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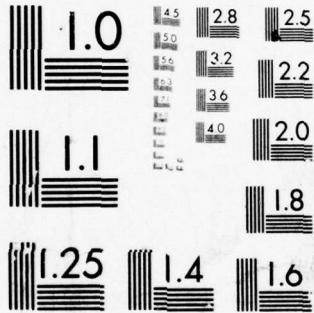
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APPLICATION OF CHEMLUMINESCENCE ANALYSIS IN AIR
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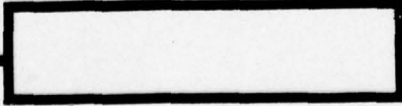
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Chen Chu Cheun

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APPLICATION OF CHEMILUMINESCENCE ANALYSIS IN
AIR POLLUTION RESEARCH

Chen Chu Cheun
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Introduction

The monitoring of air pollution is evolving into a new field in the realm of environmental protection. One of the important tasks of the air pollution research is the establishment of a sensitive, efficient and complete system of automatic detection-monitor system. In the development of this area, the technique of chemiluminescence has played an important role since the late 1960's, and especially in recent years.

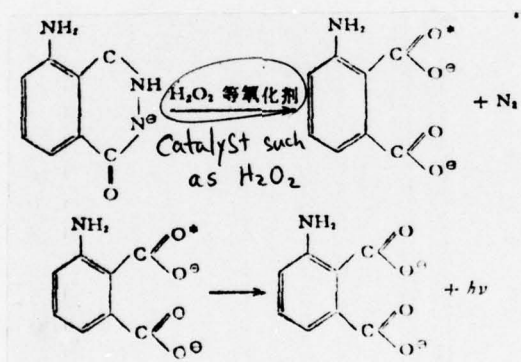
Chemiluminescence analysis makes use of the light emitting phenomenon in certain chemical reactions and enables analytical study of the chemical composition. During chemical reactions, some substances absorb the chemical energy released in the reaction and, as a result, the atoms or molecules are raised to their excited states. Energy in the form of light radiation is released when the excited atoms and molecules return to their ground state. The magnitude and spectral frequency of the radiation are determined entirely by the substances and their chemical reaction--each chemiluminescence reaction has its own characteristic chemiluminescence spectrum.

There are two basic requirements for chemiluminescence:

- (1) There must be enough chemical energy released in the reaction and the energy must be absorbed by the molecules to produce the excited states.

- (2) The atoms and molecules of excited states must be able to release photons upon de-excitation or transfer their energy to other molecules which in turn release photons upon de-excitation.

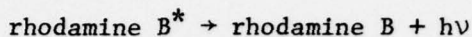
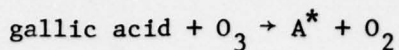
For example, in slightly basic solutions, luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) can be oxidized by oxidizing agents such as hydrogen peroxide in the presence of catalysts of Cu(II), Co(II), Fe(II), Cr(III) and produces chemiluminescence reaction. The mechanism of this reaction⁽¹⁾ is as follows:



* indicates atoms or molecules of excited state.

and the maximum wavelength of the light radiation (λ_{\max}) is 425 m μ .

As another example, ozone reacts with the ethyl alcohol solution of rhodamine B and gallic acid and undergoes chemiluminescence. The molecules of gallic acid are raised to their excited states by absorbing the reaction chemical energy when the gallic acid is oxidized by the ozone. These excited molecules rapidly transfer their energy and excite rhodamine B. As the excited rhodamine B molecules return to their ground state, photons are emitted.⁽²⁾



where A^* is the excited intermediate product in the reaction of ozone and gallic acid, and B is the final product of oxidation. The maximum wavelength of this radiation is 584 m μ .

The sensitivity of chemiluminescence is defined in terms of the efficiency ϕ_{CL} :

$$\phi_{\text{CL}} = \frac{\text{Number (or velocity) of photons emitted}}{\text{Number (or velocity) of participating molecules}}$$

The chemiluminescence efficiency ϕ_{CL} is equal to the efficiency for producing excited states, which is defined as the ratio of the number of excited molecules to the number of participating molecules. The value of ϕ_{CL} is generally less than 0.01 for most reactions.

The luminescence intensity is related to the efficiency I_{CL} and the concentration of reactants:

$$I_{\text{CL}}(t) = \phi_{\text{CL}} \cdot \frac{dC(t)}{dt}$$

The concentration of the substances in the reaction can easily be determined by measuring the intensity I_{CL} with a single photomultiplier.

