GASEOUS/PARTICULATE ABSORPTION STUDIES AT WSMR
USING LASER SOURCED SPECTROPHONES

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Field absorption measurements of ambient gases and desert dust were taken using uniquely designed resonant subcavity spectrophones. The gas measuring spectrophone contains an inner acoustical subcavity which essentially eliminates the "window" noise problem and the dust spectrophone was designed to allow laminar air flow through the microphone so that particle size distributions will be unaltered during measurements. A review of past and present gaseous and particulate absorption measurements in the Atmospheric
20. ABSTRACT (cont)

The Chemical Sciences Laboratory (ASL) shows frequently good agreement with other independent results such as White cell measurements of methane at deuterium fluoride laser lines (3.5-4.1 micrometer wavelengths), AFGL predictions at CO$_2$ laser lines (9.2-10.8 micrometer wavelengths) for ozone, and Lorenz-Mie calculations for quartz and calcite aerosol particles at the CO$_2$ laser wavelengths. In a number of cases, significant changes to prior published values have also been well substantiated. Using verified absorption coefficients for the atmospheric gases, an on-line/off-line gas analysis at DF laser frequencies was performed for a site at Oscura Peak, White Sands Missile Range (WSMR), NM. Atmospheric gases at the field site were retained in sampling tanks and taken to the laboratory where concentrations of the known gaseous constituents (water vapor, N$_2$O, and CH$_4$) were determined using a self-consistency calculational scheme. Real-time field measurements of atmospheric absorbing gases and dust were then made at a WSMR desert site. Field spectrophone measurements of absorption by desert dust lofted by a driven vehicle were also made and were correlated with Lorenz-Mie predictions based on measured "Knollenberg" particle size distributions. The theoretical calculations overestimate the spectrophone values by various amounts up to a factor of three. Possible errors and uncertainties that are introduced into the measurement technique and into the "Knollenberg" instrument are discussed.
In the past decade, great interest has been generated concerning the use of photoacoustical devices, so-called spectrophones, for measuring small absorption coefficients of trace gases and relatively large concentrations of particulate matter in the atmosphere. This interest is well-justified because of the wide applicability of spectrophones in such fields as laser communications, high energy laser propagation, electro-optical sensing instrumentation, and detection of atmospheric pollutants. For high energy laser systems, absorption of radiation can be extremely variable, depending upon the media through which the beam is being transmitted (for instance, fog, dust, haze, or smoke environment). Atmospheric conditions may result in complete or partial obscuration of the emitted laser wavelengths. Effects such as thermal blooming of the laser beam are based on accurate absorption calculations. For electro-optical systems, proper characterization of common atmospheric gases and particulates is important. Target ranging, laser guidance, target designation, and forward looking infrared devices are highly dependent upon the transmission losses due to these common atmospheric gaseous and particulate constituents. For detection of atmospheric pollutants, atmospheric coefficients of the constituent gases and/or particulates of interest (such as ozone and various industrial and vehicular pollutants) must be known before the concentration levels are deduced. In this report we shall demonstrate the applicability of the spectrophone for measuring absorption coefficients of gases as well as dust particulates in laboratory and field environments by using CO₂ and DF laser sources.
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INTRODUCTION

Since the advent of laser-sourced spectrophone systems by Kerr and Attwood\(^1\) to measure gaseous absorption, the technique has been improved considerably for measuring ultralow gas concentrations in the laboratory (Dewey,\(^2\) Kreutzer,\(^3\) Deaton et al.,\(^4\) and Bruce et al\(^5\)). In addition to gaseous measurements, the versatility of the spectrophone has led to characterizing ground particulates in the laboratory (Bruce and Pinnick\(^6\)). Inherent in both types of measurements is an acoustically resonant cell in which standing sound waves are produced to enhance the spectrophone's low absorption signals and to suppress the amplifier noise level by way of phase-locking the amplified signal with the laser chopping frequency. In this manner absorption sensitivities as low as 0.001 km\(^{-1}\) for trace atmospheric pollutants have been observed (Adamowicz and Koo\(^7\)). Other spectrophone systems have made use of laser light sources with the added advantages of high power densities and high


\(^{5}\)C. W. Bruce, 1976, Development of Spectrophones for CW and Pulsed Radiation Sources, R&D Technical Report, ECOM-5802, US Army Electronics Command, Atmospheric Sciences Laboratory, White Sands Missile Range, NM.


spectral resolution to measure liquids and solids (Rosencwaig\(^8\) and Harshbarger and Robin\(^9\)).

This report describes two techniques for absorption measurements of field atmospheric gases and dust particulates. The first technique uses a state-of-the-art Atmospheric Sciences Laboratory (ASL) developed spectrophone with an acoustically isolated microphone which essentially eliminates the "window" noise problem. The first on-line/off-line gas analysis was conducted at Oscura Peak, White Sands Missile Range (WSMR), New Mexico, and its main purpose was to measure atmospheric absorption spectra and deduce gas concentrations at field sites. The second technique employed a specially designed flow through spectrophone system in which the dust particles were slowly drawn through the resonant cavity of a vertically mounted spectrophone. In the former technique the ambient gases were sampled by stainless cylinders at the field site and then cryogenically transported to the laboratory for analysis. The latter technique for atmospheric gas and dust measurements was used in situ at the Arky Site, WSMR. Both systems operate at CO\(_2\) laser frequencies from the 9- to 11-micrometer IR region. The gas measuring system also used a deuterium fluoride (DF) laser source from 3.5 to 4.1 micrometers to obtain on-line/off-line field gas concentrations for water vapor, N\(_2\)O, and CH\(_4\). Experimental procedures and results of the field gas and dust tests are discussed. Correlated results with meteorological measured parameters and theoretical absorption calculations based upon commercial Knollenberg particle size distributions are included in the analysis. Recommended improvements for further tests are also reported.

