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Differential optical absorption spectroscopy system used for atmospheric mercury monitoring

Hans Edner, Anders Sunesson, Sune Svanberg, Leif Unéus, and Svante Wallin

A high-resolution differential optical absorption spectroscopy (DOAS) system for long-path atmospheric pollution monitoring is described. The system, consisting of a broadband lamp and a dispersive, fast-scanning optical receiver, separated by a few kilometers, was used in measurements of different pollutants, highlighted by the monitoring of the local concentration of atomic mercury. Mercury levels in the ppt ($1:10^{12}$) range were assessed by comparisons with laboratory measurements.

I. Introduction

Atmospheric pollution is a matter of increasing public concern calling for powerful measures to reduce industrial and automotive emissions. Adverse effects of air pollution include primary health effects, environmental acidification, and possible long-term changes in the global climate and in UV radiation levels. Clearly, efficient methods for the measurement of atmospheric pollution concentrations are of great interest in any program for air pollution control. In many contexts remote-sensing techniques have important advantages over point monitors. Optical techniques for atmospheric remote sensing are reviewed in a recent monograph.¹ One of the most versatile techniques is the differential absorption lidar (DIAL) method, which is a monostatic active technique allowing range-resolved measurements and 3-D mapping of important pollutants such as SO₂, NO₂, and O₃. Powerful DIAL systems have been constructed and applied in air quality assessment (see e.g., Refs. 2-5). In long-path laser absorption measurements, path-averaged concentrations are obtained, generally employing retroreflector techniques (see, e.g., Refs. 6-8). Although very powerful and versatile, most laser-based systems tend to be complex and costly, which may render their widespread application difficult. The recently introduced gas-correlation lidar concept⁹ provides some possibilities for system simpli-

fications. Passive remote-sensing techniques are simple but have limited applicability. Active long-path absorption systems employing classical light sources have the disadvantage of being bistatic in nature but can be used for reliable and cost-effective measurements of numerous pollutants. An early example of this type of approach was the ROSE (remote optical sensing of emissions) system,¹⁰ operated in the IR region employing a Fourier transform spectrometer. A particularly powerful technique was recently put forward by Platt *et al.*¹¹ In their DOAS (differential optical absorption spectroscopy) approach a powerful broadband lamp is mounted in a reflector arrangement at a distance of a few kilometers from an optical receiver system that operates in the UV and visible spectral regions. A repetitive fast scanning of a dispersive spectrometer is made over a small spectral region at a rate that leaves even minute atmospheric absorption features unaffected by air turbulence, which otherwise frequently limits optical atmospheric measurements. A sufficient number of signal photons is obtained by adding a very large number of scans in the system computer. A similar elimination of turbulence effects is obtained in an approach put forward by Johnston and McKenzie,¹² in which the ratio between a high- and a low-resolution signal is used. Using optical techniques that are insensitive to turbulence even very low concentrations of atmospheric species can be measured corresponding to differential absorption effects as low as 10^{-4} . Platt and Perner and co-workers have thus, apart from monitoring major pollutants such as SO₂, NO₂, and O₃, applied the technique in studies of trace intermediates in atmospheric chemistry, e.g., NO₃, HNO₂, CS₂ and OH.¹³⁻¹⁸

In this paper we describe a DOAS system that is characterized by a particularly high spectral resolution. This was accomplished by using a specially designed compact high-resolution spectrometer in com-

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bination with a new fast-scanning device. We have used the system for atmospheric SO₂ and NO₂ monitoring and, more critically, in measurements of the background atmospheric concentration of atomic mercury, which is of the order of 1 ppt (1 part in 10¹²). The high spectral resolution attained, better than 0.1 Å, is necessary because of the intrinsically small linewidth of the atomic absorption feature at ~253.6 nm in combination with strong interference due to forbidden O₂ bands.

Interest in atmospheric Hg monitoring is increasing because of widely spreading concern about pollution from coal-powered plants, refuse-burning plants, and chloralkali industries. Further, atomic Hg gas is very interesting as a pathfinder gas associated with various geophysical conditions such as ore deposits, geological faults, and stored geothermal energy.¹⁹⁻²²

A description of the optical and electronic arrangements in our DOAS setup is given in Sec. II. Since laboratory measurements are of great importance for the correct evaluation of data from the atmosphere, a brief description of a multipass White cell, used in conjunction with the DOAS system, is included. The operation of the DOAS system is demonstrated in cell and atmospheric measurements on SO₂ and NO₂. The experimental work on Hg and the spectrally interfering O₂ is described in Sec. III. In a final section conclusions are drawn.

