

Spectrophotometric Determination of Ozone in Ozonized Air Currents Using a Flow Injection System

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Neste trabalho, propõe-se procedimento alternativo para a determinação espectrofotométrica de ozônio em correntes de ar ozonizado ($\text{mg O}_3 \text{ L}^{-1}$ de ar). Com o objetivo de aumentar o número de determinações, com uma mesma solução absorvedora e a velocidade analítica na determinação de ozônio, investigou-se a redução nos tempos de contato gás-líquido (ar/ O_3 - solução absorvedora) e o uso do sistema de análise por injeção em fluxo (FIA). O procedimento proposto envolve a oxidação pelo ozônio de uma solução de iodeto de potássio 1% em ácido bórico 0,1 M e posterior medida espectrofotométrica do íon triiodeto liberado. Duas configurações são apresentadas: uma para a faixa de trabalho de 0,30 a 5,60 $\text{mg O}_3 \text{ L}^{-1}$ (sistema A) e outra para a faixa de 0,50 a 18,90 $\text{mg O}_3 \text{ L}^{-1}$ (sistema B). Esses sistemas, além de ampliarem a faixa de trabalho, permitem maior velocidade analítica e redução de consumo de reagentes/amostra, com boa precisão (0,2 e 0,9%, respectivamente). Os resultados obtidos da aplicação do procedimento proposto na determinação de O_3 em correntes de ar são comparáveis aos do procedimento convencional (erros relativos: -2,2 e -5,0% para os sistemas A e B, respectivamente).

This study proposes an alternative procedure for the spectrophotometric determination of ozone in ozonized air currents ($\text{mg O}_3 \text{ L}^{-1}$ air). In order to increase the number of determinations using the same absorbing solution and analytical speed in ozone determination, the reduction in the time of gas-fluid contact (air/ O_3 - absorbing solution) and the use of the flow injection analysis (FIA) system were investigated. The proposed procedure involves the oxidation of a 1% potassium iodide in 0.1 M boric acid solution by ozone, followed by the spectrophotometric measurement of the released triiodide ion. Two configurations are presented: one for the working range of 0.30 to 5.60 $\text{mg O}_3 \text{ L}^{-1}$ (system A) and the other for the range of 0.50 to 18.90 $\text{mg O}_3 \text{ L}^{-1}$ (system B). These system, in addition to expanding the work range, permit greater analytical speed and a reduction in the consumption of reagents/sample, with good precision (0.2 and 0.9%, respectively). The results obtained by applying the proposed procedure to O_3 determination in air currents are comparable to those obtained with the conventional procedure (relative errors of -2.2 and -5.0% for systems A and B, respectively).

Keywords: *FIA, spectrophotometry, ozone, ozonization*

Introduction

The ozonization process has proven to be an efficient and economical alternative for the treatment of water and effluents¹⁻³. As a consequence, the use of ozone for these purposes has increased considerably and new automatic (and/or automated) analytical procedures have been developed for its determination^{4,5}.

Most of the colorimetric analytical methods reported for the determination of ozone in the gas phase have been based on ozone absorption in collecting systems containing absorbing solutions which provoke a reduction of the absorbed gas⁶⁻⁹. These methods usually present drawbacks such as excessive manipulation and the low frequency of determinations. To obviate these difficulties, we developed an analytical procedure for ozone determination in ozon-

ized air currents using flow injection analysis (FIA), as well as reduced gas-fluid contact times.

Ozone concentration was determined from standard iodine solutions (1 mL of a 0.001 N iodine solution is the equivalent of 240 μg of ozone). The procedure is based on the spectrophotometric measurement, at 390 nm, of the triiodide ion formed by the passage of ozone through an absorbing solution of 1% potassium iodide and 0.1 M boric acid. We used the FIA technique in the sampling and reading of the ozonized absorbing solution, and compared this procedure with the conventional one⁶.

Experimental

Apparatus

The ozonization unit illustrated in Fig. 1 was mounted according to the description in L egube *et al.*¹⁰, with some modifications. A modified commercial ozone generator was used (ddp 3000 V) and air at variable flow rates was used as the feeding gas.