**SPECIALY DESIGNED SPECTROPHONES FOR FIELD OPERATIONS**

ASL developed spectrophones (Bruce\(^6\)) were used for these field tests. Basic to these spectrophone designs is an acoustically isolated microphone. The microphone's inner cavity, shown in figure 1, utilizes radially acoustical waves into which longitudinally resonant modes are generated. The microphone's diaphragm is made of a gold-coated mylar sheet and is inserted into an inner stainless steel tube. Narrow mylar strips between diaphragm and tube act as spacers and provide resilience.

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\(^6\)C. W. Bruce, 1976, Development of Spectrophones for CW and Pulsed Radiation Sources, R&D Technical Report, ECOM-5802, US Army Electronics Command, Atmospheric Sciences Laboratory, White Sands Missile Range, NM
The diaphragm which comprises the inside electrode surface; the stainless steel tube forms the outside electrode of the capacitance microphone. The cylindrical teflon carrier provides acoustical and electrical isolation from extraneous noises. For the gaseous portion of the measurements, the gaseous absorption signals within the microphone must be isolated from the "window" absorption signal. This isolation is accomplished by inserting the microphone unit (resonant subcavity) into a long outer cylinder whose end windows are spaced well away from the apertures of the inner resonant subcylinder. This provided the desired losses by misphasing and dispersing the unwanted signals. Further isolation is provided by conical teflon acoustical filters, placed between the microphone ends and the end \( \text{BaF}_2 \) windows of the outer aluminum casing. For flow through dust measurements (figure 2) the end \( \text{BaF}_2 \) windows are removed and a vacuum line connection is made on the side of the aluminum casing near the bottom of the spectrophone. The dust particles enter the spectrophone's subcavity at the top and are drawn through the central aperture. The inner diameter of the microphone and acoustic filters was designed to match the intake aperture on the aluminum casing (double open ended organ pipe type microphone\(^5\)). This was to insure as nearly laminar aerosol flow as possible. Spectrophones with large inner resonant cavities can cause divergent and turbulent flow through the microphone cell allowing alteration of particle densities with passage through the microphone cavity. Another improvement in construction of the dust spectrophone was to place the microphone unit near the top of the aluminum casing to minimize the losses due to impaction of the large particles due to orthogonal wind velocity components near the intake.

Signal processing for the CW source spectrophone is shown in figure 3 and is based on the use of phase sensitive detection to create a very narrow noise bandwidth. Signal processing for both CW and pulsed sources is discussed in more detail in reference 5.

For the measurements discussed here, either a Sylvania 950 cw \( \text{CO}_2 \) laser source or a Lumonics pulsed DF laser source is used. The \( \text{CO}_2 \) laser can be tuned to about 80 spectral lines within the 9- to 11-micrometer window region. The DF laser has a total of about 30 fixed lines ranging from 3.5 to 4.1 micrometers.

The following discussion reviews the ASL measurements of various atmospheric gases and common particulates found in the natural environment. The current efforts to characterize atmospheric gases and particulates in the field are also discussed.

Figure 2. The flow-through dus measuring spectrophone. (The dashed line shows the laminar air flow construction of the microphone unit.)

Figure 3. The electrical circuit of a laser sound spectrophone.
Laboratory Measurements With the Spectrophone Units

Both gaseous and particle spectrophones as previously described were extensively used under controlled laboratory conditions before being adapted to field measurements (figure 4). Early methane absorption studies at DF laser frequencies using a pulsed source spectrophone, for example, show relatively consistent spectral profile with various White (multipass transmission) cell results (Bruce et al.1') and Spencer's11 White cell measurements. The same measurements disagreed strongly with the then current AFCRL [now Air Force Geophysics Laboratory (AFGL)] predictions of McClatchey et al.12 and with measurements of Deaton et al.4 Differences of the normalized values range from 3 to 13 percent with no apparent trends with amplitude of absorption value or frequency. The ARGL line-by-line predictive values, generally much lower than the other referenced values, were later revised and are now in good agreement with the ASL values. During this same period, ozone measurements for sea level and simulated higher altitudes were conducted using the optical setup shown in figure 5. A tiny UV lamp within the spectrophone housing was used to generate the equilibrium concentration of ozone (about 1 to 10 ppm). Figure 6 schematically shows details of the cooled ozone spectrophone. The laser output power was measured using a calorimeter and the spectrophone container was insulated to stabilize the temperature of the system to -70°C. Tables 1 and 2 compare ASL spectrophone absorption coefficients for 9-micrometer CO₂ laser lines with those of the AFGL,12 the White cell results of Patty,1' and the Jet Propulsion Laboratory (JPL) values in km⁻¹/ppm for T = 300 K and T = 210 K for various pressures. Pattern comparison shows very


Methane absorption coefficients for nine DF laser wavelengths are plotted in Figure 4. The results from the spectrophone and White cell are compared.

Figure 4. Comparative spectrophone and White cell results. Methane absorption coefficients are plotted for nine DF laser wavelengths.

