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ABSTRACT

Mercury is the only atmospheric pollutant that is present in the atmosphere in atomic form. Range-resolved Hg mapping can be performed using the differential absorption lidar (dial) technique employing the 254 nm Hg resonance line. We have used the lidar technique both for mapping of industrial plumes and for background concentration measurements. Our studies also include mercury of geophysical origin. A field test has been performed in Icelandic geothermal fields. We have also attempted studies of Hg emission from lake surfaces.

1. INTRODUCTION

Atomic mercury is present in very low concentrations as a pollutant in the atmosphere. Great interest is being taken in environmental mercury, since this species is known to have very adverse effects. Mercury is the only atmospheric pollutant that is present in atomic form and this leads to an increase in detection sensitivity over molecular species. Since the optical absorption is not spread out over a large number of rotational-vibrational transitions a sensitivity gain of a factor of almost 1000 over typical molecular compounds is obtained. We have taken advantage of this high sensitivity to perform absorption monitoring of the very low atmospheric atomic mercury concentrations using the 254 nm resonance line. The lidar (light detection and ranging) technique was used, allowing range-resolved measurements.

Atomic mercury is generated from chlorine-alkali plants, coal-fired power plants and refuse incineration plants and refuse deposits. Recently, a discussion on the substantial mercury emissions from the cremation of human cadavers has emerged. Mercury of natural origin is also present in the atmosphere, related to geothermal, seismic and volcanic activities. Mercury has also been observed to be a tracer gas for ore deposits. Typical background concentrations of atomic mercury are a few ng/m^{3}, requiring high measurement sensitivities.

Our first attempts to detect atmospheric mercury using lidar techniques date back to 1982[1]. When high-power, narrow-bandwidth tunable lasers became available the sensitivity of the technique could be improved to allow practical applications[2]. Measurements of ambient background concentrations and industrial emissions could then be performed. The differential absorption lidar (dial) technique was used, tuning the laser on and off resonance every second pulse. We have also used the mercury lidar technique for measurements in Icelandic geothermal fields, investigating possible connections between geothermal water and mercury emissions[3]. We have also investigated an alternative lidar technique, which could be of considerable interest for mercury monitoring; gas correlation lidar[4]. In parallel, atmospheric atomic mercury monitoring using long-path absorption of light from classical light sources has been developed[5]. In such measurements, referred to as doas (differential optical

absorption spectroscopy) mean concentration values are derived using basically classical absorption techniques. The unusually narrow lines encountered for mercury calls for a high spectral resolution, especially in view of the interference from absorbing molecular oxygen.

In the present paper a review of our continuing work on atomic mercury monitoring is given. In the next section a description of our current differential absorption system for mercury is given. In Sect. 3 the mapping of elevated concentrations, e.g. industrial plumes is discussed, while background measurements are covered in Sect. 4. The gas correlation and the doas techniques for atomic mercury detection are discussed in Sect. 5, followed by a concluding section.

2. LIDAR SYSTEM DESCRIPTION

A mobile laser radar system, as illustrated in Fig. 1, was used in our atomic mercury measurements. The basic construction of the system is presented in Ref. 6 and special arrangements pertaining to mercury are further elaborated on in Ref. 2. Here a brief description of the system will be given.
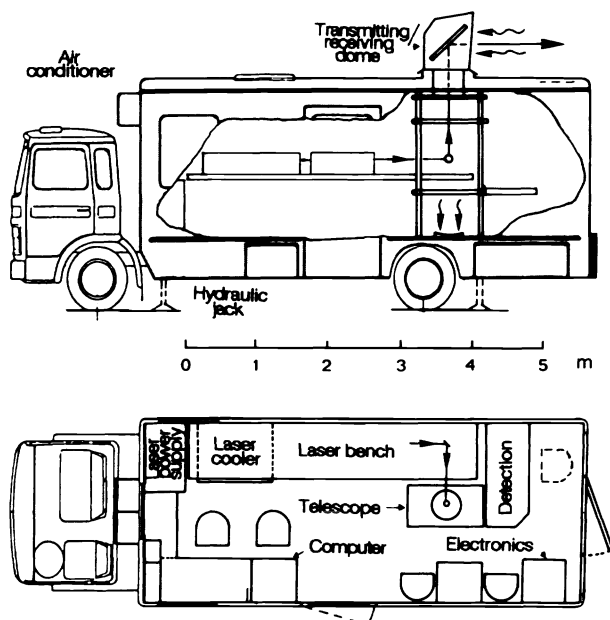

Fig. 1. Lay-out of the Hg lidar system (From Ref. 6).

