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A FOUR-CHANNEL PORTABLE SOLAR RADIOMETER FOR MEASURING PARTICULATE AND/OR AEROSOL OPACITY AND CONCENTRATION OF NO_2 AND SO_2 IN STACK PLUMES

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16. Abstract

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SUMMARY

Solar absorption radiometry has been investigated as a method of measuring stack-plume effluents. A simple and inexpensive instrument was constructed for observing the Sun at four wavelengths: 800, 600, 400, and 310 nm. Higher wavelength channels measured the effect of the particulates and NO_2 and an ultraviolet channel measured the contribution of SO_2 to the attenuation. Stack-plume measurements of opacity and concentration of NO_2 and SO_2 were in basic agreement with in-stack measurements. The major limitation on the use of the radiometer is the requirement for an accessible viewing position which allows the Sun-plume-observer relationship to be attained. It was concluded that the solar radiometer offers an inexpensive method for monitoring plume effluents when the viewing position is not restricted.

INTRODUCTION

The regulation of pollution by controlling the emissions at their source is a primary task of the Environmental Protection Agency (EPA). Pursuant to the Clean Air Act, standards of performance for new stationary sources, such as coal- and oil-fired power plants, have been set forth in reference 1. These standards include emission limits for one or more of four pollutants (particulate matter, sulfur dioxide, nitrogen oxides, and sulfuric acid mist) for each source category. The Ringelmann standards have been deleted as a visible emission control standard and all future limits will be based on opacity. Many states, however, still use opacity-equivalent Ringelmann values in order to comply with state laws established over the years. For the gases and aerosols, specific in-stack sampling techniques and analyses are described in detail.

The standards referred to in the preceding paragraph relate only to in-stack methods of sampling. These methods are difficult and time-consuming and usually require that special access ports be installed in the facility. For these reasons, and for enforcement monitoring, it would be desirable to develop alternative remote test methods of measuring these pollutants at the stack lip. Among the sophisticated remote techniques presently being developed are laser backscatter (ref. 2), infrared (IR), spectral emission (ref. 3), and correlation spectroscopy (ref. 4).

The purpose of this paper is to describe a simple inexpensive instrument for determining opacity and concentration of NO_2 $\left([NO_2]\right)$ and SO_2 $\left([SO_2]\right)$ in stack plumes. The technique uses the Sun as a background source and determines the attenuation of sunlight at four selected wavelengths (800, 600, 400, and 310 nm). An IR channel is employed which measures the effect of particulates and/or aerosols. Two visible channels trace the opacity variation with wavelength and superimpose the effects of NO_2 absorption. A fourth channel, in the ultraviolet range, provides a measure of the sulfur dioxide concentration. In practice, the radiometer is alined as shown in figure 1 to look directly at the Sun in order to establish the instrument incident solar intensity I_o. The radiometer is then moved a few meters to a location where the Sun is fully occulted by the plume, and another reading is taken. The latter reading gives the transmitted solar intensity I, hence the transmittance $\tau = I/I_o$. Measurements are made in this manner for each of the four channels by alternating the various filter inserts. A similar single-channel instrument for measuring opacity has been developed which has a spectral response approximating eye sensitivity (ref. 5).

SYMBOLS

A	projected area per particle, cm^2
I	transmitted solar intensity, arbitrary units
I_o	incident solar intensity, arbitrary units
k	Boltzmann constant, 1.38×10^{-23} J/K
L	path length, cm
N	total number density of molecules, cm^{-3}
N_p	number density of particulates, cm^{-3}
n	number density of absorbers, cm^{-3}
P	total pressure, atm
p	partial pressure, atm

p_o	partial pressure at T_o, atm
Q	extinction coefficient
T	temperature of plume, K
T_o	temperature of calibration cells, K
Z	concentration of absorbers, ppm
α	absorption coefficient, $(\text{cm-atm})^{-1}$
λ	wavelength, nm
σ	attenuation coefficient, cm^{-1}
τ	transmittance, I/I_o

FACTORS AFFECTING PLUME ATTENUATION

Factors which affect the plume attenuation as it occurs in coal-fired power plants are considered in this section. The factors discussed generally apply to other facilities such as oil-fired power plants and sulfuric acid plants if particulate emissions are neglected.

For the path lengths encountered and concentrations expected, there are only a few pollutants which will appreciably affect the attenuation in the near-UV—visible-near-IR region. These pollutants are discussed in the following sections.

