

A NEW SENSITIVE METHOD FOR MEASURING PHOTOSENSITIVE GAS POLLUTANTS BY MEANS OF CONCENTRATION MODULATION*

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Abstract—*In order to discriminate the IR spectroscopic absorption lines of a certain pollutant from the IR absorption lines of the background molecules (H_2O , CO_2 , etc.), it is proposed here that a flash light is applied to the sampled air such that the concentration of the pollutant under measuring is subject to a step change. This step modulation of concentration can be discriminatively detected from the background noise by a differentiator connected to the output of a spectroscopic IR detector. The final output can be calibrated to read directly the concentration of the pollutant.*

The improvement of signal to noise ratio due to the background molecular noise has been calculated to be six-order increase in magnitude over the conventional IR spectroscopic schemes. The physical reason for this large improvement is due to the fact that the imposed concentration modulation proposed here is spatially coherent, while the fluctuation of background molecular concentrations is not, therefore the "signal" is additive spatially while the background noise is not.

A practical scheme is described and signal to noise ratios due to background molecular noise as well as due to circuit noise are calculated in detail. Research in the related fields has been surveyed and evaluated.

I. INTRODUCTION—BACKGROUND SURVEY OF THE CURRENT METHODS

There are two major groups of methods for measuring gas pollutants in the air—the chemical methods and the optical methods. The first group¹⁻⁵ includes principally, colorimetric method, conductometric method, coulometric method, chemiluminescent method, and titration method.

The principal idea of colorimetric method is that⁶⁻⁹ some pollutants are very sensitive to certain reagents, and when they react, the product will be colored. Consequently, measuring the decrease of intensity of a certain monochromatic light beam passing through this "dye" will give, within a scaling factor, the amount of pollutant reacted. This amount is, in turn, proportional to the concentration of the pollutant contained in the air sample. NO_2 , O_3 , SO_2 , CO , etc., have been measured

* This work was done at Jet Propulsion Laboratory, California Institute of Technology

by this method using KI and inorganic and organic compounds as reagents.

The second method¹⁰⁻¹² employs the fact that when a certain pollutant is absorbed by a certain sensitive solvent, the solution will be acidified. Measuring the electric conductivity of the solution thus gives a proportional measurement to the amount of pollutant absorbed. SO₂ using H₂O₂ as reagent has been measured by this method.

The third method¹³⁻¹⁵ measures the negative charge (actually the integrated current) lost from a negative electrode immersed in a KI solution. The charge is captured by I which is released from the KI+O₃ reaction. Therefore, measuring the charge will give us a proportional amount of the O₃ absorbed.

The three methods described here are most commonly used today, although more or less, they all have the following handicaps.

One, the interference of other pollutants on the measurement of one particular pollutant may be very high if the air sample is not correctly purified so that other pollutants are completely eliminated before entering the measuring device.¹⁶ Two, sampling flowing rate needs accurate control and sampling devices require critical designs and careful attending, otherwise the accuracy of the measurements will be seriously damaged.^{17,18}

The fourth method, or the chemiluminescent method^{19,20} is derived from the fact that O₃ mixing with Rh-B (or NO_x) will emit light in a certain range of wavelength.³ Therefore, if one measures the intensity of light emitted in a dark chamber, one would get a proportional measurement on the amount of O₃ (or NO_x) in the chamber. Finally, the titration method²¹ requires an accurate measurement on the amount of standard alkali used to neutralize the acid formed by mixing a certain pollutant (e.g., SO₂) with a certain reagent (e.g., H₂O₂). The method is time consuming and sometimes introduces large errors due to contamination of other gases or acid residuals.

The second group of pollutant measuring methods concerns optical techniques. There are two major sub-groups in this group, the non-dispersive type and the dispersive type. The nondispersive methods include the interferometric spectrometer and the thermal-acoustic transducing schemes. The first one^{22,23,23a} used a Michaelson interferometer. Shifting one of the mirrors of the interferometer along its optical axis at a constant speed will allow the frequency components in the two beams to beat at *different* phases. It is shown by Hurley²² that the recombined intensity at the output is just the Fourier cosine transform of the frequency components in the original beam, and the position x of the moving mirror takes the place of the time variable in the conventional Fourier transform. Therefore, if the output intensity, or the "interferogram" is recorded with respect to time (therefore to x), and if we apply, by means of a digital or analogue computer, the inverse transform to this interferogram we will obtain the frequency spectrum of the original light beam. When absorption material is placed in the optical path, the spectrum will change. Comparing the spectra with and without the absorbent, one will have a quantitative measurement on the concentration of the absorbent. The main advantage of this scheme is that total energy (in contrast to partial energy used in conventional

spectroscopy) in the beam is used to obtain the spectrum. Therefore it is claimed that higher resolution has been obtained. The disadvantages are that it does not render any improvement of signal to noise ratio against the noise due to background molecules, and it needs computer analysis for fast results.

