

1.1 HISTORICAL OVERVIEW OF THE DEVELOPMENT OF CHEMILUMINESCENCE DETECTION AND ITS APPLICATION TO AIR POLLUTANTS

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1. INTRODUCTION

"It is so hard to find out the truth of anything by looking at the record of the past. The process of time obscures the truth of former times, and even contemporaneous writers disguise and twist the truth out of malice or flattery." - Plutarch (AD 46?-120)

By necessity, we will surely slight someone in this overview of the use of chemiluminescent reactions to monitor air pollutants, but that will not be out of "malice or flattery." We take this opportunity to review some of the scientific efforts that have contributed to the discovery, understanding, and application of chemiluminescent reactions in atmospheric chemistry.

Chemical reactions occur when atoms or molecules interact with sufficient energy to overcome the potential energy barrier for the reaction. In many cases, chemical reactions release energy in the form of light and heat. These are called exothermic reactions. A special case of an exothermic reaction in which light is produced without heat (or with minimal heat) is a chemiluminescent reaction. Some common examples of chemiluminescent chemistry have been known for ages; in their historical texts the ancient Greeks and Chinese reported chemiluminescence in biological systems. Indeed, emission of cold light is known to occur in a variety of biological organisms, the best known being the firefly. In this case an enzyme, luciferase (meaning light-bearing), reacts with oxygen in the firefly's abdomen to produce the familiar blue-green light. Fireflies are actually beetles (order Coleoptera, family Lampyridae). Other examples of bioluminescent organisms include bacteria and deep-sea fishes. The bioluminescence reactions can be considered a special case of chemiluminescence.

Another example of chemiluminescence is the atmospheric phenomenon called airglow. Light is produced by the recombination of nitrogen and oxygen atoms to form excited nitrogen and oxygen

species that emit under the low-pressure conditions in the upper atmosphere. At low pressure, the recombined molecules emit light rather than undergoing third-body collisional quenching to the ground states. These reactions have been of interest for some time (1). Indeed, in 1937 Chapman explained that some airglow emission is due to oxygen recombination (2). Previously, Chapman had suggested that the stratospheric ozone layer was formed by the well-known Chapman cycle (3).

Both bioluminescence and the northern lights phenomenon have stimulated an interest in the chemistry of luminescent reactions. This subject has developed over the years into a very large body of literature that will not be examined here. Rather, this paper will focus on the use of chemiluminescent reactions in atmospheric chemistry applications, principally in the troposphere. In applications for the detection of pollutants, these reactions are inherently simple, inexpensive, and very sensitive. In contrast to other spectroscopic methods, only a phototube and a suitable chemical reaction cell are required. Sensitivity, a natural result of detecting light produced on a black background, typically is on the order of ppb or less.

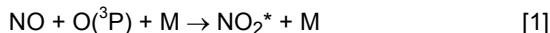
Because of these factors, chemiluminescence detection has been used to monitor a number of key species. Below, we will review some of them, beginning with the most familiar chemiluminescent reaction in the analytical chemistry of the troposphere, $\text{NO} + \text{O}_3$.

2. THE NITROGEN OXIDE ANALYZER, $\text{NO} + \text{O}_3$

Early work of the fourth Lord Rayleigh ("airglow" Rayleigh) in 1920-1930 showed that an electric discharge through oxygen and nitrogen under reduced pressures would result in the production of an airglow. Robert John Strutt began his investigations in the early 1920s. Interestingly, his father, John William Strutt (the third Lord Rayleigh) was the very well known "scattering Rayleigh," who won the Nobel Prize in physics. The son, Robert, was a very noteworthy physicist in his own right and has a unit of luminescence, the rayleigh, named in his honor. After John McLennan and G.M. Schurm in 1929 identified the green glow as atomic oxygen, Sydney Chapman suggested that the phenomenon was also due to chemical recombination.