Particulates and Aerosols

In coal-fired plants, the particulates are the most visible of all emissions. The particulate and/or aerosol opacity $(1 - \tau)$ depends on the size, number, shape, and refractive index of the particles as well as on the wavelength of the incident light. The transmitted light for monodisperse spherical particles is given by

$$\tau = e^{-\sigma L} = e^{-N_p AQL} \tag{1}$$

where σ is the attenuation coefficient, L is the path length, N_p is the particle concentration, A is the projected area per particle, and Q is the extinction coefficient (ref. 6). For particle sizes much smaller than the illuminating wavelength (Rayleigh region), the extinction coefficient varies as λ^{-4} for transparent particles, and λ^{-1} for absorbing particles. The value of the extinction coefficient is very low, however, and therefore particles in this size range contribute little to the overall opacity. Particles having sizes comparable to the illuminating wavelength (Mie region) exhibit complex oscillatory behavior in the extinction coefficient. This oscillatory behavior is smoothed considerably for polydisperse emissions of varying composition. For particle sizes larger than the illuminating wavelength (geometric region), a limiting extinction coefficient (≈ 2) is attained which exhibits little oscillatory behavior. The coal-fired plant investigated in this report exhibits a mean particle size of approximately 4 μm (EPA impactor and microscopy measurements) and thus falls into this latter category.

Nitrogen Dioxide

The nitrogen dioxide component of the NO_x emitted exhibits absorption over a wide spectral range in the visible (ref. 7) as shown in figure 2. The absorption peaks at about 400 nm and has a half-power breadth of approximately 150 nm. A dimer (N_2O_4) exists which exhibits absorption below 400 nm (a peak at 350 nm) but is expected to be only a small percentage of the NO_2 at the temperatures encountered in typical stack-plume conditions.

Sulfur Dioxide

The pollutant sulfur dioxide is one of prime concern, particularly in coal-fired plants, where the burning of high-sulfur-content coal has come under careful scrutiny. A strong band system of SO_2 exists just at the stratospheric ozone cut-off shown in figure 2. Another weaker band system exists, centered at about 370 nm, which will not result in any measurable attenuation for the path lengths encountered (ref. 8). The shaded area in figure 2 denotes the region which is inaccessible to solar radiometry due to the effects of ozone absorption in the stratosphere.

The attenuation factors described are well-known, spectrally broad features which can be resolved adequately by filters. By measuring the plume attenuation at selected wavelengths and by working the analysis from longer to shorter wavelengths, one should be able to unfold the opacity, $[NO_2]$, and $[SO_2]$.

INSTRUMENT DESIGN

The Sun subtends about 0.5° at the surface of the Earth. Experience has shown that the angle subtended by smoke stack plumes at the observer can usually be made larger than 0.5°. The entire Sun can, therefore, be used as a background source and the need for imaging optics in the radiometer can be eliminated. The radiometric optics consist only of apertures designed to encompass the entire Sun.

Another simplification is possible in choosing a detector since the Sun is such a bright source and since only low-resolution (wide-band-pass) measurements are required. A UV extended PIN photodiode was chosen which has sufficient detectivity over the entire range of wavelengths employed. This detector is small, inexpensive, and requires little power to operate. The detector was operated in a photovoltaic mode, and the output was amplified and displayed on a dc ammeter. The radiometer is shown in figures 3 and 4. The side-mounted scale is used to determine the elevation angle and thus provides a measure of the slant-path length through the plume. Two optical arrangements can be seen, one for coarse pointing of the radiometer and a parallel one for radiometric measurements.

Pointing (Alinement) Optics

The pointing (alinement) optical system consists of a lens for imaging the Sun and stack on a reticle having a circular alinement grid. The innermost circle defines the position that the image of the Sun should occupy while measurements are being taken. A small neutral density filter is located in this central circle in order to attenuate the intensity of the Sun and thereby allow easy viewing of the remainder of the scene.

Radiometric Optics

The radiometric optical path is boresighted to the pointing optics. No imaging optics are used in this path since the field of view will encompass the entire Sun and since the Sun-plume angular fields define a light path through the central section of the plume. Several apertures are employed which define a field of view of about 6°. The radiometer is therefore easy to aline and relatively insensitive to pointing errors. This field of view necessarily includes some scattered skylight but this is an insignificant amount relative to the direct sunlight for the wavelengths used (ref. 9).

The four channels are selected by the threaded inserts shown in figure 3. Each insert consists of machined apertures, an interference filter, and necessary color filters. Neutral density filters are used, as required, to render an appropriate intensity on the detector. The channels are selected by interference filters having the following characteristics:

Characteristic	Channel			
	UV	Visible	Visible	IR
Peak wavelength, nm	309.0	400.7	601.8	799.6
Full-width half-maximum, nm	9.8	9.4	10.0	10.4
Peak transmission	30	40	52	52
Rejection ratio	1.0×10^4	0.5×10^4	1.6×10^4	5.0×10^4

The rejection ratio is the ratio of the peak transmission to that outside the passband (i.e., far wings).

