

LECTURE

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Early problems in the analysis and the determination of ozone

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Abstract Schönbein's correspondence with Berzelius (1836–1847) and with Faraday (1836–1862) are shown to be excellent accessible sources for his changing views as to the nature of ozone. Two of Schönbein's qualitative tests for ozone, namely the reaction with neutral potassium iodide solution and that with indigo have current quantitative application. Andrew's quantitative studies of the ozone reaction with potassium iodide (1856) and his work with Tait on the volumetric gas phase decomposition of ozone (1860) confirmed the allotropic nature of ozone but did not yield the structure which was first proposed by Odling (1861). Modern spectroscopic studies owe their origin to Hartley's studies of 1881.

1 Introduction

Following the discovery of oxygen, Priestley's "Vital air", large numbers of experiments on oxygen were made in various countries. For example Van Marum of Holland noted in 1785 the peculiar odour after passing an electrical discharge through oxygen and that the gas then acted on mercury [1], but was however unaware of the cause. The first serious study of ozone was that by Schönbein starting in 1839; the first monograph on ozone was by Scoutetten in 1856 [2], Fig. 1, five years before its structure was elucidated by Odling (1861).

The story of ozone from Schönbein's view or changing views is quite confusing as he was for most of his studies unaware of, or unable to accept its true composition. As an alternative to reading all the numerous original papers, at least 364 [3], the details can be followed via Schönbein's correspondence with Berzelius over the period 1836–1847 [4], Fig. 2, and that with Faraday from 1836–1862 [5], Fig. 3. For details of later work Fox's

monograph "Ozone and Antozone" of 1878 [6] is most useful.

The outstanding characteristic of Schönbein's work and writings was the independent line he took. He had little interest in and disregarded the three then current main themes of chemical orthodoxy, namely, quantitative mea-

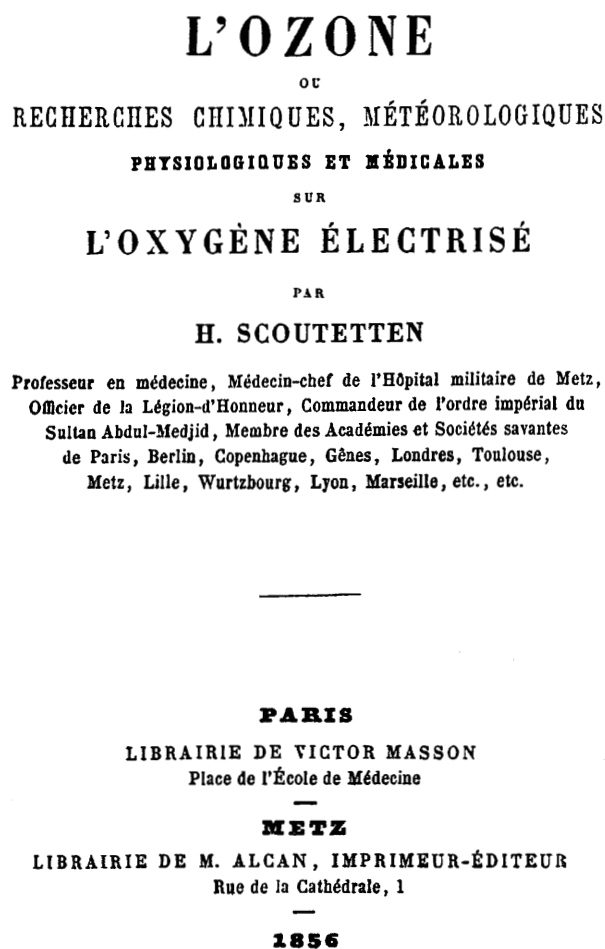


Fig. 1 Title page of the first monograph on ozone by Scoutetten (1856)

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THE LETTERS
OF
JÖNS JAKOB BERZELIUS
AND
CHRISTIAN FRIEDRICH SCHÖNBEIN
1836-1847

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1900

Fig. 2 Title page of "Letters between Berzelius and Schönbein" (1900)

surements, organic formalism and the atomic viewpoint. He relied almost entirely on qualitative reactions, many of which have since formed the basis of quantitative methods [7, 8].