The FIA system, set up as illustrated in Fig. 2, consists of an acrylic 2-channel commutator¹¹, an 8-channel peristaltic pump (Abimed Gilson), polyethylene tubes (0.8 mm internal diameter) and tygon tubes directly connected to the peristaltic pump. The measurements were carried out using a visible-UV spectrophotometer (Perkin Elmer, model 124, double beam) at 390 nm, with a quartz flow cuvette with an optical path of 10 mm. The corresponding signals were recorded with a Perkin Elmer 56 recorder, and the evaluation was based on peak height.

Reagents and solutions

All glassware was washed with neutral detergent solutions, 1% (v/v) nitric acid, and finally with distilled and deionized water to prevent contamination by reducing substances. All reagents used were analytical grade.

The absorbing solution of 1% potassium iodide and 0.1 M boric acid was prepared according to Flamm⁶, and the standard iodine solutions were prepared from a stock 0.1 N iodine solution in 0.6% potassium iodide. The iodine solutions were titrated against a 0.1 N sodium thiosulfate solution, and the titer of the thiosulfate solution was confirmed by standardization with a 0.1 N KIO_3 solution. The preservation of dilute iodine stock solutions during these standardizations was confirmed by absorbance measurements, and the solutions were kept in stoppered volumetric flasks and in quartz-stoppered cuvettes. The solutions were a maximum of 2-3 weeks old at the time they were used in these calibrations.

Method

Figure 1 illustrates the ozonization unit. The air passes through the ozone generator (3) and the ozonized air current is sampled in an ozone collecting flask (a Pyrex glass

reactor tube with a sintered glass dispersion tube, having a volume of 250 mL) containing 100 mL of the absorbing solution (at a temperature of 25 $^\circ\text{C}$). A three-way stopcock was adapted for the adjustment and equalization of the air/ozone flow (4, 5, 6). After equalization, the three-way stopcock was positioned for collecting flasks 7 and 8, and a contact time of 10 s for a work range of 0.30 to 5.60 $\text{mg O}_3 \text{ L}^{-1}$ was fixed for system A. A contact time of 60 s for a working range of 0.50 to 18.90 $\text{mg O}_3 \text{ L}^{-1}$ was fixed for system B. After 60 s, the samples were collected with the aid of the FIA system, with 150 μL of the sample injected into system A and 10 μL into system B. The injected samples were carried to the detector at a flow rate of 8 mL min^{-1} , and the signal was recorded at 390 nm. Sequential determinations (without replacement of the absorbing solution) were carried out up to the saturation time (7 min) of the potassium iodide and boric acid solution.

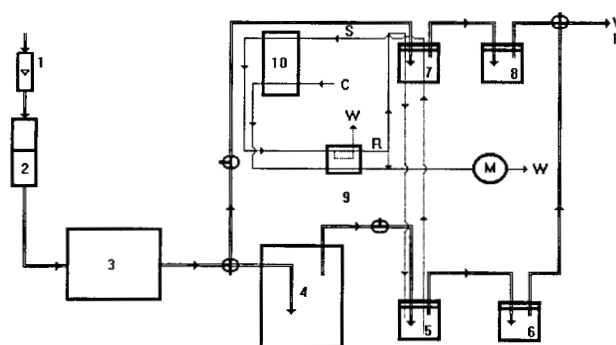


Figure 1. Ozonization unit: 1) flow meter, 2) drier, 3) ozone generator 4) ozonization reactor 5, 6, 7 and 8) ozone collecting flasks, 9) FIA system, 10) peristaltic pump, S) sample, C) carrier, W) waste, M) spectrophotometer (390 nm), R) recirculated sample, VP) vacuum pump.

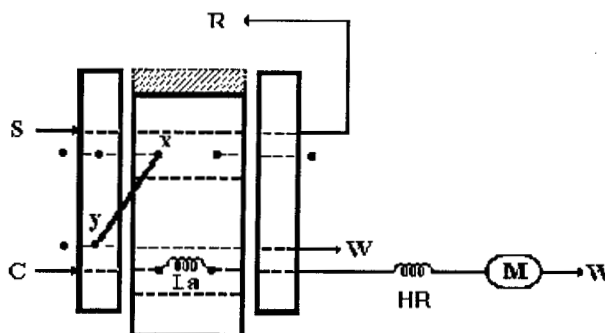


Figure 2. Configuration of the FIA systems. System A: S) sample (8 mL min^{-1}), C) sample carrier (1% potassium iodide solution / 0.1 M boric acid, 8 mL min^{-1}), La) sampling loop (150 L), HR) helicoidal reactor (25 cm), R) recirculated sample, W) waste, x-y) 7 cm connection, M) spectrophotometer (390 nm). System B: The same as System A except La) sampling loop (10 L), and HR) helicoidal reactor (125 L).