II. DOAS System Description

A. General Considerations for DOAS

One of the major advantages with the DOAS technique is the fast scanning rate. Measurements in the atmosphere using optical techniques normally suffer from problems of signal variation due to atmospheric turbulence. These effects are suppressed by using fast spectral scanning, since the frequency spectrum of atmospheric scintillations near the ground peaks at ~0.1–1 Hz. Above 100 Hz the frequency spectrum contains very little energy.²³ If a single scan is accomplished in a time that is considerably shorter than 100 ms, the atmosphere appears to be almost frozen. Several tens of thousands of scans are then averaged during several minutes of integration time to obtain a satisfactory signal-to-noise-ratio.

A raw recorded spectrum usually contains a wide-band feature caused by small spectral variations in the lamp output, wavelength-dependent mirror reflectivities, or atmospheric scattering. Since this structure is much wider than the narrow absorption features, it can be removed by dividing the raw spectrum by a polynomial (first to fifth order). This polynomial is obtained by a least-squares fit to the absorption spectrum, which generally leaves the trace gas absorption unaffected. An alternative method is to smooth the spectrum over a sufficiently broad spectral region and then divide the signals as described above (see also Ref. 12).

As the name DOAS implies, this method can only be applied for detection of the differential absorption of gaseous atoms or molecules. The atomic concentration C is given by the Lambert-Beer law:

$$C = \log(I_0/I)/(\epsilon L), \quad (1)$$

where I_0 = light intensity without differential absorption,

I = light intensity due to trace gas absorption,

ϵ = differential absorption cross section of the trace gas, and

L = length of absorption light path.

Note that the differential absorption coefficient, ϵ is generally lower than the total absorption coefficient.

When evaluating trace gas concentrations in practical applications a reference spectrum is least-squares fitted to the received absorption spectrum. This improves the system accuracy, since the spectral fingerprint over the whole scanning range contributes to the result. Often several species absorb in the same spectral region. This usually presents no problem. On the contrary, since it is possible to extract the concentrations of several components with good accuracy, it can be an advantage. Platt and Perner and co-workers have, for example, made simultaneous measurements of NO₂ and HNO₂ and also NO₂, CH₂O, and O₃ concentrations in ambient air.^{11,15}

According to Eq. (1), the detection limit for a particular substance can be calculated if the differential absorption coefficient, the minimum detectable optical density [OD = log(I_0/I)], and the length of the light path are known. The detection limit cannot always be improved by increasing the light path due primarily to two effects; geometrical light losses and light attenuation in the atmosphere.

As discussed by Platt *et al.* in Ref. 11, the signal-to-noise ratio of a DOAS system with no geometrical losses is optimal for a light path length $L = 2L_0$. The absorption length L_0 is determined by a combination of atmospheric broadband absorption and Mie and Rayleigh scattering. For bad weather conditions there is no lower limit for L_0 , while the upper limit is determined by Rayleigh scattering and background aerosol scattering. For wavelengths over 300 nm, optimum path lengths of 10 km or more are reached.

B. Optical and Electronic Setup

A diagram of the setup used in the DOAS experiments is shown in Fig. 1. The light source used in this system is a 450-W high-pressure Xe arc lamp (Osram 450). The spectral emission from the lamp is relatively smooth although some peaks are present between 450 and 500 nm. The radiation in the UV region is high, which is necessary when high-resolution classical spectroscopy is performed. The maximum luminance is located around the cathode at a spot <1 mm in diameter. The lamp is placed in front of a concave mirror with a diameter of 30 cm and a focal length of 25 cm. The light source, which is described in more detail in Ref. 24, gives a collimated beam with a divergence of <3 mrad.

