

Simultaneous measurement of N and O densities in plasma afterglow by means of NO titration

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Abstract

In this work we describe a method based on NO titration that permits us to measure at the same time the absolute concentrations of N and O atoms in the gas phase. This method is suitable for low concentrations of oxygen atoms. We also discuss the validity of the titration method, especially the influence of the reaction time. It was used to study the influence of O₂ admixture on the degree of dissociation of nitrogen in the afterglow. The results of the NO titration technique were compared with those obtained by means of electron paramagnetic resonance and with the relative values determined from emission of N₂(B³Π_g–A³Σ_u⁺).

1. Introduction

One can observe growing interest in non-equilibrium kinetics of low pressure plasmas in nitrogen, oxygen and their mixtures. It is caused by the need of various branches of science, for example, physics of the upper atmosphere or plasma physics and technology (cleaning of pollutants, plasma processing).

In many studies various authors [1–5] have observed that even a small admixture of oxygen into nitrogen (or inversely, nitrogen into oxygen) changes the dissociation degree of the main gas substantially. In order to obtain a better understanding of this phenomenon it is necessary to know the absolute densities of both N and O.

There are also many other types of experiment, where the absolute concentration of atomic nitrogen and/or oxygen in a plasma afterglow is needed. As the atoms are radical species, their detection may be difficult. There are only a few methods giving reliable absolute data, for example, two photon absorption laser induced fluorescence (TALIF) [6], nitrogen oxide, titration [7, 8] and electron paramagnetic resonance (EPR) [9, 10]. Due to its simplicity, NO titration is the most widely used. However, in most published works the experimental data are evaluated using the theory for an ideal case. In some circumstances, this can introduce substantial errors.

Recently, a method using NO titration for simultaneous measurement of N and O concentrations was reported [11] and then used [12, 13]. It is carried out in the region where [NO] ≥ [N]. It is well suited for higher oxygen atom concentrations but is quite insensitive for lower O densities.

Unfortunately, this low [O] region is very interesting for studying the increase of the dissociation rate of nitrogen when a very small molecular oxygen admixture (under 1%) is added [14, 15]. We have developed an NO titration variant especially for this range, which is presented in this paper. It is based on fitting data in the [NO] ≤ [N] region by a theoretical curve and gives the absolute values of [N] and [O] rather easily.

As we wanted to test its correctness, the results from the NO titration were compared with those of various other methods, such as EPR and optical emission spectroscopy (OES).

2. Titration by NO in nitrogen

Into a flow of partially dissociated nitrogen gas a small quantity of NO is added. Among the possible chemical reactions, these are the most important:

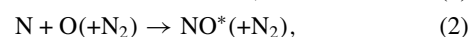
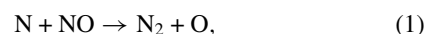


Table 1. Values of rate constants of reactions (1)–(3) that were used in our calculations. For reaction (2) we assumed the nitrogen pressure to be 400 Pa, which gives $k_2[\text{N}_2] = 9.1 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$.

Reaction	Value	Reference
(1)	$k_1 = 1.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	[16]
(2)	$k_2 = 9.1 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}$	[17]
(3)	$k_3 = 6.4 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$	[18]

Reaction (1) is very fast (see table 1) and converts all the available N atoms and NO molecules to O atoms. If there are more N atoms than NO molecules, reaction (2) follows and produces excited NO^* . It then radiates in the UV region as an $\text{NO}\beta$ system ($B^2\Pi-X^2\Pi$, $\lambda \approx 320 \text{ nm}$). On the other hand, if $[\text{NO}] > [\text{N}]$, then reaction (3) produces NO_2^* , which radiates as a green–yellow continuum ($A^2B_1-X^2A_1$) around 570 nm.

This can be used to measure the absolute concentration of N atoms by NO titration. It is sufficient to slowly increase the flow of NO and record the optical emission spectra of NO^* and NO_2^* . At the moment (the so-called dark point) when the NO^* bands have decreased to zero and NO_2^* continuum is just about to appear, the densities of the introduced NO and the initial N are the same. As the NO flow is easily measurable by a flow-controller, this method has been used by many authors.