Figure 5. Optical diagram for spectrophone gas analysis of ozone at CO₂ laser wavelengths.
Figure 6. Schematic diagram of the temperature controlled CW source spectrophone. (Absorption coefficients were normalized to Patty's values.)
## Table 1. Ozone Absorption Coefficients for ASL Spectrophone Measurements, AFGL Line-by-Line Predictions, Patty's Values, and/or JPL Values at 9-Micrometer CO₂ Laser Lines

Absorption Values at T = 300 K for Pressures of 1.0, 0.35, and 0.18 atm

Ozone Absorption Coefficients (ppm-km⁻¹)

<table>
<thead>
<tr>
<th>CO₂ Lines</th>
<th>p = 1.0 atm</th>
<th>p = 0.35 atm</th>
<th>p = 0.18 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASL</td>
<td>AFGL</td>
<td>Patty</td>
</tr>
<tr>
<td>P-6</td>
<td>0.811</td>
<td>0.200</td>
<td>0.063</td>
</tr>
<tr>
<td>P-8</td>
<td>1.09</td>
<td>0.455</td>
<td>0.298</td>
</tr>
<tr>
<td>P-10</td>
<td>0.624</td>
<td>0.134</td>
<td>0.044</td>
</tr>
<tr>
<td>P-12</td>
<td>1.24</td>
<td>0.953</td>
<td>1.22</td>
</tr>
<tr>
<td>P-14</td>
<td>1.20</td>
<td>1.09</td>
<td>1.27</td>
</tr>
<tr>
<td>P-16</td>
<td>0.934</td>
<td>0.771</td>
<td>0.90</td>
</tr>
<tr>
<td>P-18</td>
<td>0.642</td>
<td>0.514</td>
<td>0.64</td>
</tr>
<tr>
<td>P-20</td>
<td>0.479</td>
<td>0.365</td>
<td>0.55</td>
</tr>
<tr>
<td>P-22</td>
<td>0.201</td>
<td>0.228</td>
<td>0.18</td>
</tr>
<tr>
<td>P-24</td>
<td>0.074</td>
<td>0.066</td>
<td>0.07</td>
</tr>
<tr>
<td>P-26</td>
<td>0.626</td>
<td>0.527</td>
<td>0.60</td>
</tr>
<tr>
<td>P-28</td>
<td>0.945</td>
<td>0.713</td>
<td>0.94</td>
</tr>
<tr>
<td>P-30</td>
<td>0.644</td>
<td>0.551</td>
<td>0.64</td>
</tr>
<tr>
<td>P-32</td>
<td>0.565</td>
<td>0.468</td>
<td>0.59</td>
</tr>
<tr>
<td>P-34</td>
<td>0.369</td>
<td>0.339</td>
<td>0.30</td>
</tr>
<tr>
<td>P-36</td>
<td>0.742</td>
<td>0.550</td>
<td>0.67</td>
</tr>
<tr>
<td>P-38</td>
<td>0.632</td>
<td>0.429</td>
<td>0.345</td>
</tr>
<tr>
<td>P-40</td>
<td>0.496</td>
<td>0.125</td>
<td>0.049</td>
</tr>
</tbody>
</table>
### Table 2. Ozone Absorption Coefficients for ASL Spectrophone Measurements, AFGL Line-by-Line Predictions, Patty's Values and/or JPL Values at 9-Micrometer CO₂ Laser Lines

Absorption Values in (ppm-km)⁻¹ at T = 210 K for Pressures of 1.0, 0.35, and 0.18 atm

<table>
<thead>
<tr>
<th>CO₂ Lines</th>
<th>p = 1.0 atm</th>
<th>p = 0.35 atm</th>
<th>p = 0.18 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASL</td>
<td>AFGL</td>
<td>ASL</td>
</tr>
<tr>
<td>P-6</td>
<td>1.25</td>
<td>1.05</td>
<td>0.292</td>
</tr>
<tr>
<td>P-8</td>
<td>1.74</td>
<td>1.59</td>
<td>0.635</td>
</tr>
<tr>
<td>P-10</td>
<td>1.03</td>
<td>1.01</td>
<td>0.216</td>
</tr>
<tr>
<td>P-12</td>
<td>2.03</td>
<td>1.65</td>
<td>0.763</td>
</tr>
<tr>
<td>P-14</td>
<td>2.28</td>
<td>1.99</td>
<td>0.709</td>
</tr>
<tr>
<td>P-16</td>
<td>1.68</td>
<td>1.57</td>
<td>0.495</td>
</tr>
<tr>
<td>P-18</td>
<td>1.09</td>
<td>1.00</td>
<td>0.526</td>
</tr>
<tr>
<td>P-20</td>
<td>0.815</td>
<td>0.749</td>
<td>0.280</td>
</tr>
<tr>
<td>P-22</td>
<td>0.360</td>
<td>0.409</td>
<td>0.0936</td>
</tr>
<tr>
<td>P-24</td>
<td>0.116</td>
<td>0.108</td>
<td>0.0375</td>
</tr>
<tr>
<td>P-26</td>
<td>1.11</td>
<td>1.11</td>
<td>0.386</td>
</tr>
<tr>
<td>P-28</td>
<td>1.46</td>
<td>1.19</td>
<td>0.699</td>
</tr>
<tr>
<td>P-30</td>
<td>0.911</td>
<td>0.826</td>
<td>0.362</td>
</tr>
<tr>
<td>P-32</td>
<td>0.847</td>
<td>0.694</td>
<td>0.249</td>
</tr>
<tr>
<td>P-34</td>
<td>0.587</td>
<td>0.625</td>
<td>0.128</td>
</tr>
<tr>
<td>P-36</td>
<td>1.05</td>
<td>1.00</td>
<td>0.516</td>
</tr>
<tr>
<td>P-38</td>
<td>1.43</td>
<td>1.14</td>
<td>0.625</td>
</tr>
<tr>
<td>P-40</td>
<td>0.973</td>
<td>0.913</td>
<td>0.218</td>
</tr>
</tbody>
</table>
close agreement with the results of Patty, which were used for calibration of the spectrophone. The spectrophone measurements were then extended to pressures and temperatures unsuitable for White cell measurements since White cells are limited by their bulkiness and sensitivities. For a majority of the CO₂ laser lines, the ASL spectrophone values are slightly higher (about 15 percent) than the AFGL values. However, the agreement is still closer than most comparisons between published values. Differences become more pronounced at lower pressures, possibly because the predictive models (Lorentz line shapes assumed) are inexact and/or the input parameters cannot be accurately extrapolated to markedly different atmospheric conditions.

