

Z. PARISHEVA\*, A. DEMIREV\*

## THE EFFECT OF OZONE ON HARMFUL, OXIDIZABLE SUBSTANCES IN INDUSTRIAL WASTE GASES

The ozone oxidation of sulphur dioxide, nitrogen monoxide, carbon dioxide and vapours of organic compounds present in industrial waste gases was studied. The oxidation was carried out in liquid phase and monitored by measuring the electroconductivity of the solution. The conductometric measurements were performed in DC and AC regimes. The results presented are for data measured in AC regime. The quantitative transformation of the initial substances into compounds in stable oxidation states was considered to be completed when the solution electroconductivity was no longer dependent on the quantity of ozone. By measuring the potential of the anode versus a standard calomel electrode (SCE) it was proved that only a chemical oxidation with ozone took place. The possibility of minimizing the quantity of the organic compounds contained in liquid phase by oxidizing them with ozone to carbon dioxide and water and the possibility of their quantitative determination were studied.

### 1. INTRODUCTION

The gaseous emissions of harmful substances into the atmosphere cause a number of ecological problems. Some of the major impurities in the industrial waste gases and the combustion products of organic energy carriers, which need to be removed, are mainly oxides of carbon, oxides of nitrogen and sulphur and various low-molecular hydrocarbons.

The main basic anthropogenic sources of sulphur dioxide and nitrogen monoxide are thermal power stations, industrial plants, transport and aviation.

It has been established that sulphur dioxide is mainly produced due to combustion of sulphur-containing fuels – 95% of the sulphur escapes into the atmosphere as sulphur dioxide [1]. Nitrogen monoxide occurs chiefly in industrial waste gases as well as in combustion products emitted by thermal stations. The vapours of some organic compounds also pollute the atmosphere, and their concentration in the air in the vicinity of some industrial plants exceeds the permissible limits.

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\* Technical University, Plovdiv, Bulgaria.

These compounds play an important part in the chemistry of the atmosphere: they have a deleterious effect on man and the biosphere, and are powerful corroding agents accelerating the damage and structural failure of equipment and monuments of culture.

The concentration of these gases in the atmosphere is not constant. It depends not only on their quantities emitted but also on a number of other factors which determine their chemical transformations. Oxidation, for example, is one of the ways allowing us to reduce the initial concentrations of nitrogen monoxide and sulphur dioxide in the atmosphere.

The ozone oxidation of nitrogen monoxide, carbon dioxide, sulphur dioxide and such organic compounds as acetone and glycerine adsorbed in aqueous phase was studied in the present paper. The possibility of reducing the quantities of these harmful compounds is based on the fact that during their oxidation with ozone only oxygen and the stable nitrogen and sulphur compounds in the highest oxidation states are produced.

## 2. EXPERIMENTAL DETAILS

Two-electrode electrolytic cell with platinum electrodes was used for the determination of the electroconductivity of the aqueous solutions of the adsorbed sulphur dioxide, carbon dioxide and nitrogen monoxide. The cell was kept at 293 K ( $\pm 0.1$  K), and its constant  $-k = I/s$  [m] was determined by measuring the resistance of a standard solution of KCl of a known specific resistance [2].

The specific conductivity of the solutions was determined in DC and AC regimes. In the first case, a regulated voltage supply source TEC-21 with a working voltage of 2 V and a numeral multimeter V560 measuring the current in the system were used. In the second case, an alternating current bridge BM 599 RLCG with a working frequency of 20 kHz was applied.

