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Invited Paper

Chemiluminescence applied to air pollutants assessment

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Air pollution from both stationary (e.g. factories) and mobile (e.g. cars) sources includes many substances such as sulfur dioxide, nitrogen oxides, carbon monoxide, ammonia, hydrazine etc. Chemiluminescence (CL) method for monitoring these pollutants is based on production of electromagnetic radiation as a result of a chemical reaction. One of the reaction products is in an excited state and emits light on returning onto its ground state. In a reaction chamber placed in front of photomultiplier the reactants are mixed. The chemiluminescent emission is proportional to the concentration of pollutant. A detection limit of a few ppm can be achieved. The detailed description on the CL method and suitable instruments are given. Atmospheric ozone is an important component leading to the formation of photochemical smogs. Detection and measurements of ozone by CL are also discussed. Response characteristics of the CL instrument are presented including its sensitivity to ozone detection, calibration curves and flow rate influence.

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1. Introduction

Atmospheric ozone is an important factor leading to the formation of photochemical smog, together with the oxides of nitrogen and certain hydrocarbons [1-5]. Ozone may be formed as a natural component in the upper atmosphere by solar radiation [1,2]. High levels of ozone in the lower atmosphere result also from photochemical reactions. Ozone is also generated in ionizing irradiation processing.

Chemiluminescence consists of a chemical reaction forming an excited-state product which undergoes one or more relaxation processes to attaing its ground state.

Chemiluminogenic reactions which occur in the gas phase must be exoenergetic to generate a significant fraction of products in an excited state. The chemiluminogenic properties of ozone can be attributed to the weak O-O (104.0 $kJmol^{-1}$) bond in ozone which is broken to form stronger O=O (497.42 $kJmol^{-1}$) in molecular oxygen and much stronger C=O (718.96 kJ mol^{-1}) bonds in reactions with many organic compounds.

The chemiluminescence from ozone includes the following reactions [3]:

(a) Nitrogen monoxide

$NO + O_3 \rightarrow NO_2^* + O_2$

$NO_2^* \rightarrow NO_2 + (h\upsilon)_{CL}$ (600-800 nm)

The reaction is used for continuously monitoring nitrogen monoxide with linearity over 6 orders of magnitude in polluted atmospheric air [6].

Nitrogen dioxide does not interfere with the measurement and can be determined only after photolytic [7] or thermal [8] conversion to nitrogen monoxide.

(b) Ethylene

The overall reaction can be written as [9]:

$2C_2H_4 + 2O_3 \rightarrow 4CH_2{=}O + O_2 + (h\upsilon)_{CL}$ (400 nm)

Many other alkenes such as: propylene, isobutylene, 2,3-dimethyl -2-butane,1-pentene, cyclopentene, cyclohexene were olso used in O_3 detection [10].

(c) Carbon monoxide

The chemiluminescent reaction can be written [11]:

$CO + O_3 \rightarrow CO_2 + O_2 + (h\upsilon)_{CL}$ (410 nm)

(d) Sulfur compounds

Ozone reacts with sulphur compounds to generate excited SO_2 [12]. Hydrogen sulphide and methyl mercaptan generate CL:

$H_2S + O_3 \rightarrow SO_2 + H_2O + (h\upsilon)_{CL}$ (280 nm)

$CH_3SH + O_3 \rightarrow CH_3OH + SO_2 + (h\upsilon)_{CL}$ (280 nm)

The introduction of H_2S into the hydrogen diffusion flame take place formation of excited S_2 molecules [4]:

$H_2S + H \rightarrow HS + H_2$

$HS + H \rightarrow S + H_2$

$S + S \rightarrow S_2^* \rightarrow S_2 + (h\upsilon)_{CL}$ (300 – 460 nm)

(e) Nickel carbonyl

When nickel carbonyl is mixed with O_3 and CO, the following reaction occur [13]:

$Ni(CO)_4 + O_3 \rightarrow NiO + products$

$NiO + CO \rightarrow Ni + CO_2$

$Ni + O_3 \rightarrow NiO^* + O_2$

$NiO^* \rightarrow NiO + (h\upsilon)_{CL}$ (500 nm)

Nickel tetracarbonyl is a toxic compounds heaving a threshold limit value in air of 1ppb.