There are four advantages in using the technique of chemiluminescence:

- (1) It has a higher sensitivity for environmental protection work than the usual absorption colorimetric spectrum and the coulometric methods. For example, the sensitivity of the ozone and rhodamine B reaction is 1 ppb O_3 and the sensitivity of the gas phase reaction of ozone and NO enables the detection of 1 ppb NO (3). Using the flame chemiluminescence reaction of sulfur, 0.002

microgram of Sulfur^[1] can be detected; 1 ppb level of CO^[3, 4] can be detected by the gas phase reaction of carbon monoxide and oxygen atoms. The luminal-oxygen reaction with iron ions as the catalyst can be used to detect Fe(II) to 0.005 microgram/liter,^(5,6) and the same reactions with hydrogen peroxide catalyzed by ions of chromium, cobalt and copper are able to detect 0.025 ppb Cr(III) 1 ppb Co(II) and 3 ppb Cu(II).⁽⁷⁻¹¹⁾

- (2) Since there are not too many chemiluminescence reactions in existence and the spectrum of the emitted light is determined by the excited atoms or molecules, or loosely speaking, by the chemical reaction, it is only very rare that different chemiluminescence reactions produce the same light emitting substances. The technique of chemiluminescence analysis is therefore effective and possesses high selectivity. It can be used to determine different pollutants in air pollution research and no separation of the pollutants is required.
- (3) Because of the high sensitivity and selectivity, instrumentation set up is relatively simple. Sophisticated spectrum analysis and intensity measurement equipment are not necessary. Generally, only a few interference filters and the ordinary photomultipliers are needed.
- (4) Measurements are rapid--each analysis can be carried out in a matter of a few minutes, and the method is therefore appropriate for automatic monitor systems.

Three types of chemiluminescence reactions are generally used in analysis work: in the solution, in the gas phase and in the flame. In the environmental protection research, the reaction in solution is often

used in monitoring the poisonous pollutants in natural water and industrial waste water. The latter two reactions are employed in air pollution monitoring. (12,13)

The major pollutants in air such as SO_2 , H S, NO, NO_2 , O_3 and CO can be monitored automatically by the chemiluminescence analysis technique with easily assembled instrumentation systems. This article deals mainly with the applications of this method in air pollution research.

Ozone

I. Chemiluminescence Reaction of Ozone and Rhodamine B

Many organic compounds undergo luminescence upon oxidation by ozone. People have used such reactions in identifying more than forty different kinds of organic compounds at the milli-microgram level. The reaction of ozone and rhodamine B has the highest luminescence efficiency. (14-16) Two methods can be used in detecting the trace ozone in air.

The first method uses the above-mentioned reaction of ozone and the ethanol solution of rhodamine B and gallic acid. (2) In this reaction, the gallic acid is used as the acceptor of ozone and the rhodamine B is the emitter of photons. The concentration of rhodamine B is kept constant throughout the detection process and the response speed (proportional to the chemical reaction rate) is faster than the direct reaction of ozone and rhodamine B. Based on this principle, an automatic detection scheme for ozone content in the atmosphere has been designed (see Fig. 1).

Tube K contains granular potassium hydroxide and reactor C contains chemical luminescent solution prepared as follows: dissolve 2.5 grams of gallic acid and 0.03 gram of rhodamine B into one liter of 95% ethanol. The luminescence efficiency of the solution is constant for the first 20

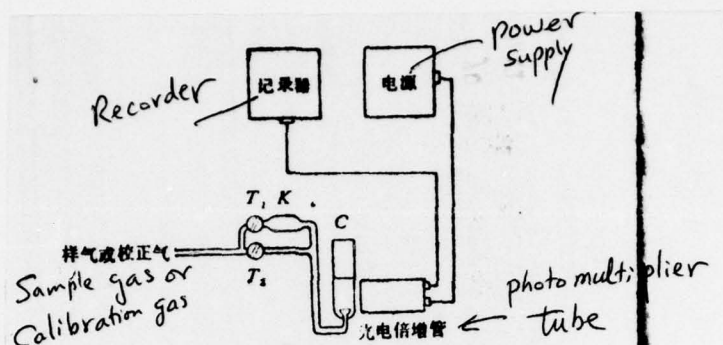


Fig. 1. Automatic detector of ozone.

hours of use. Sample gas or calibration gas is fed in with a mechanical pump at a constant flow rate and the photomultiplier is used to amplify the light intensity. The ozone concentration is directly proportional to the luminescence intensity in the 3-140 ppm range.