It is interesting to speculate how Schönbein's work might have changed if he had, as at one time he wished, studied under Berzelius, a master exponent of quantitative methods.

2 Schönbein's correspondence with Berzelius and Faraday

Schönbein first wrote to Berzelius about ozone 11 September 1840 [4a] and in great detail on the same topic on 14 April 1844 [4b], he was of the opinion that nitrogen was ozone and hydrogen. Berzelius replied (18th May 1844) that he should produce its compounds in weighable amounts [4d]. Later [4e] (14th February 1845) he wrote "It would be therefore better to put on one side all theoretical conjectures as to the constitution of ozone and nitrogen and to study the properties of ozone itself. Then

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WITH NOTES, COMMENTS
AND
REFERENCES TO CONTEMPORARY LETTERS

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AND
FRANCIS V. DARBISHIRE

"C'est un chéri et grand plaisir que cette
correspondance avec un homme comme vous."
Oct. 20. 1838.
AUGUSTE DE LA RIVE TO SCHÖNBEIN.

BÄLE 1899 LONDON
BENNO SCHWABE WILLIAMS & NORGATE

Fig. 3 Title page of "Letters between Faraday and Schönbein" (1899)

once you have caught it, it will be earlier to theorise about it. I hope you will excuse my candid remarks" [4f]. By March 1845 Schönbein considered ozone to contain oxygen and hydrogen [4g]. Berzelius in due course explained that since ozone could be produced from dry air it contains no hydrogen (12th March 1847) [4h]. Thus, Schönbein could not accept as explained in his last letter to Berzelius (29 March 1847) where he quoted from a letter he had written to de la Rive, "For ambitions sake I must wish that you and Berzelius are in the right, and Mr. Schönbein in the wrong for ozone being mere oxygen modified by electricity would be a substance infinitely more interesting than my peroxide of hydrogen" [4i]. Kahlbaum to assist in following the views expressed to Berzelius gives in an appendix to the correspondence a previously unpublished Schönbein paper "On various states of oxygen" [4j].

The story unfolds in a similar manner in the Faraday [5] correspondences, but covers a longer period and includes the element murium [5a] and antozone [5b] in the account. The name murium is a throw-back to old name for hydrochloric acid, muriatic acid (muriatic-brine). The Schönbein-Faraday correspondence in addition to its sci-

entific content has very human aspects and shows the close relationship which developed between the two scientists. For example, Faraday arranged for an expenses paid British Association for the Advancement of Science lecture (1845) for Schönbein [5c]. Schönbein sends Faraday details of his latest work on ozone for Faraday's Royal Institution evening discourse [5d] (25th February 1859). Faraday arranged an extended trip to London for Schönbein's daughter [5e], Emilie, this ended in tragedy due to her sudden and unexpected death, 13th February 1859 [5f]. The exchange of supportive letters [5g] one to the other further illustrates the mutual affection between the two scientists.

3 Andrews and Tait's quantitative studies on ozone

Thomas Andrews [9] was the first to prove that ozone, from what ever source it was derived, was a single substance namely oxygen in an altered and allotropic condition. Andrews made a series of quantitative analytical studies both gravimetric and volumetric on ozone prepared by electrolysis and by silent electrical discharge.

In the first series of experiments [10] (Fig. 4), Andrews generated ozone by electrolysis and passed the oxygen plus ozone via a U tube (CC') packed with pumice moistened with pure sulphuric acid to dry the gases to an absorption bubbler (D) containing slightly acidified potassium iodide solution then to a bubbler (E) filled with concentrated sulphuric acid, then via a guard tube (F) filled as U-tube CC' finally to the graduated collection vessel, G. The increase in weight of D and E gave the entire weight of ozone be it allotropic oxygen or an oxide of hydrogen.