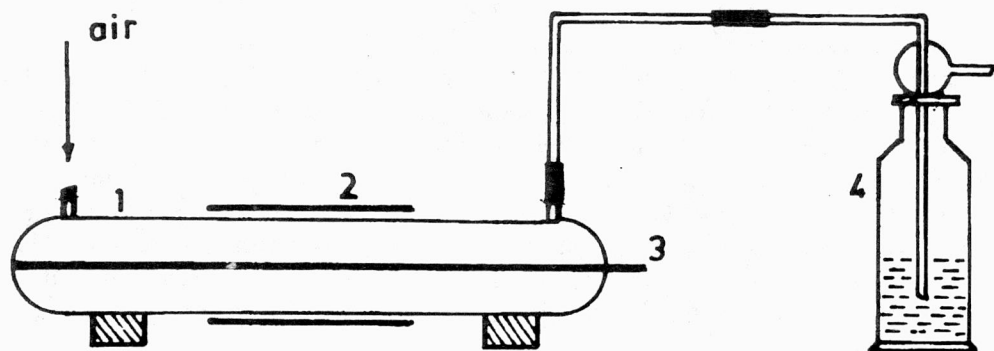


Fig. 1. Sketch of the laboratory ozonizer

1 - glass tube, 2 - low-voltage electrode, 3 - high-voltage electrode, 4 - solution studied

A lab ozonizer, described in [3], was used as a source of ozonized air. The ozonizer is sketched out in figure 1. The discharge part is a glass tube (1), and a high-voltage electrode (3) is placed on its axis. Electric impulses with amplitude 14 kV were supplied to the high-voltage electrode. The air to be ozonized was compressed by means of a ventilator and passed through the tube; then the ozonized air passed through the solution studied (4). The amount of ozone produced was regulated by changing the frequency and duty factor of electric impulses supplied to the high-voltage electrode. The amount of the ozone in the gas mixture was determined by iodometry [4].

Sulphur dioxide, carbon dioxide and nitrogen dioxide needed for the experiment were prepared under laboratory conditions and adsorbed in redistilled water until the desired concentration of the solution was reached.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

#### 3.1. OXIDATION OF SULPHUR DIOXIDE TO SULPHUR TRIOXIDE

The dependence of the electroconductivity of an aqueous solution of sulphur dioxide (sulphurous acid) on the time of treatment with ozone is shown in figure 2.

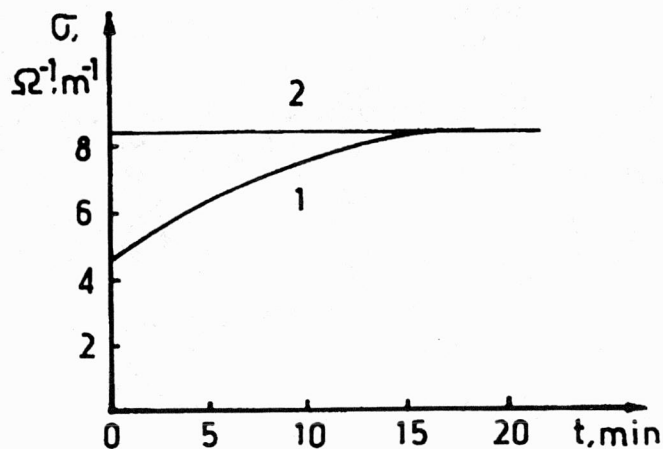


Fig. 2. Dependence of the specific electroconductivity of  $0.7646\text{ M H}_2\text{SO}_3$  (curve 1) and  $0.7646\text{ M H}_2\text{SO}_4$  (curve 2) on the time of treatment with ozone

The electroconductivity of the solution increased with the increase of the ozone amount passed through the solution. After a 15-minute treatment with  $27.93 \cdot 10^{-6}$  g of ozone introduced (table 1), the electroconductivity reached a constant value corresponding to the electroconductivity of sulphuric acid with a molarity equal to the molarity of the solution obtained.

Table 1

Time of treatment with ozone, min.	5	10	15	20	25
Ozone amount, $10^{-6}$ g	9.41	18.82	27.93	37.64	49.36

This indicates that full amount of sulphur dioxide (sulphurous acid) was oxidized to sulphur trioxide (sulphuric acid). The complete quantitative transformation of sulphur dioxide into sulphur trioxide was confirmed by the concentrations of the initial sulphurous acid and the produced sulphuric acid determined experimentally (by titration). The experimental and theoretical values of the respective concentrations are shown in table 2. The theoretical values were calculated using the data for the solubility of the sulphur oxides in water under the given conditions.