CALIBRATION

Calibration of the radiometer for particulate opacity requires that the transmittance τ be measured accurately at an appropriate wavelength in the visible, preferably at the peak sensitivity of the eye (green light). However, this is also a region in which NO_2 could influence the measurement of opacity. Therefore, the IR channel is used to determine the opacity with an estimated accuracy under user conditions of about ±20 percent at 5 percent opacity. A relationship between the opacity and the mass concentration is often desired, but this relationship can be expected to vary considerably from source to source due to particle size distributions and particle characteristics. For sources with stable characteristics, an opacity—mass-concentration relationship is usually determined by empirical calibration of an in-stack transmissometer (ref. 6). The use of the solar radiometer to obtain mass concentration would also require a similar empirical calibration.

Calibration for gases such as NO_2 and SO_2 requires that the concentration be determined by using the equation

$$\tau = e^{-\alpha p_o L} \tag{2}$$

where α is the spectral absorption coefficient, p_o is the partial pressure of the absorbers at temperature T_o, and L is the path length through the sample. For stack exit conditions at temperature T,

$$p = nkT \tag{3a}$$

and

$$P = NkT \approx 1 \text{ atm} \tag{3b}$$

where n is the number density of absorbers, N is the total number density of molecules, and P is the total pressure. The concentration of absorbers in parts per million Z is given by

$$\frac{Z}{10^6} = \frac{n}{N} = \frac{p}{P} \tag{4}$$

Hence the transmittance becomes

$$\tau = e^{-\alpha \frac{ZP}{10^6} \frac{T_o}{T} L} \tag{5}$$

With the Sun as a source, calibration was performed in quartz cells which had been evacuated and then filled to selected pressures of the absorbing gas. Nitrogen was added to atmospheric pressure. The measured transmittance values were then plotted as a function of ZL/T. The results of such a calibration for SO_2, obtained by using three calibrated cells, are shown in figure 5. The dashed curve represents the increased attenuation expected, based on the absorption coefficient determined at the point where $\tau = 0.70$. The deviation of the measured attenuation from the dashed curve results from the following effects associated with spectral purity and resolution:

(1) Mean absorption coefficient: The filter passband employed encompasses several peaks of the SO_2 band system; this results in a mean value of the absorption coefficient which does not obey Beer's law (ref. 10, p. 150).

(2) Spectral purity of the filter:

(a) Near wings – The near wings of the filter on the long-wavelength side encompass spectral regions where the absorption coefficient is very small but the incident light intensity is very high.

(b) Far wings – Although the far-wing blocking is good, the integration of an intense source over a large spectral interval can still produce a nonnegligible impurity. Secondary maxima in the filter $\left(10^{-3}\right.$ blocking at peak$\left.\right)$ exist at 370 nm and 650 nm which enhance this effect.

The effect of the spectral impurities mentioned is minimal at high values of transmittance, which renders the technique most accurate in this range.

The spectral purity problems do not appreciably affect the measurement of $[NO_2]$ since the absorption coefficient for NO_2 is more uniform and since the filter is located at a wavelength where the signal is strong.

STACK MEASUREMENTS

Tests have been conducted in conjunction with the EPA at a coal-fired power plant operated by the Carolina Power and Light Company in Asheville, N.C. The results are summarized in the following sections.

Opacity

Measurements were made on a clean plume at the Asheville plant (stack 2, November 9, 1972) which indicated an opacity of approximately 4 to 5 percent. This result corresponds to a 3 to 5 percent range in opacity measured earlier by a remote lidar system at the same site. The lidar system measures the opacity at 694.3 nm (ruby laser) by using the clear air backscatter from the near and far sides of the plume (ref. 2).

Nitrogen Dioxide

The attenuation measured for NO_2 by the visible channels differed very little from the IR channel (opacity). The results indicate an upper limit of about 10 ppm for NO_2 in this plume. This is consistent with in-stack sampling which indicates that most of the NO_x is emitted as NO $\left([NO_x] \approx 300 \text{ to } 500 \text{ ppm}; \; [NO_2] \approx 0.05[NO_x]\right)$. Additional instrumentation was employed to verify this trend with wavelength. This instrumentation was a small-grating spectrometer with 3 nm per millimeter of dispersion and 1 nm resolution, outfitted with a telescope, and having photomultiplier detection. The results showed that the attenuation increased very slowly with decreasing wavelength (less than 1 percent per 100 nm). This is consistent with a smoke emission having a mean particle size greater than 2 μm in which the transmittance in effect does not vary with wavelength (ref. 6, p. 12).