Results and Discussion

The effect of potassium iodide concentration on the absorbing solution

As previously reported by Schechter¹², increased concentrations of potassium iodide provoke an increase in the absorbance of the triiodide ion solution, this effect being more pronounced at lower ozone concentrations ($0.01\text{--}0.3\text{ mg L}^{-1}$). At higher ozone concentrations ($> 0.3\text{ mg L}^{-1}$), the effect is not significant and it is possible to use potassium iodide concentrations of 2, 5 and 10%. On this basis, the values prescribed by Flamm⁶ were maintained, since the 1% potassium iodide concentration does not provoke an appreciable fall in the analytical signal. Also, no appreciable increase in the absorbing solution saturation time as a function of the potassium iodide concentration was observed.

The effect of gas-fluid contact time

The objective was to use the lowest amount of contact time possible per determination in order to obtain the largest possible number of determinations with the same absorbing solution (obtained by the joint use of systems A and B). In the conventional procedure⁶, the time established is 10 min (a working range of $0.1\text{ to }3.5\text{ mg O}_3\text{ L}^{-1}$), a time exceeding the saturation time of the absorbing solution, which is 7 min under the conditions employed (observed by the formation of triiodide ion in a second ozone collecting flask - collecting flask 8 in Fig. 1). This is the maximum time for the sequential determinations without replacing the absorbing solution. Of the contact times studied, those obtained after 10 s or more were the times which provided results comparable to those of the conventional procedure. For a concentration of $0.80\text{ mg O}_3\text{ L}^{-1}$, relative errors of -2.2% (system A), and -5.0% (system B) were observed for contact times of 10 and 60 s, respectively. The ozone production rate (mg h^{-1}), the operability of the ozonization system, and the sensitivity of the method (and/or procedure) for ozone determination are limiting factors in the selection of the gas-fluid contact time. The gas-fluid contact time is proportional to the volume of absorbing solution used, since it is directly related to the iodine concentration produced by oxidation with ozone. Thus, the use of 20 mL of absorbing solution requires a contact time 5 times lower than that required with the use of 100 mL (in order for the same number of determinations to be maintained).

The configuration of the FIA system

FIA systems A and B were mainly developed in order to expand the working range and reduce sample consumption (ozonized absorbing solution) per determination. Thus, the sample was recirculated and the dispersal factors

in the injection zone were evaluated. For contact times up to 2.5 min, we used system A, and for up to 7 min, we used system B, which has a lower sensitivity. Both systems (A and B) provide linear analytical curves along the sequential determinations, as can be observed in Figs. 3 and 4. This behavior confirms the feasibility of sequential determinations, since the ozone production rate ($\text{mg O}_3\text{ h}^{-1}$) was kept constant (controlled by the feeding gas flow). Thus, the

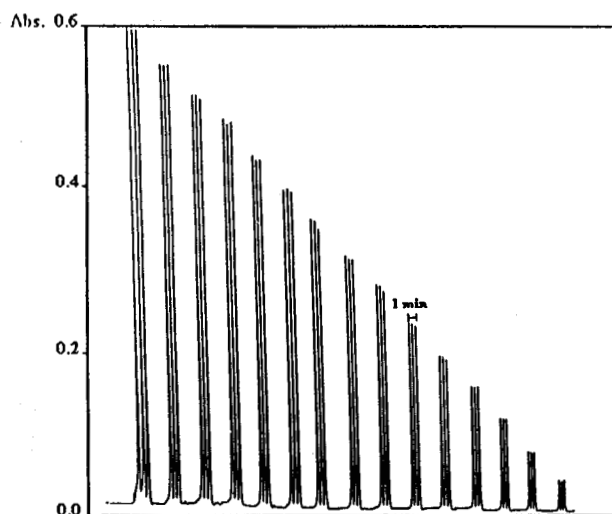


Figure 3. Sequential ozone determinations using System A. Recording of analytical signals (each set of three recordings corresponds to one determination and three samplings). The time of gas-fluid contact for each determination was 10 s, with a total contact time for all determinations of 150 s (or 15 determinations). Air/ozone flow, 60 L h^{-1} . Ozone production rate, $14.23 \pm 0.13\text{ mg O}_3\text{ h}^{-1}$.