The second method is to absorb rhodamine B onto the surface of silica gel and the ozone in air reacts directly with rhodamine B as it flows through the silica gel. The ozone content in air can be obtained by measuring the luminescence intensity.⁽¹⁷⁻²¹⁾ The detection arrangement is shown in Fig. 2.

A gas pump delivers the sample gas or the calibration gas into the reaction chamber at a fixed rate. Luminescence takes place as soon as the ozone reacts with the rhodamine B. The sensitivity and stability of the detection hinges on the way the chemiluminescent plate is prepared. Silica gel substrates (such as K301V and ECS-6061) are generally coated with water-resistant electronic silicon resin (such as SR-82). The stain absorbed can

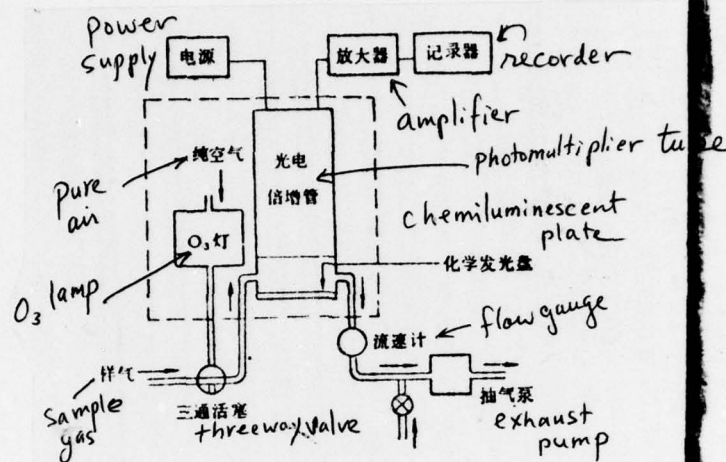


Fig. 2. Automatic ozone detector.

be rhodamine B, O (hydrochloric), $\lambda_{\max} = 584 \text{ m}\mu$. Eosin-Y with a $\lambda_{\max} = 562 \text{ m}\mu$ or ~~phenophthalein~~^{red} with a $\lambda_{\max} = 565 \text{ m}\mu$ can also be used. The preparation procedure is as follows:

1. A circular silica gel plate, with diameter equal to those of the reaction chamber and the photomultiplier, is cut and baked in an oven for 15-30 minutes at 110-120°C.
2. Dip the freshly baked silica gel plate into the benzene solution of 10% SR-82 electron silicon resin for one minute. Remove the plate and drain out excessive solution, then bake for 24-48 hours at 110-120°C.
3. Dip the baked plate in the acetone solution of 0.01% ^{rhodamine B, O} for one minute. Again remove and drain the excessive solution. Evaporate

the acetone thoroughly under a flow of nitrogen gas, then store the plate in a container filled with dry nitrogen gas until use. The luminescent plate prepared with this method is moisture-resistant and has high sensitivity (5 microampere photocurrent/1 ppm O_3).

The sensitivity of the luminescent plate has a positive temperature coefficient, hence, the reactor must be stored in a constant temperature chamber and kept at $25^\circ \pm 2^\circ C$. The flow rate of the sample gas or the calibration gas is 50-850 milliliters/minute. If the pressure of the gas is in the 0.6-1.0 atm range, the luminescence intensity is proportional to the product of the gas pressure and the ozone concentration. Under constant pressure, the intensity is therefore directly proportional to the ozone concentration.

$$I = KP[O_3] = K'[O_3].$$

The ozone content in the sample gas can be obtained by calibrating the luminescent plate with the calibration gas under the same conditions.

$$\frac{I_{\text{sample gas}}}{I_{\text{calibration gas}}} = \frac{KP[O_3]_{\text{sample}}}{KP[O_3]_{\text{calibration}}} = \frac{[O_3]_{\text{sample}}}{[O_3]_{\text{calibration}}}$$

The limit of this detection method is 1 ppb O_3 and the range of detection is 1-400 ppb.

In the above two methods, especially when the rhodamine B and the silica gel luminescent plate are used, the luminescence sensitivity will show signs of weakening with prolonged reaction time. A calibrated ozone generator is therefore necessary to serve as the standard of detection and for the calibrator of the system.

