# COLORIMETRIC AZO DYE METHODS FOR THE ATMOSPHERIC ANALYSIS OF NITROGEN DIOXIDE; HISTORICAL DEVELOPMENT*

By

E. L. SZONNTAGH

Honeywell Inc. Fort Washington, Pennsylvania, USA

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Presented by Prof. Dr. F. SZABADVÁRY

The various oxides of nitrogen today constitute a group of important air pollutants. Table I shows the percentage of various pollutants typical for the 1960. Oxides of nitrogen with 8.5% of the total occupy the fourth place among gaseous contaminants. The same table also marks transportation as the major source of nitrogen oxides.

**Table I**
Sources on major air pollutants in the United States (1966)

| % | | Industry | Power Generation | Space Heating | Refuse Disposal | Total % |
|---|---|---|---|---|---|---|
| CO | 46.0 | 1.5 | <1 | 1.5 | <1 | 50 |
| Sulfur Oxides | <1 | 6.5 | 8.5 | 2.0 | <1 | 17.5 |
| Hydro-Carbons | 8.5 | 3.0 | <1 | <1 | <1 | 12.5 |
| Nitrogen Oxides | 4.0 | 1.5 | 2.0 | <1 | <1 | 8.5 |
| Particulate Matter | <1 | 4.0 | 2.0 | <1 | <1 | 8.5 |
| Misc. Others | <1 | 1.0 | <1 | <1 | <1 | 3.0 |
| Total % | 60% | 17.5% | 14.0% | 5.5% | 3.0% | 100 |

Nitric oxide, nitrogen dioxide (or peroxide) nitrogen tetroxide and others are present in the atmosphere in a state of equilibrium. Under ordinary atmospheric circumstances nitric oxide dominates [1] but nitrogen dioxide is of deep concern because of its high toxicity [2]. $NO_2$ dissolves in water and at moderate temperature nitric acid and nitrous acid are formed. In this article we will focus on the colorimetric determination of the nitrous acid through azo dyes formed by the processes illustrated in Fig. 1.

During the past decades this analytical method gained considerable popularity and the Saltzman Method [3], as it is frequently referred to [e.g. 5, 5a], is the widely accepted method for the quantitative determination of minute $NO_2$ quantitites in the atmosphere. Even the controversy over the "Saltzman-factor" [4, 5] did not seriously affect its popularity.

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## The Griess—Ilosvay Reaction

The azo dye method of detection was first described by the German organic chemist **Peter Griess** [6]. Actually, his correspondence was read at a session of the German Chemical Society and was submitted for publication on March 10, 1879. **Griess'** article contains criticism of a publication by **Weselsky** and **Benedict** [7], in which they failed to mention **Griess'** work published 15 years earlier on certain azo compounds [8]. In his publication [6] **Griess** described a new and very sensitive reaction for nitrous acid:

"Versetzt man nämlich eine Flüssigkeit, welche auch nur Spuren von salpetriger Säure enthält, nachdem man sie mit reiner Schwefelsäure angesäuert, mit etwas Sulfanilsäurelösung und ungefähr 10 Minuten nachher mit einigen Tropfen einer durch Thierkohle entfärbten schwefelsauren Napthylamin lösung, so bemerkt man nach kurzer Zeit das Auftreten einer rothen Färbung."

Prior to this disclosure of analytical importance, in 1861 **Griess** described the properties of diazobenzoic acid [9] and even earlier he reported the first diazotization in history and the discovery of a diazonium salt [10]. Tab. II