To find the dark point with good accuracy in a classical way, one needs to carry out many measurements. However, it is possible to achieve the same accuracy with fewer experimental points if the shape of the solution of (1)–(3) is considered. If reaction (1) is finished, the intensity of NO^* radiation is proportional to the actual values of $[\text{N}]$ and $[\text{O}]$. As a result of reaction (1) each NO molecule produces one O atom and consumes one N atom. The dependence $I_{\text{NO}} = f([\text{NO}]_0)$ is then

$$I_{\text{NO}} \propto [\text{N}][\text{O}] = ([\text{N}]_0 - [\text{NO}]_0)[\text{NO}]_0 = [\text{N}]_0[\text{NO}]_0 - ([\text{NO}]_0)^2, \quad (4)$$

where the subscript 0 denotes the initial densities (without the influence of the products of reactions (1)–(3)). This is the equation of a parabola with one root at zero and the second root at the dark point. A good use of this fact is that by fitting of experimental data by a parabola we can determine the position of the dark point precisely even from sparse data.

In spite of the ease of use of the NO titration method certain problems may arise. The ‘ideal’ behaviour (see figure 1) is observed only for a limited range of reaction times. However, in many published works the authors have recorded emission spectra from a region too close to the NO inlet. In that case the reactions are not over and the observed results are distorted (see figure 2). The experimental evidence of this effect is presented later in figure 8. It is clear that there is no longer even a dark point. As a quick cure some authors [19] suggest taking the intersection of the two lines as the dark point. Unfortunately this is not valid, because (i) the scaling of curves will influence the position of the dark point and (ii) even for the same scale for both curves the position of the intersection depends on the reaction time. In some cases the error of such quick estimation may be relatively important as is demonstrated in figure 2. Therefore it is necessary to either correct for insufficient reaction time or, even better, to avoid short reaction times altogether. Because we neglected

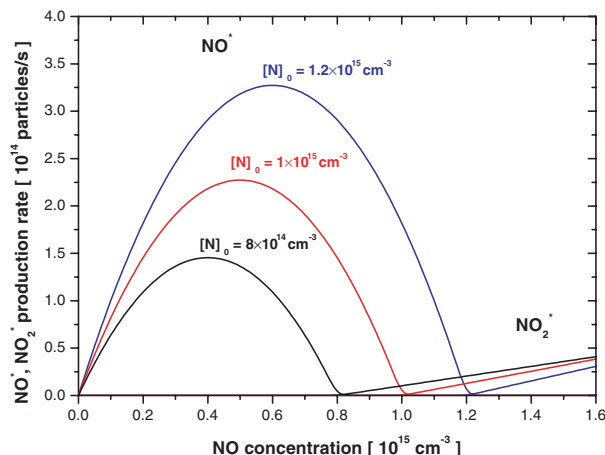


Figure 1. Production of excited molecules in the course of NO titration in nitrogen afterglow at a pressure of 400 Pa. The three curves correspond to different concentrations of N atoms: $8, 10$ and $12 \times 10^{14} \text{ cm}^{-3}$.

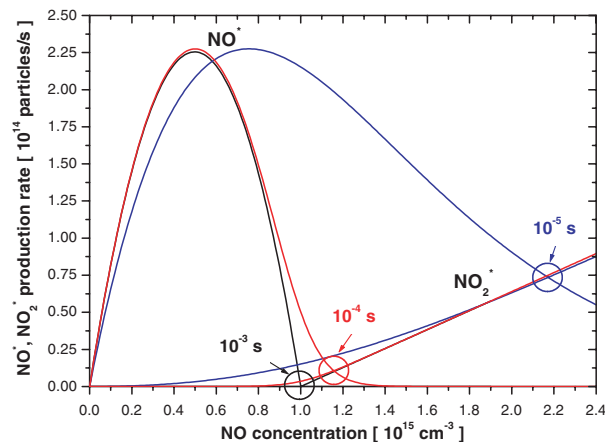


Figure 2. Distortion of the ideal case due to insufficient reaction time. The intersection of the NO^* and NO_2^* curves moves away from the correct value of $1 \times 10^{15} \text{ cm}^{-3}$ for too-short reaction times.

all other processes except (1)–(3), long reaction times pose no problem.