The thermal-acoustic transducer scheme uses the principle that when a pollutant, say, CO, absorbs energy from an IR beam, its volume expands slightly. Measuring the amount of expansion by a microphone which converts the acoustic pressure into electrical signal, one can obtain a proportional amount of CO under expansion.²⁴ Also one can measure the differential expansion between an absorbing CO chamber and a non-absorbing chamber separated by a diaphragm by measuring the change of capacitance of the pressure-distorted diaphragm. From this, one can also obtain proportionally the amount of CO contained in the sampled air.²⁵

The main methods using optical dispersion schemes are the longpath spectroscopy. 250 feet longpath UV spectroscopy has been used to measure the O₃ concentration in the air^{26,27} although there exist some alignment problems and other practical difficulties.²⁸ The correlation spectrometer developed by Barringer and others²⁹⁻³⁴ uses a vibrating correlation mask placed at the output of a monochromator. The mask is a multi-slit plate matching the positions of the dispersed absorption lines of a certain pollutant to be measured. During the vibration there is only one position of the mask such that perfect match between the slits and the pollutant lines is reached, but no such full correlation can be reached between the mask and the lines of other pollutants or background molecules. It is claimed that by means of a phase-locked detector matching the vibration of the mask, and by using an optical path greater than 1000 meter long*, one can measure the average NO₂ concentration up to 0.1 ppm or to 1 ppb^{32,33}. But it is obvious that the background noise due to absorption of other molecules cannot be suppressed significantly in this scheme, because, although not perfectly correlated to the mask, the background lines do give periodical time variation after passing through the vibrating mask.** The 1000 meter long path used in Barringer's scheme may have contributed significantly to the sensitivity they have obtained. Furthermore, remote sensor using correlation mask actually measures the *average* pollutant concentration along the long path. It is not a *point* measuring device.

Apart from the ideas of all the above schemes, the author feels that since the background noise due to background molecules has about the same random variation as that of the signal due to the pollutant to be measured,*** if one intends to

* Barringer and his associates used remote lamp (quartz iodine or xenon arc) or sunlight as the remote light source.

** The author had some private communications (letters) with Dr. Barringer's group concerning the signal to (background) noise ratio of their correlation scheme from detailed theoretical and experimental point of view. It was informed that they are still working on this point at the time being.

*** This is not like the case in electrical communication. The electrical noises always have a large degree of randomness as compared to the signal. Therefore most of the electrical communication technology for detecting signal from noise is based on this contrast of degrees of randomness.

separate the signal from the noise by non-chemical means, the most logical way, from an electrical communication point of view, is to impose a controlled time variation on the concentration of the pollutant to be measured and *not* to the background molecules. Then detect this imposed variation by a selective circuit which responds *only* to this imposed variation. In the following, this idea, being tentatively called as "concentration modulation", will be extensively discussed and improvement of signal to noise ratio will be calculated.

II. PRINCIPAL IDEA

A practical scheme based on the above idea is shown in the following.

As shown in Fig. 1, if we flash a chamber containing polluted air with a UV light containing enough energy above the dissociation limit of a certain pollutant (for example, NO_2), then this pollutant will have an imposed concentration decrease—a "step" decrease with respect to time as shown by the lower curve in Fig. 2-b, where it shows that the signal is *buried* in the noise due to background molecules. Now if we detect the IR spectrum of this concentration modulated NO_2 by inserting a stationary correlation mask placed between the monochromator and the photo-detector, and connect the output to an electronic differentiator (Fig. 1), the final output as shown on the oscilloscope will give a spike corresponding to the differentiation of the step change in Fig. 2-b. This spike will now stand out from the background noise (Fig. 2-c) because the thermal fluctuation of concentration of the background molecules (H_2O , CO_2 , etc.) cannot be so fast and so spatially coherent as is the imposed step change of NO_2 concentration. As to be shown shortly, the amplitude of this spike is proportional to the initial concentration of NO_2 . Consequently, a calibration of the reading of the spike amplitude on the oscilloscope will give a direct reading of the initial concentration of NO_2 in the polluted air.