Several schemes are available for the design of the standard ozone source; (2,13,19) among them, the most convenient method makes use of a

Fig. 3

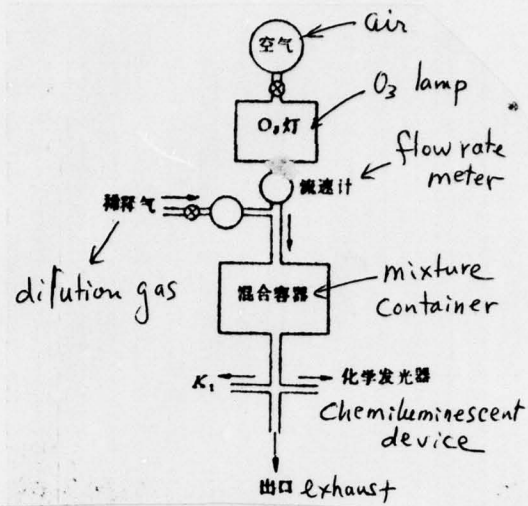


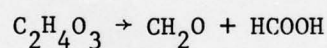
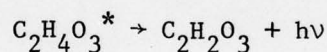
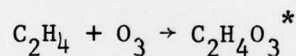
Figure 3. Low Voltage Mercury Dissociation Lamp

low voltage mercury dissociation lamp (Fig. 3), such as the ones generally used in spectrophotometers.

The amount of ozone generated from the air flow will remain constant under fixed lamp voltage, flow rate of air and temperature. The concentration of ozone can be varied by adjusting the voltage of the lamp and the air flow rate. The absolute value of the concentration can be calibrated by potassium iodide. The stable ozone concentration produced by such a source is in the 0.1-4 ppm range. Reports on the ozone source and automatic monitor system for ozone in the atmosphere can be found in the literature. (22)

II. Gas Phase Chemiluminescence Reaction of Ozone and Ethylene (23-25)

Ozone and ethylene react in the gas phase according to the following equations:



The emission spectrum of this gas phase reaction is in the 300-600 m μ range. The maximum emission wavelength (λ_{max}) is equal to 435 m μ . This reaction is most efficient for atmospheric ozone detection since no separation and pretreatments are required. The sensitivity of the detection is 0.003 ppm and the luminescence intensity and the ozone concentration follow a linear relationship in the 0.003-30 ppm range. An automatic monitor system is shown in Fig. 4. (22)

During the measurements, the air flow rate is 1 liter/minute and the ethylene flow rate is 0.8-1.2 liter/minute. Detection sensitivity can be

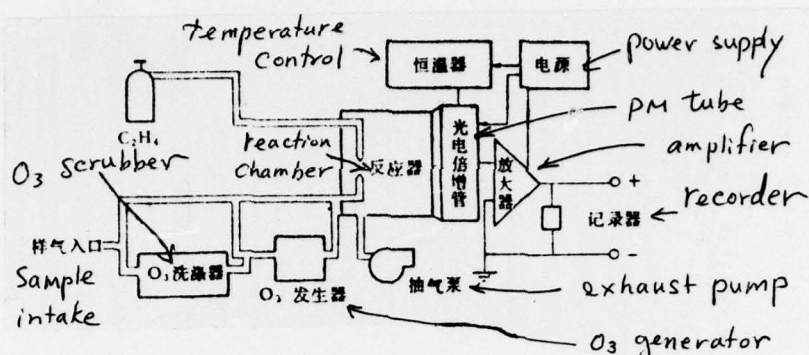


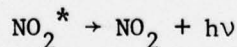
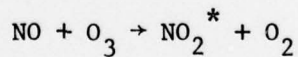
Fig. 4. Automatic monitor system of ozone gas phase chemiluminescence.

further enhanced by increased ethylene flow rate and cooling of the photocathode. In addition to the two schemes described here, the gas phase luminescence reaction of ozone and nitrogen monoxide can also be used, although the last reaction is generally used in the detection of nitrogen monoxide.

Oxides of Nitrogen

I. Nitrogen Monoxide-Ozone Gas Phase Reaction

Detailed studies have been made on the high chemiluminescence efficiency in the gas phase reaction of ozone and nitrogen monoxide. (26,27)



The luminescence intensity of this reaction is given by:

$$I = 12\{\exp(-4180 \pm 300)/RT\} \{[\text{NO}][\text{O}_3]/[\text{M}]\} \text{sec}^{-1}$$

where $[M]$ is the air concentration. The air has quenching effect on the NO_2^* . The emission spectrum falls in the 600 to 75 μ range. The overall reaction rate constant is given by

$$-\frac{d[\text{O}_3]}{dt} = -\frac{d[\text{NO}]}{dt} = K[\text{NO}][\text{O}_3].$$