Recent spectrophone measurements of ammonia (NH₃) by Brewer¹ have been completed for 9- and 10-micrometer CO₂ laser wavelengths. The ASL spectrophone measurement program was focused at resolving disagreements in published ammonia absorption values. The ammonia was buffered with N₂ to 1 atmosphere at 295 K. The absorption coefficients at 77 laser lines are tabulated (table 3) and 95 percent of these coefficients range between 3 to 20 percent probable errors for single measurements. Once again pattern agreement with that of measurements by Patty et al² is quite good through the amplitudes span several orders of magnitude. The values given in table 3 are generally within 15 percent of Patty's values with the exception of the 10-micrometer R branch; the White cell technique used by Patty resulted in a consistent overestimation of the very low absorptions present. The following is an example of the importance of verifying absorption coefficients: the values obtained by another group (Mayer³) have a claimed accuracy of ±5 percent for all lines having coefficients greater than 10⁻⁶km⁻¹/ppm and has stated that its results are in good agreement with those of Patty. However, the absorption at the P(18) line in the 9-micrometer CO₂ emission band is a factor of 10 higher than that reported by Patty and a comparison of the remaining results does not substantiate the statement that the two groups' results are (for ammonia) in agreement since the average ratio between the two sets is 2.6.

For the particulate measurement portion of ASL's tests, known dust particles were finely ground and then uniformly dispersed into an environmental chamber. The general procedure to characterize the absorption


### TABLE 3. ABSORPTION COEFFICIENTS OF NH₃ (295 K, 1 ATM)

<table>
<thead>
<tr>
<th>Spectral Line</th>
<th>Coefficients (ppm-km)⁻¹</th>
<th>Error (%)</th>
<th>Coefficients (ppm-km)⁻¹</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ (air)</td>
<td></td>
<td></td>
<td>μ (air)</td>
<td></td>
</tr>
<tr>
<td>00'1-02'0 CO₂ Band</td>
<td></td>
<td></td>
<td>00'1-10'0 CO₂ Band</td>
<td></td>
</tr>
<tr>
<td>1/4(0)</td>
<td>9.171</td>
<td>0.170</td>
<td>4.0</td>
<td>10.122</td>
</tr>
<tr>
<td>R(38)</td>
<td>9.180</td>
<td>0.0377</td>
<td>4.0</td>
<td>10.133</td>
</tr>
<tr>
<td>(1/4)</td>
<td>9.189</td>
<td>0.00739</td>
<td>7.0</td>
<td>10.144</td>
</tr>
<tr>
<td>R(34)</td>
<td>9.198</td>
<td>0.0212</td>
<td>3.9</td>
<td>10.156</td>
</tr>
<tr>
<td>R(32)</td>
<td>9.208</td>
<td>0.0356</td>
<td>3.4</td>
<td>10.168</td>
</tr>
<tr>
<td>R(30)</td>
<td>9.217</td>
<td>0.062</td>
<td>5.2</td>
<td>10.180</td>
</tr>
<tr>
<td>R(28)</td>
<td>9.227</td>
<td>0.0407</td>
<td>3.7</td>
<td>10.192</td>
</tr>
<tr>
<td>R(26)</td>
<td>9.237</td>
<td>0.0096</td>
<td>5.9</td>
<td>10.204</td>
</tr>
<tr>
<td>R(24)</td>
<td>9.247</td>
<td>0.00583</td>
<td>7.0</td>
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<tr>
<td>R(22)</td>
<td>9.258</td>
<td>0.00489</td>
<td>7.3</td>
<td>10.230</td>
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<tr>
<td>R(20)</td>
<td>9.269</td>
<td>0.00514</td>
<td>8.3</td>
<td>10.244</td>
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<td>R(18)</td>
<td>9.280</td>
<td>0.0107</td>
<td>5.4</td>
<td>10.258</td>
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<tr>
<td>R(16)</td>
<td>9.299</td>
<td>1.12</td>
<td>5.4</td>
<td>10.272</td>
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<tr>
<td>R(14)</td>
<td>9.303</td>
<td>0.0639</td>
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<td>R(12)</td>
<td>9.315</td>
<td>0.0282</td>
<td>4.2</td>
<td>10.301</td>
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<tr>
<td>R(10)</td>
<td>9.327</td>
<td>0.0223</td>
<td>4.2</td>
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<td>R(8)</td>
<td>9.340</td>
<td>0.165</td>
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<td>9.352</td>
<td>0.0112</td>
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<tr>
<td>R(4)</td>
<td>9.365</td>
<td>0.0431</td>
<td>6.6</td>
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<td>P(4)</td>
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<td>P(8)</td>
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<td>0.00488</td>
<td>10.0</td>
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<td>P(10)</td>
<td>9.470</td>
<td>0.0331</td>
<td>3.6</td>
<td>10.492</td>
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<tr>
<td>P(12)</td>
<td>9.486</td>
<td>0.0965</td>
<td>5.2</td>
<td>10.510</td>
</tr>
<tr>
<td>P(14)</td>
<td>9.501</td>
<td>0.0348</td>
<td>5.5</td>
<td>10.529</td>
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<tr>
<td>P(16)</td>
<td>9.517</td>
<td>0.0162</td>
<td>3.2</td>
<td>10.549</td>
</tr>
<tr>
<td>P(18)</td>
<td>9.533</td>
<td>0.0230</td>
<td>2.7</td>
<td>10.568</td>
</tr>
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<td>P(20)</td>
<td>9.550</td>
<td>0.0293</td>
<td>3.6</td>
<td>10.588</td>
</tr>
<tr>
<td>P(22)</td>
<td>9.567</td>
<td>0.0356</td>
<td>5.8</td>
<td>10.603</td>
</tr>
<tr>
<td>P(24)</td>
<td>9.584</td>
<td>0.0348</td>
<td>3.4</td>
<td>10.629</td>
</tr>
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<td>P(26)</td>
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<td>0.00817</td>
<td>4.5</td>
<td>10.650</td>
</tr>
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<td>0.0965</td>
<td>3.8</td>
<td>10.832</td>
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*aThese errors represent the maximum fluctuation in a single measurement.

