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"Introduction to the DOAS Methodology Applied to Atmospheric Minor Gas Measurements"

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Introduction to the DOAS methodology applied to atmospheric minor gas measurements

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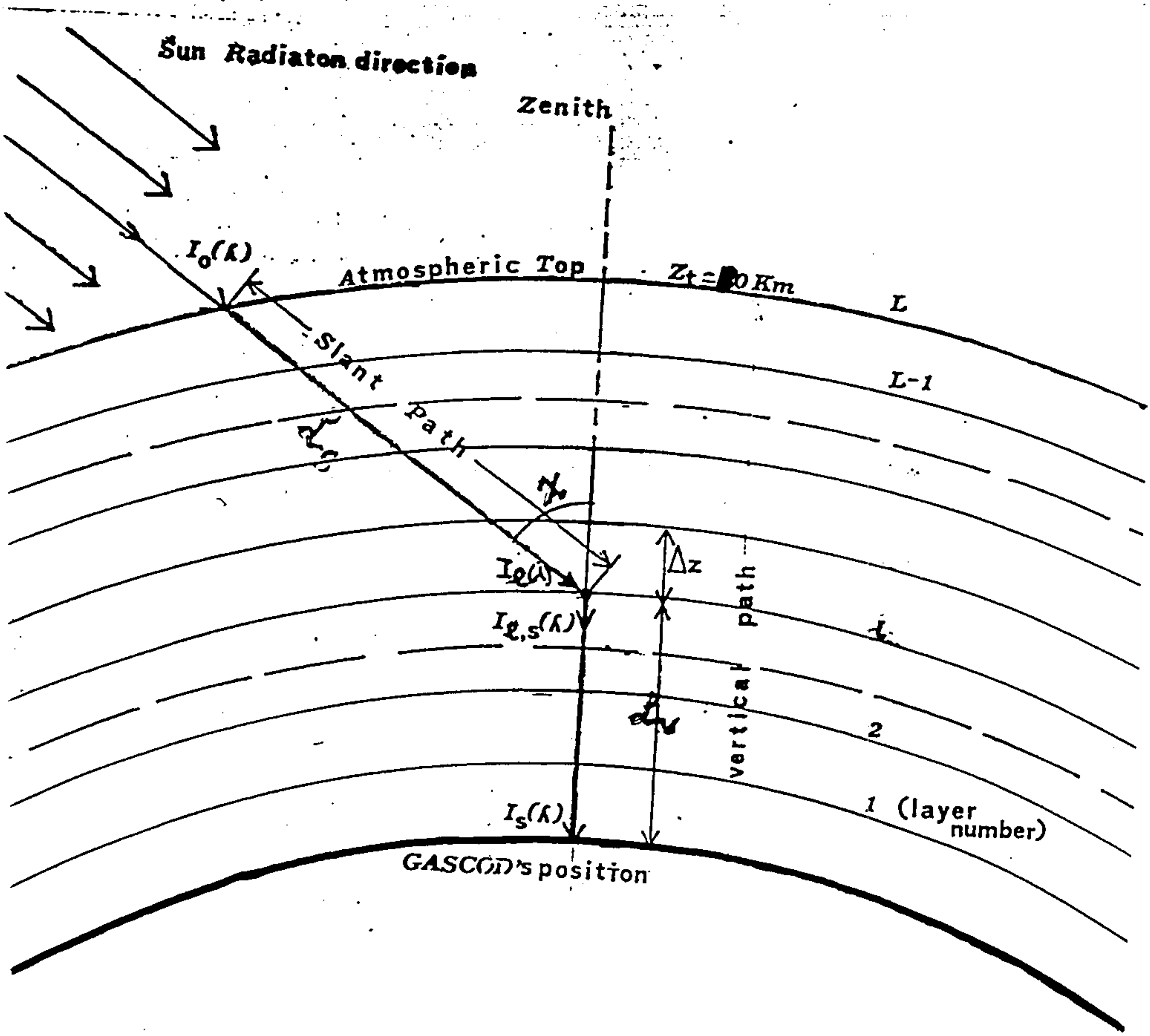
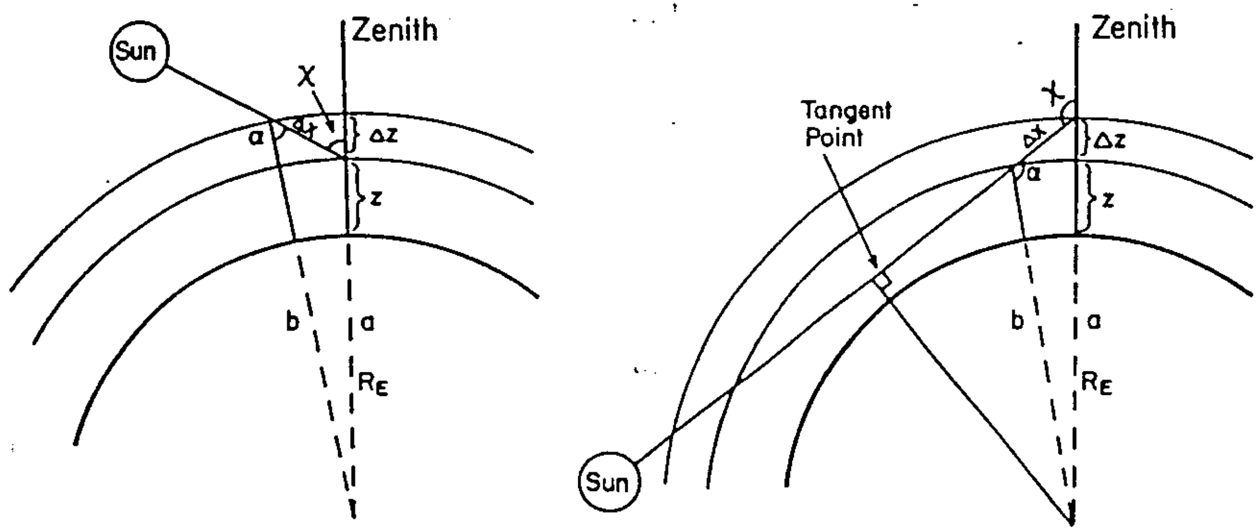
1 - The atmospheric transfer equation for zenith sky measurements,