At room temperature,

$$K = 1 \times 10^7 \text{ liter} \cdot \text{gram molecule}^{-1} \cdot \text{sec}^{-1}.$$

A chemiluminescence nitrogen monoxide detector based on this reaction is shown in Fig. 5.^(3,28) The sample air and the ozone gas are pumped into the reaction chamber by a vacuum pump. The two gases mix and react in the chamber where luminescence reaction takes place. Photomultiplier is used to detect the intensity of the emitted light. Interference filters with cutoff wavelength of 6000 Å are used to filter out the shorter wavelength emissions due to reactions of the ozone and the alkane and hydrocarbon molecules in the air. Once the detection system is calibrated by a sample gas of known ϕ nitrogen monoxide concentration, it can carry out continuous measurement of NO content in the air. The NO concentration follows a linear relationship to the luminescence intensity in the 4-100 ppm concentration range of NO in air, as shown in Fig. 6.

A different design of an automatic monitor system is shown in Fig. 7.⁽²²⁾ Upon cooling the photocathode to -25°C and reducing the pressure of the input gas to reduce the quenching effect of NO_2^* , the sensitivity of the system can be raised to 1 ppb NO and the linear relation region of the intensity and the NO concentration can be expanded to 0.01-10,000 ppm.

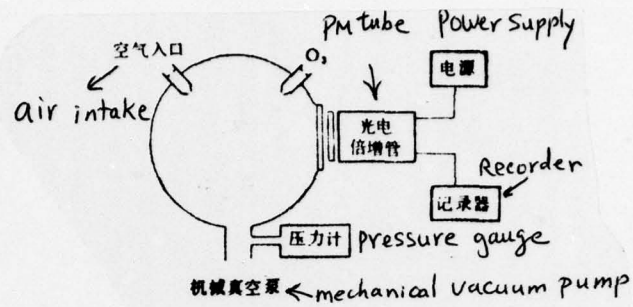


Fig. 5. Nitrogen monoxide detector.

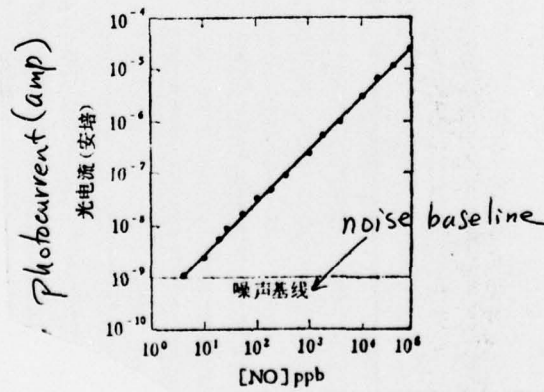


Fig. 6. Nitrogen monoxide reaction response relationship.

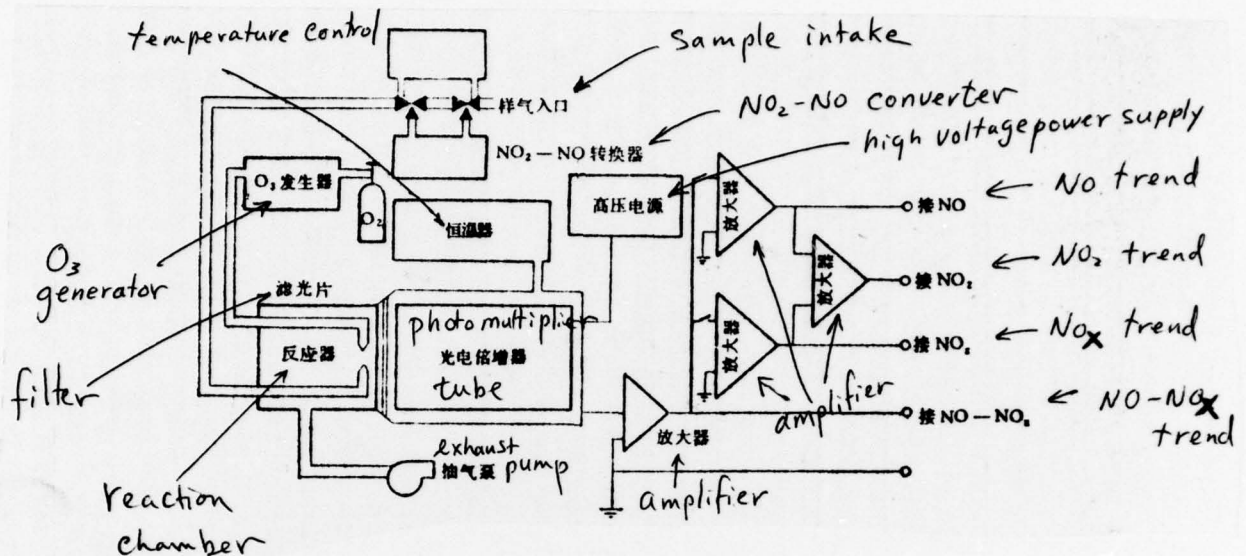
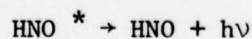
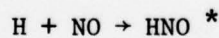


Fig. 7. Automatic monitor system using the gas phase reaction of NO.