3. NO titration in N_2 – O_2 mixtures

When the afterglow of nitrogen–oxygen discharges is studied, the set of reactions (1)–(3) remains the same but the initial conditions are different. The solution for sufficient reaction times (reaction (1) completed) has the form

$$I_{\text{NO}} \propto ([\text{N}]_0 - [\text{NO}]_0)([\text{O}]_0 + [\text{NO}]_0) - ([\text{NO}]_0)^2 + ([\text{N}]_0 - [\text{O}]_0)[\text{NO}]_0 + [\text{N}]_0[\text{O}]_0. \quad (5)$$

In comparison with the case of pure nitrogen, a new factor appears—the initial concentration of O atoms. It is again an equation of a parabola,

$$I_{\text{NO}}(x) = ax^2 + bx + c, \quad (6)$$

where the coefficients a , b and c follow $b/a = [\text{O}]_0 - [\text{N}]_0$ and $c/a = -[\text{N}]_0[\text{O}]_0$. So by fitting the experimental dependence

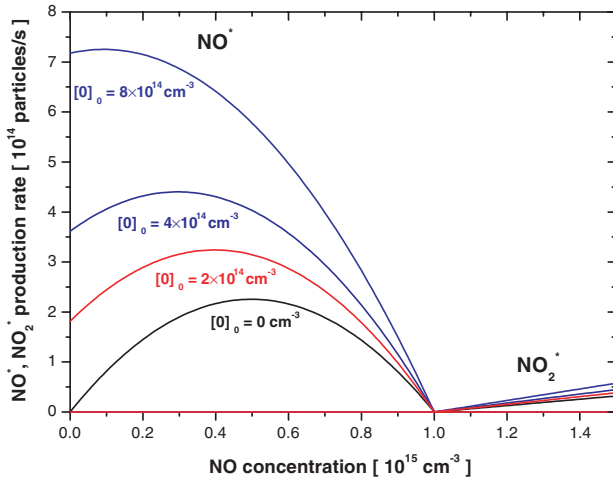


Figure 3. Production of excited molecules in the course of NO titration in nitrogen + oxygen afterglow for various oxygen atom concentrations. The nitrogen atom concentration is fixed at $1 \times 10^{15} \text{ cm}^{-3}$ and the pressure is 400 Pa. It is seen that for rising oxygen content the dark point does not move but the shape of the NO^* curve changes.

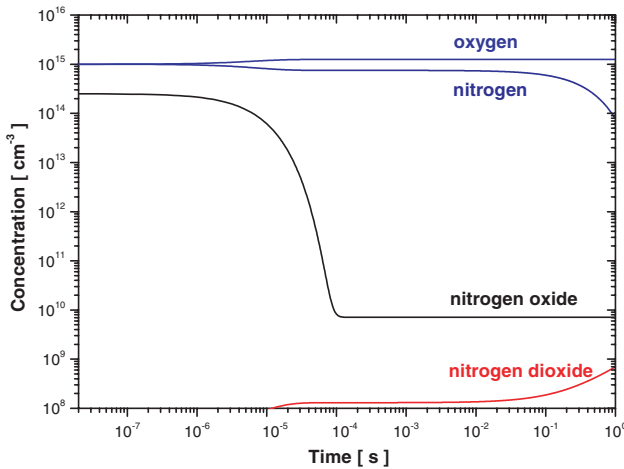


Figure 4. Time development of important species in the course of NO titration in nitrogen + oxygen afterglow. Curves were calculated for a pressure of 400 Pa, $[\text{N}]_0 = 1 \times 10^{15} \text{ cm}^{-3}$ and $[\text{O}]_0 = 2.5 \times 10^{14} \text{ cm}^{-3}$.

$I_{\text{NO}} = f([\text{NO}]_0)$ by a parabola, we obtain the results

$$[\text{N}]_0 = \frac{-b - \sqrt{b^2 - 4ac}}{2a}, \quad (7)$$

$$[\text{O}]_0 = -\frac{-b + \sqrt{b^2 - 4ac}}{2a}. \quad (8)$$

Now one of the roots moves with the initial O concentration to the value $-[\text{O}]_0$, but the second one remains fixed at $[\text{N}]_0$ as shown in figure 3. Therefore, the dark point does not shift and even in the presence of O atoms the standard method of $[\text{N}]$ measurement by NO titration works. Measured data exhibiting these parabolic dependences are shown later in figure 9 in the experimental part of this paper.

