Instrument for long-path spectral extinction measurements in air: application to sizing of airborne particles

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A novel instrument that is capable of taking spectral extinction measurements over long optical paths (approximately 1–100 m) in the UV, visible, and IR ranges is described. The instrument is fully automated, and the extinction spectrum is acquired in almost real time (approximately 5–10 s) with a resolution of ~3 nm. Its sensitivity and accuracy were estimated by tests carried out in a clean room that showed that, for optical paths between 50 and 100 m, the extinction coefficient can be detected at levels of ~10^{-2} m^{-1}. Tests carried out on calibrated latex particles showed that, when it was combined with an appropriate inversion method, the technique could be profitably applied to characterize airborne particulate distributions. By carrying out measurements over optical paths of ~100 m, the instrument is also capable of detecting extinction coefficients that are due to aerosol concentrations well below the limits imposed by the European Economic Community for atmospheric pollution (~150 μg/m^3). Scaled over optical paths of ~10 m, the limit imposed for particle emissions from industrial plants (10 mg/m^3) can also be detected sensitively. © 2001 Optical Society of America.

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1. Introduction
Atmospheric particle pollution and particle emissions from industrial plants are extremely deleterious to human health because they can enter the airways of the lung and remain trapped in various regions of the respiratory tract, down to the interstices in the pulmonary alveoli.\(^1\),\(^2\) Indeed, the diameters of these particles (approximately 0.1–5 μm) are too small for the particles to be retained by the upper respiratory system and too big for them to be expelled during exhalation. It is therefore evident that their harmfulness depends greatly on both their size distribution and concentration. As a consequence, the simultaneous detection and size characterization of the airborne particulates are of extreme interest, but this is a difficult task to accomplish.

To control and possibly to reduce the emission rates of such substances it is often convenient to monitor large areas (usually in the open air) and to perform a real-time analysis. To our knowledge, most of the available standard instrumentation provides information on the total aerosol concentration or on some fraction of it, such as the PM10 and PM2.5 fraction.\(^2\) However, it does not permit the determination of the airborne particulate size distribution. That task is commonly carried out by use of a cascade of impactors, which separate airborne particles into different classes according to the particles’ aerodynamic diameters. Analysis of the fractions deposited upon the various plates of the impactor gives information on the mass size distribution of the airborne particles. However, this technique has several limitations; the most important ones are related to the fact that the procedures for sampling and handling the particles inside an impactor are rather invasive and somewhat unreliable as well. Moreover, in many cases the data analysis is carried out a second time, and so is clearly time-consuming and demanding in terms of costs and labor.

A well-known optical technique that is capable of overcoming the limitations mentioned above and of recovering both the size distribution and the concentration of airborne particulates is the spectral extinction method.\(^3\) The technique is based, first, on...
measurement of the extinction coefficient spectrum that is due to particles dispersed in the atmosphere and, second, on an analysis of the data that provide information on the particle size distribution and concentration. The data analysis is a somewhat delicate process, which requires the inversion of a Fredholm integral equation of the first kind and knowledge of the particles' refractive index. In the past these issues were addressed in a number of numerical and experimental works in which the technique was profitably exploited for detecting and characterizing atmospheric aerosols under many different conditions. Examples can be found for marine, continental, dry-rural, and urban aerosols as well as for air columnar aerosols, aerosols generated in a tunnel, and tomographic two-dimensional mappings of spatial aerosols. In more recent years, the spectral extinction method was extensively exploited in connection with lidar techniques, from which information on the altitude profile of columnar atmospheric aerosols can be inferred (see, for example, Ref. 11 and references therein).

One can carry out the measurement of the extinction coefficient by shining a laser beam operating at a number of different wavelengths or a beam of white light in air and detecting the spectrum of the transmitted radiation after its propagation over a long optical path. By comparing this spectrum with the one obtained from a short path it is possible to determine the spectral extinction coefficient that is due to the substances dispersed in air. Using a long path ensures that two fundamental requirements are encountered at once: On the one hand, the data are efficiently averaged against local or spatial inhomogeneity, and, on the other hand, achievement of high sensitivity can be guaranteed. However, using a long path implies that it is impossible to have a reference measurement over the same path over which the particles are dispersed. Thus designing the instrument is accomplished by different methods, depending on which type of radiation source is utilized. If the source is a set of laser lines, the layout of the apparatus is simple, and optical paths as long as 200 m, with a resolution of ~3 nm, corresponding to ~200 λ. We overcame the difficulty associated with the reference measurement by taking the transmission spectrum over a short path that was collinear with the long path of the sample measurement and by using a laser beam aligned onto the optical axis for normalization. We estimated the instrument's characteristics (sensitivity, accuracy, and reliability) by carrying out measurements in a clean room over several optical paths and following different procedures. The findings of these investigations show that, for optical paths between 50 and 100 m, the instrument sensitivity, i.e., the minimum detectable extinction coefficient is \( \alpha_{\text{min}} \approx 10^{-5} \text{ m}^{-1} \) over almost the entire spectral range. For shorter paths, \( \alpha_{\text{min}} \) increases in inverse proportion to the path length, and, for example, is \( 10^{-4} \text{ m}^{-1} \) at 10 m. These values are much smaller than typical extinction coefficients encountered in a (clean) atmosphere and expected for aerosols released in the atmosphere as a product of combustion in industrial plants.