**Table II**

Development of the Griess reagent for $NO_2$ analysis

| Year | Author | Reference | Description |
|---|---|---|---|
| 1784 | Bergman | [12] | Color Reactions |
| 1838 | Lampadius | [13] | Color Comparison |
| 1845 | Heine | [28] | Bromine Determination |
| 1846 | Jacquelain | [29] | Copper Determination |
| 1852 | Herapath | [30] | Iron Determination |
| 1860 | Griess | [10] | Azo Dyes |
| 1864 | Hofmann | [14] | Diphenylamine for $NO_2^-$ |
| 1872 | Kopp | [15] | Colorimetric Method for $NO_2^-$ |
| 1879 | Griess | [7] | Determination of $HNO_2$ by α Naphthylamine and Sulfanilic Acid |
| 1889 | Ilosvay | [16] | Same but Acetic Acid Medium |
| 1889 | Lunge | [17] | Mixed Reagent |
| 1930 | Bennett | [20] | Griess Reagent for NO |
| 1937 | Marshall et al. | [18] | Determination of Sulfanilamid |
| 1939 | Liebhafsky and Winslow | [44] | Nitrite and NO by Spectrophotometer |
| 1939 | Bratton and Marshall | [19] | N-(1 Naphthyl) Ethylene Diamine Dihydrochloride for Sulfanilamid |
| 1941 | Shinn | [45] | Same Coupling agent for Nitrite |
| 1943 | Patty and Petty | [21] | Griess Reagent for $NO_2$ |
| 1947 | Averell et al. | [22] | $NO_X$'s with Spectrophotometer and Color Standards |
| 1954 | Saltzman | [3] | Marshall version of Griess Reagent for $NO_2$, Single Solution |
| 1956 | Thomas et al. | [23] | Automatic Apparatus for NO and $NO_2$ |
| 1960 | Saltzman | [25] | Color Development in 4—5 Minutes |
| 1965 | Lyshkow | [26] | Color Development in 1 Minute |
| 1966 | Kothny and Mueller | [27] | Color Development in 30 seconds |

lists the major developments in the history of colorimetric determinations in general and later for $NO_2$ in chronological order. Prior to GRIESS' publications, BERGMAN, LAMPADIUS, HEINE, JACOUELAIN and HERAPATH worked on color development and on the color comparison of various substances. It is believed that their work, as well as the contributions of HOFMANN and KOPP, greatly enhanced the evolution of the method.

Organic reagents causing color development were used long before GRIESS' time. The gallnut extract for the identification of iron e.g. was used in ancient times and was described by PLINY the elder [11, p. 172]. TORBERN BERGMAN in 1784 described the observation of shadings in color reactions [12]. Quantitative estimates, however, were not common until 1838 when LAMPADIUS published his method for color comparison with known solutions using cylindrical tubes for the estimation of Fe and Ni in ores [13]. HOFMANN's diphenylamine method for nitrites [14] was developed into a colorimetric technique by KOPP in 1872 [15], however, the method was still lacking specificity.

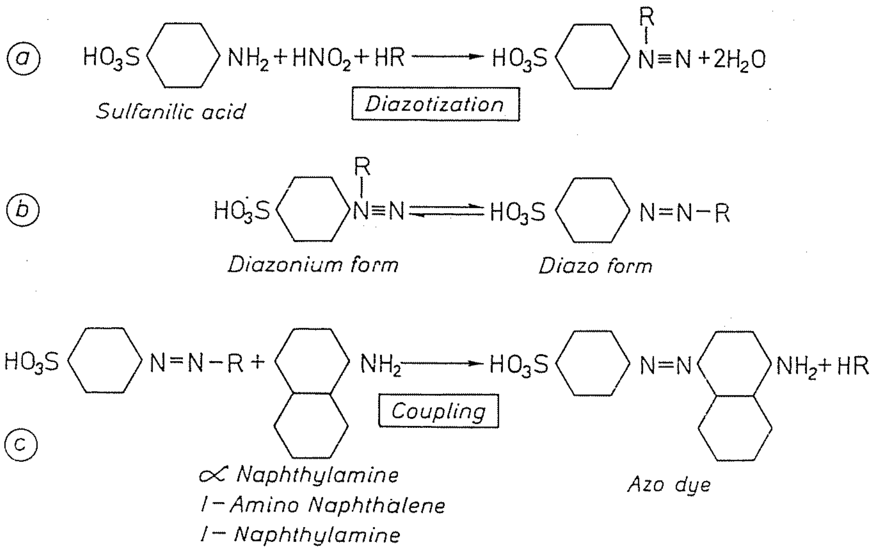

*Fig. 1.* The Mechanism of Griess Reaction

The GRIESS reagent appears to be the first organic reagent in the history of analytical chemistry featuring specificity. Figure 1 shows the mechanism of the formation of azo dyes by the GRIESS reagent. Sulfanilic acid reacts with nitrous acid in the presence of another acid, marked HR. The diazonium salt and water are the products of this reaction (a). At some point rearrangement occurs (b), and the diazo form is coupled with an amine, in the illustrated case with $\alpha$ naphthylamine, thus forming a red azo dye and the acid is regained (c).