If the amount of nitrogen dioxide in the air is to be measured, the nitrogen dioxide can first be reduced to nitrogen monoxide by carbon-covered metal and the total amount of NO_x is measured. The NO_2 content is obtained by subtracting the NO content from the total amount_x^(29,30).

II. Flame Chemiluminescence of Nitrogen Monoxide.

When nitrogen monoxide is burnt in a hydrogen-rich flame, strong flame luminescence reaction takes place according to the following equations:^(31,33)



The emission spectrum, as shown in Fig. 8, is in the 660-770 $\text{m}\mu$ range with the maximum emission wavelength (λ_{max}) being 690 $\text{m}\mu$. The emission

intensity is directly proportional to the NO concentration.

$$I = I_0 [H][NO]$$

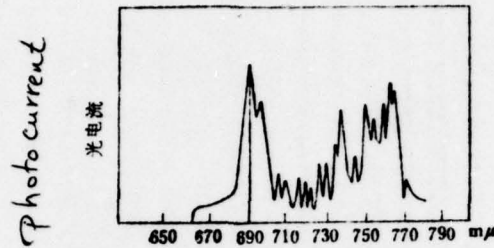


Fig. 8. Emission spectrum of the flame reaction of NO.

During the detection, the sample air and the carrier gas are pumped into the device where they are mixed with hydrogen and burnt (Fig. 9). The flow rate of hydrogen is 200-300 milliliter/minute and the detection sensitivity is 0.150 ppm NO.

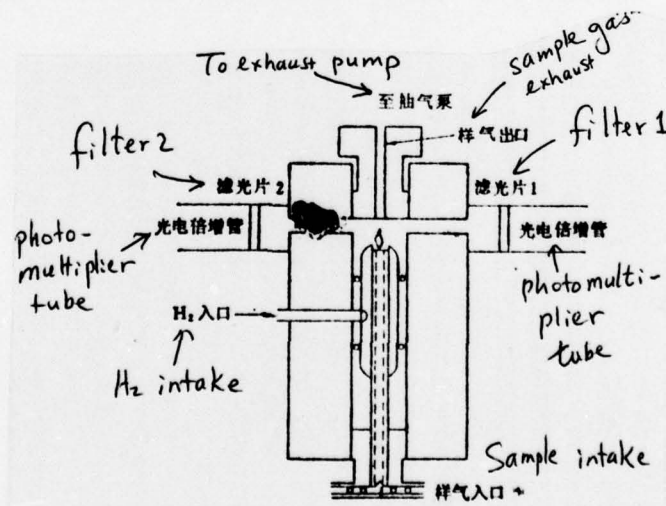
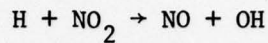


Fig. 9. Nitrogen monoxide flame reaction detector.

This method can be used in detecting the total amount of NO_x in air since the nitrogen dioxide is rapidly reduced to NO by the hydrogen atom in the hydrogen-rich flame:

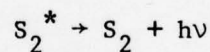
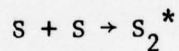


$$k = 2.9 \times 10^{10} \text{ liter/gram molecule} \cdot \text{sec.}$$

The flame luminescence reaction and detection device may also be used together with the gas phase color spectrometer for detecting and identifying nitrogen compounds.

Sulfur Dioxide and Hydrogen Sulfide

Various sulfide pollutants can be monitored by the flame chemiluminescence reaction. (2, 34-36, 42) A strong blue chemiluminescence occurs when volatile sulfides are burnt in a hydrogen-rich flame. The origin of this blue luminescence is from the fact that sulfides are reduced to sulfur atoms by the hydrogen and the atoms combine to form molecules of S_2 .



The emission spectrum of S_2^* is between 350 and 460 $\text{m}\mu$ (see Fig. 10).

The maximum emission wavelength (λ_{max}) is ~~391~~ $\text{m}\mu$.