The NO exhibits absorption band heads at 226.9 and 226.3 nm (ref. 11), but this is far beyond the stratospheric ozone cut-off and is therefore not accessible by solar radiometer techniques. It should be mentioned, however, that a simple mercury pen lamp (ref. 12) exhibits an emission line at 226.2 nm which overlaps the NO band sufficiently to make attenuation measurements. An inexpensive, in-stack, interference-filter device could be built to monitor this important pollutant.

Sulfur Dioxide

The attenuation measured in the SO_2 channel is greater by about an order of magnitude than that measured in the other three channels. A stack-gas exit temperature of 408 K was employed which was determined from in-stack thermocouple measurements. The radiometer measurements from the UV channel indicated an SO_2 concentration of approximately 625 ppm (estimated accuracy of ± 50 ppm) compared with in-stack sampling measurement at that time of about 750 ppm. The fact that the radiometer averages over an appreciable section of the plume could explain the lower reading, but such an interpretation will not be stressed based on a single data point. Rather, it should be emphasized that fluctuations of concentration in the plume and instability of the plume dimensions can lead to large uncertainties in the path length which have a much greater effect on the radiometer accuracy.

The radiometer has also been applied to the measurement of SO_2 in an oil-fired power plant and at a sulfuric acid plant. In these facilities, the radiometer results and associated spectrometer scans indicate that the technique will also be applicable here. No comparisons could be made, however, since no in-stack instrumentation was available at either location.

The major disadvantage of the solar radiometer is the requirement that the Sun be viewable behind the plume. Physical restraints such as plant location and surrounding terrain often restrict the use of the radiometer to a few observing positions or to a limited viewing time. Consequently, only limited calibration and stack tests have been performed. Applications may arise where these physical restraints are minimal. For these cases, an imaging telescope may be desirable to sense only a segment of the Sun's disc and thereby increase the spatial resolution through the plume.

CONCLUDING REMARKS

The four-channel portable solar radiometer represents a simple and inexpensive method of obtaining opacity and concentration of NO_2 and SO_2 $\left([NO_2] \text{ and } [SO_2]\right)$ in power-plant stack plumes and other stationary sources. Plume attenuation is measured in the four channels (800, 600, 400, and 310 nm) by alternately observing the Sun directly and through the plume. Higher wavelength channels measure the effect of the particulates and $[NO_2]$, and an ultraviolet channel measures the $[SO_2]$. Calibration is performed by absorption cells loaded to selected gas concentrations.

The concentration of NO_2 was very small in the power plant investigated and the radiometer provides only an upper limit for NO_2 concentration. In essence then, the visible channels provide a means of extrapolating an opacity-corrected incident solar intensity I_o for SO_2 measurements by using the ultraviolet channel. For situations where $[NO_2]$ is large, an additional channel at approximately 340 nm may be desirable in order to provide another data point on the short-wavelength side of the NO_2 band. This additional channel would verify the presence of NO_2 and also provide an additional data point on the particulate opacity at lower wavelengths.

Field tests indicate that the radiometer can be applied to the measurement of $[SO_2]$ in coal- and oil-fired power plants and in sulfuric acid plant plumes. The major difficulties encountered are with plume instabilities and with physical limitations (terrain, etc.) imposed on the viewing location.