Table 2

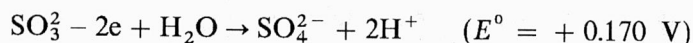
C, mol/dm <sup>3</sup>	Theoretical values	Titration with NaOH	Titration with residual iodine
H <sub>2</sub> SO <sub>3</sub>	1.7656	1.7432	1.7646
H <sub>2</sub> SO <sub>4</sub>	1.7656	1.7646	—

The electroconductivity was measured in DC and AC regimes. The values obtained for both regimes are given in table 3. Figures 2–5 are constructed using the data measured in AC regime.

Table 3

Treatment time, min	Electroconductivity, $\Omega^{-1} \text{ m}^{-1}$	
	DC regime	AC regime
0	0.626	5.105
5	1.926	5.432
10	2.696	6.936
15	3.371	8.284
17	3.371	8.824

The idea of electrooxidation of the sulphite anion to sulphate one by the reaction:



was ignored after measuring the potential of the anode versus a standard calomel electrode (SCE). The values obtained for the electrode potential: + 0.01 V, -0.02 V

and  $-0.12$  V show that under the conditions selected, the oxidation of the sulphite anion to sulphate one is a pure chemical process completed under the effect of ozone.

### 3.2. EFFECT OF OZONE ON THE OXIDATION OF NITROGEN OXIDE TO NITROGEN DIOXIDE

The dependence of the specific electroconductivity of aqueous solution of nitrogen oxide on the amount of ozone introduced is given in figure 3. In this case, the specific electroconductivity was also increased proportionally to the amount of ozone introduced, i.e., a reaction of oxidation of nitrogen monoxide (nitrous acid) to nitrogen dioxide (nitric acid) took place.

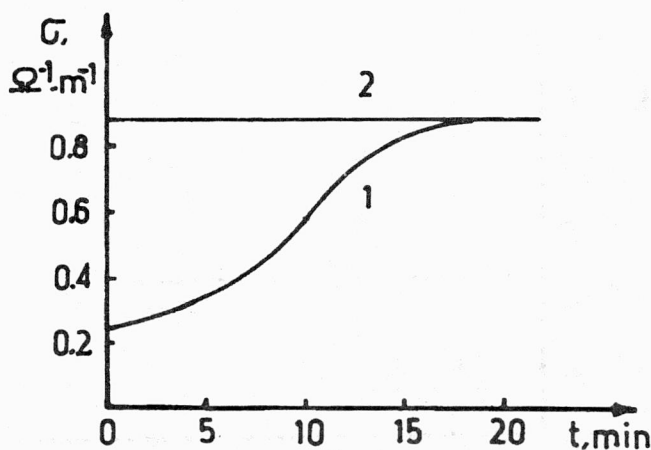
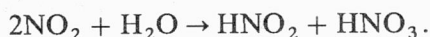
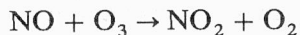


Fig. 3. Dependence of the specific electroconductivity of 0.0769 M  $\text{HNO}_2$  (curve 1) and 0.1143 M  $\text{HNO}_3$  (curve 2) on the time of treatment with ozone

At the beginning of the treatment with ozone, the solution was a mixture of nitric and nitrous acids because part of the nitrogen monoxide had been oxidized to nitrogen dioxide by the oxygen in the air:

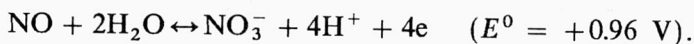


At the end of the process, full amount of the dissolved nitrogen monoxide was oxidized to nitrogen dioxide according to the following equation:



and new quantities of nitric acid were obtained.