We performed the data inversion by using a non-linear iterative algorithm proposed some time ago for the inversion of simulated and experimental spectral extinction data taken with a commercial spectrophotometer. The instrument’s ability to retrieve particle size distributions with particles in the range of diameters and concentrations that are typical of environmental conditions was investigated by computer simulations and tested on aqueous solutions of calibrated latex particles of various diameters and concentrations. The computer simulations showed that, when the particles’ refractive index is known, the inversion algorithm can handle and retrieve broad size distributions, such as those expected in the atmosphere and described, for example, by the LOWTRAN model. At the same time, the tests with the latex particles indicated that the instrument is suitable for detecting and characterizing atmospheric pollution and emission products of chimneys and other combustion processes with particles with a range of radii of approximately 0.05–2.5 μm. In both cases the instrument’s sensitivity is amply sufficient to permit easy detection of the minimum particle concentrations imposed by European Economic Community (EEC) regulations.

2. Spectral Extinction Technique

Spectral extinction techniques are based on measurement of extinction coefficient \( \alpha \) at various vacuum wavelengths \( \lambda \). \( \alpha(\lambda) \) is defined by the relation

\[
P_T = P_0 \exp[-\alpha(\lambda)d],
\]

which is known as the Beer–Lambert law. Equation (1) describes the attenuation of a monochromatic beam through a sample of length \( d \). \( P_0 \) and \( P_T \) denote the incident and the transmitted power, respectively, and Eq. (1) is valid only for samples for which multiple scattering can be neglected.

The experimental detection of \( \alpha(\lambda) \) requires quite different procedures, depending on whether the sample to be tested is confined within a container (cell) or dispersed in the atmosphere. In the first case, one carries out the measurement by first determining \( P_0(\lambda) \), i.e., the spectrum of the transmitted power with no particles in the cell. Then, without changing the optical layout, the measurement is repeated with the sample in the cell, and \( P_T(\lambda) \) is determined.
In this way, provided that during the time elapsed between the two measurements the emission spectrum of the source has not changed, \( P_0 \) and \( P_T \) are related by Eq. (1), and \( \alpha(\lambda) \) can be determined.

In the second case, the measurement is more troublesome because the sample cannot be removed from the optical path, and therefore no direct determination of the incident power is possible. In this case, the measurements of \( P_0 \) and \( P_T \) are carried out over two collinear optical paths of different lengths, \( d_0 \) and \( d_1 \), respectively (see Fig. 1). Provided that the emission spectrum of the source does not change during the two measurements and that there are no distortions of the transmitted spectrum as a result of the different layouts of the two optical paths, \( P_0 \) and \( P_T \) are related by Eq. (1) with \( d = d_1 - d_0 \). Thus \( \alpha(\lambda) \) represents the mean extinction coefficient averaged over \( d \). It should be pointed out that the second of the above requirements is quite crucial and is not easily fulfilled. Indeed, this condition implies that any difference between \( P_0 \) and \( P_T \) is to be attributed to the presence of particles in the region under test, implying that, had no particles been present in this region, \( P_0 \) and \( P_T \) would have been the same. In practice, however, because of experimental noise or unavoidable differences in the collection optics of the two paths, there is always some residual difference. This difference sets the sensitivity of the instrument and therefore has to be reduced as much as possible. Thus the design and the test of the instrument demand special care, as is described below in Sections 4 and 5.

As anticipated in Section 1, the spectral extinction technique requires that the particle size distribution be recovered by inversion of a Fredholm integral equation of the first kind. Let us suppose that the sample is a dilute dispersion of noninteracting polydisperse spheres and that all the spheres are optically homogeneous, i.e., are characterized by the same refractive index. Thus the spectral extinction coefficient is given by

\[
\alpha(\lambda) = \int \pi r^2 Q_{\text{ext}}(r, \lambda', m) N(r) dr,
\]

where \( N(r) \) is the number concentration of particles with radii from \( r \) to \( r + dr \) (cm\(^{-3}\)μm\(^{-1}\)) and \( Q_{\text{ext}} \) is the extinction efficiency and is given by Mie theory.\(^{16}\) Here \( \lambda' \) is the wavelength of the radiation in the medium, and \( m \) is the refractive index of the particles relative to the medium. Equation (2) is a Fredholm integral equation of the first kind, where \( \alpha(\lambda) \) is provided by the experiment, \( \pi r^2 Q_{\text{ext}} \) is the known kernel, and \( N(r) \) is the distribution to be recovered. As is known, this is a typical example of an ill-posed problem, which means that different distributions can fit the data \( \alpha(\lambda) \) with the same level of accuracy when some noise is present in the data.\(^{17}\) Therefore the inversion of Eq. (2) is not a trivial task and has to be carried out by use of stable and reliable algorithms. In this study we carried out the inversion of Eq. (2) by using the nonlinear iterative algorithm reported and described in Ref. 12.

3. Experimental Setup

The instrument, whose schematic diagram is shown in Fig. 1, has two parts: a measuring unit that contains the light sources and the photodetectors, and two retroreflectors, which reflect back the radiation that comes from the measuring unit.