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May 4, 1976

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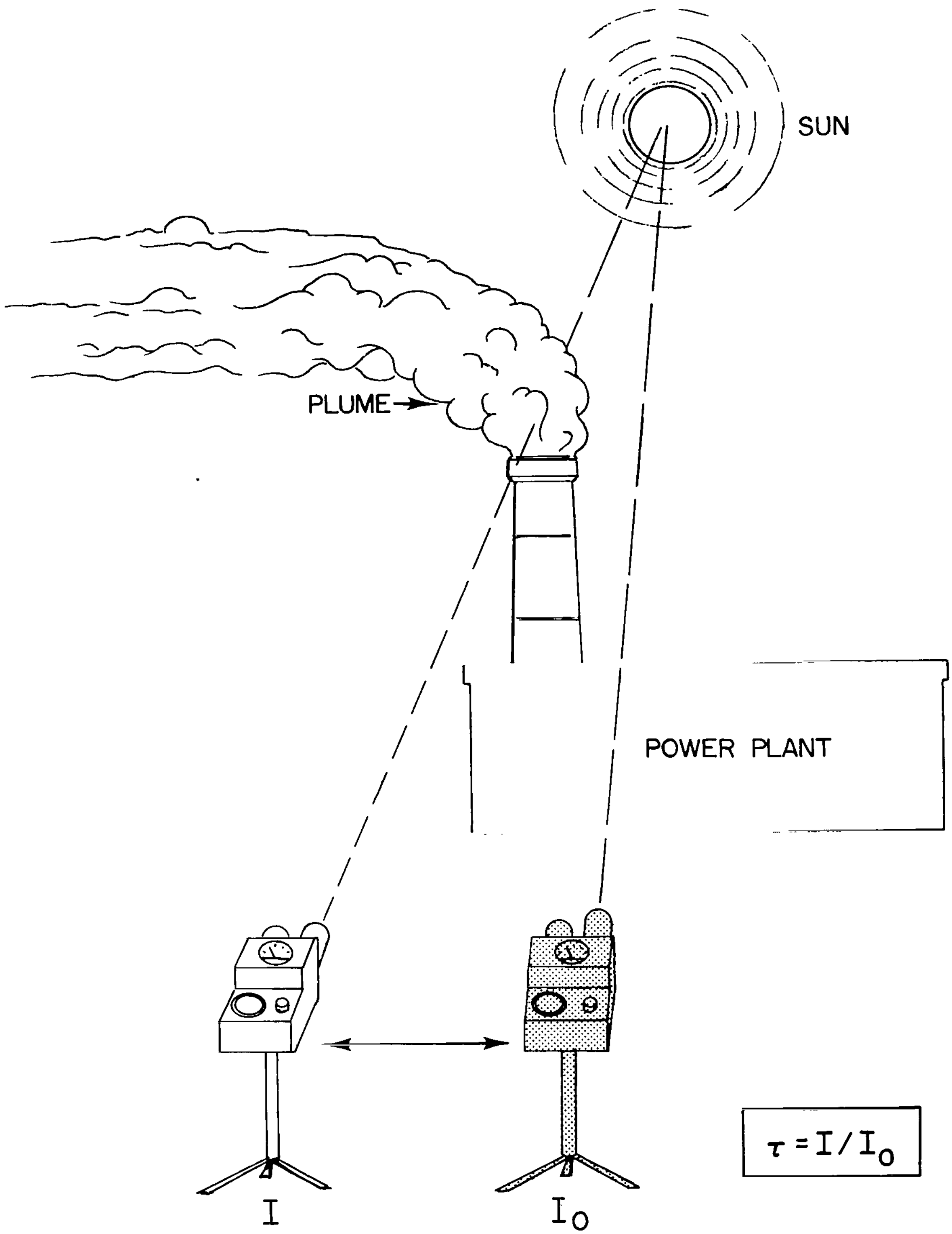

Figure 1.- Radiometer positions used in determining plume transmittance.