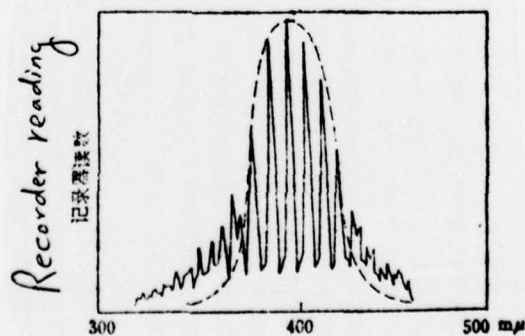


Fig. 10. Emission spectrum of S_2^* .

The sensitivity of this method is 0.2 millimicrogram. The intensity of the emitted light is proportional to the square of the sulfide concentration in the 0.2-100 millimicrogram SO_2 range since the reaction involves the combination of every two sulfur atoms to form one S_2 molecule.

A hydrogen-air-rich flame is used in this scheme since the flame luminescence efficiency of sulfur is greatest below 390°C . The flow rates of the hydrogen gas and the air are both 200 milliliter/minute. When the sulfur dioxide is in coexistence with hydrogen sulfide, the sample gas can be passed through a silver tube heated to 135°C to remove the hydrogen sulfide, and the contents of sulfur dioxide and hydrogen sulfide in the atmosphere are measured separately (see Fig. 11).

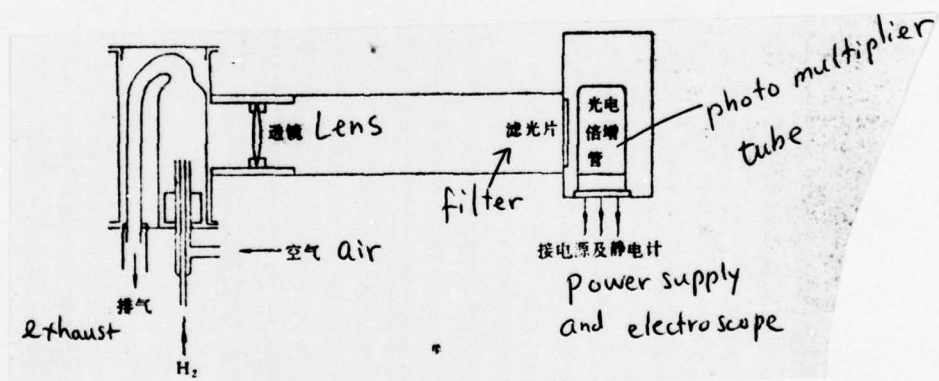


Fig. 11. Sulfur dioxide detector.

The standard sources of the sulfur dioxide and the hydrogen sulfide are kept in diffusion tubes at constant temperature. See Fig. 12 for the calibration system. The diffusion tube is made of polytetrafluoroethylene. Pure sulfur dioxide or hydrogen sulfide in their liquid state are kept in

the tube and the vapor pressure in the tube is maintained constant by the constant temperature bath. Under these conditions, the amount of gas diffused out of the tube is a constant. A constant gas source in the 1-100 ppm range can thus be obtained by proper adjustments of the diffusion area and the amount of air used for dilution. The output of the diffusion tube is steady before the liquid inside has completely evaporated. Its maximum life is six months.