After a distance of between 100 m and 10 km some of the light is collected in a telescope, which has a diameter of 35 cm and a focal length of 2 m. The light beams are made parallel after the telescope by an $f = 5$ -cm

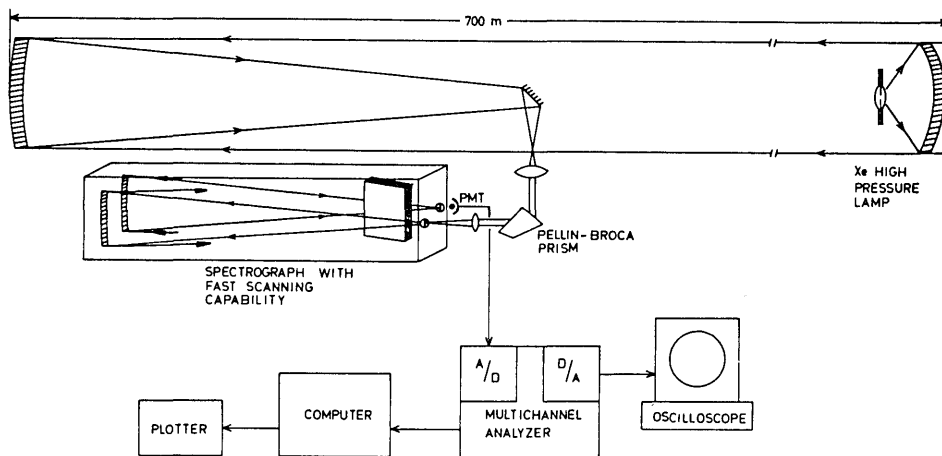


Fig. 1. Experimental setup.

quartz lens, which was chosen to fit the aperture of a Pellin-Broca prism. The prism is used as a predispersive element and the light is spectrally divided along the slit of a monochromator. By changing the slit height, the bandwidth of the light transmitted through the slit can easily be adjusted. This is necessary because the monochromator was often run at higher orders, and overlapping orders have to be efficiently suppressed. In the Hg measurements a slit height of 1 mm was used, which gave a selected region of 5 nm. This technique proved to be more efficient than the use of interference filters. The major dispersive part of the system is a 1-m monochromator in a Czerny-Turner arrangement. The monochromator is equipped with three exchangeable gratings with 600 r/mm, that are blazed at 500 nm, 2.5 μm , and 4 μm , respectively. This makes it possible to choose orders of the different gratings that fit the absorption spectra of most species that absorb between 200 nm and 4 μm with the same system.

Two approaches for the wavelength scanning are used. In our basic setup we use a rotating disk in front of the photomultiplier tube (PMT).¹¹ There are several slits in the disk with a width of 200 μm and only one slit at a time can transmit light. The slits are moved through the spectrum in front of the PMT which has a 5-cm (2-in.) diam photocathode. One advantage with this technique is that the scanning is almost linear in the wavelength domain. When extremely high resolution is necessary, the wavelength scanning is performed by a rotating mirror, which is placed inside the monochromator in front of the exit slit. In this way both the entrance and exit slits can be adjusted and this substantially improves the system flexibility. The scanning effect caused by the rotating mirror is best understood in conjunction with Fig. 2. A round mirror, slightly tilted with respect to the axis of rotation, reflects the light that is coming in at a 45° inclination angle. As the mirror rotates, the tilt causes the beam to rotate, tracing out the shape of an ellipse at the exit slit. The distance to the center is determined by the tilt angle and the distance between the mirror and the exit slit. Note that an inclination effect on the

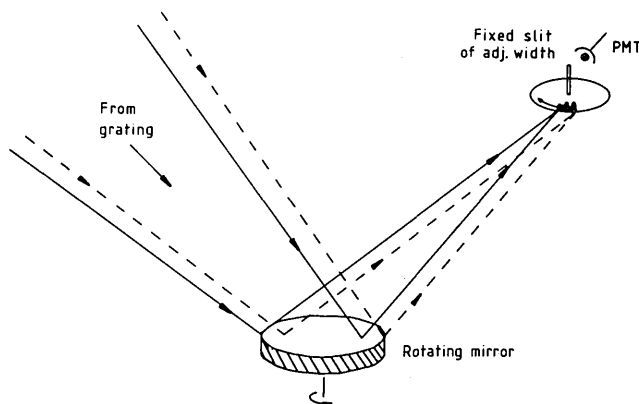


Fig. 2. Rotating mirror scanning unit.

spectral lines arises which lowers the resolution of the monochromator. To keep this inclination effect negligibly small the tilt angle is limited to 10 mrad. The width of the scanned spectral region is determined both by the plate factor of the monochromator and the distance from the rotating mirror to the exit slit. The distance was set at ~ 20 cm giving a spectral scan of 0.5 nm. As the mirror revolves, the spectral region is scanned back and forth in one turn. Using a pin obstacle on the side of the rotating mirror and an infrared light barrier, a trigger signal is sent to the computer and the analog signal is digitized and added to the corresponding channels in the computer memory. Since only the scan in one direction is digitized the duty cycle is reduced. The scan repetition frequency is ~ 40 Hz. For preservation of the spectral resolution while superimposing several thousands of scans, the rotational speed of the mirror is kept constant to within $\pm 0.05\%$.