The laser source is a Nd:YAG system pumping a tunable dye laser. The dye laser is operated at wavelengths around 507 nm with Coumarine 500 dye. The pulse energies are 25-30 mJ and the pulse repetition rate is 10 Hz. The dye laser output is frequency doubled to the UV region by using a beta barium borate (BBO) crystal (CSK Co., Los Angeles), yielding pulse energies up to 5 mJ at 254 nm. The dye laser wavelength is calibrated by separating 10% of the frequency-doubled beam and by monitoring the absorption of this beam in a cell of mercury vapor.

The UV beam is directed into the atmosphere by two right-angled quartz prisms and a large plane mirror. The mirror can be rotated around the horizontal axis and the vertical axis, thus determining the direction of the output beam. Backscattered radiation is received by the same mirror and directed to a 40 cm diameter Newtonian telescope. An interference filter selects the appro-

priate wavelength range and a photomultiplier detects the radiation. In order to reduce the requirements of dynamic range in the detection electronics, the photomultiplier gain was ramped up to reach its full value at a range of about 400 m.

A transient recorder performs A/D conversion of the signal with a time resolution of 10 ns, giving a range resolution of about 1 m. The digital signals are averaged on a computer which subsequently stores them on floppy disks. During a measurement the computer controls laser firing, dye laser wavelength setting, beam direction, and data acquisition.

For Hg measurements, the resonance line at 254 nm is used. The laser radiation is tuned on and off the resonance and the "on-" and "off-" signals are stored separately. By calculating the ratio of the on- and off- signals the absorption from Hg at a certain distance can be monitored, and the concentration as a function of distance can be calculated. By measuring in several directions through a plume containing Hg, concentration mapping of the plume can be obtained.

Molecular oxygen lines close to the mercury line had to be studied in detail in order to avoid interference problems. In Fig. 2 a laboratory spectrum obtained with a White multipass absorption cell (pathlength 340 m) filled with pure oxygen is shown, together with an atomic mercury absorption profile. Clearly, it is important to choose the off-resonant wavelength in such a way that no oxygen absorption is encountered. The figure also includes a more detailed mercury line profile with the different isotopic and hyperfine components indicated.
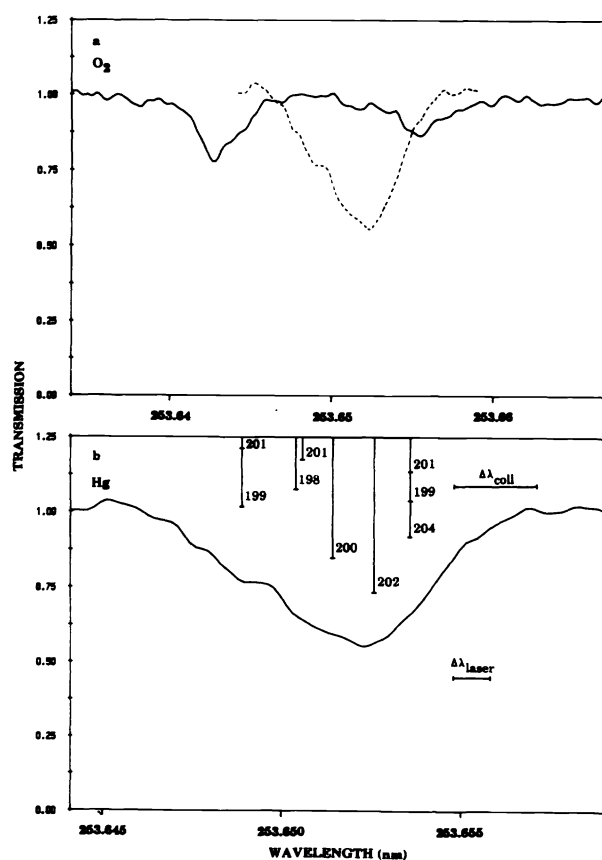

Fig. 2. White-cell spectrum of oxygen lines close to the Hg line (From Ref. 2).