2 - DOAS methodology,

3 - Air-Mass factor.


Sun Radiaton direction
Zenith
Io(λ)
Atmospheric Top
Zt
0 Km
L
L-1
Slant path
Iℓ(λ)
Iℓ,s(λ)
Δz
vertical path
2
1 (layer number)
Is(λ)
GASCOD's position



(a) $\chi \leq 90°$

$a = R_E + z, \; b = R_E + z + \Delta z$

(b) $\chi > 90°$

$a = R_E + z + \Delta z, \; b = R_E + z$

$$\alpha = \sin^{-1}\left[\frac{a}{b}\sin\chi\right]$$

$$\Delta x = \left[a^2 + b^2 - 2ab\cos(\chi - \alpha)\right]^{1/2}$$

Fig. 1. Schematic diagram of viewing geometry and path lengths.

- Determination of gas column contents by solar zenith radiation measurements

1- The Atmospheric Tranfer Equation for zenith sky measurements by UV-Vis Ground-Based Spectrometer

In ground-based measurement of zenith scattered solar radiation, the irradiation can be calculated by integrating the value of the radiation flux along the vertical path.

It is possible to define a transfer equation of solar radiation scattered along the vertical path .

The calculations can be simplified if the atmosphere is divided into equal layers. We consider an atmospheric model divided into 50 spheric layers, each Δz = 1 km thick and if, in the calculations, the summation is used instead of the integral.