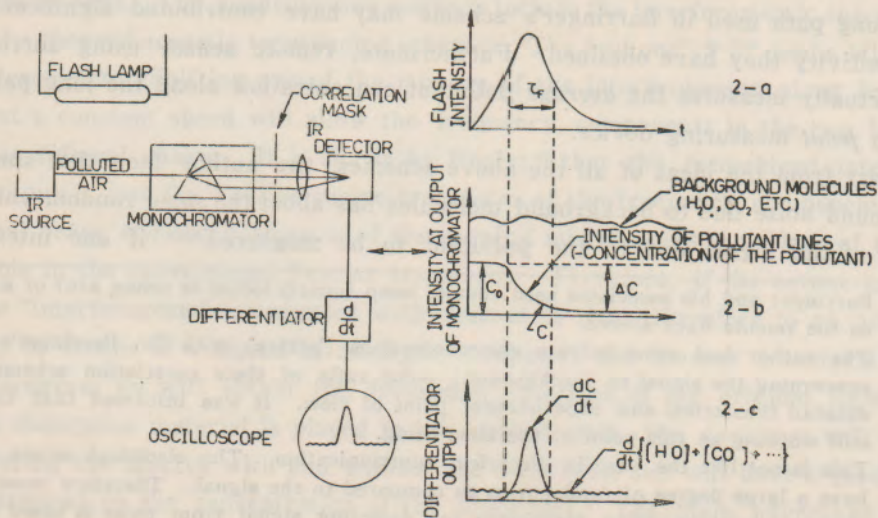


Fig. 1. Schematic Arrangement

Fig. 2. Waveforms at Different Stages

It is easy to show that dC/dt due to flash photolysis is proportional to C_0 , where C and C_0 are the concentrations of NO_2 at time t and time zero (beginning of the flash). Since only the primary photochemical reaction is important in the calculation of the "step" concentration change,* we have $\frac{dC}{dt} = -KI(t)C$ where K is the primary photochemical reaction constant. I is the intensity of the flashing light beam. The solution of this equation with $C=C_0$ at $t=0$ is

$$C = C_0 e^{-K \int_0^{t_1} I(t') dt'} \quad (1)$$

and
$$\frac{dC}{dt} = C_0 K I(t) e^{-K \int_0^{t_1} I(t') dt'} = C_0 f[I(t)] \quad (1')$$

where f is a function of the flash intensity $I(t)$ only. Therefore, dC/dt and hence, $(dC/dt)_{max}$, the amplitude of the spike, are proportional to C_0 , the initial concentration of the pollutant.

III. IMPROVEMENT OF SIGNAL TO NOISE RATIO DUE TO MOLECULAR NOISE

There are two major sources of noise in a system of an IR spectroscopic detection of pollutants—the background molecular noise and the circuit noise. The former is usually the major factor limiting the sensitivity of the detection. In this section, we will calculate the improvement of S/N due to the background molecular noise. In Appendix III, we will calculate and show that for a typical case, the circuit noise does not present a serious problem to the detection at all.

Smoluchowski³⁵ has derived a well known relation that if there are n molecules of an ideal gas occupying an average volume V_0 at the standard condition, then the root-mean-square thermally fluctuated volume of these n molecules at standard condition will be³⁶

$$\Delta V_{rms} = V_0 \frac{1}{\sqrt{n}} \quad (2)$$

Since the volume fluctuation for a fixed number of molecules can be converted to density fluctuation by the following relations

$$\rho = \frac{n}{V} \quad \Delta \rho = -\frac{n \Delta V}{V^2}$$

we have $\frac{\Delta \rho}{\rho_0} = \frac{\Delta V}{V_0}$ and from (2), $\frac{\Delta \rho_{rms}}{\rho_0} = \frac{1}{\sqrt{n}}$ ** (3)

* It is shown in Appendix I that the recovery rate of NO_2 after the flash is too slow to affect the step change due the flash photolysis. Therefore, the recovery reactions can be neglected properly in this calculation.

** This equation can also be derived from a general statistical point of view as shown in Davidson' *Statistical Mechanics*³⁷ for a statistical grand ensemble of certain gas molecules:

$$\frac{\Delta \rho^2}{\rho^2} = \frac{kTK}{V_0'} \quad (\text{eq. 14-11 of Davidson})$$

k is Boltzman constant, V_0' is the molar volume, T is the absolute Temperature and $K \equiv -1/V_0' (\partial V_0' / \partial p)_T$ is the compressibility of the gas. Substituting the ideal gas equation, $pV_0' = NkT$ (where N is Avogadro's number) and the relation at standard condition that $N/n = V_0'/V_0$ into the above equation one obtains (3) accordingly.