The white-light source is a 300-W, 1000-h lifetime xenon lamp (ILC Model Cermax) emitting in the 0.25–1.1-μm spectral range. Its emitting spectrum is broadband, with several relevant peaks in the 800–1000-nm region that, however, do not affect the performance of the instrument (see below). The beam is 25 mm in diameter and has a ±4° divergence.
The power emitted by the lamp is stabilized by means of a feedback mechanism that makes use of beam splitter BS1, photodiode PD1, and appropriate electronics (not shown). The overall stability achieved in typical measurement conditions is within a few parts in $10^3$. The beam emitted by the lamp shines toward the two retroreflectors. The first one (RR1) is placed at a distance $d_0/2$ (typically ~10 m) and is used for measuring the reference spectrum. The second (RR2) is placed at a distance $d_1/2$ (maximum, ~60 m) and (with RR1 rotated by 90°) is used for measuring the sample spectrum. From the ratio of these two spectra the shape of the extinction coefficient that is due to particles that are present in the region between RR1 and RR2 is determined. Its normalization is carried out with a laser beam, as described further below in this section. The two retroreflectors are identical, made from two flat mirrors (M1 and M2) oriented at 90° to each other and ~30 cm apart. In this way they reflect the radiation to the measuring unit, and the axes of the incoming and outgoing beams are sufficiently separated. The two mirrors measure 80 mm × 113 mm wide and have a surface flatness better than $\lambda/2$ over the whole surface and a reflectivity that is larger than 95% over the whole emission spectral range of the lamp. The mirrors are clamped onto a plate that is mounted upon a standard photographic tripod. The plate can be translated, rotated, and tilted with respect to the tripod to permit easy alignment of the retroreflectors. Between the two mirrors there is a diaphragm (DP), whose diameter is slightly larger than half the diameter of the collecting lens, L1. This diaphragm ensures that, regardless of the distance between the retroreflector and the lamp, only the light collected by lens L1 is reflected back to the measuring unit. Indeed, at such long distances the lamp can be considered almost a point source, and therefore, as the diaphragm is halfway between the source and lens L1, the beam spot size on the plane of L1 is always twice the diaphragm’s diameter.

The transmitted light is collected by lens L1, a quartz achromat with a focal length of 500 mm and a diameter of 90 mm. In its focal plane there is a 2-mm entrance pinhole of a homemade Spectralon integrating sphere with a 10-mm-diameter cavity. The L1–pinhole system acts as a spatial filter and determines the maximum acceptance angle, or field of view, of the optics, which turns out to be $\pm 2 \times 10^{-3}$ rad. This applies to all particles that are less than 45 m from L1. For the rest of the scattering volume, this value progressively decreases with the distance from L1, down to $\pm 0.5 \times 10^{-3}$ rad for a maximum distance of 100 m. It is worth noting that such a small field of view guarantees that the effects of both the singly forward-scattered and the multiply scattered light reentering the collection optics are quite negligible. A bundle of optical fibers is positioned upon the 1-mm exit pinhole of the sphere. After it has been unraveled and aligned, the fiber bundle delivers the light at the entrance slit of a polychromator (Zeiss Model MM1) working in the spectral range 0.3–1.0 μm with a resolving power of 7 nm. The light emerging from the polychromator is detected by a linear array of photosensors (Hamamatsu Model S904) made from 256 pixels. The electric signals that emerge from the array are amplified at low noise and digitized by a 16-bit analog-to-digital converter on a multifunction input–output board (National Instruments, Model AT-MIO16XE50). The board also provides the signals for controlling the linear array and varying the detector’s integration time in the range 10 ms–10 s, with an increase in the dynamic range of the analog-to-digital conversion by a factor of ~1000. In this way the reference and the sample spectra can be measured with the same level of accuracy, in spite of the fact that the power gathered by the collection optics depends sensitively on the distance $d$ between the lamp and the retroreflectors (it varies as $\sim d^{-2}$).

Moreover, each single spectrum is measured by a double-exposure procedure, i.e., by combination of two integration times. The spectral regions close to the sides of the range ($\lambda < 0.4$ μm and $\lambda > 0.7$ μm) are indeed the most critical (due to the reduced efficiencies of the lamp and of the polychromator and to the smaller detectors’ sensitivity) and are measured with an integration time approximately a factor 15 longer than that used in the central region. Finally, after corrections for the different reflectivities of the mirrors, for the nonlinearity of the polychromator, and for the spurious effects that are due to the higher diffraction orders of the grating, a relative accuracy of better than $10^{-5}$ is achieved for both the reference and the sample spectra.

As we mentioned above, because the power gathered by the collection optics depends on the distance between the lamp and the retroreflectors, the reference and the sample spectra are not directly comparable on an absolute scale. Thus the extinction coefficient is determined apart from a multiplicative constant. Its normalization is carried out by use of a He–Ne laser (0.5 mW, $\lambda = 0.6328$ μm), which is shone along the same optical path of the lamp. As shown in Fig. 1, the laser beam is divided by beam splitter BS2 into two parts: A fraction is forwarded onto photodiode PD2 and used for monitoring the laser power and the remaining part is expanded by lenses L2 and L3 and collimated to a beam with a size of ~10 mm at 1/e². When the measurement with the laser is performed, light from the lamp is blocked and the laser beam is superimposed upon the lamp axis by the two mirrors M4 and M5. The latter mirror is mounted upon a pivotable holder that permits the mirror to be moved in and out of the lamp axis easily and reliably. At the same time, mirror M3 is inserted by use of a stepper-motor-controlled stage, and the transmitted power is detected by photodiode PD3. The signals emerging from photodiodes PD2 and PD3 are handled by standard electronics and digitized by the same input–output board that was used for the polychromator.