After the exit slit the light is detected by an EMI 9558 QA PMT. The PMT can be placed in a cooled housing for reduction of the dark current if the light level is low. A preamplifier with a low-pass filter matching the spectral resolution is used to transform the current output of the photomultiplier ($\sim 10 \mu\text{A}$) into a signal level of 1–10 V. The output signal is

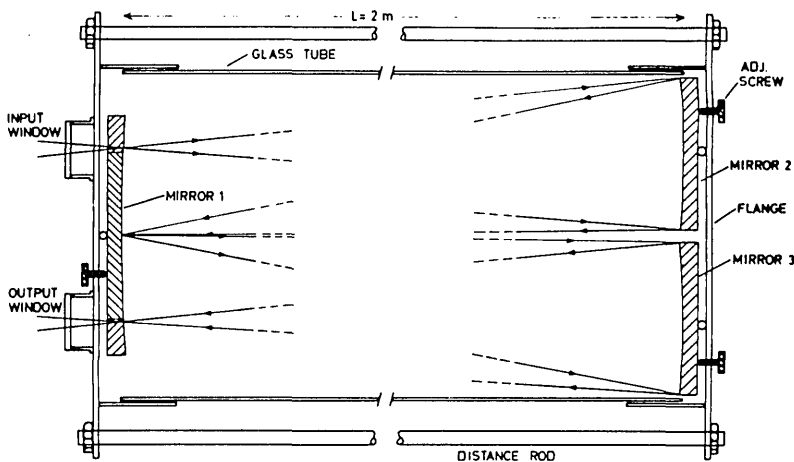


Fig. 3. Diagram of the White cell. The alignment is illustrated for four passes, which is the minimum number of passes. The absorption length is then 8 m.

digitized by a high-speed 12-bit analog-to-digital converter (ADC) and read by a microcomputer. As the spectral region of interest sweeps over the exit slit, one thousand digitized signal samples are taken during a period of 11 ms. The computer software then takes care of adding the digitized samples into separate wavelength channels. Atmospheric flicker due to turbulence and variations in lamp output are found to have a negligible effect because of the fast scan rate and the large number of superimposed spectra. Other effects, caused, e.g., by wavelength-dependent mirror reflectivity and spectral output of the light source or by variations in the sensitivity of the photocathode area, are eliminated afterward by mathematical processing.

The main hardware of the DOAS spectrometer computer system consists of the following two parts:

(a) A signal averager²⁵ based on a computer setup with four 4-MHz Z80 central processing units (CPU) working in parallel, thus making it possible to use the fast averaging rate necessary for the DOAS technique. An ADC, which accomplishes a 12-bit conversion in 3 μ s, presents digitized samples to the microprocessors one after the other. The averaged signal is displayed via a digital-to-analog converter (DAC) on an oscilloscope screen.

(b) A P80 microcomputer, also based on a Z80, performs the necessary steering and timing of the signal averager. After the completion of data acquisition the spectral information is transferred to the P80 unit for further evaluation. As described earlier, several mathematical functions could be executed, thus enabling the extraction of the trace gas concentration from the spectrum. The spectra can also be stored on floppy disks or drawn on a plotter. The programs are written in Microsoft FORTRAN-80 and Z80 ASSEMBLER code for a CP/M operating system. The software consists of a menu-selected program for interactive usage. Several functions can be chosen and performed in automatic sequences, thus allowing unattended operation and evaluation of gas concentrations.