The potentials measured versus a standard calomel electrode (SCE) proved that only a chemical oxidation with ozone took place. The values of the electrode potential ( $+0.097$  V at the starting point and  $+0.333$  V after a 15 minute treatment with ozone) were different from those of the electrochemical oxidation taking place according to the reactions:



### 3.3. ELECTROCONDUCTIVITY OF AQUEOUS SOLUTION OF CARBON DIOXIDE

The dependence of the electroconductivity of the aqueous solution of carbon dioxide on the time of treatment with ozone is given in figure 4. As can be seen, the electroconductivity does not depend on the amount of the ozone passed through. The carbon atom in carbon dioxide is in its highest oxidation state and a reaction with ozone is impossible.

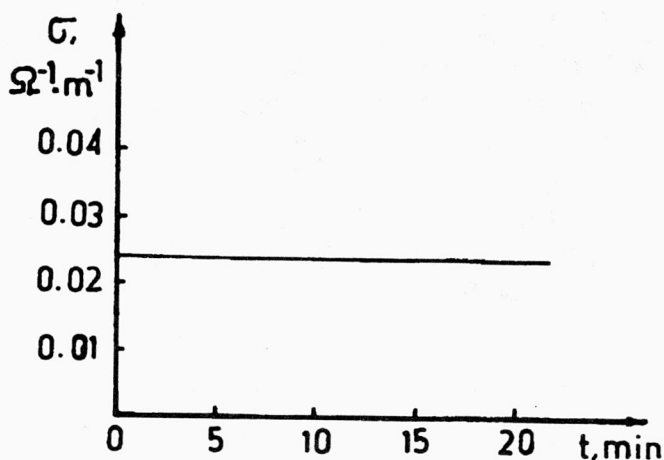
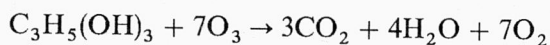


Fig. 4. Electroconductivity of aqueous solution of carbon dioxide

### 3.4. OXIDATION OF ORGANIC SUBSTANCES

Ozone oxidizes organic compounds to form carbon dioxide. The decomposition of acetone and glycerine taking place according to the equations [5]:



was established by measuring the electroconductivity of their aqueous solutions. Such organic compounds as acetone and glycerine were chosen because their molecular weights are close to those of the hydrocarbons of low molecular weights. In addition, acetone and glycerine are readily soluble in water due to the presence of polar groups in their molecules. The increase in the electroconductivity observed during the treatment with ozone results from the release of carbon dioxide which reacts with water to form carbonic acid.

The results obtained during the treatment of 10 cm<sup>3</sup> of organic substance dissolved in 40 cm<sup>3</sup> of distilled water by means of ozone are given in table 4 and figure 5.

Table 4

Treatment time, min.	Electroconductivity, $\Omega^{-1} \cdot \text{m}^{-1} \cdot 10^3$	
	Acetone	Glycerine
30	1.200	1.150
60	1.836	1.634
90	3.692	3.486
120	5.046	5.046
140	5.046	5.597

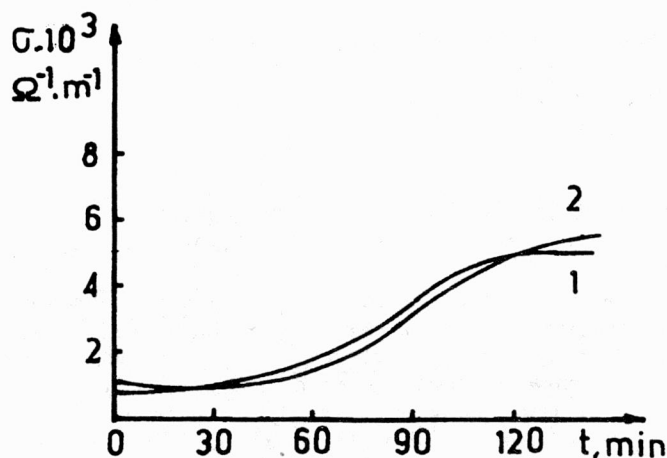


Fig. 5. Dependence of the specific electroconductivity of aqueous solutions of 2.727 M acetone (curve 1) and 2.736 M glycerine (curve 2) on the time of treatment with ozone

The oxidation of the organic substances to carbon dioxide and water allows the determination of their concentrations by plotting a standard curve representing the electroconductivity of the solution as a function of known concentrations of carbon dioxide aqueous solution. The details concerning these relationships are a subject of further investigation.