In figure 4 the time evolution of the densities of important species during the course of NO titration is shown. At time $t = 0$, NO molecules ($2.5 \times 10^{14} \text{ cm}^{-3}$) were ideally

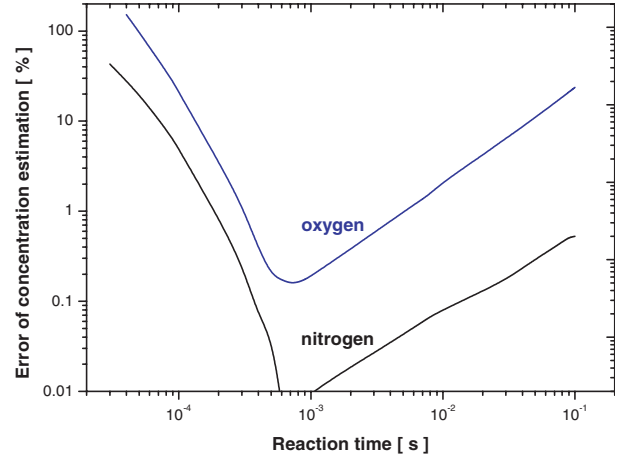


Figure 5. Relative error of $[\text{N}]$ and $[\text{O}]$ estimation as a function of the reaction time. Curves were calculated for a pressure of 400 Pa, $[\text{N}]_0 = 1 \times 10^{15} \text{ cm}^{-3}$ and $[\text{O}]_0 = 5 \times 10^{14} \text{ cm}^{-3}$.

mixed with N of concentration $1 \times 10^{15} \text{ cm}^{-3}$ and O atoms of concentration $1 \times 10^{15} \text{ cm}^{-3}$.

We can see that for $t < 10^{-4} \text{ s}$ $[\text{N}]$ and $[\text{NO}]$ decreases due to reaction (1). At time t_{eq} , in this case around $1 \times 10^{-4} \text{ s}$, an equilibrium between the NO loss due to reaction (1) and the production due to reaction (2) is established. For times higher than $1 \times 10^{-4} \text{ s}$, the resulting $[\text{NO}]$ value is given by

$$[\text{NO}] = \frac{k_2[\text{N}_2][\text{N}][\text{O}]}{k_1[\text{N}] + k_3[\text{O}]}, \quad (9)$$

where $[\text{O}]$ is the total density of O atoms, which includes not only the initial O atoms but also those produced by reaction (1). Because $k_3[\text{O}] \ll k_1[\text{N}]$, the previous equation reduces to

$$[\text{NO}] = \frac{k_2[\text{N}_2]}{k_1}[\text{O}]. \quad (10)$$

Although the NO and O equilibrium is established, there is always continuous N atom loss due to reactions (1) and (2), which removes O and N and produces NO, which in turn is removed by another N and produces O and N_2 . The time dependence of the N atom density is given by

$$[\text{N}] = ([\text{N}]_0 - [\text{NO}]_0) \exp(-2k_2[\text{N}_2]([\text{O}]_0 + [\text{NO}]_0) \times (t - t_{\text{eq}})), \quad (11)$$

which is an exponential decay.

In the case of NO titration into pure nitrogen a prolongation of reaction time reduces the error of measurement (when only (1)–(3) are considered, of course). However, in the case of an $\text{N}_2 + \text{O}_2$ mixture, the long reaction time is not optimal because it negatively affects the error of O concentration estimation. The dark point position does not move with reaction time, as it is governed by the fast reaction (1) and therefore the N atom concentration is well determined for higher reaction times, too. However, the NO^* intensity is proportional to the concentration of oxygen atoms (which does not change with time) and to the concentration of nitrogen atoms (which decreases exponentially) and thus longer reaction times deform the shape of the parabola. This results in a larger error in the fitting procedure needed for