(f) Ammonia

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
$4NO + 4O_3 \rightarrow 4NO_2^* + 4O_2$
$NO_2^* \rightarrow NO_2 + (h\upsilon)_{CL}$ (600 – 875 nm)

(g) Hydrides

When ozone reacts with AsH_3, chemiluminescence is generated by a complex reaction sequence, with components in ultraviolet and visible, region respectively [14].

The visible emission is due to the following reactions:
$AsH_3 + O_3 \rightarrow HO_2 + H_2AsO$
$HO_2 + O_3 \rightarrow OH + 2O_2$
$OH + AsH_3 \rightarrow H_2O + AsH_2$
$AsH_2 + O_2 \rightarrow AsO + H_2O$
$AsO + O_3 \rightarrow AsO_2^* + O_2$
$AsO_2^* \rightarrow AsO_2 + (h\upsilon)_{CL}$
The UV emission is due to the reactions:
$AsO_2^* + O_3 \rightarrow AsO_2 + O_2 + O$
$AsO + O \rightarrow As + O_2$
$As + O_3 \rightarrow AsO^* + O_2$
$AsO^* \rightarrow AsO + (h\upsilon)_{CL}$

This study was concerned with the development of a fast-responding analyzer based on the chemiluminescence reaction between ozone and a fluorescent dye. Also, the destructive effect on ozone of some halogenated solvents is described.

2. Experimental

The schematic diagram of the chemiluminescence ozone detecting system used in our experiments is shown in Fig. 1.

Ozone was directed across the chemiluminescent disk and was transported by an oxygen stream. A flow-meter we used to check the flow rate. The chemiluminescent disk was placed at less than 10 mm from the photomultiplier window (EMI 9558 QA type). The disk was located in a reaction cell (made from teflon) having the same diameter as the PM light-tight box (Fig. 2).

The ozone source was a small ozonizer based on electric discharge in pure oxygen. The ozone yield was measured by bubbling through neutral buffered KI and the resulting iodine was titrated using standard thiosulphate [15]. Several porous ceramic disks were impregnated with 10^{-3} M alcoholic solution of various organic dye compounds such as: rhodamine B, eosin Y; fluorescein, erythrosine etc. Halogenated compounds (chloroform, bromform, dichlorethane, dibromethane, dibrompropane, dibrombutane, n-butyl bromide, isopropyl bromide, ethyl chloride, carbon tetrachloride, methylene chloride, tetrachlorethane, ethyl bromide) were used to study ozone depletion. The reagents had analytical purity degree.

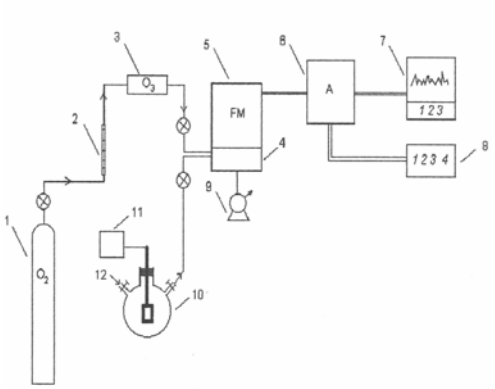

Fig. 1. Schematic diagram of the chemiluminescent ozone analyser: (1)oxygen cylinder; (2) flow-meter; (3) ozone generator; (4) detecting cell; (5) photomultiplier; (6) current-to-voltage converter; (7) graphic & digital recorder; (8) integrator; (9) aspiration pump; (10) photochemical reactor; (11) timer; (12) rectant inle.

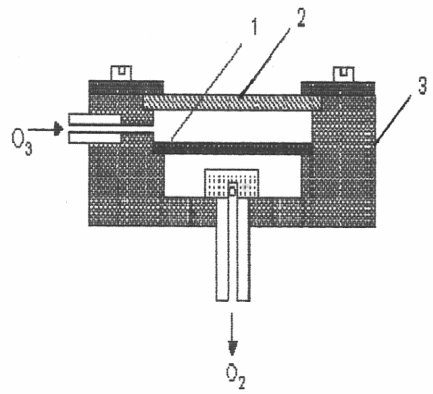

Fig. 2. Reaction cell: (1) ceramic disk; (2) glasswindow; (3) teflon housing.

3. Results and discussion

3.1 Ozone concentration measurement

A home made ceramic tablet was used as an absorbent. This is a disk shaped 30 mm diameter and 5 mm thick.

The signal obtained by permanent ozone measurement when the tablet was coated with 0.7 mg erhytrosin is shown in Fig. 3.