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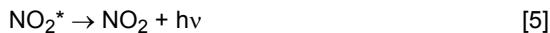
This work led to the use of the O + NO reaction in the earliest kinetic and mechanistic studies of O atoms (4). The two ground-state reactants form the excited product nitrogen dioxide, which is the chemiluminescent species:



The excited NO_2^* emission extends from the far visible into the infrared. Its maximum intensity at approximately 630 nm allows the species to be monitored quite sensitively for kinetic studies with reasonably inexpensive photomultipliers and associated electronics. Detection sensitivities of this method are on the order of 10^{10} O atoms cm^{-3} for the NO titration, or less than one part per billion in a cubic centimeter of air at standard temperature and pressure (STP).

Other methods were developed similarly for generation of ground-state oxygen atoms. For example, one can use the titration of nitrogen atoms, $\text{N}({}^4\text{S})$, with NO to produce ground-state molecular oxygen and ground-state oxygen atoms. When the nitrogen atoms combine, they yield excited molecular nitrogen, which produces a long-lived yellowish afterglow. Oxygen atoms reacting with the nitrogen atoms will produce excited NO^* , which gives a bluish chemiluminescence. Thus, one can follow the titration with the naked eye in a dark room, if one adds NO to a discharge of nitrogen gas. Initially the mixture is yellow, then yellowish blue. At the endpoint of the gas titration, the products N_2 and $\text{O}({}^3\text{P})$ are in the ground state, and no emission is observed. When additional NO is added past the N atom titration endpoint, the yellow-greenish NO_2^* is observed at low pressure because of reactions 2 and 3. Similarly, H atom chemistry methods were also developed (4).

These chemical kinetic approaches were used quite successfully to obtain absolute reaction rates for a number of $\text{O}({}^3\text{P})$ reactions. These studies led to the work of Thrush and coworkers (5-6) on the mechanism of the reaction of NO and O_3 to form electronically excited NO_2 and oxygen:



This work gave the quantum yields for the emission and the spectral region. The NO_2^* formed was observed to be in lower energy states, as expected, and the very broad emission was found to begin at about 600 nm, with a maximum in the near infrared at 1200 nm (1.2 μm). Red-sensitive photomultiplier tubes could detect the weak front edge of the emission at 600-900 nm before the photomultiplier quantum efficiencies dropped off significantly.

At about the same time, the chemistry of NO and NO_2 in photochemical air pollution became very apparent (4,7). Francis Blacet had shown that NO_2 was the source of oxygen atoms for the formation of ozone, and sensitive monitoring of NO, its precursor, was a significant need.

Arthur Fontijn and coworkers were the first to develop a prototype instrument that could measure NO both over the concentration range of interest for ambient monitoring and at higher concentrations (8,9). Shortly thereafter, Hiromi Niki and colleagues at Ford Motor Company adapted the method to monitor NO in automobile exhaust (10). Further work confirmed that the method was linear in response and insensitive to other common air pollutants at the concentrations encountered in the troposphere (9-11).

The sensitivity of Professor Fontijn's detection method was approximately 1 ppb. Specially selected photomultiplier tubes, high-efficiency ozone discharge sources, and low pressures in the reaction chamber were used for application to the stratosphere with sensitivity of about 0.03 ppb (12-14) soon after the initial demonstration of the method for work in the polluted troposphere. This work was done to address the concern in the early 1970s that the flight of supersonic transports (SSTs) would increase NO in the stratosphere and deplete ozone (15).

The first instruments used reagent oxygen containing about 1% ozone produced from corona discharge. Sample air flow rates were on the order of $1 \text{ cm}^3 \text{ s}^{-1}$, with the reactant ozone mixture at STP and operation at about 1 torr pressure in a spherical reactor of approximately 1-L volume. The mechanical vacuum pump used for the measurement made the first research systems developed rather bulky. Once this method was demonstrated, commercial interest grew rapidly, and better reaction cell designs and ozone sources, along with the application of chopping, quickly improved the method.