The direct solar irradiation, which intersects the l-th layer at the height $z=l\ \Delta z$ will be:

$$I_l(\lambda) = I_o(\lambda)\ e^{-\sigma_o(\lambda)\ L_{s,l}(\chi) \sum_{i=l}^{L} N_o(i)}\ e^{-L\ \Delta z \sum_{g=1}^{n} \sigma_g(\lambda)\ \mu_g(l)\ \bar{N}_g}$$

Along the vertical path, the $I_{l,e}(\lambda)$ contribution of the radiation towards the earth produced by scattering in the l-th layer is given by:

$$I_{l,e}(\lambda)=I_l(\lambda)\sigma_o(\lambda)f(\chi)N_o(l)\Delta z_l \; e^{-\sigma_o(\lambda) l \Delta z \sum_{j=l}^{L} N_o(i)} \; e^{-\sum_{g=1}^{n} \sigma_g(\lambda) l \Delta z \bar{N}_g}$$

where, in addition to the known symbols,

$f(\chi)$ is the molecular scattering function, derived from the Rayleigh scattering formula, which defines the fraction of the scattered radiation flux in the ground direction, versus the diurnal variation of SZA χ.

Thus in zenith-sky ground measurements using a visible and close ultraviolet spectrophotometer the scattered irradiance can be calculated by summing the $(I_{l,e}(\chi))$'s along the vertical path

$$I_e(\lambda) = \sum_{l=1}^{L} I_{l,e}(\lambda)$$

This is the Atmospheric Transfer Equation for each of the zenith-sky measurements obtained with a ground-based spectrophotometer as the GASCOD.

$$I_l(\lambda) = I_o(\lambda)\, e^{-\sigma_o(\lambda)\, L_{a,l}(\chi) \sum_{i=l}^{L} N_o(i)}\; e^{-L\,\Delta z \sum_{g=1}^{n} \sigma_g(\lambda)\, \mu_g(l)\, \bar{N}_g}$$

where:

$I_o(\lambda)$ is the incident solar monochromatic radiation flux density at the top of the atmosphere (Z_T = 50 km);

$I_l(\lambda)$ is the solar irradiance which reaches the layer Δz at the altitude $z=l\Delta z$, obliquely crossing part of the atmosphere (direction χ);

$I_{l,a}(\lambda)$ is the solar irradiance reaching the ground, produced by scattering towards the ground in the Δz layer;

$I_a(\lambda)$ is the irradiance scattered along the vertical path, received on the ground;

$\sigma_o(\lambda)$ represents the cross section scattering of air molecules;

$\sigma_g(\lambda)$ with $g=1,2,..,n$ represents the mass absorption cross section (or simply the absorption coefficient) of the g-th gas, present in the l-th layer;

$N_o(i)$ for $i=1,1+l,..,L$ represents the average air molecule density in the l-th layer;

$\bar{N}_g$ with $g=1,2,..,n$ is the average air molecule density along the entire atmosphere of the g-th absorber;

μ_g with $g=1,..,n$ is the air-mass factor of the g-th species;

χ is the solar zenith angle;

L=50 is the total number of atmospheric layers;

$L_{a,l}(\chi)$ is the slant path which crosses the vertical pat in the l-th layer;

2- Intensity-weigted optical path

Another possibility of simplifying even further the calculations necessary to obtain the column contents of stratospheric gases is that of obtaining an intensity-weighted optical path for zenith solar radiation measurements.

The radiation, which has crossed the l-th layer and has been scattered downwards by the air molecules present in the same layer, contributes to the solar radiation diffused along the vertical path with the quantity $I_{l,*}(\chi)$ is made explicit in previous eqautions.
It is possible to define the probability that this radiation flux has reached the ground with the relationship:

$$p_l = \frac{I_{l,*}}{\sum_{l=1}^{50} I_{l,*}} = \frac{I_{l,*}}{I_*}$$

where the values $I_{l,*}$ and I_* correspond to those made explicit in previous equations, without the contribution of gas absorption and with the condition, implicit in the same definition of p, that:

$$\sum_{l=1}^{50} p_l = 1$$

It is also possible to obtain an average intensity-weighted optical path for zenith solar radiation measurements thus defined:

$$L(\chi,\lambda) = \sum_{l=1}^{50} L_l(\chi)\, p_l(\chi,\lambda)$$

This Average Intensity-Weighted Optical Path may be written as the sum of 2 terms:

$$\bar{\mathcal{L}}(\chi,\lambda) = \bar{\mathcal{L}}_S + \bar{\mathcal{L}}_T$$

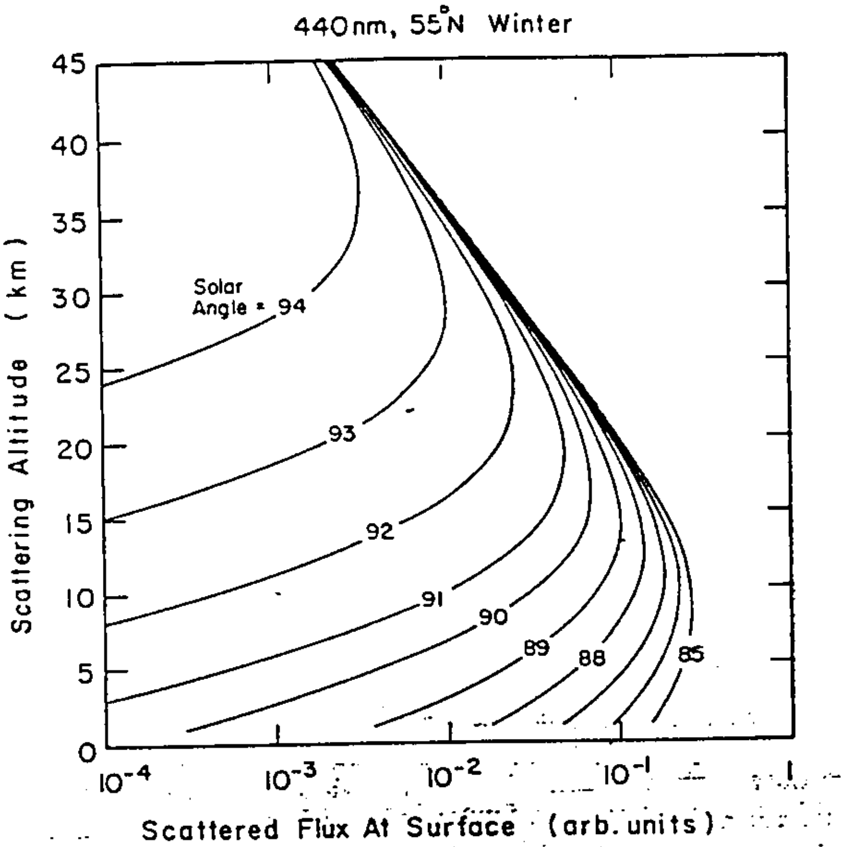
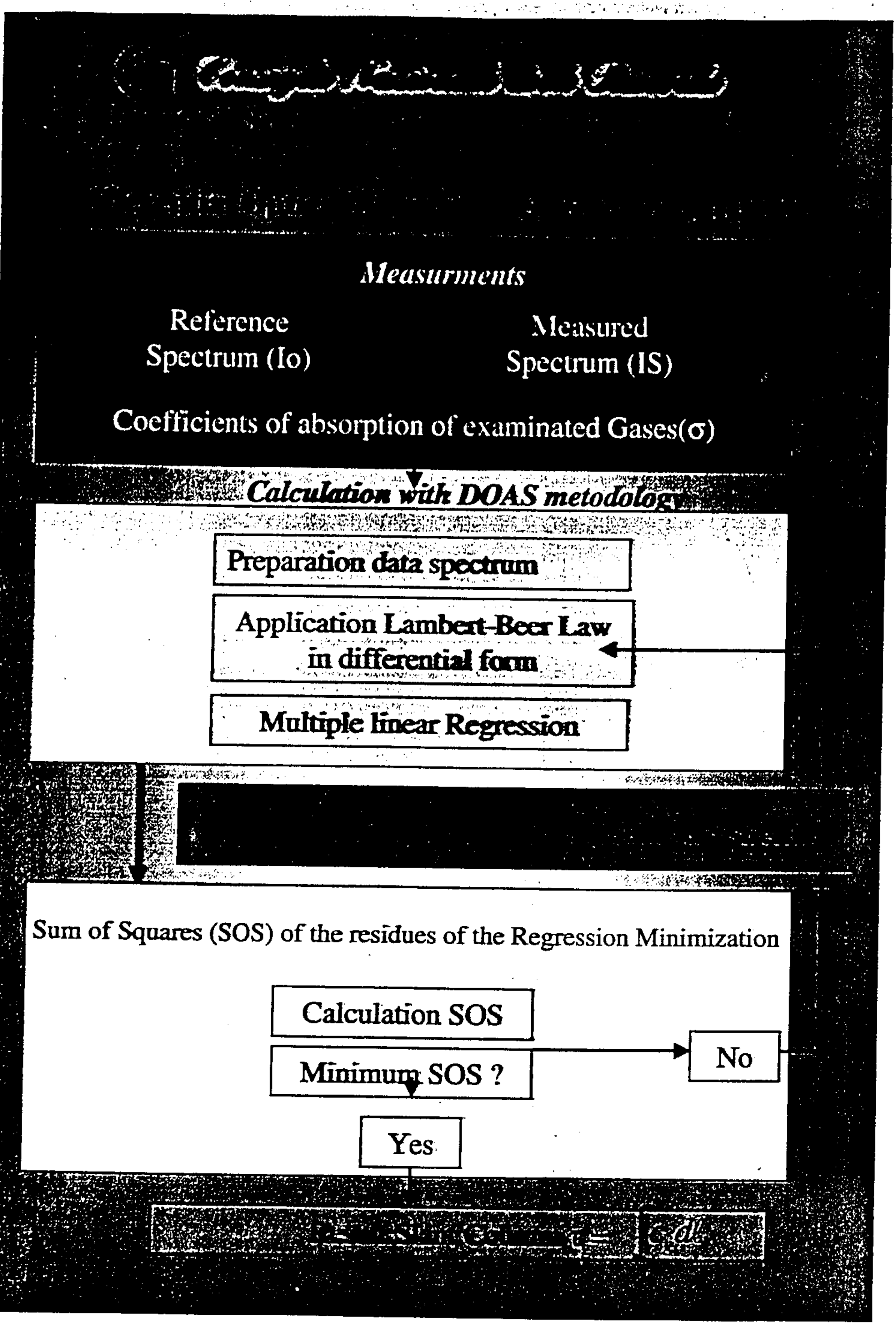