GRIESS in his previously mentioned work [6] suggested sulfuric acid medium for the reaction. ILOSVAY in 1889 recommended the more advantageous acetic acid [16] which cut down reaction time and intensified the color of the dye. The acetic acid is still used today with most azo dye methods. LUNGE, also in 1889, suggested the preparation of a ready mixed reagent and the regeneration of the reagent by zinc [17].

## Period of Stagnation and Recurrance

From 1889 the historical development of the GRIESS reagent as an analytical tool stagnated for about forty years. Some of the papers published during this period were dealing with various applications such as the determination of $NO_2^-$ in water, milk, body fluids, etc. An interesting and important sideline occurred, however, in 1937 when E. K. MARSHALL and his co-workers applied the GRIESS—ILOSVAY method to the determination of the drug sulfanilamide in the blood and in the urine of certain patients [18]. In 1939, BRATTON and MARSHALL suggested the use of the coupling agent N-(1-Naphthyl) Ethylenediamine Dihydrochloride [19]. Higher reproducibility, greater rapidity and increased sensitivity were claimed.

The first publication on the quantitative determination of a nitrogen oxide by the GRIESS—ILOSVAY reagent appeared in 1930 [20]; Bennett at the University College in London absorbed nitric oxide in NaOH and tested for nitrite. The first useful field method for $NO_2$ and other nitrogen oxides, however, was not published until 1943 [21]. AVERELL et al. in 1947 used a spectrophotometer and they employed dyed cellophane strips for color standards [22]. SALTZMAN in a previously mentioned paper [3] used a single solution with a midget fritted bubbler to improve the absorption efficiency of the nitrogen dioxide. THOMAS and his co-workers two years later improved absorption by spirals fitted in the inside of the tube for the continuous automatic determination of NO and $NO_2$ [23]. Another automatic method was reported by JACOBS and HOCHHEISER in 1958 [23a] for the determination of $NO_2$ using a sequential apparatus. The speed of color development has improved tremendously during the dozen or so years after 1953. The original GRIESS—ILOSVAY method was quite fast for qualitative test purposes; however, for quantitative analysis a rather long waiting time was necessary to ensure full color development. Figure 2 shows the decreasing trend in the duration of color development with various modified GRIESS reagents. JACOBS and BRODY reported 30 minutes in 1945 [24], SALTZMAN achieved 10—15 minutes in 1954 [3], and 4—5 minutes in 1960 [25]. LYSHKOW decreased this value to 1 minute in 1965 by the addition of a promoter [26], and KOTHNY and MUELLER achieved a development time of 30 seconds in 1966 by using an entirely different azo salt and coupling agent [27].

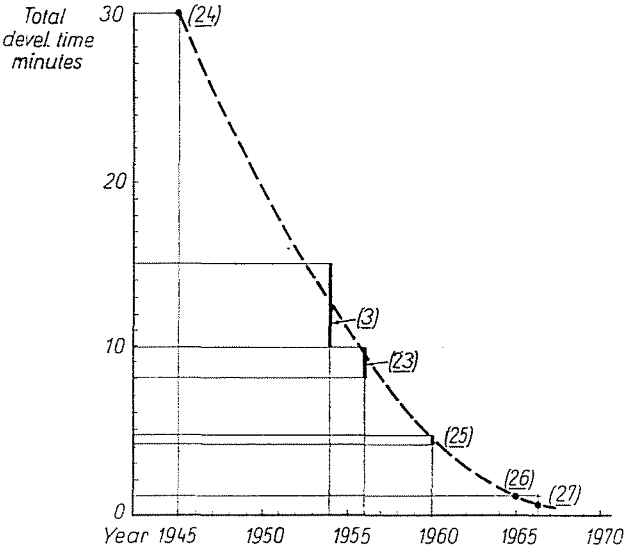

*Fig. 2.* The Decrease of Development-Time of Analytical Azo Dye Methods at Room Temperature