The overall functioning of the instrument is controlled by a PC with a 100-MHz Pentium processor.
By using a homemade program developed with LabVIEW (National Instruments), the PC controls data acquisition and elaboration and drives all the motors and other servo mechanisms in the instrument. Data inversion (see Section 2) and recovery of the particle size distribution and sample concentration are also implemented in the program.

4. Test of the Instrument

In this section we discuss the tests that we carried out on the instrument to estimate its sensitivity, reliability, stability, and accuracy and to ascertain its suitability for retrieving distributions of particles dispersed in the atmosphere. Below, three tests are reported: measurements carried out in a clean room (Subsection 4.A), which allowed us to determine the sensitivity of the instrument; measurements of calibrated polystyrene spheres (Subsection 4.B), in which the range of recoverable radii and the minimum concentration detectable by the instrument were estimated; and numerical simulations of a standard atmospheric model (Subsection 4.C), where the capability of the inversion algorithm to retrieve typical atmospheric size distributions was discussed.

A. Clean Room Measurements

We ascertained the reliability and sensitivity of the instrument to determine the extinction coefficient over the entire spectral range of the instrument, and we investigated how these properties depend on the optical path of the measurement. Because typical values of the extinction coefficient in the atmosphere are $\sim 10^{-4}$ to $\sim 10^{-3}$ m$^{-1}$, the expected attenuation over optical paths of $\sim 100$ m is of the order of $\sim 10^{-2}$ to $\sim 10^{-1}$. Therefore, if the extinction coefficient is required to be determined with an accuracy of at least 10%, the measurements of the transmitted power must be carried out with a relative uncertainty of less than $10^{-3}$. If the same accuracy is desired over much shorter optical paths, this requirement becomes much stricter, and the transmitted power should be detected with extremely low uncertainty.

Now, the limits of the accuracy of the measurement may be ascribed to two different types of noise. On one hand, there is an electronic noise derived from the detection process that limits the uncertainty associated with the measurements of the transmitted power. For our instrument, this uncertainty is $\sim 10^{-3}$, and, up to $\sim 100$ m, is almost independent of the optical path. On the other hand, as we mentioned in Section 2, the accuracy is also limited by what we can call optical noise of the instrument, i.e., all the sources of uncertainty related to the fact that the reference and the testing beams follow two different optical paths. As a consequence, any difference between the transmitted powers that is due to differences in the collection optics of the two paths may be incorrectly attributed to the presence of particles along the beam. The dimensions of this problem clearly depend on the optical path, and the problem becomes more critical as longer paths are considered.

Thus the sensitivity of the instrument is expected to be limited at short optical paths by the electronic noise and at longer optical paths by the optical noise. To test this assumption we carried out several measurements in a 50-m-long clean room, generously made available by Alenia Spazio, Turin, Italy. The room was ranked as a class 100,000 clean room (U.S. Federal Standard 209E), which means that the number of particles of sizes 0.5 μm and larger should not exceed 3.5 particles/cm$^3$ and that the number of particles 5 μm and larger should not exceed $2.5 \times 10^{-2}$ particles/cm$^3$. We carried out the test by placing the reference retroreflector at a distance of 12 m from the measuring unit. The sample retroreflector was placed at two different distances, 29 and 46 m, from the unit. The corresponding optical paths were 34 and 68 m, respectively. The measurements were then repeated over the same optical paths but with a single retroreflector used for both the reference and the sample beams. The last-named procedure obviates the need to correct for the different reflectivities of the mirrors but lengthens the overall time required for the measurement because the reflector has to be moved and realigned. Therefore that method is not suitable for automatic measurements and, in addition, is more susceptible to errors as a result of changes in the spectrum emitted by the lamp. However, a cross check between the two methods is a valid test for the overall reliability of the technique and helps to reveal possible systematic errors in the measurements.

The behavior of the extinction coefficient relative to the four measurements described above is illustrated in Fig. 2 as a function of the wavelength. The high peaks in the figure are due to absorption bands of the gases (O$_2$ and H$_2$O) dispersed in air and are discussed in Subsection 4.B. Remarkably, the four curves match one another rather nicely, showing high instrumental reproducibility. In particular, over most
of the entire spectral range, from 0.35 to 0.80 μm, the spread among four curves is always less than $\sim 10^{-5}$ m$^{-1}$. Outside this region the differences are somewhat larger but are always within $\sim 5 \times 10^{-5}$ m$^{-1}$. For wavelengths smaller than 0.35 μm, the main sources of error are the reduced emitting power of the lamp and the low sensitivity of the detector. For wavelengths larger than 0.85 μm, however, the spread among the curves is probably due to our limited ability to correct for the effect of higher diffraction orders of the polychromator grating. For this reason, and because of the high absorption bands that are present in this spectral region, we did not consider wavelengths larger than 0.90 μm when we were inverting atmospheric data.

