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

CHIA-LUN HU*

College of Engineering, National Chiao Tung University

(Received October 27, 1972)

Abstract—In order to discriminate the IR spectroscopic absorption lines of a
certain pollutant from the IR absorption lines of the background molecules
(H₂O, CO₂, 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 con-
ventional IR spectroscopic schemes. The physical reason for this large im-
provement is due to the fact that the imposed concentration modulation proposed
here is spatially coherent, while the fluctuation of background molecular con-
centrations is not, therefore the “signal” is additive spatially while the back-
ground 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 group includes prin-
cipally, colorimetric method, conductometric method, coulometric method, chemilu-
minescent method, and titration method.

The principal idea of colorimetric method is that 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. NO₂, O₃, SO₂, 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 method 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 method 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+O₂ reaction. Therefore, measuring the charge will give us a proportional amount of the O₂ 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. 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.

The fourth method, or the chemiluminescent method is derived from the fact that O₂ mixing with Rh-B (or NOₓ) will emit light in a certain range of wavelength. Therefore, if one measures the intensity of light emitted in a dark chamber, one would get a proportional measurement on the amount of O₂ (or NOₓ) in the chamber. Finally, the titration method 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 used a Michelson 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 Hurley 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. 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.

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, although there exist some alignment problems and other practical difficulties. The correlation spectrometer developed by Barringer and others 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 NO₃ concentration up to 0.1 ppm or to 1 ppb. 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 responses 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, NO₂), 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 NO₂ by inserting a stationary correlation mask placed between the monochromator and the photodetector, 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 (H₂O, CO₂, etc.) cannot be so fast and so spatially coherent as is the imposed step change of NO₂ concentration. As to be shown shortly, the amplitude of this spike is proportional to the initial concentration of NO₂. Consequently, a calibration of the reading of the spike amplitude on the oscilloscope will give a direct reading of the initial concentration of NO₂ in the polluted air.

![Schematic Arrangement](image1)

![Waveforms at Different Stages](image2)
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$_x$ 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 $rac{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

$$C = C_0 e^{-k \int_0^t I(t') dt'}$$  \hspace{1cm} (1)

and

$$\frac{dC}{dt} = C_0 K I(t) e^{-k \int_0^t I(t') dt'} = C_0 / [I(t)]$$  \hspace{1cm} (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.

Smoluchowski$^{25}$ 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 be$^{25}$

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

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

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

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

---

* It is shown in Appendix I that the recovery rate of NO$_x$ 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$^{21}$ for a statistical grand ensemble of certain gas molecules:

$$\frac{\Delta \rho^2}{\rho_c^2} = \frac{kT}{V_0}$$  \hspace{1cm} (eq. 14-11 of Davidson)

$k$ is Boltzmann constant, $V_0$ is the molar volume, $T$ is the absolute temperature and $K = -1/V_0^e (\partial V'_e/\partial p)_T$ is the compressibility of the gas. Substituting the ideal gas equation, $pV'_e = NkT$ (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 $\Delta C$ is the step change of concentration of NO$_2$ due to the flash and $\tau_f$ is the pulse width of the flash (Fig. 2-b), also if we approximate $d\phi/dt$ (due to background molecule fluctuation) by $\sqrt{2}\Delta \rho_{rms}/\tau_e$, where $\tau_e$ 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 $(S/N)_{fed}$ (due to flash, correlation mask, and differentiator) to $(S/N)_e$ (due to correlation mask alone) equal to:

\[
\text{Improvement factor } r = \frac{(S/N)_{fed}}{(S/N)_e} = \frac{(\Delta C / \tau_f)}{\left(\frac{\sqrt{2} \Delta \rho_{rms}}{C_0 / \rho_0} \right) \frac{\tau_e}{\tau_f}} = \frac{\Delta C}{C_0 / \sqrt{2} \Delta \rho_{rms} \rho_0} \frac{\tau_e}{\tau_f} \sqrt{n}
\]

or, by (3),
\[
r = \frac{\Delta C}{\sqrt{2}C_0} \frac{\tau_e}{\tau_f} \sqrt{\frac{n}{C_0}}
\]

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

\[
\frac{\Delta C}{C_0} = C_{e-ex} - C_{e-x} = 1 - e^{-\kappa \int_0^{\tau_f} G(t') dt'} = 1 - e^{-\kappa E/A}
\]