*bAbsorptions at these lines were used to calibrate the spectrophone.
properties of various common atmospheric particles such as quartz, calcite, and ammonium sulfate is outlined.

1. First, the particles were finely ground using a mortar and pestle and sifted through a 38-micrometer screen mesh. This process was repeated numerous times so that large densities of smaller particles less than 2 micrometer radius were produced. A heat lamp was used to minimize the particle clumping caused by dampness.

2. The particles were dispersed into a 0.5 cubic-meter chamber illustrated in figure 7. Approximately 5 minutes after dispersion of the dust, particles with radii larger than 5 micrometers had settled to the bottom of the chamber. The particle sizes contributing most to the absorption were in the range 0.5- to 2-micrometer radius (Bruce et al.6).

3. As the finely ground dust settled through the dust spectrophone, time decay measurements were taken at selected CO$_2$ laser lines.

4. Particle filter samples were taken at various time intervals to determine number size densities. Histograms of the number density of particles versus mean radii were compiled from electron micrographs reproduced at magnifications of 200X, 500X, 1000X, and 2000X. From the interpolated particle density distributions and the index of refraction of the known particle composition, calculated Mie absorption coefficients were computed.

5. The absorption contribution due only to the ambient gas in the chamber as measured by the gas spectrophone was subtracted from the total gas-plus-particle absorption as measured by the dust spectrophone.

6. Finally, the spectrophone measured absorptions were correlated with Lorenz-Mie absorption calculations and/or spectrophotometer measurements.

Figure 8 shows spectrophone absorption of quartz (SiO$_2$) as compared to Lorenz-Mie calculations at 9.4 to 10.3 micrometers as a function of time after the dust is introduced into the environmental chamber (Bruce and Pinnick6). The time interval between dust sampling measurements was

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Figure 7. Schematic arrangement of spectrophone and particle sampling apparatus showing light scattering particle counter, six filter particle collectors, and spectrophone cutaway. The insert depicts a cross-sectional view of the filter carousel. To obtain a filter sample, the top disk is rotated to expose a filter, and the appropriate valve to the flowmeter is opened.

Figure 8. Absorption coefficients of quartz dust as a function of the time after the dust was dispersed in the holding chamber, as predicted by Lorenz-Mie theory, and as measured with a spectrophone for two wavelengths. The predictions are based on particle size distributions measured at times $t_1$, $t_2$, and $t_3$. 
approximately 15 to 20 minutes with continuous spectrophone sampling. Discrepancies appear between the spectrophone measured and the calculated absorption coefficients. The settling dust provides a range of size distributions over which the comparison time dependencies is in close agreement while the spectral dependence differs by about a factor of two. However, for the theoretical calculations, the particles were assumed to be spherical and as seen in figure 9, the particle shapes are highly irregular and particle density was inhomogeneous. Considering the uncertainties in the theoretical calculation, the experimental results are considered to be in good overall agreement.

Calcite (CaCO₃) dust was dispersed into the environmental chamber, but since it proved to be a very weak and spectrally flat absorber in the 9- to 11-micrometer wavelength region, it was not studied extensively. Figure 10 demonstrates a relative correlation comparison with a segment of a low resolution spectrophotometer measurement using the potassium bromide pellet technique. The spectral nature of the calcite in this IR wavelength region is rather flat with no characteristic structure to its profile. The actual particle absorption values were well below the gaseous absorption levels, which accounts for some of the random scatter in the spectrophone measurements.