Now, if we approximate dC/dt by $\Delta C/\tau_f$ where ΔC is the step change of concentration of NO_2 due to the flash and τ_f is the pulse width of the flash (Fig. 2-b), also if we approximate $d\rho/dt$ (due to background molecule fluctuation) by $\sqrt{2}\Delta\rho_{rms}/\tau_c$ where τ_c is the statistical correlation time of the background noise at the output of the photodetector—It is the correlation time of the *integrated* density fluctuation of the background molecules along the optical path, —then we have the ratio of the $(S/N)_{fcd}$ (due to flash, correlation mask, and differentiator) to $(S/N)_c$ (due to correlation mask alone) equal to:

$$\text{Improvement factor } r \equiv \frac{(S/N)_{fcd}}{(S/N)_c} = \frac{\left(\frac{\Delta C}{\tau_f}\right) / \left(\frac{\sqrt{2}\Delta\rho_{rms}}{\tau_c}\right)}{C_0/\rho_0} = \left(\frac{\Delta C}{C_0} / \sqrt{2} \frac{\Delta\rho_{rms}}{\rho_0}\right) \frac{\tau_c}{\tau_f}$$

$$\text{or, by (3), } r = \frac{\Delta C}{\sqrt{2}C_0} \frac{\tau_c}{\tau_f} \sqrt{n} \quad (4)$$

where n is the average number of molecules in the optical path of the spectroscopic arrangement Fig. 1, and $\frac{\Delta C}{C_0}$ can be related to the flash energy in the following way. From (1), we have

$$\frac{\Delta C}{C_0} = \frac{C_0 - C_{t \rightarrow \infty}}{C_0} = 1 - e^{-K \int_0^{\infty} 1(t') dt'} = 1 - e^{-RE/A} \quad (5)$$

where E is the total energy released during the flash. A is the cross-section of the "flashing path", and K is the primary photochemical reaction constant. K for NO_2 as calculated in Appendix II is equal to $0.45 \text{ cm}^2 \text{ watt}^{-1} \text{ sec}^{-1}$. Other variables in (4) can be calculated numerically as shown in the following. With 2 meter length, and 1 mm^2 cross-section of a typical optical path in Fig. 1, the number of molecules n for a background gas, say, H_2O , contained in the path is

$$n = 6.024 \times 10^{23} \times \frac{200 \times 0.01 \times 10^{-3} \text{ liter}}{22.4 \text{ liter}} \times 0.018 = 5 \times 10^{19} \quad (6)$$

for a flash tube giving 500 joules of UV energy per burst (e.g., a small-size Norrish-Porter type flash tube³⁸) and for an effective flashing cross-section of 100 cm^2 , we have, from (5)

$$\Delta C/C_0 = 0.92 \quad (7)$$

Also for a Norrish-Porter flash tube, τ_f is approximately equal to 10^{-3} sec .³⁹

As for τ_c , the post-detector (output of the photodetector of Fig. 1) statistical correlation time for H_2O density fluctuation, it is difficult to calculate because of the lack of experimental data on hand. But from our experience (e.g., by means of an oscilloscope connected to the output of an IR spectrometer, we can observe the fluctuation of the intensity of an IR line of H_2O is a certain domain of the atmosphere.), 1 microsecond is probably the shortest correlation time we could expect for the fluctuation. If we take

$$\tau_c = 10^{-6} \text{ sec} \quad (8)$$

and substituting (6) to (8) into (4), we then obtain

$$r=5 \times 10^6$$

That is, an improvement of S/N of the order of 10^6 can be achieved by the present scheme over the conventional scheme of stationary correlation spectroscopy!

Physically, this significant improvement of S/N is due to the fact that the random thermal fluctuation of the background molecular density is *not* spatially coherent along the optical path, therefore it is *not additive* along the path.* While the change of density of NO_2 due to flash photolysis is spatially coherent, and therefore is *additive* along the optical path. Consequently, if one detects this *density change* by a differentiator and a correlation mask instead of detecting the *density itself* by correlation mask alone, one would expect a *large* improvement of signal to noise ratio.

V. SOME PRACTICAL CONSIDERATIONS

Two important factors of a practical system are considered here. One, the isolation between the flash emission and the spectroscope source emission.** Two, multiple path, e. g., 5 to 10 paths, must be used if the absorption chamber is not to be very long, e. g., 1 meter. The scheme shown in Fig. 3 may meet both these ends.