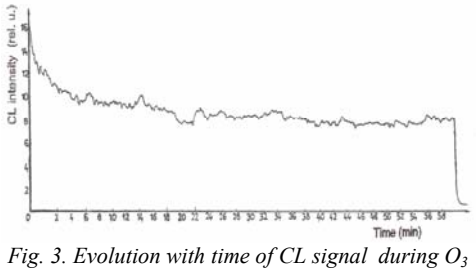

Fig. 3. Evolution with time of CL signal during O_3 permanent measurement.

As can be observed in Fig. 3, the reactin between O_3 and erythrosin is very rapid and a sudden increase of the signal is observed, followed by its diminution and stabilization for long time. Several different organic dyes have proven effective for the chemiluminescent reaction with ozone (Table 1).

The mechanism for the obtained CL signal can be written as follows:

$$2O_3 \rightarrow 3O_2 + (h\upsilon)_1$$

$$F + (h\upsilon)_1 \rightarrow F^* \rightarrow F + (h\upsilon)_2$$

The energy of the first reaction is transferred to the fluorescer wich play the role of a chemical amplifier.

Table 1. Sensitivity of some dyes coating a ceramic disk.

Dye	CL (rel. u.) integrated signal		
	1200 V	1300 V	1400 V
None	4	7	12
Rhodamine B	626	1160	1936
Eosin Y	197	313	493
Kresol red	120	130	183
Eosin red (aq)	100	180	300
Azur II eosin	43	62	97
Erythrosin	38	58	87
Dimethyl yellow	23	30	44
Evans blue	23	28	38
Bromphenol blue	22	29	41
Fluorescein	19	21	32
9-methyl-2,3,7-trioxifluoron	16	27	42
Alizarin S	13	16	28
Crystal violet	8	13	21
Methyl green	7	15	31
Indigo carmine	5	9	16

The influence of the amount of dye coating the disk and also the influence of voltage supplied to the photomultiplier tube were tested. The results are shown in Fig. 4.

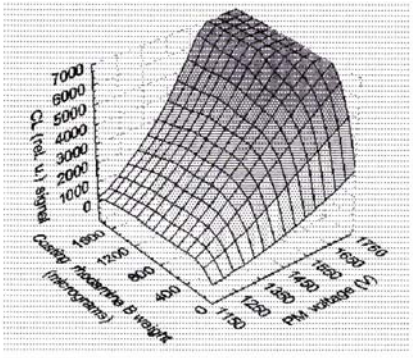

Fig. 4. Influence of rhodamine B amounts coating the porous disk and of the voltage supplied to the photomultiplier tube.

As can be seen in Fig. 4 when the disk coating dye amount increases, the CL signal also increases up to 250 μg coating rhodamine B, after wich a plateau is obtained. Fig. 4 also show that as the voltage supplied to the PM tube increases, the signal increases to at the same time with the noise.

The calibration curves for two voltages 1200 V and 1500 V were plotted (Fig. 5 and 6).

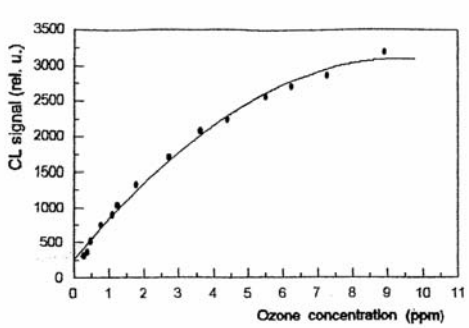

Fig. 5. Calibration curve for U_{PM}=1200 V.

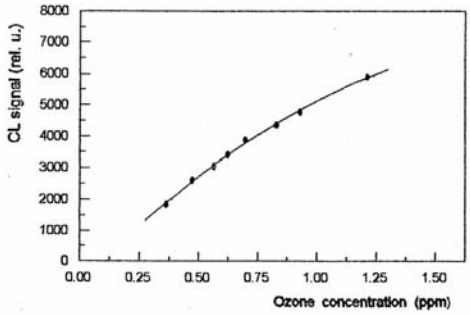

Fig. 6. Calibration curve for U_{PM}=1500 V.

Figs. 5 and 6 show that these calibration curves follows quadratic equations: $Y=248.271 + 605.191X - 32.173X^2$ and $Y= -626.303 + 7594.4678X - 1843.547X^2$ respectively, having a correlatio coefficient of 0.9978.