3. PLUME MEASUREMENTS

The elevated concentrations present in plumes from chlorine-alkali plants can easily be mapped out with the lidar system described above. As an example, the result from a horizontal scan across a plant is shown in Fig. 3. The data were plotted directly on a map of the industrial area. Vertical scans perpendicular to the wind direction showed that about 30 g/h of mercury were emitted from the plant. For mercury emissions of this order the on-resonance radiation was reduced to about a third of the off-resonance radiation. On the other hand, plumes from a geothermal power plant in Iceland did not contain any appreciable amount of Hg as, illustrated in Fig. 4. The upper figure contains both on- and off- resonance curves which look identical, leaving the ratio as a horizontal line for zero mercury concentration.
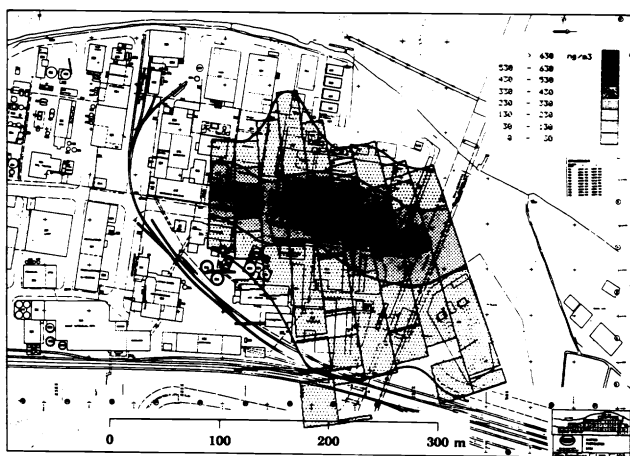

Fig. 3. Horizontal lidar scan over an industrial area with evaluated Hg concentrations (From Ref. 2).

The absence of elevated concentrations of atomic mercury in the air over at least three geothermal fields in Iceland presents a puzzle. There can, on the one hand, be no doubt about the presence of significant amounts of mercury in well fluids in these areas. The lidar technique is sensitive only to atomic mercury, however. Mercury in a form other than elemental vapor would therefore not have been revealed in our search. At present, we thus consider the occurrence of the mercury in some form other than elemental vapor to be the most probable explanation for the failure of the lidar search to detect significant concentrations.

The lidar technique should also be useful for measurements from incineration plants and crematories. In Sweden the latter sources are now expected to contribute more to environmental mercury contamination than the incineration plants. An assessment for optical measurement techniques for Hg emissions from crematories has been made[7].

4. BACKGROUND MEASUREMENTS

While no concentration could be observed in Fig. 4, the lidar technique has the required sensitivity to allow measurements of background concentrations, which are typically a few ng/m^3 in industrial countries. This is illustrated in Fig. 5, where 1.5 ± 1.0 ng/m^3 Hg over a 1 km path is detected.