Like quartz, ammonium sulfate is a strong absorber in the 9- to 11-micrometer region. The methodology is similar to the previous particulate aerosols; filter samples were taken 4, 9, 14, 20, and 33 minutes after dust dispersal. The peak absorption contribution came from approximately 1-micrometer radius particles. Eighty percent of the total absorption is from particles between 1.3 and 6.3 micrometers in radius. In figure 11, spectrophone measurements (solid lines) are plotted with time for the 9.25-micrometer (R-24) CO₂ laser line and for the 10.22-micrometer (R-24) CO₂ laser line. Here, there seems to be more spectral dependence for the spectrophone values than for the corresponding Lorenz-Mie calculations, but there are not enough absorption points to extrapolate to earlier or later times. The results correlate very well for the 9.25-micrometer line falling within a factor of two although the slopes of the time decay curves differ slightly. For the 10.22-micrometer case, the particle counting statistics for the calculated absorption coefficients are poor and the calculated absorption value at 21 minutes after dust dispersal seem to reverse the trend, opposing that of the spectrophone values. The dust samples at the various times are collected onto 13 mm diameter 0.2-micrometer Nuclepore filters, but the electron micrographs are enlargements covering only about one ten-thousandth of the area from these filters, that is, approximately 0.016 sq mm out of the 133 sq mm total filter area. Therefore, electron micrograph enlargements may contain some statistically poor particle distributions. Also, the actual counting and sizing of the particles from the micrographs are inexact since the particles are not uniform or spherical. Figure 12 is a 2000X micrograph enlargement of ammonium sulfate particles; as in quartz, clustering and irregularity of particles are predominant. The 10.22-micrometer absorption dropped quickly toward the ambient gaseous value (also measured
Figure 9. Photographic electron microscope enlargements of quartz dust collected onto Nuclepore filters. The particle samples were taken at times $t_1$, $t_2$, and $t_3$ corresponding to figure 4. Each photograph contains the geometric mean radius $r_g$ and geometric standard deviation $\sigma_g$ for lognormal size distributions obtained by determining the radii of spheres of equivalent cross sections from SEM photomicrographs. Also shown are the corresponding aerosol mass loading $m$, as determined from the lognormal size distribution parameters by using a quartz density of 2.6 g cm$^{-3}$. The dark circles are holes in the Nuclepore filter substrate.
Figure 10. Relative spectral absorption coefficients for calcium carbonate as measured by a spectrophotometer and an uncalibrated CW CO₂ laser sourced spectrophone.

Figure 11. Absorption coefficients of ammonium sulfate dust as a function of time after dispersal, as predicted and measured with a spectrophone for two wavelengths.
Figure 12. A 2000X photographic enlargement for ammonium sulfate particles using a scanning electron microscope.
using a spectrophone) effectively increasing the spectral dependence. The dust spectrophone measures the total absorption due to both gases and particles. The gaseous contribution must be subtracted from the total absorption in order to obtain the particle absorption coefficient, but unless the dust particles are weak IR absorbers, the gaseous absorption component is negligible compared to the particle absorption levels. If the particle density in the chamber approaches the ambient particle densities, the ambient gaseous absorption may cause another source of error. With these error factors in mind, correlated results that are several factors apart are not unreasonable for these types of absorption measurements. The worst agreement for the measured spectrophone and the calculated values for ammonium sulfate occurred at 10.22 micrometers where a factor of three difference occurred.

This review of ASL developed spectrophone measurements on known atmospheric gaseous and particulate absorbers has illustrated the instruments' basic suitability for flow through, real-time field applications. The gaseous absorption measurements at CO₂ and/or DF laser wavelengths have been strongly substantiated by the best of independent results, when they have been applicable. As for the particulate absorption comparisons, reliable theoretical Lorenz-Mie calculations for irregularly shaped particles are lacking so that assumptions regarding particle sphericity must be made. The automatic counting and sizing of small particles is an extremely difficult problem. Many particle measuring instruments such as the forward scattering Knollenberg particle counter have limitations involving the wavelength of the light source, knowing the exact response characteristics for each substance, and assuming the proper index of refraction for each substance. Even simply collecting the settling dust particles onto filter samples and sizing printed enlargements of electron micrographs are subject to inaccuracies and assumptions. Nevertheless, in general, the correlation results between measured spectrophone values and calculated values for quartz, calcite, and ammonium sulfate particles appear promising enough to do actual field absorption measurements in situ.

ON-LINE/OFF-LINE GAS ANALYSIS AT OSCURA PEAK

The first on-line/off-line gas analysis was attempted at Oscura Peak, WSMR. The purpose of this analysis was to determine atmospheric absorption spectra and gas concentrations at field sites. The gaseous constituents were sampled at the field and then cryogenically transported to ASL for analysis. The stainless steel sampling bottles were pumped and baked to insure a high degree of purity. Before sampling the field gases, the stainless steel bottles were evacuated and cooled down

17C. Samuel, C. W. Bruce, and R. J. Brewer, 1978, Spectrophone Analysis of Gas Samples Obtained at Field Site, ASL-TR-0009, US Army Atmospheric Sciences Laboratory, White Sands Missile Range, New Mexico 88002
in a bath of liquid nitrogen. At the field site the evacuated bottles were opened to receive the ambient field gases. When returned to the laboratory, the bottles were allowed to warm up to ambient air temperatures creating a positive pressure differential inside the bottle with respect to the ambient pressure. The sample gas could then be valved into a gas spectrophone cell for laboratory measurements described earlier. This procedure was verified prior to its use on field gaseous samples. DF laser lines were used to determine the spectral profile of eight gas samples and the average absorption of these samples are plotted in figure 13. Assuming standard pressure and temperature concentrations of CO₂ and N₂, concentrations of water vapor, N₂O, and methane (CH₄) were computed from the spectrophone measurements. Numerous guess values of the partial pressures or concentrations of the gases of interest are input into a computer program which calculates a scaling factor for each of the gases. The total atmospheric absorption for a particular laser line frequency is calculated and plotted. The program increments the partial pressures of water by -10, -5, 0, 5, and 10 percent of its input value. At each of these five pressures, the absorption contribution due to each of the gases under consideration is calculated subtracted from the measured absorption coefficients. The resulting residual absorption coefficients are shown by the dashed line in figure 13, representing unknown gases and impurities within the system. A summary of concentrations of known constituents for nine gas samples is tabulated in table 4. Nitrous oxide and methane gas concentrations are measured approximately two times higher than the standard values. The water vapor concentration varies with meteorological measurements (taken with sling psychrometers and not necessarily at the same location) but generally the correlation agrees.