An adjustment of the movable pinhole M in the exit chamber can select *critically* the optical path for the emission rays coming from the point source provided by the pinhole S in front of the source lamp. The emission from the flash lamp practically cannot pass the fixed pinhole E in the exit chamber because no ray of such emission from the flash lamp or from the reflecting walls can follow *exactly* the path selected by the two pinholes in the exit chamber. Would there be any stray emission from the flash lamp entering M, this stray light should practically be completely absorbed by the absorbing walls in the exit chamber.

The adjustment of the movable pinhole M can also allow us to select the number of multiple paths in the absorption chamber. This number can be obtained in the following way. When the flash lamp is off and the source lamp is on, shift M along the screw axis until a maximum of photodetector output is obtained. Then shift the unit further until the next maximum is observed. Measuring the shifting

* The incoherency of thermal fluctuation also reflects in the physical meaning of the Smoloukowski's equation

$$\frac{\Delta \rho_{rms}}{\rho_0} = \frac{1}{\sqrt{n}}$$

Physically this equation means that the more the number of molecules contained in a fixed volume, the more the average density ρ_0 , but the fluctuation will not change too much because of the incoherency. Consequently $\Delta \rho_{rms}/\rho_0$ will decrease as the number of molecules n increases as shown by the equation.

** Although the monochromator in Fig. 1 will reject the UV light from the flash tube, yet if the latter has some traced amount of emission in the IR or visible range, it will enter the spectroscopic detection channel and seriously affect the accuracy of the measurements. Because the change of IR or visible line intensities due to concentration modulation of a pollutant is very small and may be of the same order of this "leaking" flash intensity. Consequently it is safe to have further isolation means set up between the flash and the detecting channels to obtain sensitive and accurate measurements.

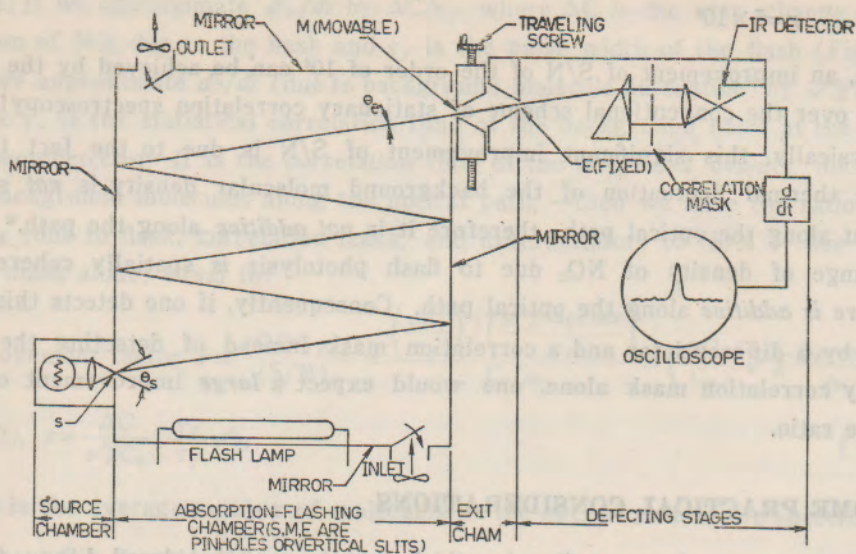


Fig. 3. Outline of a Practical Scheme

distance of the unit between the two maximums, one can calculate the number of multiple paths if the positions of S, E and the length of the chamber are known.

The mirrors on the walls are designed for two purposes—to provide multiple-path reflections and to homogenize as well as to strengthen the flash radiation in space. The inlet and outlet doors for polluted air should be closed during measurements to minimize the flow perturbations.

Pinholes S, M, E can be replaced by vertical slits to enhance the intensity of the exit light beam, hence the signal strength.

V. CONCLUSION

The principal idea of the present scheme is to impose a spatially coherent modulation on the concentration of a certain pollutant by means of flash photolysis. Then selectively detect this coherent modulation against the spatially incoherent concentration fluctuation of the background molecules. The improvement of sensitivity of this scheme over that of the conventional spectroscopic schemes has been calculated for a practical case to be six-order increase in magnitude!

The major advantages of this scheme are seen to be

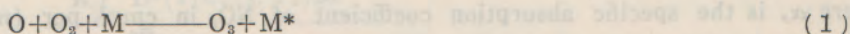
1. High sensitivity against the background molecular noise.
2. Same set-up may be used for detecting any photosensitive pollutant, for example, NO_2 , SO_2 , O_3 , etc. with just a change of the correlation mask for each pollutant.
3. It is a "point" measuring device, not a long-path measurement on the *average* concentrations.
4. It does not need continuous supplies of chemicals as required by wet chemical methods.
5. It does not need critical alignments once the zero point is adjusted.