## The Development of Optical Methods

We mentioned before that the azo dye formed in the GRIESS reaction has a red color. Maximum absorbance occurs at about 550 millimicrons. The degree of color development can be measured conveniently by colorimeters, photometers and spectrophotometers. It is appropriate at this point to list the major developments in the optical field. The development of colorimetric methods ran about parallel with the development of the chemistry of azo dyes. SZABADVÁRY in his "History of Analytical Chemistry" [11] gave an excellent account of the historical development of optical methods; the following outline is based on his work. We have mentioned the primitive techniques of BERGMAN [12] and LAMPADIUS [13]. HEINE in 1845 determined bromine by color comparison [28]. JACOUELAIN analyzed copper-ammonia complexes in 1846 [29] and HERAPATH determined iron with rhodanide in 1852 [30].

The first colorimeter is believed to have been constructed by MÜLLER in 1853 [31] and in 1863 the double path system of DEHM become known [32]. DUBOSCQ's well-known colorimeter dates from 1870 [33]. The theoretical ground work for colorimetry was laid down much earlier: BOUGOUER's work dates from 1729 [34], LAMBERT's law was published in 1760 [35] and BEER's adaptation of this law to solutions was reported in 1852 [36]. BAHR and BUNSEN in 1866 for the first time used absorption spectroscopy for analytical purposes [37]. But they did not realize the analytical possibilities of the absorption coefficient previously defined by Bernard [38] and independently by Beer in 1853. Vierordt, a German physician was the first who made use of the absorption coefficient in 1870 [39] and is generally regarded as the father of photometry. The first photometer using a selenium element, however, was not developed until 1911 [11, p. 343] and this technique did not come into general use until 1925.

From the foregoing description it is evident that by the time Greiss published and Ilosvay improved the method on the detection of nitrous acid, a substantial knowledge in theoretical optics existed and colorimeters were available. Yet, neither Griess nor other scientists of the 19th Century applied colorimeters to quantitative nitrite ion analysis or to the analysis of nitrogen oxides.*

## Possible Explanations of the Stagnation-Period

The question arises: what are the reasons fo the gap between the development of the Griess—Ilosvay method in the 1870's and the instrumental application of it to the analysis of oxides of nitrogen in the 1940's. For a better overall view of the evolution of the Griess reagent we refer again to Table II in which the dates of important publications are shown together with the author's name and brief description of their contributions.

By studying the publications in this table interesting facts can be revealed: all major publications prior to 1900 were authored by Europeans and the papers listed after 1937 were written by Americans. Bennett's paper in 1930 originated in London. This pattern of shifting from European to American domination is in agreement with Doctor Price's findings on the "size of Science"- versus various world regions [40]. In his schematic graph (Figure 3)

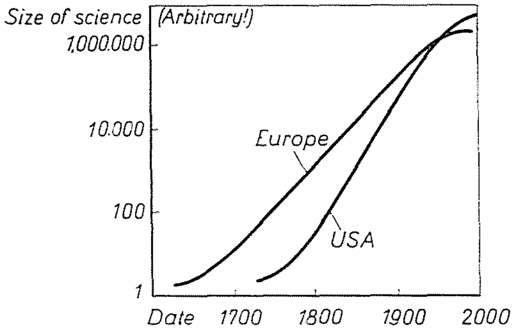

*Fig. 3.* Schematic Graph of the Rise of Science; Based on a Graph by Dreek J. de Solla Price (*40*)

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* Prof. F. Szabadváry of the Technical University of Budapest, winner of the ACS 1970 Dexter Award, in a private communication amended this statement. According to him Prof. Ilosvay in the last decade of the 19th Century applied the Griess method to colorimeters and to the quantitative determination of nitrite in drinking water: Ilosvay, L.: Bull. soc. chim. (3) *11*, 216 (1894); Math. und Phys. Berichte aus Ungarn *12*, 208 (1893/94).

