection of Hg^0 to be performed in parallel to PFE detection of $HgCl_2$.

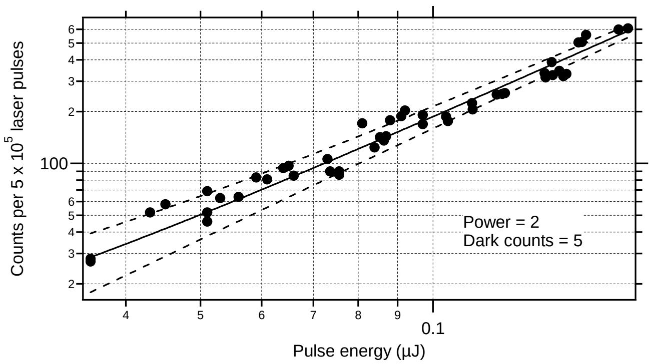

Figure 2. $HgCl_2$ PFE signal strength versus laser pulse energy obtained with 5×10^{-5} Torr of $HgCl_2$ in 760 Torr of air. Each data point (filled circle) comprises 5×10^5 laser shots (representing an acquisition time of 100 s for a 5-kHz pulse repetition rate). The solid line is included to display the agreement of the data with the expected quadratic dependence. The dashed lines represent +/-2σ departure from the solid line fit, where σ is the standard deviation due to Poisson counting statistics. The dark count rate is 10^{-5} counts/pulse.

Acknowledgment

This work was supported by the DOE Office of Fossil Energy's National Energy Technology Laboratory Advanced Research Program through award FEW03-011948. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

References

1. P. Monkhouse, Prog. Energy Combust. Sci. **2002**, *28*, 331-381.
2. J. B. Simeonsson and R. C. Sausa, Appl. Spectrosc. Rev. **1996**, *31*, 1-72.
3. C. Roxlo and A. Mandl, J. Appl. Phys. **1980,** *51***,** 2969–2972.
4. D. Spence, R.-G. Wang, and M. A. Dillon, J. Chem. Phys. **1985**, *82***,** 1883–1889.
5. A. A. Hoops and T. A. Reichardt, Appl. Opt. **2006**, *45*, 6180-6186.
6. R. B. Barat and A. T. Poulos, Appl. Spectrosc. **1998**, *52***,** 1360–1363.
7. T. A. Cool, J. A. McGarvey, Jr., and A. C. Erlandson, Chem. Phys. Lett. **1978**, *58***,** 108–113.
8. C. Whitehurst and T. A. King, J. Phys. B **1987**, *20***,** 4053–4064.
9. U. Gottwald and P. Monkhouse, Appl. Phys. B **1999**, *69*, 151-154.
10. D. A. V. Kliner, F. Di Teodoro, J. P. Koplow, S. W. Moore and A. V. Smith, Opt. Commun. **2002**, *210*, 393-398.
11. A. A. Hoops, T. A. Reichardt, D. A. V. Kliner, J. P. Koplow, and S. W. Moore, Appl. Opt. **2007**, *46*, 4006-4014.
12. L. L. Baxter, Biomass and Bioenergy **1993**, 4, 85-102.
13. A. A. Hoops, T. A. Reichardt, P. Schulz, R. L. Farrow, R. P. Bambha, R. L. Schmitt, and D. A. V. Kliner, "Development of a compact, narrow-linewidth, tunable ultraviolet laser source for detection of Hg^0," Submitted for presentation at the 2007 Laser Applications to Chemical, Security, and Environmental Analysis (LACSEA) meeting of the Optical Society of America, St. Petersburg, FL, March 17-20, 2008.