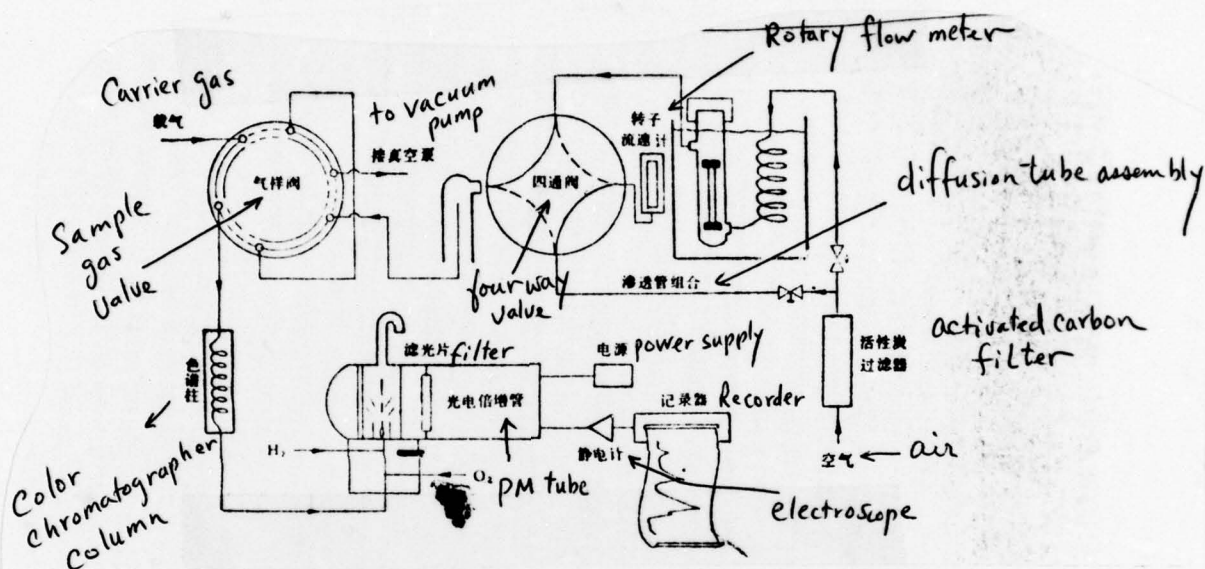


Figure 12. Automatic gas phase color spectrometer for the detection of trace sulfides in the atmosphere by flame photometer.

The flame luminescence detector of sulfur can be conveniently combined with gas phase color spectrometer and used in the sensitive and efficient detection and identification of sulfides. The combination, when used in the study of air pollution, is capable of rapid detections of all kinds of sulfide pollutants [37-39] of the ppb class in the atmosphere including SO_2 , H_2S , CH_3SH , CH_3SCH_3 , etc. Its arrangement is as shown in Figure 12.

The gas chromatographer column is made of polytetrafluoroethylene. Its length is 36 feet and the inner diameter is 1/8 inch, packed with No. 40-60 Haloport-F (beads of polytetrafluoroethylene). Fixing solution is 12 grams of polyphenylether and 0.5 gram of phosphoric acid. The temperature of the column is kept at 50°C and the ambient temperature of the detector is $105 \pm 3^\circ\text{C}$. Nitrogen is used as the carrier gas and its flow rate is 100-120 milliliter/minute. The flow rates of hydrogen and oxygen are 80 and 16 milliliter/minute, respectively. The total separation time is eight minutes and the separation spectrum is shown in Fig. 13. External standard is used in the detection process and the system is calibrated by 10 milliliters of sulfide gas of known concentration.

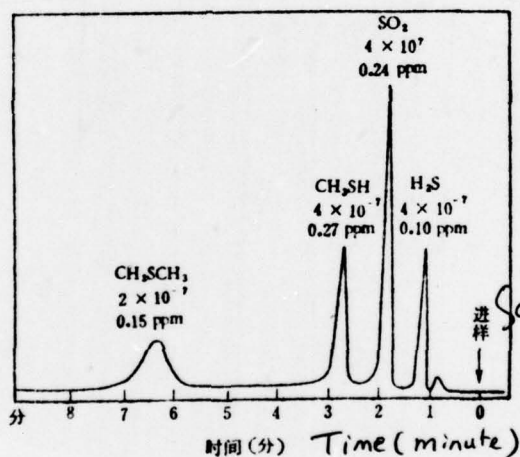
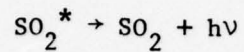
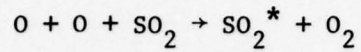
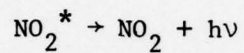
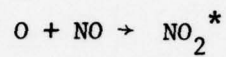


Fig. 13. Spectrum of the SO_2 , H_2S , CH_3SH and CH_3SCH_3 mixture below 1 ppm level.

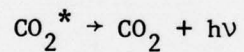
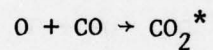
In the atmosphere, SO_2 , NO , NO_2 and CO can all be detected by their gas phase chemiluminescence reactions with the oxygen atom. Their reactions and detection ranges are summarized below.



$$\lambda_{\text{max}} = 200 \text{ m}\mu, \text{ sensitivity} = 0.001 \text{ ppm SO}_2. \text{ (1)}$$



$$\text{Spectrum range} = 400\text{-}1400 \text{ m}\mu, \text{ sensitivity} = 0.001 \text{ ppm NO. (32,33,40)}$$



$$\text{Spectrum range} = 300\text{-}500 \text{ m}\mu, \text{ sensitivity} = 1 \text{ ppb. (34,41)}$$

The key to the above reactions is a source of oxygen atoms. To date they are not widely used because a stable source of oxygen atoms is not yet readily available.

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