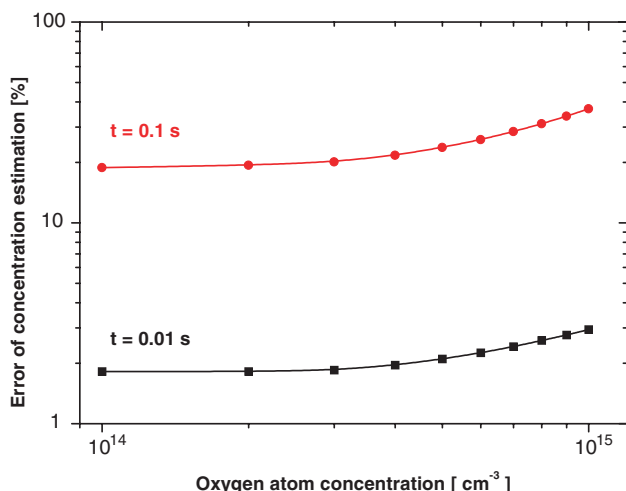


Figure 6. Relative error of [O] estimation for two reaction times. We used a pressure of 400 Pa and $[N]_0 = 1 \times 10^{15} \text{ cm}^{-3}$ for the calculation.

calculation of [O]. In figure 5 it is shown how the relative error of [N] and [O] estimation depends on the reaction time. The graph was calculated for a pressure of 400 Pa, $[N]_0 = 1 \times 10^{15} \text{ cm}^{-3}$ and $[O]_0 = 5 \times 10^{14} \text{ cm}^{-3}$, and the density of N and O atoms was calculated from a parabola fit of the NO^* curve and compared with the initial values introduced into the simulation.

From the analysis presented here it might seem that we are able to calculate a correction to the measured value. However, the situation is more complicated due to the fact that the mixing of reactants is not immediate [20]. In fact, for short distances between the NO inlet and the photodetector it is nearly impossible to determine the value of the reaction time and as a consequence to calculate the correction factor. So the only solution is to increase the reaction time to a value at which the error in N and O atom estimation is sufficiently low. For longer reaction times, the [N] estimation is rather precise, with a relative error under 1%, which is much lower than the error in [O] estimation. Increasing the reaction time results in an increase in the relative error of O atom estimation, and so it is necessary to choose the position of the photodetector carefully.

How the error in [O] estimation depends on the density of [O] atoms is presented in figure 6 for two reaction times. The loss of [N] with increasing [O] is due to the production of NO, which in turn quickly reacts with another N, producing N_2 . In figure 6 it is clearly seen that for a ten times higher O atom density the relative error in [O] determination increases only twice.

Therefore on the basis of the presented analysis we conclude that the choice of correct reaction time is more important than the influence of O atoms on measurement errors.

4. Experimental set-up

A schematic drawing of the apparatus is presented in figure 7. A microwave discharge is produced in a quartz discharge tube with an inner diameter of 13 mm by means of a surfatron

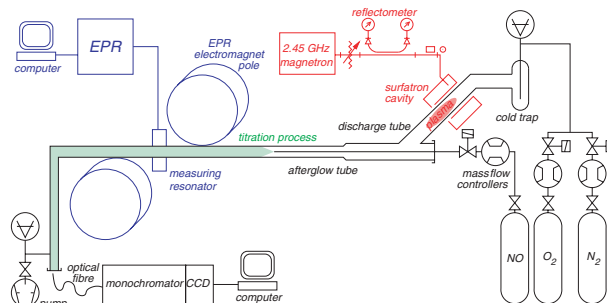


Figure 7. Experimental set-up.

cavity, powered by a 100 W magnetron working at 2.45 GHz. Our experiments being carried out in a flowing regime, the afterglow is observed downstream in a 1 m long quartz tube with an inner diameter of 8 mm. A small amount of oxygen admixture is added to the main nitrogen gas before being passed through the discharge.

The gases passed from gas bottles through the mass flow controllers to a cold trap, which removes traces of unwanted impurities, like water or hydrocarbons. The purities of N_2 and O_2 were better than 99.995% according to the manufacturers' certificates. The flow rates of the O_2 admixture was varied between 0 and 2.5 sccm, then the nitrogen flow rate being kept constant at 100 sccm. The pressure in the discharge was 480 Pa.