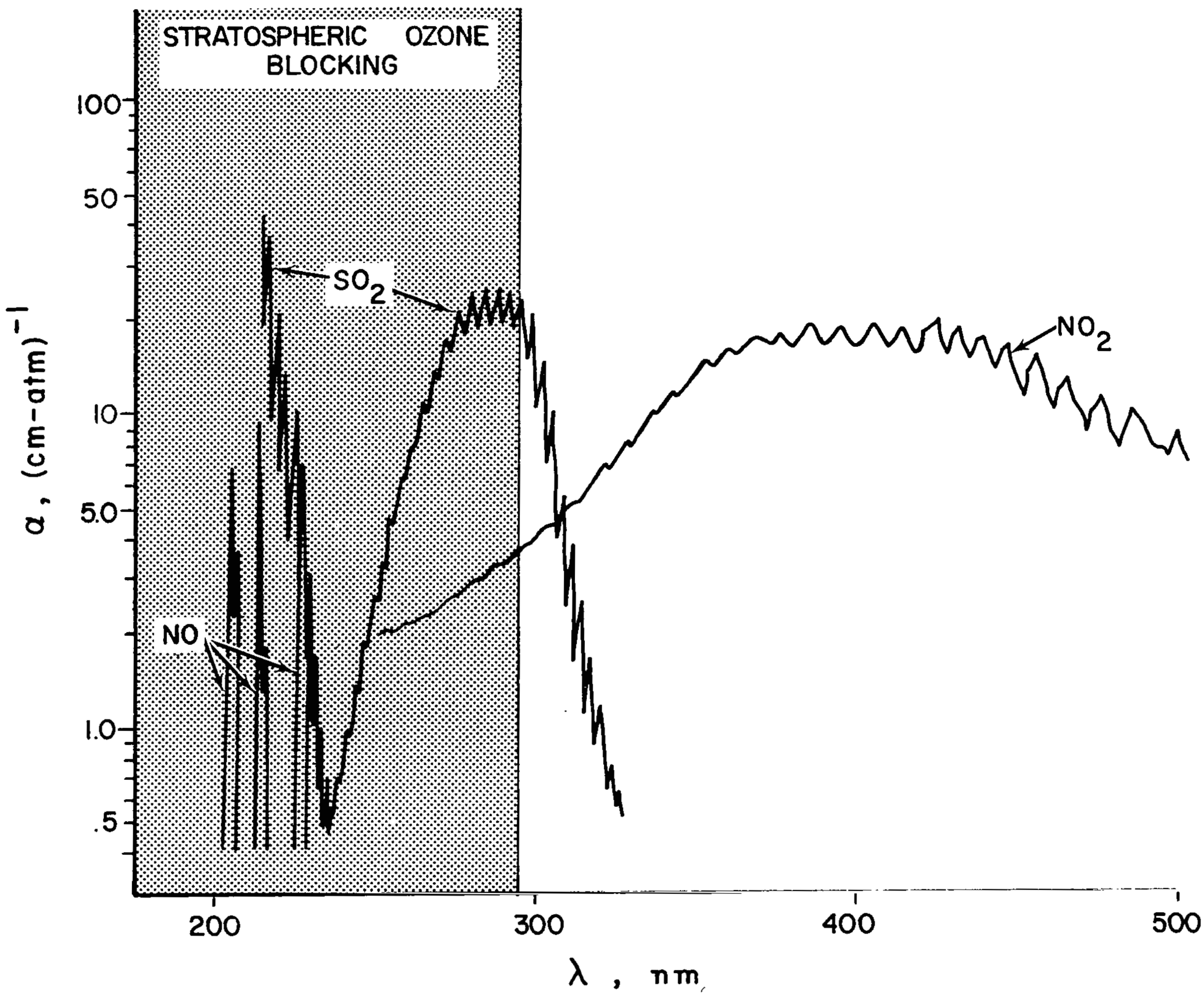

Figure 2.- Spectral absorption coefficients for the gaseous effluents NO, NO_2, and SO_2.