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APPENDIX I. RATE OF REACTIONS TO RECOVER NO_2 FROM THE FLASH PHOTOLYSIS

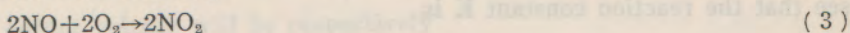
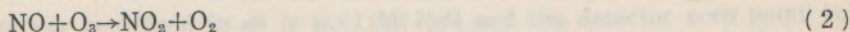
The primary photolysis of NO_2 is $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$. The chance of immediate recombination is very small because the concentrations of NO and O are very small. Since O is very active chemically, it will react with most of the other molecules encountered. Because of the dominant population of O_2 and M (a third body molecule*) in the air, most likely the O atom will react through the following pathway.



This is a three body reaction, yet due to the abundance of O_2 and M , we can safely consider that the concentrations of O_2 and M are constants in (1), and the equivalent first order reaction constant is⁴¹

$$K' = K_3[\text{O}_2][\text{M}] = 2.4 \times 10^4 \text{ sec}^{-1}$$

This means that the life time of O due to reaction (1) is only 40 usec. It would be much longer if O reacts with other molecules (10^4 seconds with O_3 ⁴², 0.1 second with NO_2 ⁴³ and 3.6 seconds with NO ⁴⁴). The NO produced from the primary photolysis will react with O_3 and O_2 to return to NO_2 through the following pathways. (Other return paths are negligible because of the smallness of reaction constants or reactant concentrations in the air.)



The reaction rates are respectively

$$\left. \frac{d[\text{NO}]}{dt} \right|_{(2)} = -K_{11}[\text{NO}][\text{O}_3]$$

$$\left. \frac{d[\text{NO}]}{dt} \right|_{(3)} = -K_{12}[\text{NO}]^2[\text{O}_2]$$

Assuming $[\text{O}_2] \approx 10$ pphm, $[\text{NO}] \approx 1$ pphm, and from Leighton^{45,46} that

$K_{11} = 1.17 \times 10^7$ liter mole⁻¹sec⁻¹, $K_{12}[\text{O}_2] = 127$ liter mole⁻¹sec⁻¹ we see that (2) is at least six order faster than (3) for returning NO to NO_2 , hence (3) can be neglected properly.

* As reported by Leighton,⁴⁰ M consists of the following species, O_3 , O_2 , N_2 , CO_2 , He with proportion of molar concentrations of 1:0.44:0.41:1.06:0.34 respectively.

Now the life time of NO due to (2) is

$$\frac{1}{K_1[O_3]} = \frac{1}{1.17 \times 10^7 \times \frac{10 \times 10^{-8}}{22.4}} \text{ sec} = \frac{22.4}{1.10} = 19 \text{ sec.}$$

Consequently we see that the main return paths for NO₂ after its photolysis are (1) and (2), but statistically it takes 19 seconds for an NO₂ molecule to do so. This is much too slow to affect the "step" change (in millisecon.) of NO₂ concentration due to flash photolysis.

APPENDIX II. REACTION CONSTANT FOR THE PHOTOLYSIS OF NO₂

Since the primary quantum yield of the photolysis of NO₂ is approximately equal to 1, we can assume that any photon absorbed with λ beyond the dissociation limit of NO₂ will decompose an NO₂ molecule into NO and O. The number of photons absorbed per cubic cm per second at the photolysis wavelength is

$$\frac{1}{h\nu} \frac{dI}{dX} \equiv \frac{\alpha I}{h\nu} \equiv \frac{\alpha_\nu [NO_2] I}{h\nu}$$

Where α_ν is the specific absorption coefficient of NO₂ in cm⁻¹ per (mole/liter of NO₂). NO₂ is the concentration of NO₂ is mole/liter. Therefore the number of moles of NO₂ decomposed per cubic cm per second is

$$\frac{\alpha_\nu I [NO_2]}{h\nu N}$$

where N is Avogadro constant, and the number of moles of NO₂ decomposed per liter per second will be

$$\frac{d[NO_2]}{dt} = \frac{1000 \alpha_\nu I [NO_2]}{h\nu N}$$

comparing this with

$$\frac{d[NO_2]}{dt} = -K I [NO_2]$$

we see that the reaction constant K is

$$K \equiv \frac{1000 \alpha_\nu}{h\nu N} = \frac{1000 \lambda \alpha_\nu}{h c N} = 0.0084 \lambda \alpha_\nu$$

K is in cm² watt⁻¹ sec⁻¹, α_ν is in cm⁻¹ liter mole⁻¹, and λ is in micron. For $\lambda = 0.36$ micron, $\alpha_\nu = 150$ cm⁻¹ liter mole⁻¹⁴⁷, we have $K = 0.45$ cm² watt⁻¹ sec⁻¹.