The titration probe is mounted at the end of the afterglow tube. NO is introduced into the flowing gas containing N and O atoms. The observing window is placed at a certain distance (40 cm) and through it the intensities of NO^* (β system, $B^2\Pi-X^2\Pi$), NO_2^* (yellow-green continuum, $A^2B_1-X^2A_1$) and N_2^* (first positive system, $B^3\Pi_g-A^3\Sigma_u^+$) are recorded. The tube is bent so that the radiation of the earlier stages does not enter into the collecting optical fibre. For OES we used a Jobin-Yvon TRIAX 320 monochromator equipped with a 1200 grooves per millimetre grating and a CCD camera.

The afterglow tube also passes through the measuring resonator of the JEOL JES-3B EPR spectrometer operating in the X-band to measure the concentration of atomic oxygen. This method is based on the resonance absorption of microwave energy by the transitions between the Zeeman split levels. In the case of oxygen, the ground levels $^3P_{1,2}$ have non-zero magnetic momentum and so they split to a system of eight levels in all. The resulting EPR spectra have a typical structure of a quartet and a doublet. After a calibration of the EPR device by molecular oxygen [9], which is paramagnetic, the absolute concentration was obtained. The advantage of such calibration is a well-defined fill factor, which is not easy to achieve with traditional diphenylpicrylhydrazyl (DPPH) standard. The use of EPR spectroscopy to determine the absolute concentrations of a wide range of radical species is described in [21].

5. Experimental results and discussion

Here we apply the method described in the theoretical part of this paper to measure the N and O density in the plasma afterglow.

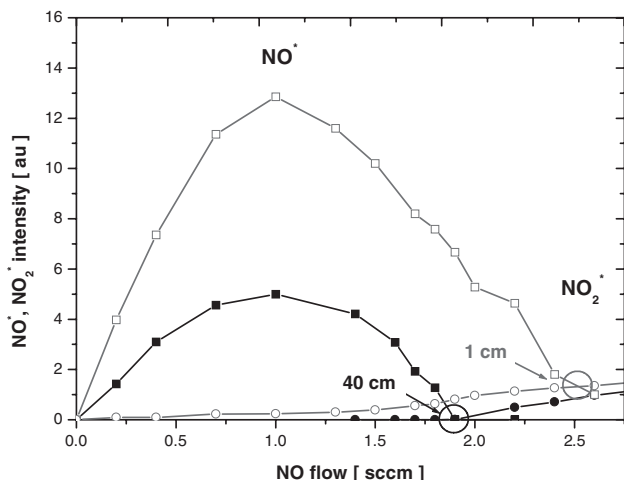


Figure 8. Recorded intensities of NO^* and NO_2^* emission during the course of titration for two distances between the NO inlet and the optical fibre. The reaction time for shorter distances is clearly insufficient.

We wish to emphasize the often neglected fact that, in order to get the N atom concentration correctly, the reaction between N and NO must be completed. In figure 8 typical examples of NO^* and NO_2^* intensities in the course of titration for two distances between the NO inlet and the optical fibre is presented. In the case of shorter distances (1 cm) the reaction of N and NO, in spite of being rather fast, is not completed yet (also due to slow mixing of the reactants [20]) and there is no well-defined dark point any more. These curves are in good accord with the numerical calculations presented in figures 1 and 2.

The best way of getting the correct N atom density in a pure nitrogen afterglow is to avoid short reaction times altogether, i.e. to increase the distance between the NO inlet and the point of optical measurement until a well-defined dark point is observed (the case for the 40 cm distance in figure 8 is well beyond such distances).

A recent paper [13] has described the use of a method, which, besides [N], permits us to measure [O] also by comparing the slope of NO_2^* intensity after the dark point—with and without oxygen admixture. This method is well suited for higher oxygen admixtures (of the order of several per cent).