Fig. 4 Andrews' apparatus (1856) to pass ozone and oxygen through potassium iodide solution

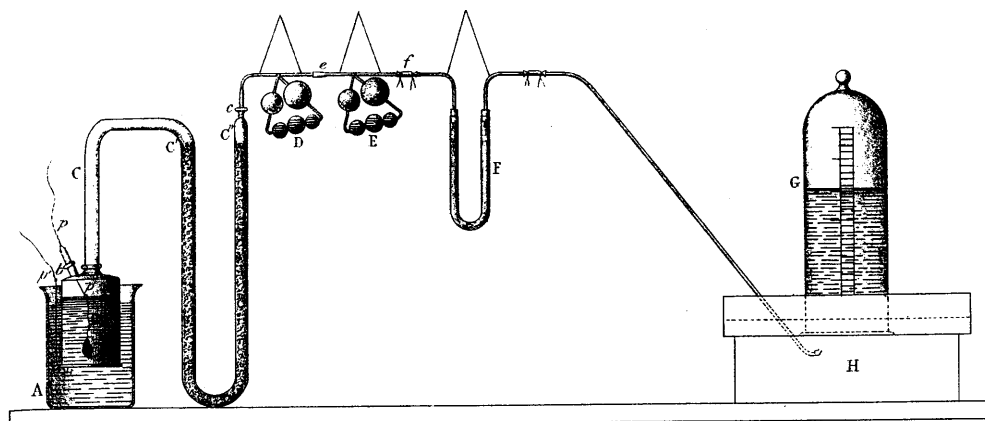
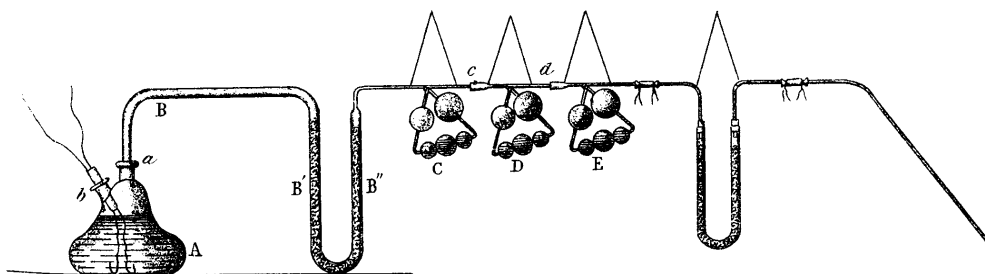


Fig. 5 Andrews' apparatus (1856) to pass ozone oxygen plus hydrogen through potassium iodide solution



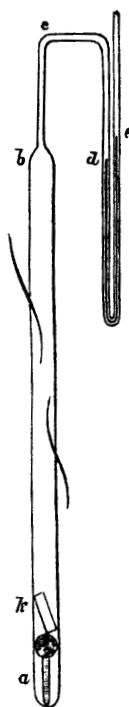
The iodine liberated in D was titrated with standardised sulphurous acid and the equivalent amount of oxygen calculated. Andrews found that, over 5 runs, the weight of ozone (0.1179 g) was the same as that deduced from the iodine liberated (0.1178 g). Hence ozone did not contain hydrogen.

In the second series of experiments (Fig. 5) both the hydrogen and oxygen plus ozone were passed through the apparatus and again increase in weight (0.0149 g) was equal to the weight of ozone (0.0178 g) deduced from the iodine set free.

There followed two brief notes on the density of ozone [11, 12] and a detailed account by Andrews and Tait "On the volumetrical relations of ozone, and the action of the electrical discharge on oxygen and other gases" [13].

The key observations were that dry oxygen contracted when subjected to silent electrical discharge, the volume was fully restored upon heating to 300°C and all ozone properties were lost. Introduction of mercury or potassium iodide by breaking a sealed capsule within the ozonised gas (see Fig. 6) removed all trace of ozone but with no further change in volume. This reaction at constant volume was not explained satisfactorily. Andrews and Tait wrote, "On the allotropic thesis these experiments lead to the conclusion that ozone must have a density at least 50 times that of oxygen. This conclusion is indeed unavoidable from the experiments just described, unless it is assumed that at the same moment that one portion of the ozone combines with the iodine, another portion changes back into oxygen, and that these quantities are so related to one another, that the expansion due to one is exactly equal to the contraction from the other. Such a supposition can however not be considered probable."