Clearly, this method would work for NO, but now a method for was needed NO_2 . Two approaches were used to adapt the NO method. The first was the conversion of NO_2 to NO and O by using the thermal equilibrium. J.E. Sigsby and his group initiated the use of a simple thermocatalytic converter consisting of a

stainless steel tube heated to 700°C to accomplish the conversion (16). This worked quite well, but NH₃ was also oxidized to NO, and the NO₂ conversion was approximately 98% efficient (16,17), leaving some room for improvement.

Chemical converters were investigated next, because NO₂ is an oxidant that a catalytic converter can reduce to NO. A number of converter approaches were demonstrated, first by Bretenbach and Shelef with carbon-impregnated molybdenum converters operated at 475°C (18). These converters changed NO₂ to NO quantitatively with a much reduced conversion of NH₃. Interestingly, acidic surfaces were used in combination with stainless steel converters to monitor the NH₃ present through differencing techniques (17), and the method was used in the early years to examine both NH₃ emissions and NO from automobiles (19).

Instruments involving converters were considered able to measure NO and NO₂ selectively. These two species were determined by two-channel instruments (one with converter and one without), and the difference was used to determine the NO₂ and NO concentrations. The total signals were commonly referred to as NO_x, meaning the converter channel that gave the two species together.

Further studies of converters quickly indicated that a number of the oxides of nitrogen were also reduced to form NO by various thermal catalytic converters that are currently used, including stainless steel, molybdenum, and others (20). These oxides included nitric acid, organic nitrates, and peroxyacetyl nitrate (PAN), indicating that considerable problems were associated with using the converters for specific NO₂ measurements. Thus, the NO_x channel actually measured other species and included NO_x plus all other oxides of nitrogen (HNO₃, PAN, organic nitrates, etc.). Thus, today we refer to the total signal that includes all of these species as NO_y. Other approaches followed, including the use of photolysis of NO₂ (21) and the use of more selective chemical catalytic converters. The latter is not significant in current applications, and photolytic methods are now preferred (22). The development of the photolytic method for NO₂ has led to a capability to determine NO and NO₂ accurately and to the definition of NO₂ as the NO_y signal in the total converter channel of the instrument, less the NO and NO₂ contributions.

This chemiluminescence instrument continues to be a workhorse for detecting NO and oxides of nitrogen in analytical atmospheric chemistry.

3. DETECTION OF OZONE AND HYDROCARBONS

One obvious approach to the detection of ozone through chemiluminescence would be the reverse of the previously discussed reaction, with NO as the reactant (4,7). This approach was used for some time as a method for ozone detection. However, the ability of ultraviolet absorption detection to make the same measurement without chemical reagents has displaced the chemiluminescence method in the field.

Another chemiluminescent reaction, that of ethene with ozone at pressures near atmospheric, was reported in 1965 by G.W. Nederbragt and colleagues (23). The authors demonstrated the use of this method for monitoring ozone in a laboratory where ozone used as a reactant was a health concern. In 1972, Hodgeson and coworkers built a prototype of this instrument that was useful for ambient ozone measurement, demonstrating a linear response from 1 ppb to 1 ppm (9). The emitting species in this reaction at atmospheric pressure was found to be formaldehyde in an excited state, HCHO ('A"-1A₁), with a broadband emission maximum at about 440 nm (24-26). Meinel band emission of HO from this reaction with ethene (and olefins in general) was demonstrated by Finlayson-Pitts and colleagues (4,25,26) to occur at reduced pressure.

Sulfides were also observed to produce chemiluminescence from ozone oxidation reactions. In the case of the sulfides, the emitting species was electronically excited SO₂^{*} with a broadband emission maximum at 340 nm (24). Other studies in this same time period showed that acetaldehyde would also react to form OH Meinel band emission (27).