C. Multipass Optical Absorption Cell

In our experiments we have used the DOAS system in conjunction with a multipass absorption cell²⁶ of the

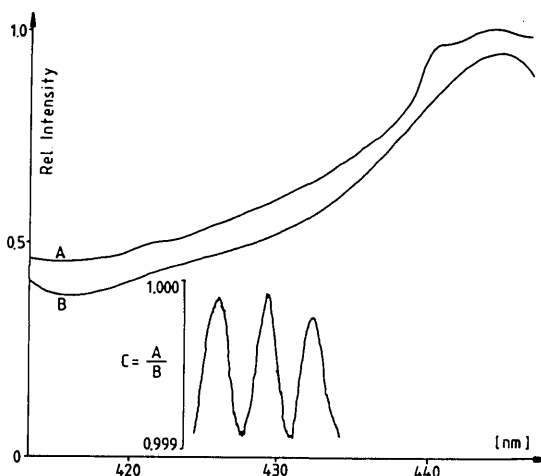


Fig. 4. A, Raw atmospheric spectrum in the blue region with NO_2 absorption (600-m path length). B, Fifth degree polynomial fit to A. (The curve is moved downward to avoid overlap.) C, A divided by B; magnification is 400 times.

type proposed by White.²⁷ The cell was built using a similar device constructed at the university of Gothenburg as the starting point.²⁸ A schematic diagram of the cell is shown in Fig. 3. So far we have achieved an absorption path of 200 m with the Xe lamp. This was performed at a wavelength of ~ 250 nm, i.e., in the region where the Hg absorption line occurs.

The cell has been used to monitor the spectrum of NO_2 in the blue region, SO_2 around 300 nm, and in the UV region around 250 nm. It provides a powerful means of measuring absorption spectra from many gases of low concentrations. Even very weak transitions can be observed, for example, the O_2 bands in the UV region (see Sec. III).

D. Illustration of System Performances

Figure 4 shows an atmospheric spectrum (curve A) in the blue region in which nitrogen dioxide has a prominent absorption profile. The path length was 600 m. The spectrum was recorded with the scanning approach using the rotating slotted disk. The visible structure in the spectrum originates from some peaks in the emission from the lamp but is also due to short-

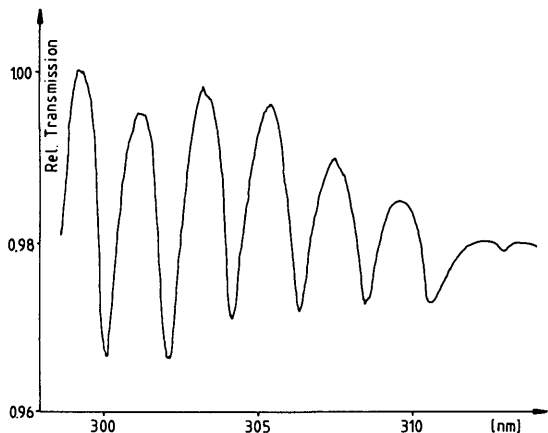


Fig. 5. An SO_2 measurement with a 600-m absorption path length.

comings in the rotating disk setup. Curve *B* is a fifth degree polynomial fitted to spectrum *A*. The curve follows the original one for the large features, but relatively sharp profiles, such as the structure due to absorption from NO_2 and the peaks from the lamp, cannot be taken into account. Thus, by dividing the original spectrum with the fitted one and multiplying by a large factor, the absorption from NO_2 can be greatly enhanced. This is shown in trace *C* in which the scale is magnified by a factor of ~ 400 . As can be seen, the noise level is much smaller than the absorption features which are of the order of 0.1%. This is equal to an NO_2 concentration of ~ 4 ppb for an absorption path of 600 m.

Another species that can easily be measured with the DOAS technique is sulfur dioxide. There is a region of strong SO_2 absorption around 300 nm, and Fig. 5 shows an atmospheric spectrum recorded with a 600-m path length in air. It yields an average SO_2 concentration of 22 ppb. It is important that the plate factor and the resolution are adjusted to the absorption profile of the specific species. SO_2 and NO_2 are easy to evaluate because they have smooth and regular profiles for

which only moderate resolution is required. If the resolution is not sufficient, the Lambert-Beer law will not be strictly valid. The instrumental broadening of the spectrum contributes to a deviation from the strict rule, which gives rise to nonlinearities. One way of overcoming this problem is to calibrate the system with cells that have the same optical depth.