Professor DEREK PRICE places the crossover point between Europe and the USA to about 1940. This scientific-technological power shift is considered by this author as one of the reasons for the stagnation period of the GRIESS reagent.

Other possible explanations might include the emphasis on production technology during the early 1900's. New coupling agents were developed for industrial purposes during this time, especially in Germany, but it took decades until these found their way into the analytical field. Furthermore, the photometric methods during the same period developed very slowly and commercial instruments were available only after 1925. The major breakthrough of the year 1895, the X-rays, seems to rule the first decades of the 20th Century and the visible range received little attention. The tremendous growth of industrial processes in the first part of the 20th Century required better quality control and therefore more sophisticated analytical techniques. The nitrogen oxide analysis efforts of the 30's and 40's are examples of this movement. As one recent account points out: Nitrogen oxides were finally analyzed "out of desperation" by classical wet methods [41]. The circumstances which demanded instrumental gas analysis methods in the 1940's simply did not exist in the late 1800's or early 1900's.

Finally, and probably most influentially the society's and government's awareness of wastes and pollution affected the development of $NO_2$ analysis methods. Although the Bureau of Mines started its air pollution research program in the early 1900's, it was mainly directed towards smoke and sulfur dioxide. Nitrogen oxides were not emphasized as a serious threat to human health until much later. The sharp increase in the number of automobiles after the Second World War contributed to society's and government's concern. The development of huge suburbs around urban areas with their associated transportation problems in the forties and fifties considerably accelerated the development of air pollution monitoring methods. The U.S. Public Health Service and many university affiliated research institutes started research programs in the 1950's on air pollutant analysis and on the continuous survey of contaminants. During the same time, it became known that only not is nitrogen dioxide dangerous to the respiratory organs, but it has a role in visibility reduction and probably in smog formation also. It is well to remember that Dr. SALTZMAN's pioneering article on $NO_2$ analysis was published in 1954 [3] and Professor SALTZMAN was with the U. S. Public Health Service at that time.

## Conclusions

The GRIESS reagent is by no means the only qualitative analytical technique which can be developed into an automatic instrumental gas analysis method and, of course, neither are optical sensors the only possibilities for detection. Many chemical reactions, now in an idling stage, can be combined with advanced instrumentation. Benzidine acetate for hydrogen cyanide, p-nitrobenzene diazonium chloride for ammonia, p-phenylene dimethyl diamine sulfate for hydrogen sulfide, pyrogallol for oxygen are a few examples of specific reactions. Sensitive reactions exist for man gases, among others for chlorine, bromine, various hydrocarbons, arsine, phosphine, etc. Sporadic publications in these fields exist but there are very few cases where an "all-out" effort is noticeable such as in the case in the diazo-colorimetric determination of $NO_2$.

Despite certain trends, which discourage wet chemical analyzers for the future [42], the author feels that there are still important possibilities for such methods. One of the solutions to eliminate maintenance problems associated with wet chemical analyzers is the use of solid adsorbents [43]. The recirculation and regeneration of the liquid reagents can also lessen maintenance. Although other methods like chromatography, solid state electrochemical sensors, laser techniques might be more convenient, adequate specificity of the last two methods is yet to be realized and gas chromatography must solve the problems associated with the analysis of reactive gases such as $O_3$, $NO_2$, $NO$, $H_2S$ and $SO_2$. It is the author's belief, that properly automated, relatively maintenance-free "wet chemical" methods can still fill the gap between high specific but slow bench chemistry and not very specific but fast solid state sensor type instrumentation.

## Summary

The author gives a historic survey of the development of nitrite determination methods with special regard to the GRIESS-ILOSVAY method and the application of it as well as other recent results in the determination of the nitric oxide contaminants in the atmosphere.

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Dr. Eugene L. Szonntagh, Honeywell Inc., Fort Washington, Pennsylvania, USA