Fig. 3. Scattered flux received at the surface by an upward looking spectrometer at 440 nm for 55°N in winter, as a function of the altitude where scattering occurs.


Measurments
Reference Spectrum (Io)
Measured Spectrum (IS)
Coefficients of absorption of examinated Gases(σ)
Calculation with DOAS metodology
Preparation data spectrum
Application Lambert-Beer Law in differential form
Multiple linear Regression
Sum of Squares (SOS) of the residues of the Regression Minimization
Calculation SOS
Minimum SOS ?
No
Yes

$$I_S(\lambda) = I_0(\lambda)\cdot e^{-\sum \sigma_g(\lambda)\int_0 c_g(l)\,dl}$$

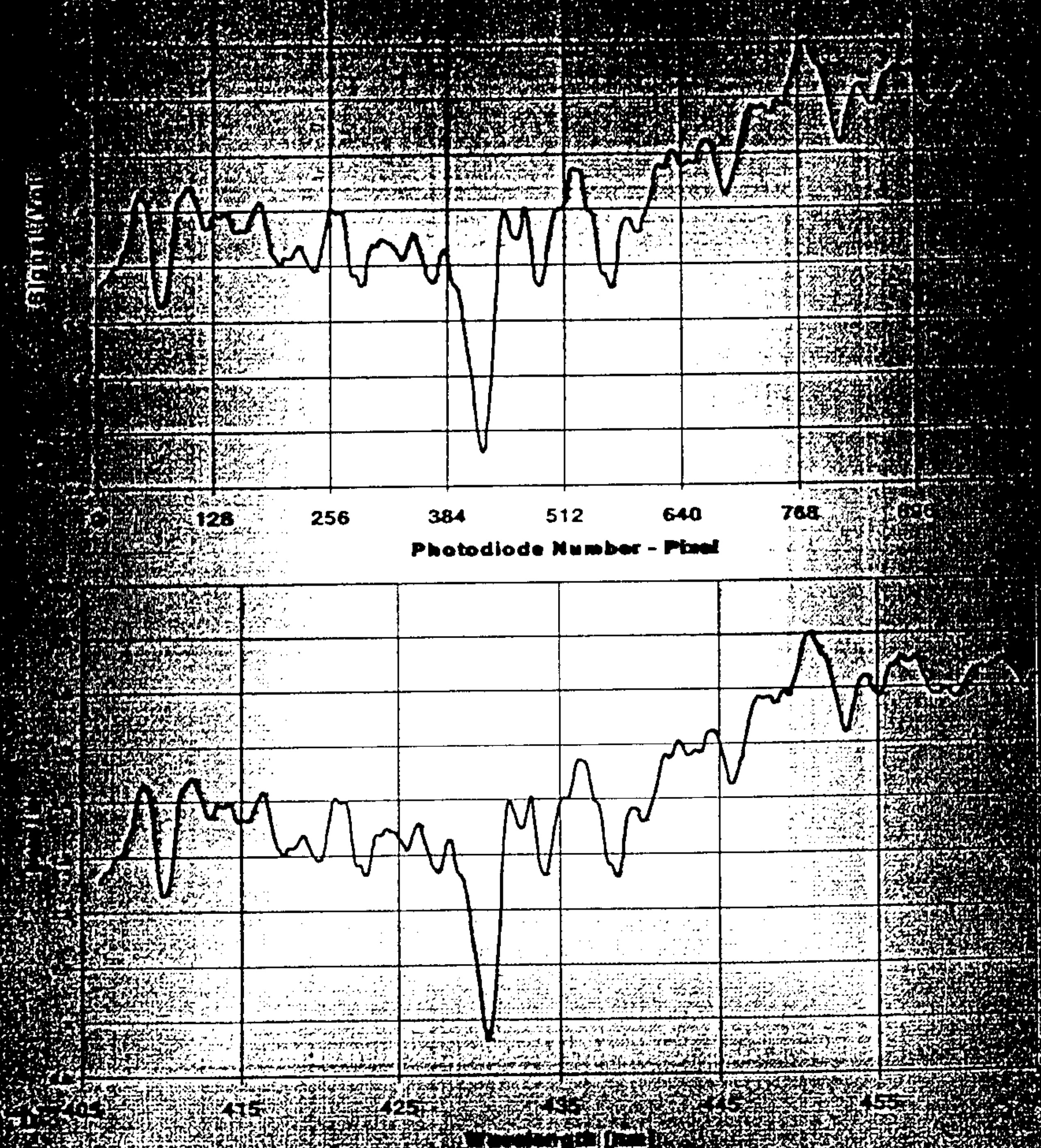
$$\log\left(\frac{I_O(\lambda)}{I_S(\lambda)}\right) = \sum_{g=1}^{n} \sigma_g(\lambda)\int_0^L c_g(l)\,dl$$

Differential Lambert-Beer Law

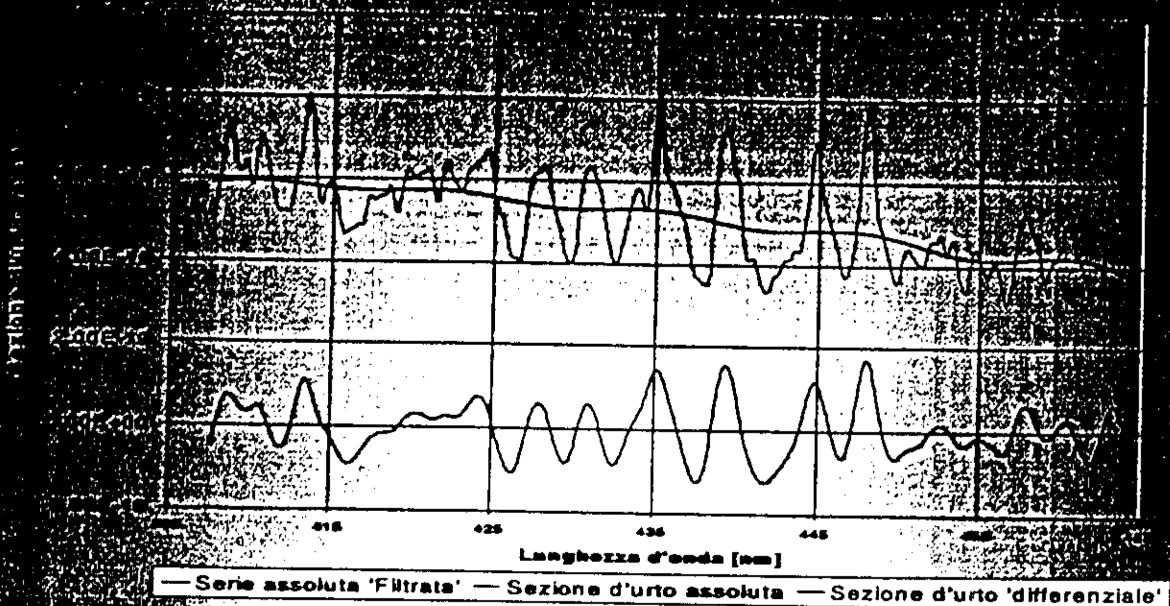
$$\log\left(\frac{I_o(\lambda)}{I_s(\lambda)}\right) - \log\overline{\left(\frac{I_0(\lambda)}{I_S(\lambda)}\right)} = \sum_{g=1}^{n} \left(\sigma_g(\lambda) - \overline{\sigma_g(\lambda)}\right)\int_0^L c_g(l)\,dl$$