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 cm$^2$watt$^{-1}$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$_2$O, contained in the path is

\[
n = 6.024 \times 10^{23} \times \frac{200 \times 0.01 \times 10^{-3}}{22.4 \text{ liter}} \times 0.018 = 5 \times 10^{19}
\]

for a flash tube giving 500 joules of UV energy per burst (e.g., a small-size Norrish-Porter type flash tube$^{38}$) and for an effective flashing cross-section of 100 cm$^2$, we have, from (5)

\[
\frac{\Delta C}{C_0} = 0.92
\]

Also for a Norrish-Porter flash tube, $\tau_f$ is approximately equal to $10^{-3}$ sec.$^{38}$

As for $\tau_e$, the post-detector (output of the photodetector of Fig. 1) statistical correlation time for H$_2$O 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$_2$O is a certain domain of the atmosphere.), 1 microsecond is probably the shortest correlation time we could expect for the fluctuation. If we take

\[
\tau_e = 10^{-6} \text{ sec}
\]

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

\[
-34-
\]
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 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 incoherence of thermal fluctuation also reflects in the physical meaning of the Smolukowski's equation

$$\Delta\phi_{rms} = \frac{1}{\rho_0}$$

Physically this equation means that the more the number of molecules contained in a fixed volume, the more the average density $\rho_0$, but the fluctuation will not change too much because of the incoherence. Consequently $\Delta\phi_{rms}/\rho_0$ 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.
distance of the unit between the two maxima, 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\textsubscript{5}, SO\textsubscript{2}, O\textsubscript{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.
ACKNOWLEDGEMENT

The author deeply appreciates Professor Nicholas George at California Institute of Technology for detailed discussions on the calculation of the signal to noise ratio. He is also in debt to Professor Arie Haagen-Smit at Caltech. Without his criticism and encouragement, this work could not have been completed. Acknowledgements are due to Professor Sheldon Friedlander and Professor Aron Kuppermann at Caltech for their interest in the idea and their constructive discussions with the author.

APPENDIX I. RATE OF REACTIONS TO RECOVER NO₂ FROM THE FLASH PHOTOLYSIS

The primary photolysis of NO₂ is NO₂ + hν → NO + 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 O₂ and M (a third body molecule*) in the air, most likely the O atom will react through the following pathway.

\[ O + O₂ + M \rightarrow O₃ + M* \]  \hspace{1cm} (1)

This is a three body reaction, yet due to the abundance of O₂ and M, we can safely consider that the concentrations of O₂ and M are constants in (1), and the equivalent first order reaction constant is

\[ K' = K₁[O₂][M] = 2.4 \times 10^4 \text{ sec}^{-1} \]

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 (10⁴ seconds with O₂, 0.1 second with NO₂, and 3.6 seconds with NO). The NO produced from the primary photolysis will react with O₂ and O₃ to return to NO₂ through the following pathways. (Other return paths are negligible because of the smallness of reaction constants or reactant concentrations in the air.)

\[ NO + O₂ \rightarrow NO₂ + O \] \hspace{1cm} (2)
\[ 2NO + 2O₂ \rightarrow 2NO₂ \] \hspace{1cm} (3)

The reaction rates are respectively

\[ \frac{d[NO]}{dt} \bigg|_{(2)} = -K₁[NO][O₂] \]
\[ \frac{d[NO]}{dt} \bigg|_{(3)} = -K₁₁[NO]²[O₂] \]

Assuming \([O₂] = 10 \text{ pphm}, \ [NO] = 1 \text{ pphm}, \) and from Leighton⁵⁵,⁶⁶ that

\[ K₁ = 1.17 \times 10^7 \text{ liter mole}^{-1}\text{sec}^{-1}, \ K₁₁[O₂] = 127 \text{ liter mole}^{-1}\text{sec}^{-1} \]

we see that (2) is at least six order faster than (3) for returning NO to NO₂, hence (3) can be neglected properly.

* As reported by Leighton,⁶⁶ M consists of the following species, O₂, O₃, N₂, CO₂. He with proportion of molar concentrations of 1 : 0.44 : 0.41 : 1.06 : 0.34 respectively.

---

37
Now the life time of NO due to (2) is

\[
\frac{1}{K_1([O_3])} = \frac{1}{1.17 \times 10^5 \times 10 \times 10^{-8}} \text{sec} = \frac{22.4}{1.10} = 19 \text{ sec.}
\]

Consequently we see that the main return paths for NO\textsubscript{2} after its photolysis are (1) and (2), but statistically it takes 19 seconds for an NO\textsubscript{2} molecule to do so. This is much too slow to affect the “step” change (in millisecond) of NO\textsubscript{2} concentration due to flash photolysis.