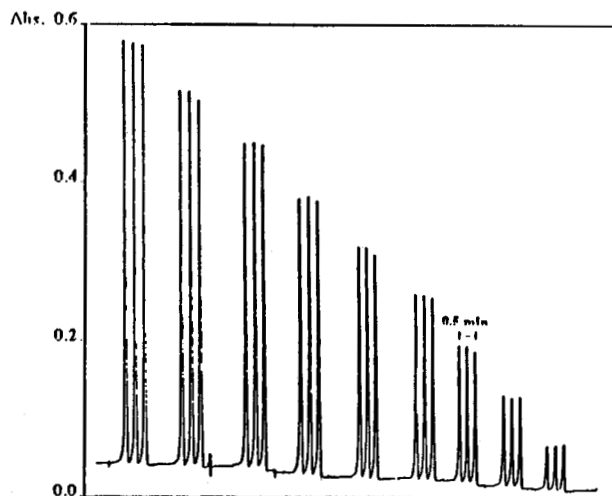


Figure 4. Sequential ozone determinations using System B. Recording of analytical signals (each set of three recordings corresponds to one determination and three samplings). The time of gas-fluid contact for each determination was 60 s, with a total contact time for all determinations of 450 s (or 9 determinations). Air/ozone flow, 60 L h^{-1} . Ozone production rate, $13.30 \pm 0.15\text{ mg O}_3\text{ h}^{-1}$.

variations along the analytical curves represent the possible ozone determinations (variations in absorbance within a given period of time related to ozone production).

The effect of potassium iodide concentration on the carrier solution

An attempt was made to fit the potassium iodide concentration in the carrier solution to the potassium iodide concentration in the absorbing solution (carrier / sample relationship). The use of water as a carrier caused a loss of sensitivity and a deformation of the analytical signal. In contrast, for potassium iodide concentrations from 0.1 to 1.0%, there was a significant increase in the sensitivity of the analytical signal, with higher concentrations (2, 5 and 10%) having no appreciable effect. Thus, the 1% concentration of potassium iodide was chosen as the concentration for the carrier solution.

The optimization of the flow injection analysis system – Evaluation of physical parameters

System A

System A was used for the working range of 0.30 to 5.60 mg O₃ L⁻¹, i.e., for gas-fluid contact times of 10 s to 2.5 min. For the configuration of the FIA systems, we followed the recommendations for single line FIA systems without chemical reactions¹³. In this case, an operation with flows exceeding 8 mL min⁻¹ is inconvenient because requires greater consumption of the sample / carrier solution, and at lower flows there is an increase in the cleaning time resulting in a decrease in the determination rate. Thus, when we selected a flow of 8 mL min⁻¹ we obtained a sampling rate of 180 samples per hour.

Sample volumes of 50, 75, 150 and 200 µL were tested and a volume of 150 µL was selected. With this volume we obtained the best cleaning time. Using the same parameters, we selected the length of the reactor. In this case, we opted for a reactor of 25 cm (internal Ø = 0.8 mm). It

should be pointed out that the selection of the sample volume in FIA systems is related to the volume of the absorbing solution used. If a volume of 20 mL were used instead of 100 mL, the volumes required for sampling in the FIA systems (size of the sampling loop) would be 5 times lower. This would guarantee the applicability of the system, since the total variation in the volume of the content of the ozone collecting flask due to sampling continues to be small (2.5%).

System B

System B was used for a working range of 0.50 to 18.90 mg O₃ L⁻¹, or for gas-fluid contact times of 60 s to 7 min. In this configuration of the FIA system, appropriate dispersals were obtained with a reactor of 125 cm (internal Ø = 0.8 mm), a sample volume of 10 µL, and the same flows as used in system A (8 mL min⁻¹). Thus, the working range was expanded, with the possibility of performing readings up to the total saturation time of the absorbing solution, with a sampling rate of 360 samples per hour. Table 1 shows a comparison of the FIA system with the conventional system.