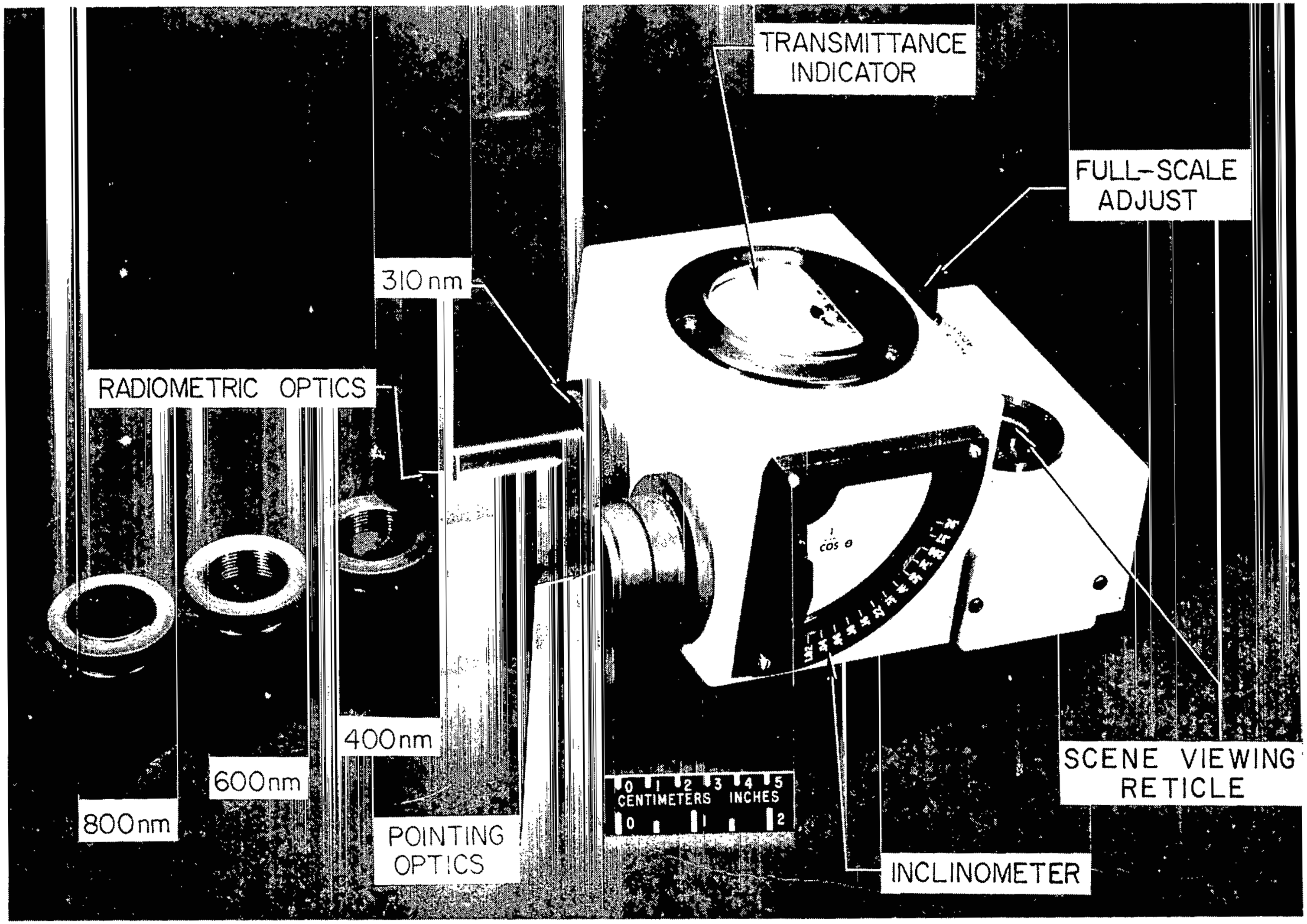

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Figure 3.- Solar radiometer and filter inserts (channels).

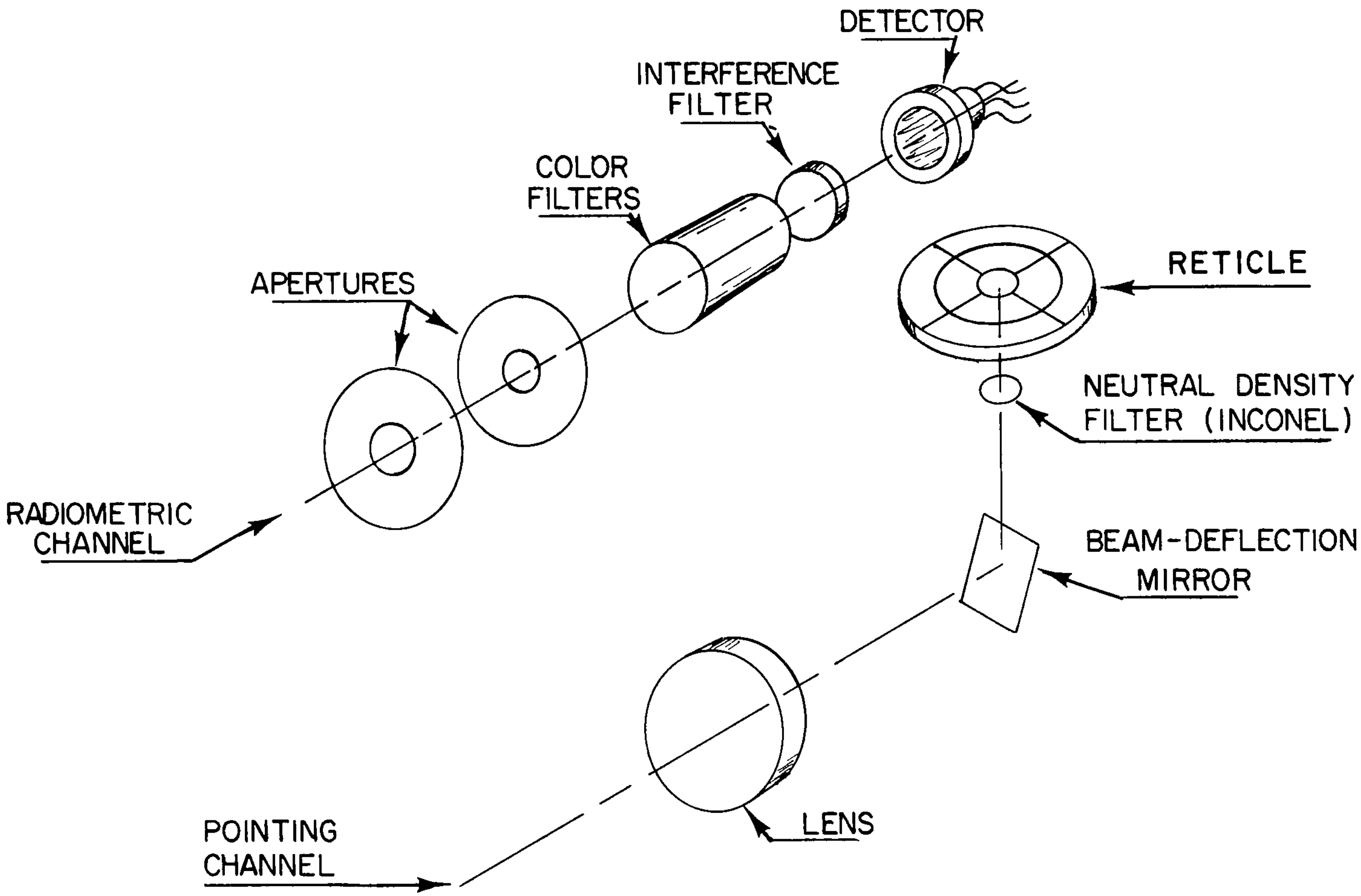

Figure 4.- Schematic of radiometer showing pointing and radiometric channel.