FIELD DUST EXPERIMENTS ARKY SITE

Under normal atmospheric conditions, the gaseous contribution to the total absorption can be as much as several orders of magnitude greater than the ambient aerosol absorption values. But when dust storms and severe thunderstorm activity in the field and/or man-made battlefield disturbances are considered, generated dust particulates in the air become extremely important as they cause drastic spatial variations of radiant obscuration.

The culminating spectrophone results in the laboratory are directly applicable to the in situ field experiments conducted at the Arky Site, WSMR. A series of dust tests during the period March through June 1978 represent the first in situ field measurements of particulate absorption using a flow-through spectrophone system. The basic design of the optics is outlined in figure 14. The CO₂ laser beam passes through a mechanical chopper at a frequency of 800 hertz; after several beam splitter and mirror deflections, the beam enters a horizontal gas spectrophone and a vertical total-absorption spectrophone. A schematic (figure 15) of the vertically positioned spectrophone shows the aluminum
Figure 13. Remote field site's average initial and residual absorption for eight gas samples at DF laser wavelengths.
TABLE 4. OFF-LINE GAS CONCENTRATION ANALYSIS FOR NINE SITE SAMPLES AT DF LASER WAVELENGTHS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water Vapor (torr)</th>
<th>N₂O (ppm)</th>
<th>CH₄ (ppm)</th>
<th>N₂ (torr)</th>
<th>CO₂ (ppm)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>4.75</td>
<td>0.462</td>
<td>18.2</td>
<td>600</td>
<td>330</td>
</tr>
<tr>
<td>2</td>
<td>3.60 3.20</td>
<td>0.397</td>
<td>4.75</td>
<td>550</td>
<td>330</td>
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<tr>
<td>3</td>
<td>3.57 3.61</td>
<td>0.398</td>
<td>4.26</td>
<td>560</td>
<td>330</td>
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<tr>
<td>4</td>
<td>3.87 2.69</td>
<td>0.748</td>
<td>5.46</td>
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<tr>
<td>5</td>
<td>2.69 2.69</td>
<td>0.760</td>
<td>4.41</td>
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<td>6</td>
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<td>5.04 3.94</td>
<td>0.346</td>
<td>3.79</td>
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Concentrations (or partial pressures) of known constituents

* Calculated from spectrophone measurements
** Obtained from meteorological sources (sling psychrometers)
*** Assumed
Figure 14. Optical arrangement and CO₂ laser alignment of the field-adapted spectrophone system, mirror (M) and beam-splitter (BS).

Figure 15. The vertically mounted total absorption spectrophone with an aluminum intake bell, microphone casing, and a detachable calorimeter.
intake bell (to damp out undesirable wind gusts, reduce particle velocities, and provide laminar flow through the spectrophone), a microphone casing which consisted of acoustic wave absorbers and a teflon incased microphone, a calorimeter, and an outlet valve from which the dust particles were drawn through the spectrophone's cavity by means of an air pump. The laser power output was recorded as well as humidity using a dew point hygrometer. The acoustical signals are electronically processed in the same manner as previously mentioned.

An army 3/4-ton vehicle was driven over the desert terrain upwind of the spectrophone system. A 5 to 10 mph wind with 15 to 20 mph gusts caused the dust clouds to drift across the measurement instrumentation giving a profile in each case. The desert terrain was relatively flat although existing winds frequently changed speed and direction. To independently correlate the spectrophone measured absorption coefficients, a PMS “Knollenberg” particle counter was positioned within 2 meters from the spectrophone probe. Gaseous absorption was in this case a negligible fraction of the total measured by the field dust spectrophone and was thus not separated. Overall, the results of these dust generated runs (figures 16 to 20) indicate good pattern correlation of the absorption coefficients versus time although the relative absorption values varied significantly—a maximum of about 350 km⁻¹ for the Lorenz–Mie calculations and 150 km⁻¹ for the spectrophone. The peaks of the absorption coefficients for the Lorenz–Mie predictions and the spectrophone values may be slightly offset in time because of the spatial distance between the Knollenberg and the spectrophone as the dust cloud passed each device. The spectrophone response time was set at about 1 second as opposed to the 5-second sampling period of the “Knollenberg,” thereby accounting for the more sensitive variations of absorption with time for the spectrophone. For runs 1, 3, 4, and 5, the Lorenz–Mie predictions are generally a factor of three greater than the spectrophone measurements. Run 2 has high spectrophone absorption peaks that match the Lorenz–Mie calculation by no worse than a factor of two. In all cases when the dust cloud appeared to have passed over the instrumentation, the “Knollenberg” particle counts produced negligible absorption values (less than 1 km⁻¹) whereas the spectrophone was still measuring the fluctuating ambient gas levels at the field site and the wind noise (5-7 km⁻¹).