The ethene reaction was used for some time in a commercial instrument to monitor ozone. However, like the NO approach, this method has been mostly replaced by long-path ultraviolet absorption measurements for detecting ozone in air pollution applications. The inverse reaction with olefins and with sulfides has been applied in a number of instances as a gas chromatographic detection system for sulfides (28-30) and olefins (31). Indeed, the method is now being applied for the detection of isoprene (alkenes) in current research efforts and in commercially available equipment. The temperature dependence of the ozone reaction with hydrocarbons might also be useful as a means of estimating the hydrocarbon reactivity in an air parcel (31,32).

4. LUMINOL CHEMILUMINESCENCE METHODS

Luminol (5-amino-2,3-dihydro-1,4-phthalazine-dione) was first synthesized in 1853, and its ability to yield a chemiluminescent reaction in basic solution in the presence of an oxidant such as hydrogen peroxide

was first reported in 1928 by H.O. Albrecht (33). Since that time, numerous uses of this system have been developed for applications in a wide variety of areas ranging from environmental to medical to forensic. For example, the presumptive luminol test for blood developed by Walter Specht at the University Institute for Legal Medicine and Scientific Criminalistics in Jena, Germany, in late 1930s has found considerable use in forensics. The early work in this area was reviewed in 1962 (34).

In atmospheric chemistry, two major applications have developed: the use of the luminol reaction to monitor liquid-phase oxidants such as hydrogen peroxide and the surface reaction with NO_2 for gas-phase monitoring of that species. The reaction of luminol was used by Kok and colleagues with aqueous detection to study concentrations of hydrogen peroxide in air (35). Earlier, the reaction was used to look at hydrogen peroxide concentrations in surface waters (36). This method has a number of interferences, including organic peroxides and peracids. Application in combination with high-performance liquid chromatography methods would seem a reasonable way to use the luminol method for organic peracids, organic peroxides, and hydrogen peroxide in gas and rainwater samples. We are pursuing this method in our laboratories.

For this paper we will focus on the more widely used application of the surface chemistry to measure NO_2 . The surface reaction of NO_2 and luminol solutions was first described by Maeda and his associates in 1980 (37). The method was quite promising and was improved further by Stedman and colleagues (38). Significant interference by PAN was observed, along with other potential analytical difficulties related to direct injection of air samples into the detector (39). The use of gas chromatography was pursued in our laboratory and by Stedman's group, with the first publication of a practical instrument published in 1988 (40). This packed-column method allowed for measurement of NO_2 and PAN with a 5-min analysis time. Further development of the method for use with fast capillary gas chromatography (41) has decreased the time for analysis of peroxyacetyl nitrates and NO_2 to 1 min. Recent developments in our laboratory, which applied photon counting to bring the analysis time for NO_2 and PAN under 30 sec, have allowed use on aircraft platforms (42).

The inherent advantage of this method is that the luminol emission has a broad maximum at approximately 440 nm. In contrast, the nitric oxide/ozone reaction has a broad maximum at 1.27 μm . The 440-nm emission is much more readily detected by present photomultiplier systems and therefore can allow detection of NO_2 at less than 10 ppt. Further developments now under way for this approach focus

on the reduction of dark current by using thermoelectric cooling of the tubes with better column temperature control and reduction of dead volumes in the detectors.

5. OTHER CHEMILUMINESCENCE DETECTORS

Other widely varying methods have been used for detection of important atmospheric chemistry species. An promising reaction noted some time ago is the reaction of ozone and PAN with triethylamine to produce chemiluminescence in two different regions (43). This reaction has not been studied further, and it would be interesting to examine it again in the light of advanced photon counting methods and emission spectroscopy.

6. CONCLUSIONS

Chemiluminescence detection methods have the advantage of being sensitive and simple to operate. As this brief overview demonstrates, these methods have found considerable application in many areas of analytical chemistry, particularly in analytical atmospheric science. Interest in using these methods for research and for routine monitoring of key pollutant species will continue in the years to come.

7. ACKNOWLEDGEMENT

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