III. Measurements

Our first attempts to measure Hg with the DOAS technique were hampered by the very dominant O_2 absorption profile in the same region around 254 nm.^{29,30} The structure is a band spectrum degraded to the red, with the bandhead at around 252 nm. Figure 6 shows the absorption over an 80-m path in the White cell filled with pure oxygen at atmospheric pressure, recorded in the ninth order of the grating. More than ten absorption peaks are clearly resolved. The ninth absorption peak, counted from the bandhead, is very close to the Hg absorption wavelength at 253.6 nm. The major bands of O_2 are situated below 200 nm, where the atmosphere absorbs all UV radiation. The bands that we observe are called the Herzberg I bands³⁰ and correspond to $A^3\Sigma_u^+ - X^3\Sigma_g^-$ transitions, that are forbidden ones of the first type.²⁹ The bands range from 240 to 280 nm and consist of *Q* branches and weak *S* and *O* branches. As described by Herzberg, the *Q*-branch in each band has a structure denoted by the rotational quantum number *K*, which takes odd values. Each line of the *Q* branch has a fine structure which consists of seven components. The system starts at 41153.3 cm^{-1} (the $v' = 11 - v'' = 0$ band) and ends with a $v' = 1 - v'' = 0$ band at 35780.0 cm^{-1} . The vibrational quantum numbers v' used here differ by one from the ones given in Ref. 29. We use the revised quantum numbers given by Pearse and Gaydon.³⁰ The mercury absorption feature is very close to the tenth component, denoted $K = 19$ in the $v' = 7 - v'' = 0$ band. This component has a fine struc-

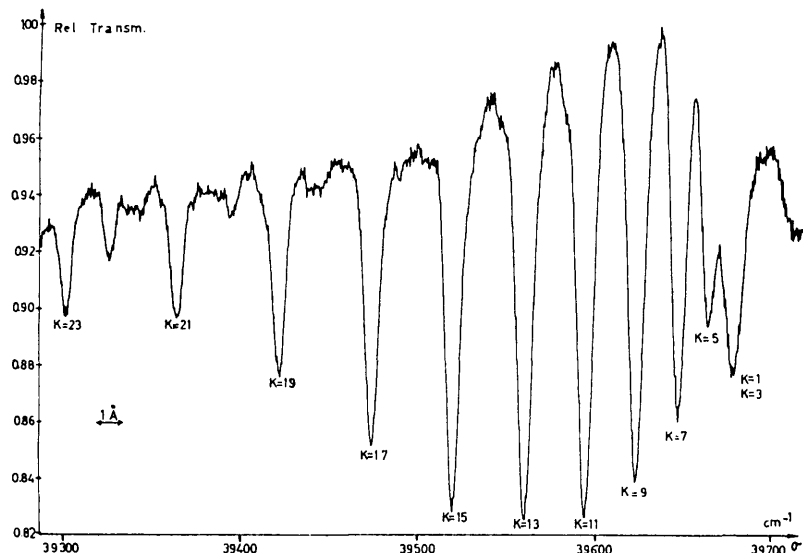


Fig. 6. Oxygen absorption in the White cell in the wavelength region around 254 nm. The absorption path length is 80 m.

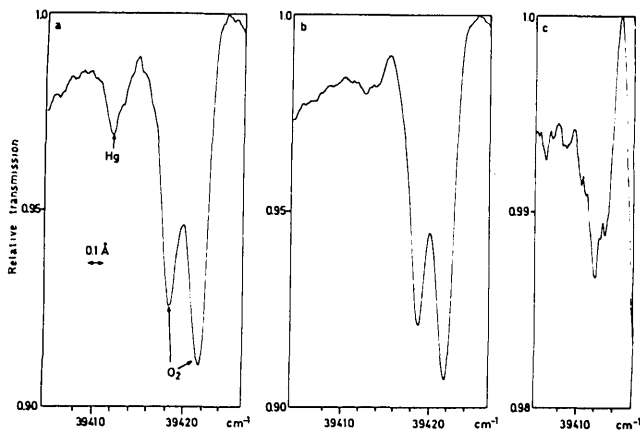


Fig. 7. Differential optical absorption recording for a 700-m atmospheric path length showing signals due to Hg and forbidden O_2 bands. In (a) the incoming light is first passed through a 1-mm Hg cell with a temperature of 18°C . In (b) the signal is due to natural Hg only. This is shown at higher amplification in (c).

ture from 39423.64 to 39417.19 cm^{-1} and the mercury absorption is at $\sim 39412\text{ cm}^{-1}$.