In conclusion, we can state that, for optical paths $d$ of 50–100 m, the instrument sensitivity is $\alpha_{\text{min}} \sim 10^{-5}$ m$^{-1}$ over the entire spectral range. For shorter paths, $\alpha_{\text{min}}$ is determined by the relative uncertainty associated with the measure of the transmitted power ($\sim 10^{-3}$) and, therefore, increases in inverse proportion to path length $d$ (for example, for $d \sim 10$ m, $\alpha_{\text{min}} \sim 10^{-4}$ m$^{-1}$). These values are much smaller than typical extinction coefficients encountered in (clean) atmospheres and therefore allow us to perform measurements with a signal-to-noise ratio of 10 or better over the whole spectral range.

### B. Tests of Latex Spheres

We performed these series of tests to check whether the instrument is suitable for detecting and retrieving particle size distributions with particles in a range of radii and concentrations that is typical of environmental conditions. In particular, we tested the ability of the instrument to detect the minimum concentration imposed by the current EEC regulations (150 μg/m$^3$ for atmospheric particle pollution and 10 mg/m$^3$ for particles emitted by chimneys of industrial plants), and we estimated the range of radii over which atmospheric aerosol distributions can be recovered. To do this we carried out several measurements of aqueous solutions of calibrated polystyrene latex spheres of known sizes and concentrations confined within a relatively thin cell placed along a long optical path. With respect to the concentration, the idea was to assume that, once the minimum concentration detectable in the cell was determined, we could retrieve the minimum concentration for a given environmental condition by simply rescaling its value for the corresponding optical path (up to 100 m for monitoring atmospheric pollution and up to 10 m for chimney emissions). Similarly, we estimated the range of recoverable radii for the atmospheric aerosols by rescaling the range found for the latex–water system after having properly taken into account the different refractive indices of the two systems (see the discussion below).

The particle samples were diluted suspensions of calibrated polystyrene spheres (Interfacial Dynamics Corporation, Portland, Ore.) characterized by typical polydispersity of a few percentage points. All the samples were diluted in distilled and filtered water (through a 0.22-μm filter) and inserted into a square cell made from two 150 mm × 150 mm quartz windows, 10 mm apart. The cell was placed along an optical path of 50 m at a distance of 10 m from the lamp. The test was repeated several times with different optical paths and different distances between the cell and the lamp, and the results were the same within the instrumental sensitivity. We determined the extinction coefficient by comparing the spectrum transmitted by the sample with the reference spectrum obtained with the cell filled only with water. Between the two measurements the cell was kept in the same position. The spectral range of the measurements was 0.3–1.0 μm. We inverted the data by taking into account the dispersion of the refractive indices of water and polystyrene over the spectral range that was measured.\(^{13}\)

The first sample comprised particles with an average radius of 0.73 μm and a relative standard deviation $\sigma/\langle r \rangle \sim 3\%$. The sample concentration spanned approximately three decades, from $1.71 \times 10^2$ to $2.02 \times 10^7$ particles/cm$^3$, or, equivalently, from $2.78 \times 10^{-8}$ to $3.29 \times 10^{-5}$ volume fractions. Figure 3 shows the extinction coefficients as a function of wavelength for several sample concentrations. The symbols refer to experimental data, whereas the continuous curves are the data reconstructed on the basis of the distributions recovered as a result of the

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**Fig. 3.** Behavior of the extinction coefficient of calibrated 0.73-μm-radius latex spheres for several sample volume fractions that vary from $3.29 \times 10^{-5}$ to $2.78 \times 10^{-8}$ (top to bottom). The spheres were dispersed in water and confined in a cell with a 10-mm optical path. Symbols represent the experimental data, whereas solid curves are the extinction data reconstructed on the basis of the recovered distributions. For clarity, the symbols for the two lowest (and noisiest) curves are different from all the others.
inversion procedure. The match between the experimental and the reconstructed data is excellent, with deviations always much smaller than the noise level that is present in the data. As expected, the signal-to-noise ratio is higher for more-concentrated samples and decreases for more-diluted samples. For the lowest concentration shown in Fig. 3 the average extinction coefficient is \(1.5 \times 10^{-2}\) m\(^{-1}\) and the noise levels at the borders of the spectrum are comparable with the amplitude of the spectrum itself. Thus, this value is an estimate of the minimum detectable concentration when the particle sample is confined within a 10-mm cell. If we spread the particles contained in the cell over an optical path of 100 m, the corresponding extinction coefficient is \(1.5 \times 10^{-5}\) m\(^{-1}\), which is consistent with the instrument’s sensitivity estimated from the clean room measurements. The recovered distributions that correspond to the data of Fig. 3 are shown in Fig. 4, where, for clarity, only some of the curves are shown. The figure shows that all the distributions are nicely bell shaped, with the peak falling exactly at the expected position. All the distributions are characterized by the same FWHM of approximately three classes, which corresponds to a relative standard deviation of \(10\%\). This can be considered a good estimate of the resolution of the instrument because the nominal standard deviation of the sample distribution is approximately one class.

To better elucidate the instrument performance, we show in Fig. 5, as a function of sample concentration, some of the errors made in the parameters that characterize the recovered distributions, i.e., the rms deviations between the experimental and the recovered data, (b) percentage deviations between the recovered average radius and the nominal one, (c) percentage deviations between the recovered and the actual sample concentrations. The dashed vertical lines indicate the equivalent limits for atmospheric pollution and emissions from chimneys imposed by the EEC (see text).
distribution parameters are retrieved less accurately. When the sample concentration and the average radius can both be recovered with an accuracy within 10–20%. Thus we can conclude that, for almost monodisperse spheres dispersed in water, a reasonable estimate of the range of recoverable radii is approximately 0.084–5.0 μm.