As the dust clouds swept over the individual probes, substantial spatial variation of the dust density was noticed. The horizontal position of the PMS particle counter made it more sensitive to the larger, crosswind particles than the vertically positioned total absorption spectrophone. Inaccuracies in the complex index of refraction of the dust and the PM1 reliability under heavy dust loading can also contribute to the amplitude differences between Lorenz–Mie predictions and spectrophone measurements. Even under ideal spherical particle conditions, errors in the response characteristics of the “Knollenberg” particle counter can result in a factor of two or more difference,¹⁴ while the spectrophone absorption values have an estimated probable error of less than 15

Figure 16. Calculated and measured absorption coefficients of vehicular dust at the Arky Site, WSMR (test run 1).
Figure 17. Calculated and measured absorption coefficients of vehicular dust at the Arky Site, WSMR (test run 2).
Figure 18. Calculated and measured absorption coefficients of vehicular dust at the Arky Site, WSMR (test run 3).
Figure 19. Calculated and measured absorption coefficients of vehicular dust at the Arky Site, WSMR (test run 4).
Figure 20. Calculated and measured absorption coefficients of vehicular dust at the Arky Site, WSMR (test run 5).
percent. However, quantitative sampling errors are unknown for both instruments (functions of the windspeed and wind direction).

CONCLUSION

Spectrophone measurements of gaseous and/or particulate absorption in the laboratory confirmed the reliability and applicability of ASL developed spectrophones and provided much of the basis for quantifying atmospheric absorption as a function of gas concentration. For the gaseous measurements, ozone absorption coefficient comparisons at 300 K and 210 K temperatures for various pressures suggest that ARGL values are about 15 percent low for the strong ozone \( \nu_3 \) absorption band coincidences at 9-micrometer \( \text{CO}_2 \) laser lines. At DF laser lines, methane absorption agreed well with published White cell results and disagreed with the then current predictions. The spectral analysis of ammonia for 9- and 10-micrometer \( \text{CO}_2 \) laser wavelengths at 295 K also produce reasonable agreement with published White cell results and illustrated problems with credibility for other results.

Inherent in all the mentioned gas studies was a spectrophone cell with internal resonant subcavity and filters, both for the purpose of eliminating the "window" noise—the perennial problem of other spectrophone designs. The microphone unit was constructed of a stainless steel tube to minimize outgasing and a perforated teflon carrier to minimize extraneous noise.

For the particulate spectrophone measurements, quartz, calcite, and ammonium sulfate were measured in a laboratory controlled, environmental dust chamber before taking in-situ field measurements. Spectrophone based results correlated with calculated results based on particle counting and sizing agreed within the expected uncertainty of the calculations (probable variation estimated to be a factor of two) and the spectrophone uncertainty (estimated maximum 15 percent). Electron micrographs of ammonium sulfate particles display roughly the same pattern of high irregularity and inhomogeneity of particle sizes and distribution as for quartz dust. Agreement between measured results and theory again is found to be within expected limits for the 9.25-micrometer \( \text{CO}_2 \) laser line. At 10.22 micrometers, the Lorenz-Mie absorption coefficient at 21 minutes after dust dispersal is abnormally higher than spectrophone by a factor of four, but the sample area from which the electron micrographs are produced is only one ten-thousandths of the total particle filter area so that the statistics may have been poor. Calcite proved to be a very weak and spectrally flat absorber in the 9- and 10-micrometer wavelength region as measured by both spectrophone and spectrophotometer.
A program to measure atmospheric gaseous constituents in an on-line/off-line spectrophone analysis for DF laser wavelengths was conducted at Oscura Peak, WSMR. Concentrations for the major atmospheric absorbers at these wavelengths (i.e., water vapor, methane, and nitrous oxide) were measured and found to be roughly a factor of two higher than predictions but water vapor was in close agreement with expectations based on known absorption coefficients and measured relative humidity. Impurities and unknown gases are recognized by the residual level of the absorption after contributions of methane, water vapor, and N\textsubscript{2}O are subtracted from the total spectrophone measured absorption. The feasibility of applying this on-line/off-line gas analysis using cryogenic sampling technique at DF and other laser wavelengths looks very promising though impurities are likely to be introduced unless great care is taken. Unstable species are not candidates for this technique.

A series of field dust tests were conducted at the Arky Site, WSMR, in which relatively large particles were lofted by a running vehicle. A specially designed laminar flow through spectrophone was used and the results were compared to Lorenz-Mie calculations of Knollenberg particle distributions. Preliminary results indicate good pattern correlation although the average amplitudes of the Lorenz-Mie absorption values are approximately three times as high as the corresponding spectrophone measurements. The combined errors of the two measurements as presented in the text represent a factor between two and three. However, other problems not currently quantified (such as sampling efficiencies and uncertainties in the complex index) may explain the differences.

After demonstrating consistently good agreement in the laboratory between spectrophone measured quantities and other independent methods of measurements, absorption tests were conducted at Oscura Peak and then in the field at Arky Site, WSMR, to determine the feasibility of using field designed spectrophones. The measured spectrophone values for the gases for both on-line/off-line and in-situ field cases were generally higher than the expected ambient values (except for the major trace constituent, water vapor) while the spectrophone values for the particulates were generally lower than Lorenz-Mie calculations, though highly correlated in fluctuations. Field and laboratory systems continue to quantify, in-situ, gaseous and particulate obscuration of military environments and to correlate these results with obcurant source densities.
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