Fig. 6 Andrews' and Tait's apparatus (1860) for the study of the volumetric relations of ozone (*a* = capsule containing mercury or iodine)



Thus, despite careful quantitative measurements, it cannot be claimed that Andrews and Tait quantitatively determined ozone. Had they reacted the ozonised oxygen with an essential oil which absorbs ozone the additional contraction considered in relation to the other volume changes should have solved the problem of the nature of ozone and thus allowed its quantitative determination. The true nature of ozone was left to the insight of Odling [14].

Andrews satisfied himself on the identity of the body in the atmosphere which decomposes potassium iodide as being ozone from its selective destruction by dry manganese peroxide and the action of heat [15].

He summarised his and other work to date in an “*Address on ozone*” delivered to the Royal Society of Edinburgh in 1873. He noted Soret’s experiments [16] using oil of turpentine or of cinnamon when the contraction was twice the increase in volume when the ozone was decomposed by heat, hence a formula O_3 . Later Soret confirmed his results by a totally different method, measurement of gaseous diffusion [17]. Andrews was somewhat critical of Brodie’s work on ozone which was somewhat unfair in view of the detailed analysis of errors given in Brodie’s paper on the ozone-iodide-iodine reaction, the absorption of ozone in turpentine and stoichiometry of various oxidations effected by ozone [18]. It is perhaps worth noting that Brodie had a good knowledge of redox chemistry from his earlier work on the oxidation and disoxidation effected by alkaline peroxides [19].

4 The longevity of some of Schönbein’s qualitative tests

Before discussing quantitative aspects of Schönbein’s tests for ozone it is worth noting the longevity of some of

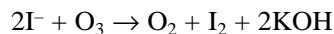
his qualitative reactions. In Wilders “*List of Tests*”. (1895) [20], seven tests appear under Schönbein’s name, for blood, copper, nitrite (2), hydrogen peroxide (3) but none for ozone. These are incorrectly credited to Boettger, Schönbein’s co-worker on guncotton, not ozone. At least one of his qualitative reactions is still cited, that for blood based on the oxidation of gum guaiac with copper (II) in the presence of cyanide ion [21 a].

4.1 Determination of ozone via reaction with potassium iodide

This reaction used qualitatively by Schönbein became the basis of the earliest quantitative determinations [4k]. Mohr [22] completed the determination of free iodine by titration with sodium thiosulphate solution. When atmospheric ozone determinations became popular because of therapeutic uses of ozone, portable monitors were developed based on potassium iodide or potassium iodide-starch reagent papers. These were exposed to the air in special houses or “ozone boxes” to avoid the effects of sunlight [6].

Although the use of the reaction continues to the present it has been subject to problems and considerable study. This is due to the unstable nature of the analyte, and also to the variation in the stoichiometry of the reactions or supposed reaction(s) dependent on the conditions, including the time element of the sampling and or post sampling reaction periods.

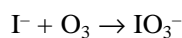
Under neutral conditions the reaction is normally represented [23] as



Since a base is formed the reaction can go on to produce iodate ion,

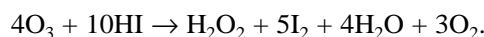


This reaction is reversed upon acidification and overall the same amount of iodine is available for titration as in the first reaction [24, 25], a fact discovered more than once [26, 27]. It has also been suggested that iodate can be formed directly [28],



which in the presence of excess iodide would upon acidification produce $3I_2$, in a six-fold multiplication as compared to the first reaction [25].

The production of hydrogen peroxide under acidic conditions has also been considered [28],



This yields 1.25 I_2 per O_3 reacted, a results confirmed in 1930 by Allen [29]. More recent careful work (1952) using a neutral absorbing solution has shown a positive bias although no mechanism was put forward [30] to explain this result.