**APPENDIX II. REACTION CONSTANT FOR THE PHOTOLYSIS OF NO\textsubscript{2}**

Since the primary quantum yield of the photolysis of NO\textsubscript{2} is approximately equal to 1, we can assume that any photon absorbed with $\lambda$ beyond the dissociation limit of NO\textsubscript{2} will decompose an NO\textsubscript{2} molecule into NO and O. The number of photons absorbed per cubic cm per second at the photolysis wavelength is

\[
\frac{1}{h\nu} \frac{dI}{dX} = \frac{\alpha[I]}{h\nu} = \frac{\alpha_r[NO_2]I}{h\nu}
\]

Where $\alpha_r$ is the specific absorption coefficient of NO\textsubscript{2} in cm$^{-1}$ per (mole/liter of NO\textsubscript{2}). NO\textsubscript{2} is the concentration of NO\textsubscript{2} is mole/liter. Therefore the number of moles of NO\textsubscript{2} decomposed per cubic cm per second is

\[
\frac{\alpha_r I[NO_2]}{h\nu N}
\]

where N is Avogadro constant, and the number of moles of NO\textsubscript{2} decomposed per liter per second will be

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

Comparing this with

\[
\frac{d[NO_2]}{dt} = -KI[NO_2]
\]

we see that the reaction constant K is

\[
K = \frac{1000 \alpha_r}{h\nu N} = \frac{1000 \lambda \alpha_r}{hCN} = 0.0084 \lambda \alpha_r
\]

K is in cm$^2$ watt$^{-1}$ sec$^{-1}$, $\alpha_r$ is in cm$^{-1}$ liter mole$^{-1}$, and $\lambda$ is in micron. For $\lambda = 0.36$ micron, $\alpha_r = 150$ cm$^{-1}$ liter mole$^{-1}$, we have K = 0.45 cm$^2$ 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,$_{\text{IR}}$ for NO\textsubscript{2} 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 $\lambda$-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. In the following, we are going to calculate, based on these $\lambda$-averaged data, the $\lambda$-distributed responsivity and the signal voltage output for a typical case in our arrangement. From this, we can then estimate immediately the $S/N_{e,k}$ value.

The $\lambda$-averaged responsivity or the “calibration responsivity” $R_\lambda$ can by expressed in the following way with variation in $\lambda$ taken into account.

$$R_\lambda = \sum (\text{contribution to the detector output voltage due to optical power absorbed in between } \lambda_i \text{ and } \lambda_i + \Delta \lambda_i)/\text{total power absorbed in the detector}$$

$$= \frac{K \int_0^\infty D^*(\lambda) U_\lambda(\lambda, T_e) d\lambda}{\int_0^\infty U_\lambda(\lambda, T_e) d\lambda} \quad (1)$$

where $u_\lambda =$ radiation power per unit area at the input aperture = radiation energy density $x$ velocity of light.

$D^*(\lambda) =$ detectivity spectrum of the detector. It has been measured by SBRC. $K =$ a proportional constant to be determined from this equation.

The $\lambda$-distributed responsivity should be

$$R(\lambda) = \text{output voltage due to radiation in } u(\lambda)d\lambda/\text{total power absorbed in } d\lambda = KD^* (\lambda) u(\lambda) d\lambda / u(\lambda) d\lambda = KD^* (\lambda) \quad (2)$$

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

$$V_z = \int_0^\infty R(\lambda) U_\epsilon(\lambda) M(\lambda) d\lambda \quad (3)$$

$$\Delta V_z = \int_0^\infty R(\lambda) \Delta U_\epsilon(\lambda) M(\lambda) d\lambda \quad (3')$$

where $M(\lambda)$ is the mask transmission function. $\Delta V_z$, $\Delta u_\epsilon$ are increments of $V_z$ and $u_\epsilon$ due to absorption by a pollutant in the absorption chamber. $\Delta u_\epsilon$ 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 $\lambda$ by the pollutant) at the exit slit $E$ will be
\[ \Delta U_e = \frac{\theta_e}{\theta_s} \left[ 1 - e^{-\mu_l(\lambda)} \right] \int_0^{\infty} U_e(\lambda, T_e) d\lambda \]  

\[ \int_0^{\infty} U_s(\lambda, T_s) d\lambda \]