However, for the very interesting region of low oxygen admixtures, where a steep rise of nitrogen dissociation is observed, this method is not sensitive enough. Therefore we developed a method for simultaneous [N] and [O] measurement using NO titration suitable for low O densities, as was described in the theoretical part. Another advantage of the presented method in comparison with [13] is that no calibration measurement with pure nitrogen is needed. From the analysis presented before, it follows that the density of nitrogen atoms can be obtained classically from the dark point as in the case of a pure nitrogen post discharge. But a quicker and more precise way is to fit the dependence of NO^* on [NO] by a parabola, and from three fitting parameters calculate both [N] and [O].

In figure 9, $\text{NO}\beta$ intensities during the course of titration for different amounts of oxygen admixture in nitrogen are presented. One can see that for zero NO flow, NO^* is zero only

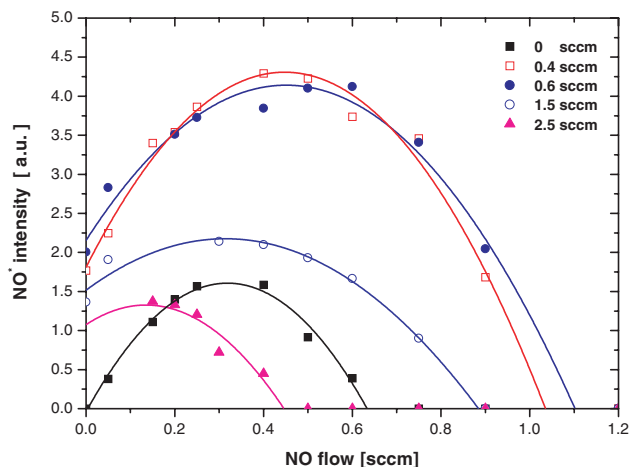


Figure 9. Intensities of NO^* (β system, transitions 0–8, $\lambda \approx 320$ nm) for varying NO titrant flow. The five curves corresponding to 0.4, 0.6, 0.8, 1.5 and 2.5 sccm of oxygen admixture in 100 sccm of nitrogen.

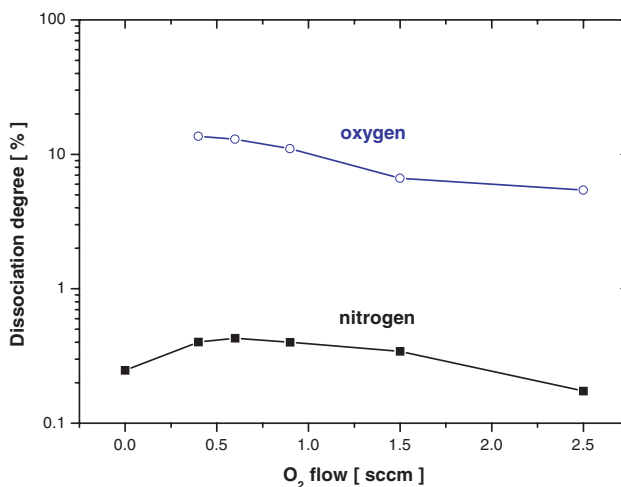


Figure 10. The degree of dissociation of nitrogen and oxygen as a function of oxygen admixture.

for pure nitrogen, as the presence of oxygen leads to production of NO^* . For different oxygen admixtures the position of the dark point moves, which indicates changing of [N]. Together with the experimental points the fitted parabolas are shown too. From the fitting parameters [N] and [O] were then calculated using relations (7) and (8).

In figure 10 the results of NO titration are shown in the form of the degree of dissociation of nitrogen and oxygen, $\eta = \frac{1}{2}[X]/[X_2]$, as a function of the oxygen admixture. The rather high oxygen dissociation degree (nearly 20%) is notable.

We compared the results of NO titration with two other methods, which were carried out simultaneously with the main measurement. The absolute density of oxygen atoms was measured by EPR. The density of nitrogen atoms was determined from OES. It is known that some vibration bands of the nitrogen first positive system (for example $\text{N}_2B^3\Pi_g v = 11 - \text{N}_2A^3\Sigma_u^+ v = 7$) are caused by recombination of atomic nitrogen and thus their intensities are proportional to [N] squared. This method gives only relative values, but it is sufficient for our purposes.