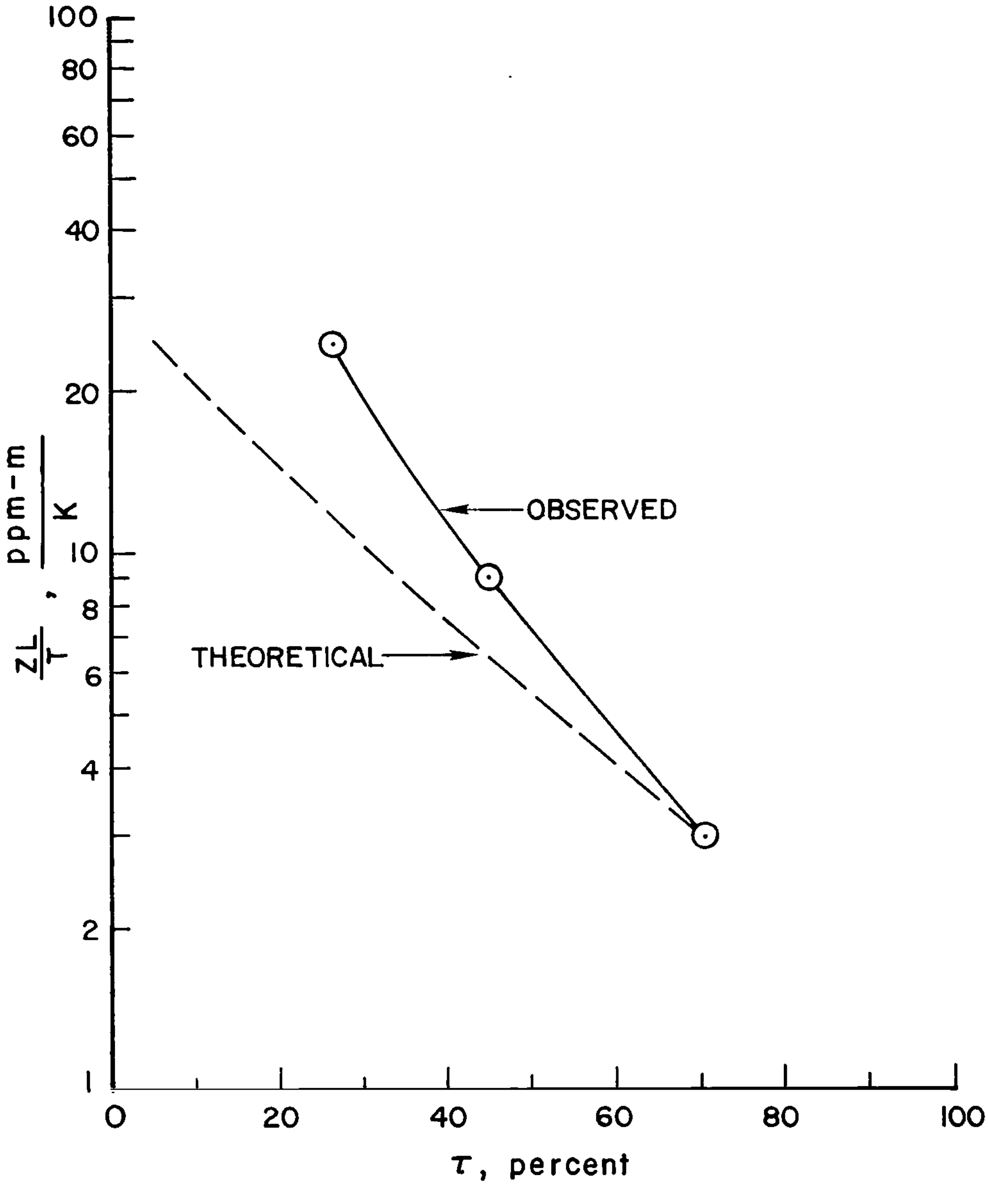

Figure 5.- Radiometer calibration for SO_2.

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