Factor I in the above equation is due to the selection of part of the "wedge" radiation at S by the exit slit E. \( \theta_s \) is the angle of the radiation wedge at S. \( \theta_e \) is the angle of the radiation wedge at S. \( \theta_s \) 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 \( \rho \alpha(\lambda) \) where \( \alpha(\lambda) \) is the specific absorption coefficient, and \( \rho \) is the pollutant concentration. Factor 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:

\[ \Delta V_s = R_e \frac{\theta_s}{\theta_e} \rho P_s \int_0^{\infty} U_e(\lambda, T_e) d\lambda \int_0^{\infty} U_s(\lambda, T_s) D^*(\lambda) d\lambda \int_0^{\infty} U_s(\lambda, T_s) D^*(\lambda) \alpha(\lambda) M(\lambda) d\lambda \int_0^{\infty} U_s(\lambda, T_s) d\lambda \]

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 \( \Delta V_s \) at the output of the IR detector for a typical concentration of NO\(_s\) 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°C blackbody. From this, we have, \( u_e = u_s = u \), \( T_s = T_e = 500°C \).

2. Only one slit centered at \( \lambda_0 \) (for example, \( \lambda_0 = 6.17 \mu \) for NO\(_s\)) with width \( \Delta \lambda_0 \) (for example, 0.5 \( \mu \)) is there on the correlation mask i.e., \( M(\lambda) \) is a function of \( \lambda \) as shown in Fig. 4.

3. The \( D^* \) v.s. \( \lambda \) curve measured by SBRC is linearized as shown in Fig. 5 for a Ge:Cu detector.

4. \( u(\lambda) \) is flat between the active range \( \lambda_2 \) to \( \lambda_1 \) given in Fig. 5. (For a 500°C blackbody, \( u(\lambda) \) is quite flat over most of the wavelengths.)
With these assumptions, (5) can be reduced to

\[ \Delta V_s = R_e \theta_s \rho \alpha(\lambda) \theta_s \int_0^{D_s(\lambda)} \frac{D_s(\lambda) \Delta \lambda}{D_s(\lambda) d\lambda} \]

(6)

The numerical values for the variables in this equation are the following. \( R_e \) for Ge:Cu is \( 3.87 \times 10^3 \) volt/watt, \( \theta_s = 10^{-6} \) (for \( \theta_s = 90^\circ \), slit width of \( E = 1 \) mm, and an optical path = 2 meter), and \( \rho \alpha(\lambda) \) at 6.17 \( \mu \) for a 0.1 ppm NO\(_2\) absorbing in an optical path of 2 meter long is \( 10^{-8} \). \( \Delta \lambda_s \), the slit width of the correlation mask shown in Fig. 4 is 0.5 \( \mu \); and from reference 50 we have \( D_s(6.17 \mu) = 7 \times 10^4 \text{ cm}^2(\text{h})^{1/2} /\text{watt} \). Finally from Fig. 5, the integral in (6) can be calculated analytically. It is equal to \( 3 \times 10^{11} \text{ cm}^2(\text{h})^{1/2} /\text{watt} \).

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

\[ \Delta V_s = 4.5 \times 10^{-4} \text{ volt} \]

The total noise of the detector with a 1-Hz-band-width electronic circuit is \( 2.7 \times 10^{-7} \) volt.\(^{51} \) Since the electronic circuit in the present scheme has about a 1000-Hz-band-width, the noise at the output will be \( 2.7 \times 10^{-7} x \sqrt{1000} = 9 \times 10^{-6} \) 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 6.17 \( \mu \)) as detector. Also, the result should be increased several times when the multiple-slit transmission of the correlation mask is taken into account.

REFERENCES

3. Public Health Service, Air Quality Criteria for \( \text{SO}_x \), Jan. 1969, Chap. 2
5. Public Health Service, Air Quality Criteria for \( \text{NO}_x \), 1971, Chap. 5
17. Public Health Service, Air Quality Criteria for \( \text{NO}_x \), p. 5-2, 1971
36. Ref. 35, equation 17-11, p. 343
41. P. A. Leighton, op. cit., p. 119, table 35, the ambient temperature is taken to be 25°C.
42. P. A. Leighton, op. cit., p. 127-128
43. P. A. Leighton, op. cit., p. 131.
44. P. A. Leighton, op. cit., p. 132
45. P. A. Leighton, op. cit., p. 154, Table 44
46. P. A. Leighton, op. cit., p. 185, Table 53
47. P. A. Leighton, op. cit., p. 54, Table 14
48. Private communication with SBRC
50. Santa Barbara Research Center Infra-Red Components Data Brochure, issued by SBRC, Goleta, California
51. Detector Data Sheet, issued by Santa Barbara Research Center, Goleta, CA