An approximate cross section for the tenth component, $K = 19$, is estimated to be $\sim 6 \times 10^{-7}\text{ m}^2\text{ g}^{-1}$. This value, together with the optical depth in a typical measurement situation, $\sim 1.4 \times 10^5\text{ gm}^{-2}$ for 500 m, gives an absorption of $\sim 10\%$. This largely exceeds the expected mercury absorption of $\sim 1\%$. Since the lower resolution used did not permit complete resolution of the O_2 line from the Hg feature, even with the grating in the tenth order, this makes Hg detection very difficult without higher resolution. It should be possible to evaluate the Hg concentration, although the absorption spectrum of the interference is known. By dividing the absorption spectrum from the air with the pure oxygen absorption spectrum, the influence of the features that are not due to oxygen should appear. However, due to Hg contamination within the laboratories this was impossible. Most cell spectra contain a very prominent mercury absorption feature. The cell could, for example, be evacuated and flushed several times with nitrogen, but the light path from the Xe lamp to the cell and from the cell to the detector would add so much in absorption that a mercury feature would appear anyway.

The remedy for these problems was the development of the rotating mirror, which made it possible to adjust the exit slit and thus the resolution. When both the entrance and exit slits were $100\ \mu\text{m}$, the absorption from Hg was totally resolved. The receiving system was placed close to an open window in an area outside the contaminated laboratories. Furthermore, the wind was blowing in through the open window. The measurements were performed in November 1984, in Lund, which has a population of $\sim 70,000$. A 700-m path, at a mean height of 20 m above the ground, was used. Figure 7(a) shows a recording with a 1-mm Hg cell at 18°C in the light path. As can be seen the absorption from Hg is totally resolved. The internal

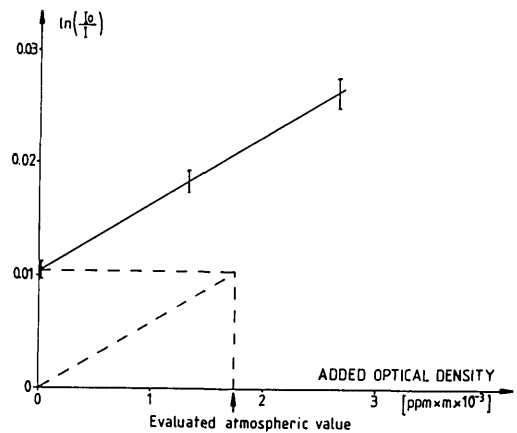


Fig. 8. Standard addition plot using two cells with 1- and 2-mm absorption paths at 18°C .

structure of the oxygen absorption gives rise to two very close peaks for this resolution. The pure atmospheric spectrum is shown in Fig. 7(b) and magnified in Fig. 7(c). The evaluation of the Hg concentration was made with a standard addition method. A plot is shown in Fig. 8 in which two cells with an absorption path of 1 and 2 mm at 18°C were used together with the local concentration in the atmosphere. This gives a differential cross section, $\sigma = 2.45 \times 10^{-19}\text{ m}^2$. About forty recordings, collected over several days, gave the same value to within 10%. Thus, the local concentration of atomic mercury was found to be $2.4 \pm 0.1\text{ ppt}$ or $20.4 \pm 1.0\text{ ng/m}^3$.

IV. Discussion

As demonstrated in this paper and previously,¹¹⁻¹⁸ the DOAS technique provides a powerful means of cost-effective atmospheric monitoring. Major pollutants such as SO_2 and NO_2 can be monitored with a relatively simple system of intermediate spectral resolution, while a high-resolution system, such as the one described in this work, allows studies of particularly weak and overlapping structures such as those encountered in atmospheric Hg monitoring. DOAS can be seen as a valuable complement to the DIAL technique. Because of its relative simplicity the DOAS technique can be expected to find increasing use in practical air pollution monitoring. Because of its ability to detect very small absorptions, the performance of a DOAS system frequently surpasses that of a DIAL system in the detection of intermediates in atmospheric chemistry. Because of the use of a broadband light source, measurements can be performed in wide spectral ranges. We are presently considering the extension of DOAS measurements to the IR region.

The limitations imposed by the bistatic nature of the DOAS technique can be partly overcome by using sufficiently large retroreflectors that can be sequentially illuminated by a light source placed adjacent to the detection system. Since the DOAS technique is a line-of-sight technique, it normally only provides path-averaged concentrations. However, by using tomographic techniques, as recently discussed by Wolfe and

Byer,³¹ spatially resolved information can be obtained through mathematical inversion of the data recorded for different measurement directions in much the same way as for an X-ray CAT scanner.

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