For system A, the analytical curve was linear from 0.30 to 5.60 mg O₃ L⁻¹, and its equation was $Y = 0.0009 + 0.02X$ (where Y is the absorbance and X is the ozone concentration in mg L⁻¹), with a correlation coefficient of $r = 0.999$. Regarding precision, the relative standard deviation ($n = 7$) was 0.2%, for a rate of 0.75 mg O₃ L⁻¹. The detection limit (3σ) was calculated according to the IUPAC¹⁴, and a value of 0.30 mg O₃ L⁻¹ was obtained. For system B, the analytical curve was linear from 0.50 to 18.90 mg O₃ L⁻¹, with an equation of $Y = -0.002 + 0.006X$ and a correlation coefficient of $r = 0.999$. Regarding precision, the relative standard deviation ($n = 7$) was 0.9%, for a concentration of 0.75 mg O₃ L⁻¹. The detection limit under the optimized conditions was 0.50 mg O₃ L⁻¹.

Table 1. Comparison of the FIA systems with the conventional procedure⁶.

Analytical properties	Conventional procedure	FIA Systems	
		A	B
Sample volume used per determination*	100 mL	150 µL	10 µL
Number of determinations per 100 mL of absorbing solution	1	15	9
Sampling rate (h ⁻¹)	5	180	360
Time of gas-fluid contact (min)	10	0.16	1
Precision (%)	< 1%	0.20	0.9
Detection limit, DL (mg O ₃ L ⁻¹)	0.1	0.30	0.5
Working range (mg O ₃ L ⁻¹)	0.1 - 3.5**	0.30 - 5.60	0.50 - 18.90***

* Proportional to the volume of absorbing solution utilized.

** $\lambda = 352$ nm.

*** $\lambda = 390$ nm.

The signals from the standard iodine solution from 0.00 to 30.00 mg L⁻¹ (system A) and from 0.00 to 100.00 mg L⁻¹ (system B), can be observed in Figs. 5 and 6.

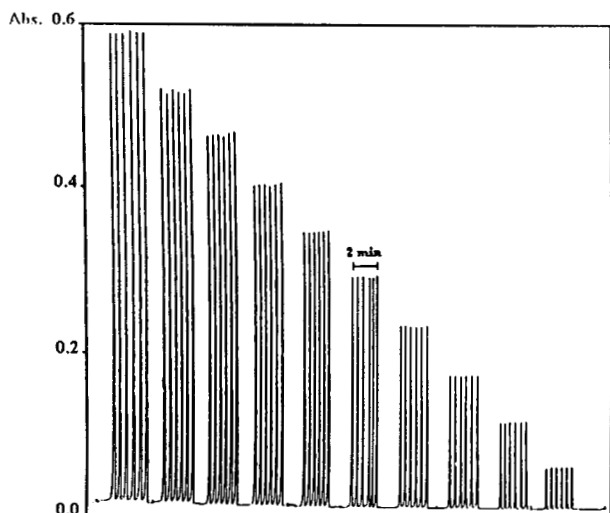


Figure 5. Recording of the analytical signals of the standard iodine solution: from right to left, standards from 0.00 to 30.00 mg l⁻¹ iodine.

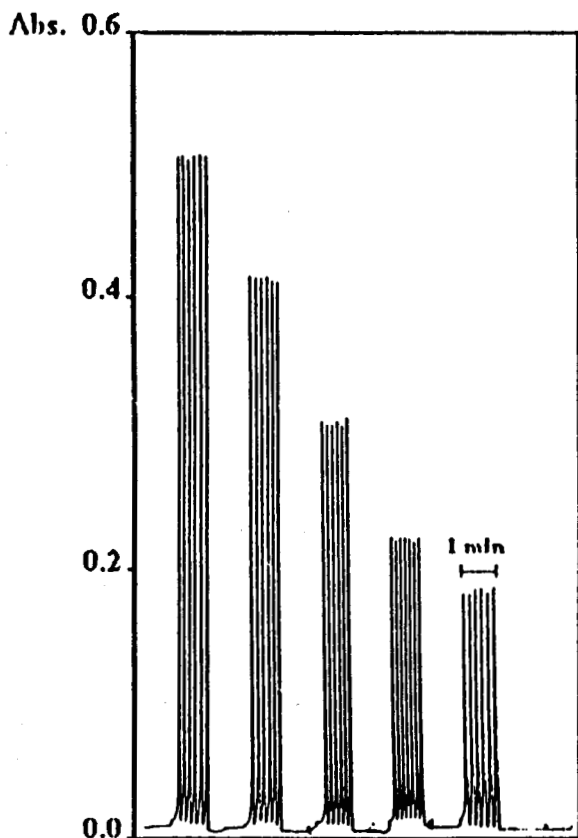


Figure 6. Recording of the analytical signals of the standard iodine solution: from right to left, standards from 0.00 to 100.00 mg l⁻¹ iodine.