APPENDIX III. CALCULATION OF SIGNAL TO NOISE RATIO DUE TO CIRCUIT NOISE

For a 50-watt IR source and a copper-doped-germanium detector or a PbSe (77°K) detector (made, for example by *Santa Barbara Research Center*). The S/N_{circuit} for NO₂ in a typical polluted air should be greater than 50 as calculated below. Therefore, the circuit noise should not be a problem for the present scheme.

SBRC measures λ -averaged responsivities for their semiconductor detectors by using a blackbody radiator as a source. The total power emitted by the blackbody at the detector input aperture is *calculated* by plank's blackbody radiation law, when then the temperature of the blackbody, the separation between the source and the detector, the aperture sizes of the source and the detector are known. Then they measure the voltage across the load resistor of the detector, and the "responsivity" is given by the "responsivity" is given by the ratio of this two numbers.⁴⁸ In the following, we are going to calculate, based on these λ -averaged data, the λ -distributed responsivity and the signal voltage output for a typical case in our arrangement. From this, we can then estimate immediately the $S/N_{c_{ht}}$ value.

The λ -averaged responsivity or the "calibration responsivity" R_c can be expressed in the following way with variation in λ taken into account.

$$R_c = \frac{\sum (\text{contribution to the detector output voltage due to optical power absorbed in between } \lambda_i \text{ and } \lambda_i + \Delta\lambda_i) / \text{total power absorbed in the detector}}{= \frac{K \int_0^\infty D^*(\lambda) U_c(\lambda, T_c) d\lambda}{\int_0^\infty U_c(\lambda, T_c) d\lambda}} \tag{1}$$

where u_c = radiation power per unit area at the input aperture = radiation energy density \times velocity of light.

$D^*(\lambda)$ = detectivity spectrum of the detector. It has been measured by SBRC.^{49,50}

K = a proportional constant to be determined from this equation.

The λ -distributed responsivity should be

$R(\lambda)$ = output voltage due to radiation in $u(\lambda)d\lambda$ / total power absorbed in

$$d\lambda = KD^*(\lambda)u(\lambda)d\lambda / u(\lambda)d\lambda = KD^*(\lambda) \tag{2}$$

In our arrangement, if the radiation power spectrum at the exit E of the absorption chamber (Fig. 3) is $u_e(\lambda)$, then, after the monochromator and the correlation mask, the power contained in $d\lambda$ is $u_e(\lambda)M(\lambda)d\lambda$ and the detector zero point voltage and signal output voltage will be respectively

$$V_s = \int_0^\infty R(\lambda)U_e(\lambda)M(\lambda)d\lambda \tag{3}$$

$$\Delta V_s = \int_0^\infty R(\lambda)\Delta U_e(\lambda)M(\lambda)d\lambda \tag{3'}$$

where $M(\lambda)$ is the mask transmission function. ΔV_s , Δu_e are increments of V_s and u_e due to absorption by a pollutant in the absorption chamber. Δu_e can be calculated in the following way.

If the source has a power spectrum $u_s(\lambda, T_s)$ at temperature T_s , and a total emitting power of P_s at the source slit S (Fig. 3), then, the incremental power spectrum (due to absorption at wavelength λ by the pollutant) at the exit slit E will be

$$\Delta U_e = \frac{\theta_e}{\theta_s} [1 - e^{-\rho I \alpha(\lambda)}] \frac{P_s}{\int_0^\infty U_s(\lambda, T_s) d\lambda} U_s(\lambda, T_s) \quad (4)$$

I II III IV

Factor I in the above equation is due to the selection of part of the "wedge" radiation at S by the exit slit E. θ_s is the angle of the radiation wedge at S. θ_e is the angle of the radiation wedge at S. θ_e is the angle extended by E at S. Factor II is due to the absorption by the pollutant in the chamber. It can be approximated by $\rho I \alpha(\lambda)$ where $\alpha(\lambda)$ is the specific absorption coefficient, and ρ is the pollutant concentration. III is a scaling factor and IV is the source spectrum.