At this point it must be recalled that, because of their different refractive indices, the range of recoverable radii for the latex–water system is different from that of the aerosol–air system. This is so because, for any given particle size distribution, the shape of the extinction coefficient \( \alpha(\lambda) \) may vary significantly when the refractive indices of the particles and the medium are varied. In particular, it can be seen that, on passing from the latex–water to the aerosol–air system, the pattern of maxima and minima in curve \( \alpha(\lambda) \) moves or is shifted (on a log scale) toward larger values of \( \lambda \). Because of the refractive dispersion of latex, this shifting factor varies within the spectral range of the measurements, going from \(~1.6\) for \( \lambda = 0.3 \mu m \) to \(~2.1\) for \( \lambda = 1.0 \mu m \). Thus we expect that, on passing from the latex–water to the aerosol–air system, the smallest and largest recoverable radii will be reduced by factors of \(~1.6\) and \(~2.1\), respectively. This implies that the range found for the latex–water system (approximately 0.084–5.0 μm) would become approximately 0.05–2.5 μm for the aerosol–air system. As a final comment, it should be pointed out that this is only an indicative estimate of the range of recoverable radii. The actual range depends on many factors, such as \( \lambda \) sampling, distribution shape, the noise present in the experimental data, and the algorithm adopted. It is beyond the scope of this research to discuss the performance of the algorithm with respect to this issue, so we limited our investigations only to calibrated (almost monodisperse) latex spheres. We have evidence from computer simulation that, as soon as broader distributions are considered, the lower limit of 0.05 μm can be further extended, but, at the same time, the upper limit has to be reduced. We give an example of this relationship in Subsection 4.C., where the highly polydisperse distribution of a standard atmospheric model will be considered.

C. Simulation of Atmospheric Distributions

The inversion algorithm adopted here was previously used and tested on relatively narrow and bell-shaped distributions. As is known, these are different from the distributions encountered in the atmosphere; the latter are highly polydisperse, with particle sizes ranging over several decades, from tens of nanometers to tens of micrometers. We report below an example of the way in which the algorithm
described here performs with a typical atmospheric distribution.

One of the accepted models that can be used to characterize such distributions is the semiempirical model LOWTRAN, which is a variation of the well-known Junge distribution. This model predicts an airborne particle distribution with particle radii in the range 0.02–10 μm. The number distribution is flat in the range 0.02–0.1 μm and decays as a power law characterized by an exponent of −4 in the rest of the range. According to this model the shape of the distribution remains fixed, with the overall number of particles depending on the local atmospheric conditions such as visibility and elevation over sea level. Once it is biased with this information, the model provides the expected transmission spectrum as a function of wavelength. From this spectrum it can be seen that the extinction derives from two main contributions, namely, the absorption of gases dispersed in air (mainly O₂ and H₂O) and the extinction that is due to scattering from the airborne particulate. An example of this spectrum is illustrated in Fig. 10 below and is discussed in Section 5. Because gas absorption is confined within fairly narrow bands, these two contributions can be separated, and it is easy to select the spectral regions where the extinction is due only to the airborne particulate.

The simulation was carried out as follows: We selected 41 wavelengths within the operating spectral range of the instrument, i.e., 0.3–0.9 μm. The values of the wavelengths were identical to those used in the real measurements and, as mentioned above, were chosen so they would not coincide with the absorption bands of the gases dispersed in air. The particulate in air was assumed to be described by a LOWTRAN distribution with a concentration of 2828 particles/cm³, which corresponds to the case of a clean rural atmosphere with a level visibility of 23 km. The particles' refractive index was assumed to be constant, with the real and imaginary parts given by 1.53 and 0.08, respectively. By using Mie theory, we calculated the extinction coefficient of such a sample, and the result is shown in Fig. 7 as a function of wavelength. The symbols refer to the simulated data, whereas the solid curve represents the result of the inversion procedure, i.e., the data reconstructed on the basis of the recovered distribution. As for latex particles, the match between the simulated and the reconstructed data is excellent, with an overall rms deviation of the order of 0.1%. Finally, within the whole range 0.02–1 μm, both the number and the volume fraction concentrations are recovered fairly satisfactorily; the recovered concentrations are higher than the expected by the order of 10% over the entire spectral range. Thus, by neglecting this contribution, we expect only minor errors in the recovered distribution. Indeed, the figure shows that the match of the two curves within the range 0.1–1 μm is excellent for almost the entire four decades of variation of the distribution. Also, the crossover to a flat distribution for r < 0.1 μm is well detected. For particles smaller than 0.1 μm, the reconstruction is somewhat poorer, but this part of the curve makes contributions to the overall extinction coefficient that are fairly negligible (a few percent rms).
pected ones by factors of ~22% and ~14%, respectively.