Spectral Dispersion

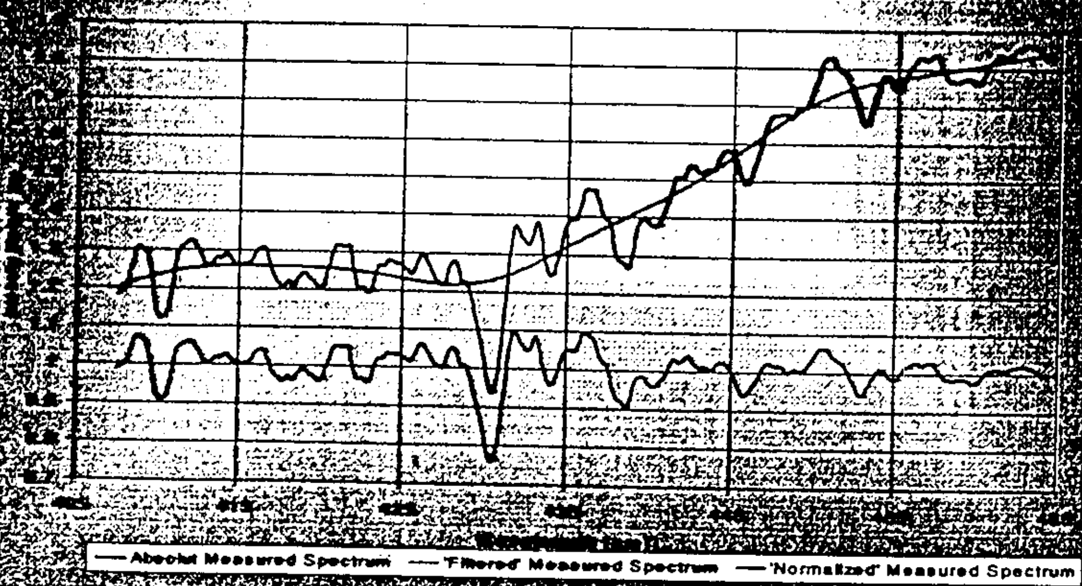
$$\gamma = K1 - K2 * \lambda$$



Spectral series received by the spectrometer:
a) Function of Photodiode Number
b) Function of Wavelength



Differential spectrum of NO2 Absorption coefficients



- Air-Mass Factor

The term "air mass" or "enrichment" factor describes the ratio between the quantity of an absorbent species integrated along a slanted atmospheric path and the quantity of the same species, integrated along a vertical path.

In general, a minor stratospheric gas has a vertical distribution of its partial pressure which can be attributed to a gaussian profile. Therefore, the appropriate air mass factor, for a minor stratospheric gas depends on the average height of the gas bulk.

Amf alla quota di 5 km in funzione della lunghezzad'onda, bulk NO2&O3 20km 3.5Km