We have also tried to use Hg lidar to study the Hg emission from the surfaces of lakes, as it has been postulated that this may account for missing
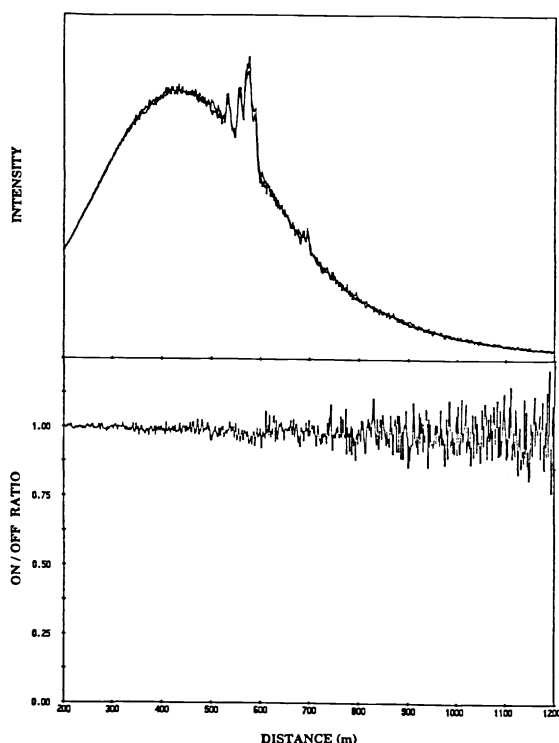
Fig. 4. Lidar measurements through the plume from an Icelandic geothermal plant (From Ref. 3).
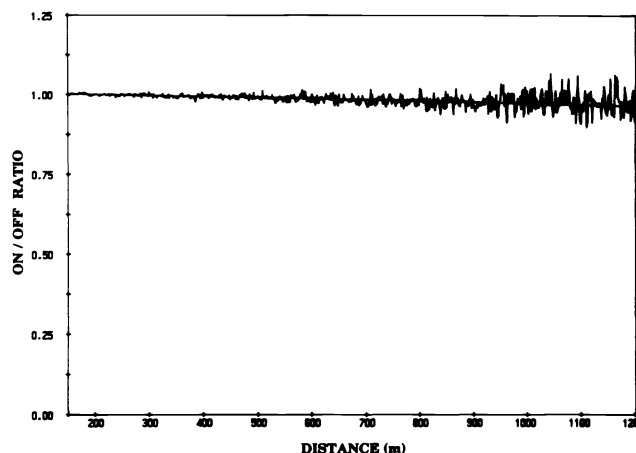

Fig. 5. Background Hg measurement in the city of Lund, Sweden, (From Ref. 2).

mercury in the full environmental cycle of this element. A measurement scenario is illustrated in Fig. 6, where our lidar system combined with flat first surface mirrors was used to obtain 1 km measurement paths across a lake at 0.5 and 2.0 m above the surface. In initial measurements the concentration gradient over the lake surface was not high enough to be detected.
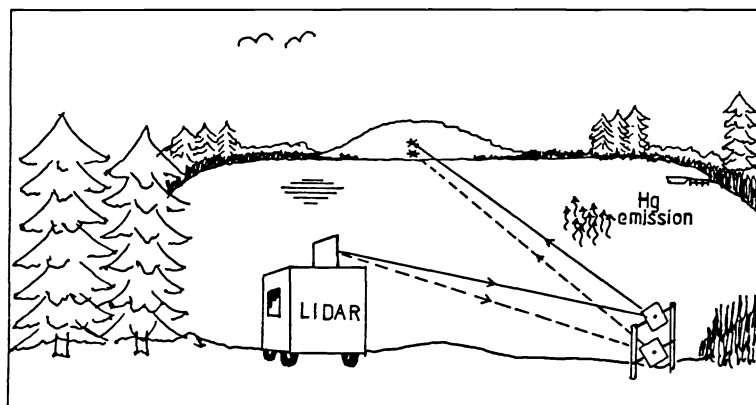

Fig. 6. Measurement scenario in lidar search for Hg emission from lake surface.

5. OTHER OPTICAL Hg MEASUREMENT TECHNIQUES

As we have noted, a narrow laser linewidth is necessary to provide a high contrast ratio between on- and off-resonance signals, which places stringent demands on the laser system used. However, it is possible to measure mercury even with a rather broadband laser if, instead, selective filtering is performed on the detection side, as illustrated in Fig. 7. The technique is called gas correlation lidar[4]. Rather than providing separate on- and off-resonance curves a combined on- and off-resonance curve (obtained in direct detection) is compared with a pure off-resonance curve (obtained through the optically dense atomic absorption cell. Since both curves can be recorded for the same laser shot problems associated with atmospheric turbulence are eliminated.
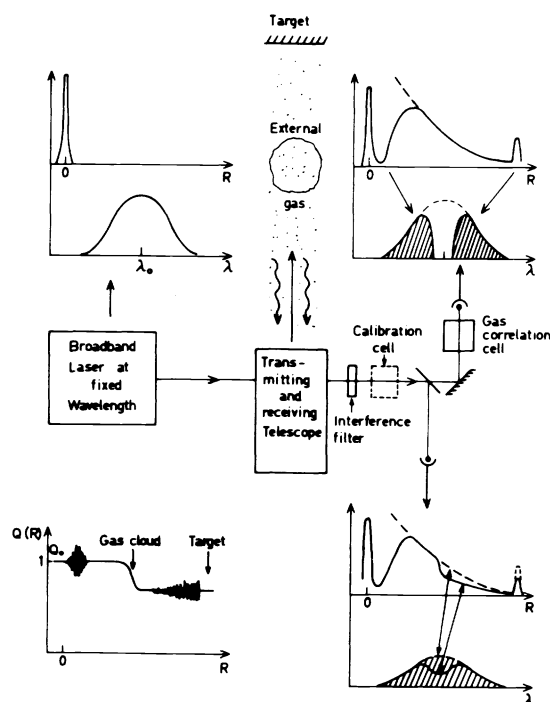