One of the main assumptions made in the above simulation was to suppose that all the particles had the same refractive index and that this was known. In reality, the refractive index of an airborne particulate can vary significantly from case to case, and it might be known only with some uncertainty. Numerical simulations\textsuperscript{12} carried out for relatively narrow distributions with radii similar to the wavelengths of the measurement have shown that the recovered distributions may be remarkably different from the expected ones, even if the error in the real part of the refractive index is of the order of only 0.1. Errors in the imaginary part are shown to be less relevant. However, for broad distributions (such as those typically encountered in the atmosphere) the dependence of the extinction coefficient on the particles’ refractive index is rather small, and the distributions can be recovered with satisfactory accuracy even if the particles’ refractive index is known with some uncertainty. As it is beyond the purpose of this paper to discuss this issue, we refer the reader to the research already reported in the literature, for example, in Refs. 4, 8, 12, and 23.

As a comment, it should be pointed out that the LOWTRAN distribution investigated here, although it is considered to be a good representation of a typical clean rural atmosphere\textsuperscript{22} is clearly only an example of the distributions that one may encounter in the atmosphere. Its main limitations are that, when it is reported as a volume distribution, it exhibits only one mode (see Fig. 12 below) and that all the particles are characterized by the same refractive index. Under some circumstances, ambient distributions can exhibit a multimodal character, such as the well-known Whitby distribution\textsuperscript{24} in which three different modes are simultaneously present. In that case, particles that belong to each mode are derived by different production mechanisms and have different optical properties as well.

Finally, we emphasize that one of the advantages in using the LOWTRAN model is the fact that this model provides the entire extinction spectrum expected in the atmosphere, in which the two contributions that derive from molecular absorption and extinction from particulates are both considered. Thus it is a useful tool for understanding raw experimental data and comparing them with expected results, as we describe in Section 5.

5. Experimental Results

We checked on the proper functioning of the instrument in real situations by measuring two aerosol distributions, one that is due to the presence of airborne particulate uniformly dispersed in air over a long optical path and the other one derived from a localized release of particles, such as a cigarette-smoke aerosol, in the air.

A. Characterization of Atmospheric Particle Pollution

Atmospheric particle pollution was measured in a polluted environment, namely, a 50-m-long underground corridor used for connecting stocking premises. A picture of the environment and of the instrumental layout appears in Fig. 9. The reference and sample retroreflectors were placed 13 and 47 m, respectively, from the measuring unit. Thus the corresponding folded optical path was 68 m. The measured transmission spectrum that corresponds to this region is shown in Fig. 10 (dotted curve) and compared with both the spectrum predicted by the LOWTRAN model (solid curve) and the measurements taken in the clean room (dashed curve). The LOWTRAN model was applied for a clean rural atmosphere characterized by a ground-level visibility of 23 km (see Subsection 4.C). For all three spectra, the molecular scattering contribution was subtracted. This correction was very small over the whole spectral range, less than 0.1% for $\lambda > 0.5$ $\mu$m and increasing slightly at lower wavelengths up to 1% for $\lambda \sim 0.3$ $\mu$m. The figure shows a remarkable match of the peak structures of all three curves. All the bands that are due to the presence of $O_2$ and $H_2O$ in the atmosphere are clearly detected, even when their amplitudes are as small as ~0.5% or less, in agreement with the instrumental sensitivity estimated in the tests described in Section 4. The high accuracy in recovering the peak positions shows that the instrument is spectrally calibrated and, as described in
Subsection 4.C, allows the spectral regions to be used for the data inversion to be selected reliably. Figure 10 shows a substantial difference among the three curves. The clean room spectrum exhibits a low attenuation, which, within experimental error, appears to be reasonably level. The spectrum for the model shows a somewhat higher attenuation, mainly at lower wavelengths. This is reasonable because the air in the clean room is expected to be cleaner than that predicted by the model, with a nominal total number of particles (in the 0.5–5-μm range) smaller by approximately a factor of 10. At variance with the first two measurements, the one taken in the underground corridor shows much higher attenuation and a substantial change in the shape of the spectrum. This is much more evident from Fig. 11, where the behaviors of the extinction coefficients sampled at 41 selected wavelengths within the 0.3–0.9-μm range are shown for both the LOWTRAN model (circles) and the underground corridor measurement (squares). The average extinction detected in the underground corridor is much higher than that of the model, and, whereas the $\alpha(\lambda)$ of the model grows monotonically toward smaller wavelengths, the experimental extinction coefficient exhibits a maximum for $\lambda \approx 0.35 \mu m$. The presence of this peak is indicative of a distribution that is widely different from that predicted by the model. This is confirmed in Fig. 12, where the recovered volume fraction distributions obtained from the inversion of the data of Fig. 11 are shown on a log-linear scale. For comparison, the theoretical distribution predicted by the model (solid curve) is shown as well. The inversions were made by use of the same parameters (refractive index and radius range) as those described in Subsection 4.C. The distribution for the experimental data (dotted curve) is by far much higher than the one for the model (dashed curve) and exhibits a pronounced peak for a radius of $\sim 0.25 \mu m$. Although a comparison with other experiments is obviously not straightforward, these findings seem to be consistent with some of the results presented in the literature, with fairly good agreement of both distribution shape and average radius. The overall volume fraction concentration of air in the corridor was a factor of $\sim 2$ higher than the one predicted by the model. If we assume that the density of the particulate is $2 \text{ g/cm}^3$, this value corresponds to a concentration of $\sim 200 \mu \text{g/m}^3$, which is a plausible value for a polluted environment such as an underground corridor.
B. Characterization of Cigarette-Smoke Aerosols