When K is solved from (1) and substituted into (2), its result and (4) can be plugged into (3') to give

$$\Delta V_s = R_c \frac{\theta_e}{\theta_s} \rho I P_s \frac{\int_0^\infty U_c(\lambda, T_c) d\lambda}{\int_0^\infty U_c(\lambda, T_c) D^*(\lambda) d\lambda} \frac{\int_0^\infty U_s(\lambda, T_s) D^*(\lambda) \alpha(\lambda) M(\lambda) d\lambda}{\int_0^\infty U_s(\lambda, T_s) d\lambda} \quad (5)$$

This is the most general result for the signal output voltage (due to pollutant absorption) in a system of Fig. 3 using any IR source and a SBRC detector.

Now, with the following assumptions and known data, we can calculate readily the ΔV_s at the output of the IR detector for a typical concentration of NO_2 in a polluted air.

1. The IR source in Fig. 3 is the same as the calibration source used in SBRC, i.e., a 500°K blackbody. From this, we have, $u_c = u_s = u$, $T_s = T_c = 500^\circ\text{K}$.
2. Only one slit centered at λ_0 (for example, $\lambda_0 = 6.17 \mu$ for NO_2) with width $\Delta\lambda_0$ (for example, 0.5μ) is there on the correlation mask i.e., $M(\lambda)$ is a function of λ as shown in Fig. 4.
3. The log. D^* v.s. λ curve measured by SBRC is linearized as shown in Fig. 5 for a Ge:Cu detector.⁵⁰
4. $u(\lambda)$ is flat between the active range λ_2 to λ_1 given in Fig. 5. (For a 500°K blackbody, $u(\lambda)$ is quite flat over most of the wavelengths.)

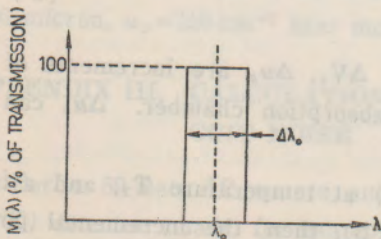


Fig. 4. Transmission Function of the Correlation Mask

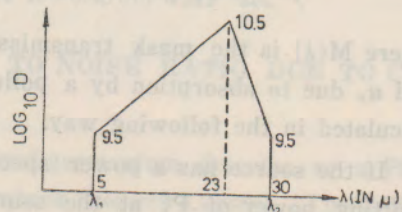


Fig. 5. Linearized log D- λ Curve for Ge:Cu Detector

With these assumptions, (5) can be reduced to

$$\Delta V_s = R_c \frac{\theta_e}{\theta_s} \rho I \alpha(\lambda) p_s \frac{D^*(\lambda_0) \Delta \lambda_0}{\int_0^\infty D^*(\lambda) d\lambda} \quad (6)$$

The numerical values for the variables in this equation are the following. R_c for Ge:Cu is 3.87×10^3 volt/watt,⁴⁸ $\frac{\theta_e}{\theta_s}$ is 10^{-4} (for $\theta_s = 90^\circ$, slit width of $E = 1$ mm, and an optical path = 2 meter), and $\rho I \alpha(\lambda)$ at 6.17μ for a 0.1 ppm NO_2 absorbing in an optical path of 2 meter long is 10^{-3} . $\Delta \lambda_0$, the slit width of the correlation mask shown in Fig. 4 is 0.5μ ; and from reference 50 we have $D^*(6.17 \mu) = 7 \times 10^3 \text{ cm}(hz)^{1/2}/\text{watt}$. Finally from Fig. 5, the integral in (6) can be calculated analytically. It is equal to $3 \times 10^{11} \text{ cm}^2(hz)^{1/2}/\text{watt}$.

Substituting all these data into (6), we have the signal voltage

$$\Delta V_s \approx 4.5 \times 10^{-4} \text{ volt.}$$

The total noise of the detector with a 1-Hz-band-width electronic circuit is 2.7×10^{-7} volt.⁵¹ Since the electronic circuit in the present scheme has about a 1000-Hz-band-width, the noise at the output will be $2.7 \times 10^{-7} \times \sqrt{1000} = 9 \times 10^{-6}$ volt. From this, we see immediately that S/N due to circuit noise at the output of the system is approximately equal to 50.

The result should be enhanced if we used a higher temperature blackbody or a special IR glower as source, and a PbSe detector (which has higher detectivity at 6.17μ) as detector. Also, the result should be increased several times when the multiple-slit transmission of the correlation mask is taken into account.

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