Fig. 7. The principle of gas correlation lidar (From Ref. 4).

The differential absorption spectroscopy (doas) method applied over a long absorption path can also be used to measure average concentrations of mercury provided that a sufficient spectral resolution can be obtained. An experimental setup with a high-pressure xenon lamp as a transmitter and a fast scanning monochromator for the analysis to eliminate the influence of atmospheric turbulence is shown in Fig. 8. An atmospheric recording over a pathlength of 700 m is given in Fig. 9, where oxygen signals and an enhanced Hg signal, obtained by placing a 1 mm Hg cell (18^0C) in front of the spectrometer slit, are shown. In order to evaluate background concentrations of Hg a higher resolution than that illustrated in Fig. 9 is required.
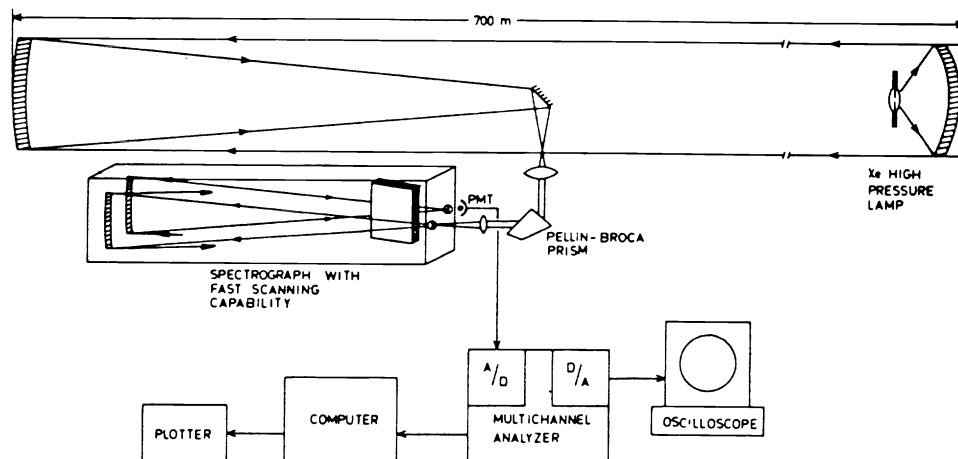
Fig. 8. Differential optical absorption spectroscopy (doas) system (From Ref. 5).
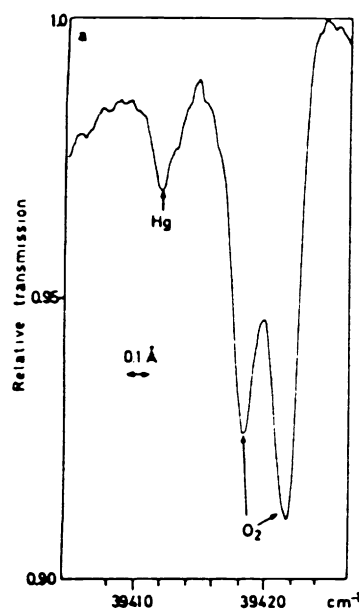

Fig. 9. Doas spectrum close to the mercury line (From Ref. 5).

6. DISCUSSION

Optical measurement techniques have been shown to allow sensitive measurements of atomic mercury in the atmosphere. The methods show promise, not only for pollution measurements, but also for interesting geophysical applications. Airborne equipment might be useful for practical exploration work.

7. ACKNOWLEDGEMENTS

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