3.2 Ozone reaction with halogenated compounds

Ozone decay in the presence of some chlorinated or brominated derivatives (RX) of methane, ethane, propane, and butane have been studies. Ozone concentration measurement in RX absence and presence led to the determination of ozone relative decrease. Figs. 7 and 8 shows the decrease rate of CL intensity versus the amount of RX introduced in photochemical reactor. The reaction of ozone decay can be schematically written as follows:

$$RX + h\upsilon \rightarrow R^{\bullet} + X^{\bullet}$$

$$X^{\bullet} + O_3 \rightarrow XO^{\bullet} + O_2$$

$$XO^{\bullet} + O_3 \rightarrow X^{\bullet} + 2O_2$$

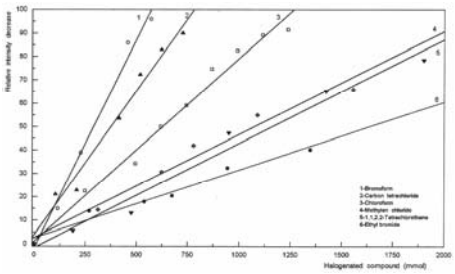

Fig. 7. Decrease rate of CL intensity with the amount of halogenated compound.

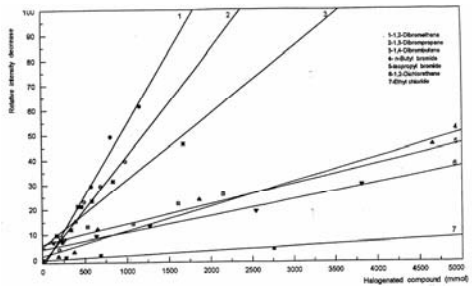

Fig. 8. Decrease rate of CL intensity with the amount of halogenated compound.

Table 2 gives the parameters of straight line equation resulting from the above mentioned measurements.

Table 2. Decrease rate of CL intensity for various halogenated compounds. Initial ozone concentration: 10 ppm.

Compound	Intercept	Slope	Correlation coefficient	No. of measurements
ethyl chloride	0.028	0.00173	0.996	7
1,2-dichlorethane	4.403	0.00652	0.971	7
isopropyl bromide	6.353	0.00794	0.975	6
n-butyl bromide	1.701	0.00979	0.985	7
1,4-dibrombutane	5.341	0.0266	0.967	7
ethyl bromide	2.559	0.0291	0.985	6
1,3-dibrompropane	-0.931	0.0425	0.989	6
methylene chloride	2.645	0.0441	0.986	6
1,2-dibromethane	-2.765	0.0570	0.989	6
1,1,2,2-tetrachlorethane	-1.821	0.0732	0.988	6
chloroform	1.135	0.078	0.984	9
carbon tetrachloride	3.954	0.123	0.988	6
bromoform	-1.720	0.178	0.995	5

By ploting the logarithm of the slopes of these straight line versus halogen weight, the straight line plotted in Fig. 9 is obtained.

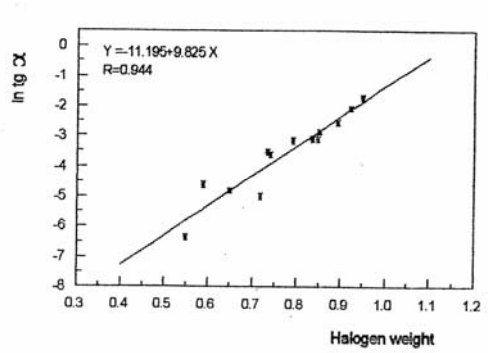

Fig. 9. Dependence of tgα on the halogen weight.

As can be observed the ozone reactivity with photohomolitically splitted halogen depends on the halogen weight in the given compound. Also, it can be seen that for chemically identical structures, brominate derivative reactivity is higher that chlorinate one. This is a consequence of C-Br bond energy is lower than C-Cl bond one.

4. Conclusions

- A new and simple instrument for the continous monitoring of ozone in air has been built.

The central unit of the apparatus is a ceramic disk wich is impregnated with a dye. Ozone flows over and through the disk generating CL relative to the concentration entering the unit;

- Various dye were tested and rhodamine B proved to generate the most intense CL radiation.

A detection limit of 1 ppb was obtained for Rhodamine B;

- The main advantage is that apparatus does not require special or dangerous gases;
- The instrument has been used successfully to estimate the ability oh halogenated solvents to consume ozone.

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