As a final test of the instrument we performed several measurements of cigarette-smoke aerosols, which are known to be characterized by submicrometer particles. In these measurements the two retroreflectors were placed 10 and 20 m from the measuring unit, and the smoke was released between them by a person who slowly exhaled it from his mouth. Two different modalities were followed. In the first case, the smoke was aspirated into the oral cavity and kept there for only a few seconds before exhalation. In the second case, it was kept longer, for \( \sim 10 \) s. Although the output of this experiment obviously depends on the conditions under which the measurement is carried out, the main features of the results appear to be rather reproducible and independent of the particular kind of smoke or specimen, as we verified during several trials. Figure 13 shows typical extinction coefficients measured following the two modalities described above. It appears immediately clear that the two curves are different, with different shapes and maxima located at different wavelengths. Whereas the data relative to the smoke kept briefly in the oral cavity peaks at \( \sim 0.35 \) \( \mu \)m [Fig. 13(a)], when the smoke is kept longer the peak is much broader and centered at larger \( \lambda \), \( \sim 0.60 \) \( \mu \)m. Note than the extinction coefficient of Fig. 13 is shown in arbitrary units on two distinct graphs.

This was done because, under the conditions of the experiment, it was not possible to control and estimate the length of the volume over which the smoke was dispersed, and therefore the determination of \( \alpha(\lambda) \) on an absolute scale was not possible. The continuous curves in Fig. 13 are the results of the inversion procedure, i.e., the data reconstructed on the basis of the recovered distributions. In this case we carried out the inversion by assuming that the smoke aerosol is characterized by a wavelength-dependent refractive index that varies according to the well-known Cauchy relation with coefficients \( A = 1.491534, B = 0.007850, \) and \( C = 0.001455 \) and with the imaginary part equal to zero. We tuned the values of coefficients A–C by minimizing the rms deviations between the experimental and the reconstructed data, and they gave rise to a refractive index that was reasonably consistent with the values found in the literature. The results of the inversion procedure are shown in Fig. 14. The distribution of the smoke that was kept for a few seconds in the oral cavity appears to be fairly narrow, with an average radius of \( \sim 0.20 \) \( \mu \)m and a standard deviation of \( \sim 0.03 \) \( \mu \)m. Conversely, for the other case the distribution is much broader, with an average radius of \( \sim 0.43 \) \( \mu \)m and a standard deviation of \( \sim 0.16 \) \( \mu \)m. Although it is beyond the purpose of this study to
interpret and compare these data with the vast amount of experiments on cigarette smoke reported in the literature, we can comment that our results are consistent with simple physical observations in which dense aerosols kept for a long time in an environment with high humidity (the oral cavity) grow larger with time. Finally, under the experimental conditions described above, the particle dimensions and the distribution shape estimated with our technique seem to be quantitatively in agreement with the typical findings that have been published.

6. Conclusions
We have described a new instrument that is capable of carrying out spectral extinction measurements for environmental applications over optical paths between 1 and 100 m. The instrument permits accurate detection of the extinction spectrum in almost real time (approximately 5–10 s), within a spectral range of 0.3–0.9 μm, with a resolution of ~3 nm.

Measurements carried out in a clean room showed that, for optical paths between 50 and 100 m, the instrument sensitivity is \( \sim 10^{-5} \text{ m}^{-1} \). This value is much smaller than typical extinction coefficients encountered in (clean) atmospheres and is amply sufficient for detection of the minimum aerosol concentrations imposed by the current EEC regulations for atmospheric pollution \((150 \text{ μg/m}^3)\). Over shorter optical paths the instrument’s sensitivity is reduced \((\sim 10^{-4} \text{ m}^{-1} \text{ at } \sim 10 \text{ m})\) but nevertheless is still high enough to detect easily the minimum concentrations allowed by the current EEC regulations for the emission rates of particles from chimneys of industrial plants \((10 \text{ mg/m}^3)\).

When it is used in conjunction with an appropriate inversion algorithm, the instrument can be profitably used for characterizing various airborne particulate distributions. We gave examples by reporting the measurements carried out in a polluted indoor environment (underground corridor) and taken from cigarette smoke, together with the corresponding particle size distributions. The findings of these investigations were consistent with previous ones reported in the literature.

In conclusion, if the performance of the instrument is compared with those of other instrumentation previously used for spectral extinction measurements, it appears that the instrument’s main features are related to the fact that the extinction spectrum can be determined over long optical paths with high accuracy and resolution. Also, the instrument exhibits a rather high degree of flexibility because the measurements can be carried out over short \((\sim 10\text{-m})\) and long \((\sim 100\text{-m})\) optical paths. This permits the use of the instrument for monitoring both atmospheric aerosols and other airborne particles, for example, particulates released from the chimneys of industrial plants. With respect to the latter point, as far as we know, no other instrument is currently available for multi-wavelength extinction measurements over such long optical paths. The characterization of this particulate is typically made by use of opacimeters, which operate at a single wavelength.

As a final comment, note that, besides its main application to the particle sizing of airborne particulates, the instrument also provides an easy way to detect and measure the absorption bands of the gases, mainly \( \text{O}_2 \) and \( \text{H}_2\text{O} \), that are present in atmosphere. This permits a simple determination of the concentration of such substances, which could be of interest in environmental monitoring.

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