The application to ozone determination at variable flows

Ozone production by electrical discharge is affected by factors such as air humidity, air pressure inside the generator, applied potential, voltage frequency, ozone concentration, and air temperature and flow through the generator¹⁵. In this respect, it is interesting to observe ozone production (in mg O₃ h⁻¹) at variable flows since this relationship can be used instead of a variation of potential in order to control ozone measurements in ozonization systems. Table 2 shows the air flow range (feeding gas) investigated and the respective ozone production in mg h⁻¹. As expected, it can be seen that the ozone production rate decreased with increasing air flow (the effect was more pronounced for higher ozone concentrations within the generator).

Conclusion

We conclude that the reduction in gas-fluid contact time and the use of the FIA system have advantages over the conventional procedure for ozone determination in ozonized air currents. Essentially, the proposed FIA systems permit a satisfactory dilution of ozonized absorbing solutions by controlling the dispersal in the injection zone. In turn, the reduction in gas-fluid contact time permits the exploitation of the total saturation time (concentration of the triiodide ion) of the absorbing solution, which is 7 min, by sequential determinations.

The results obtained with the FIA systems are equivalent to those obtained with the conventional procedure, with comparable sensitivity and replicability. However, the proposed procedure provides greater analytical speed, reduced manipulation of the solutions, and lower consumption of the absorbing solution per determination. Using systems A and B together, it is possible to carry out 24 sequential determinations with the same absorbing solution. In addition, the working range can be expanded from the conventional range of 0.1 to 3.5 mg O₃ L⁻¹ to 0.30 to 5.60 and 0.50 to 18.90 mg O₃ L⁻¹ for the FIA systems A and B, respectively.

Table 2. Variation of the ozone production rate with an air flow (feeding gas).

Flow L h ⁻¹	mg O ₃ h ⁻¹ (n = 7)
60	14.23 ± 0.13
120	15.40 ± 0.12
180	13.30 ± 0.10
240	11.59 ± 0.14
300	10.97 ± 0.12
360	10.01 ± 0.14
420	9.10 ± 0.16

References

1. Lin, K.L. Yeh, *Chem. Engineering* **May**, 112 (1993).
2. J. Marubin, Braz., Pedido PI BR 8007.642 (CL.CO2F1/78) **27 July** (1982), Appl. 80/7, 642, **24 Nov.** (1980).
3. Peroxidation Systems, Tucson - AZ, *Environtech* **April**, 5-6 (1992).
4. M.R. Straka, G. Gordon and G.E. Pacey, *Anal. Chem.* **57**, 1799 (1985).
5. G. Gordon, G.E. Pacey and M.R. Straka, *Anal. Chem.* **56**, 1973 (1985).
6. D. Flamm, *Environ. Sci. Technol.* **11** (10), 978 (1977).
7. B.E. Saltzman, *Anal. Chem.* **11** (31), 1914 (1959).
8. C.M. Birdsall, A.C. Jenkins, and E. Spadinger, *Anal. Chem.* **4** (24), 662 (1952).
9. A.W. Boyd, C. Willis and R. Cyr, *Anal. Chem.* **6** (42), 670 (1970).
10. B. Légube, B. Langlais and M. Doré, *Water Tech.* **12**, 553 (1980).
11. H. Bergamin F°, E.A.G. Zagatto, F.J. Krug and B.F. Reis, *Anal. Chim. Acta* **104** (17), (1978).
12. H. Shechter, *Water Res.* **7**, 729 (1973).
13. M. Valcárcel and M.D. Luque de Castro, *Flow-Injection Analysis: Principles and Applications* (Ellis Horwood Ltd., Chichester, 1st ed., 1987), p. 400.
14. Commission on Spectrochemical and other Optical Procedures for Analysis. Nomenclature, Symbols, Units and their Usage in Espectrochemical Analysis - II, *Spectrochim. Acta* **33** (6), 241 (1978).
15. S.D. Razumovskii and G.E. Zaikov, *Ozone and Its Reactions With Organic Compounds* (Elsevier Science, New York, 1984), p. 403.