#### 4. CONCLUSIONS

A complete chemical oxidation of industrial gases adsorbed in liquid phase was established using the conductometric method of measurements in DC and AC regimes.

The data on the complete oxidation of the organic substances in the liquid phase to carbon dioxide and water shows that these substances can be determined quantitatively by measuring the electroconductivity of standard solutions of carbon dioxide.

On the basis of the ozone oxidation of the industrial gases to non-toxic products and oxygen, the following process chart can be implemented to make them harmless:

1. Taking the industrial waste gases away and absorbing them into water filters.
2. Treating the produced sulphurous and nitrous acids with ozone to their complete quantitative transformation into sulphuric and nitric acids.
3. Neutralizing the acids obtained to harmless products.

#### REFERENCES

- [1] RAVINSKI F.Y., EGOROV P.I., *Ozon, oksii azota i sery v nizhnei atmosfere*, Leningrad, Gidrometeoizdat, 1086.
- [2] *Metody izmereniya v elektrokhemii*, 1977, Izd. „Mir”, Moscow.
- [3] ARMEJKOV E., *Oustrojstvo za ozonirane*, diplomna rabota, TU-Plovdiv, 1993.
- [4] HERCH P., DENRINGER K., *Anal. Chem.*, 1963, 35, 897.
- [5] *Alpine air products, inc.*, Minneapolis.

#### WPLYW OZONU NA SZKODLIWE, UTLENIALNE SUBSTANCJE WYSTĘPUJĄCE W PRZEMYSŁOWYCH GAZACH ODLOTOWYCH

Zbadano proces utleniania ozonem dwutlenku siarki, tlenku azotu, dwutlenku węgla i par składników organicznych występujących w przemysłowych gazach odlotowych. Proces utleniania prowadzono w fazie ciekłej i kontrolowano, dokonując pomiaru przewodnictwa roztworu. Pomiarów konduktometrycznych dokonywano, stosując prąd stały i zmienny. Przyjęto, że ilościowe przejście substancji występujących na początku procesu w stan stały z powodu utleniania zachodzi wówczas, gdy przewodnictwo roztworu nie zależy już od dawki ozonu. Mierząc potencjał anody w stosunku do standardowej elektrody kalomelowej (SCE) wykazano, iż jedynie chemiczne utlenianie ma miejsce. Zbadano możliwość zmniejszenia ilości organicznych składników w fazie ciekłej, utleniając je ozonem do dwutlenku węgla i wody.

#### ВЛИЯНИЕ ОЗОНА НА ВРЕДНЫЕ, ОКИСЛЯЕМЫЕ ВЕЩЕСТВА, ВЫСТУПАЮЩИЕ В ПРОМЫШЛЕННЫХ ОТХОДЯЩИХ ГАЗАХ

Исследован процесс окисления озонem двуокиси серы, окиси азота, двуокиси углерода и пар органических компонентов, выступающих в промышленных отходящих газах. Процесс окисления вели в жидкой фазе и контролировали, измерения проводимость раствора. Кондуктометрические измерения выполняли, применяя постоянный и переменный ток. Было принято, что количественный переход веществ, выступающих в начале процесса в жидкую фазу происходит тогда, когда проводимость раствора не зависит уже от дозы озона. Измеряя потенциал анода по отношению к стандартному каломельному электроду (СЦЭ), обнаружили, что имеет место лишь химическое окисление. Исследована возможность понижения количества органических компонентов в жидкой фазе, окисляя их озонem в двуокись углерода и в воду.