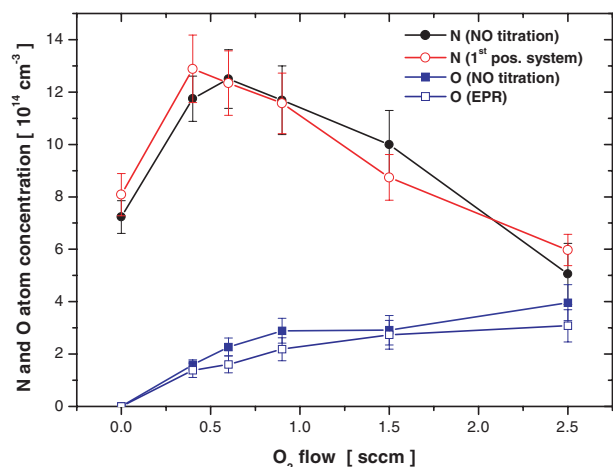


Figure 11. Concentrations of N and O atoms in the afterglow as a functions of oxygen admixture in 100 sccm of nitrogen. The values obtained from the intensities of the nitrogen first positive system are relative and so they were scaled.

From figure 11 it is seen that all the three methods are in very good accord. The absolute values of [O] given by EPR and by NO titration as well as the absolute values of [N] from titration and the scaled [N] from the square root of the nitrogen first positive system intensity coincide very well.

The variation of the concentration of nitrogen atoms versus the O₂ percentage was previously measured by [14] and the same behaviour as presented in this paper (i.e. steep increase in N₂ dissociation followed by slow decrease for increasing O₂ admixture) was observed. Often, the increase in N atom concentration for a small O₂ percentage is explained by the change in the reduced electric field, E/N [14], by various homogeneous reactions [14] or by a decrease in the wall recombination coefficient [22]. Depending on the purity [23] of the nitrogen gas, [N] can be increased even by a factor of 50 [15]. The decrease in [N] for larger O₂ percentages can be attributed to the homogeneous destruction processes.

In [24] the dissociation degree in the afterglow was increased even by adding the admixture directly to the pure nitrogen afterglow. However, all the above mentioned hypotheses are based on a presence of the admixture in the active discharge. It follows that these theories cannot be complete.

6. Conclusion

A method for obtaining simultaneously the N and O atom concentrations in N₂ and N₂-O₂ post-discharges by NO titration from the NO β system UV radiation was described and the influence of reaction time on the accuracy of such a measurement was discussed.

The method presented here is based on a fitting of the measured data points by a theoretical parabolic curve (equation 5), and it is suitable for estimation of low O atom densities. It was shown that for short reaction times (for our typical values of [N], [O] and [N₂] it is below 10⁻⁴ s) problems with estimation of the dark point still exists. Increasing the reaction time improves the accuracy of N atom density estimation in a pure nitrogen afterglow. In the case of

an N₂-O₂ post-discharge, there is a range of times, 10⁻⁴–10⁻² s (again, the numerical values depend on the given experimental conditions), where the accuracy of N and O atom concentrations is sufficient. For higher reaction times, mutual reactions between N, O and NO species affect the shape of the NO* parabola and the error of estimation becomes too high for practical purposes. To obtain accurate values, it is necessary to choose the position of the photodetector carefully.

The correctness of the measurement procedure can be verified in pure nitrogen even without any calculation. The reaction time is sufficient if (i) the dark point exists, i.e. both the NO* and NO₂ intensities are zero and/or (ii) the NO* curve is a parabola and/or (iii) after the dark point NO₂ increases linearly. In other cases a more careful approach is necessary and the reaction time should be increased.

We successfully deployed the method of simultaneous [N] and [O] measurement in the plasma afterglow based on a titration by NO. It consists of fitting the NO* intensities for increasing the NO flow by a theoretical curve. We found that the calculated values and trends are in very good agreement with the results of other methods like EPR or OES.

The measured steep increase of nitrogen dissociation, when a small oxygen admixture is added, was also observed by other authors. Up to now, the full explanation of this phenomenon has not been available. Therefore this relatively cheap and simple absolute method, which is sensitive enough even for low oxygen atom densities, can help to obtain an understanding of the complex processes involved.

Acknowledgments

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