Despite its uncertainties, due to simplicity and sensitivity it has been the basis of standard methods for many

years [31]. Interferences from other oxidants can be overcome, or ozone selectively removed [32], as in the H.S.E. Method "Ozone in the presence of nitrous fumes" [33] by passage *via* cotton wool. Recent work has confirmed the system specific characters of the iodometric method for ozone, including bubble size passing through the reagent [34]. It should be noted the ASTM have recently (1989) withdrawn [35] their standard test method for "Oxidant content of the atmosphere (Neutral KI)". Gordon et al. suggest that, long term, a defined UV-monitor method may be the best choice for laboratory based measurement [34]. This would correlate more directly with differential optical absorbance spectroscopy (DOAS) tropospheric measurements in the Hartley band region (280–290 nm) [36].

Before leaving the iodide-ozone reaction it is perhaps worth mentioning a slight mystery as to the priority of discovery of the reaction. Mellor [37], following an earlier comment by Fox [6], reports that H. Davy in his "Lectures on Agricultural Chemistry" (London, 6, 1826) states that "In 1826 Dr. John Davy recognised the existence of this principle in the atmosphere and published a formula for the preparation of chemical tests to be used in its detection resembling those adopted by Schönbein". This raises several problems, Davy's book was "Elements of Agricultural Chemistry in a course of lectures for the Board of Agriculture delivered between 1802 and 1812" [38], there was no edition in 1826. The closest edition was the 4th of 1827. The statement cannot be found in the 3rd, 5th or 6th editions. Search of the Royal Society's "Catalogue of Scientific Papers" [3] for John Davy's publications reveals two papers of interest, "Miscellaneous Chemical Observations", (1829) [39], which does not mention any reactions of potassium iodide and "Some Observations on Atmospheric Electricity," (1836) [40] in which Davy used a starch gel containing potassium iodide to detect the passage of electricity from a lightning conductor to earth, no gas phase discharge products were mentioned. Perhaps this is the source of the rare error of attribution by Mellor.

4.2 Determination of ozone via reaction with indigo [20]

Schönbein's test for ozone based on the bleaching of indigo, like that using iodide has shown considerable longevity but has a smaller literature. The reaction, the oxidative cleavage to form isatin, is the basis of the current Dräger Tube Test for ozone [41]. The reagent in a disulphonated version may be monitored spectrophotometrically [42], or from its chemiluminescence [43]. Indigo trisulphonate has been used in the flow injection analysis of residual ozone in water [44].

4.3 The reaction with gum guaiac

In Schönbein's view [5h] the best means of ascertaining the presence of ozone was that based on an alcoholic ex-

tract of guajacum or resin/gum guaiac. This reagent was criticised in 1902 by Arnold and Mentzel [45] along with other well known tests; they preferred benzidine-copper or tetramethyl-di-p-amino-phenylmethane as reagents, as, although it has not stood the test of time for ozone, gum guaiac was put forward by IUPAC as a spot-test for dichromate as late as 1848 [46] and as guaiac-copper sulphate, Schönbein-Pagenstracher paper, is given as a test for blood in the current "Merck Index" [21].

5 The spectroscopic determination of ozone

The spectroscopic study of ozone goes back over 100 years to the pioneering work of W. N. Hartley, Professor of Chemistry in the Royal College of Science in Dublin.

Hartley reported on the absorption spectrum of ozone spectrographically in the region 233–385 nm [47]. The amount of ozone within his cell was determined by absorption in neutral potassium iodide. He deduced the presence of ozone in the atmosphere from the short wavelength cut off in the solar spectrum [48] and that the blue of the sky due to the fluorescence of ozone [49]. The UV absorption method is now routine for laboratory [50] and for tropospheric measurements.

6 Conclusions

It is considered that Schönbein's correspondence with Berzelius and with Faraday along with Fox's account provide easy access to Schönbein's reactions for characterising ozone and to his views as to its nature. Interestingly, Schönbein's reactions, namely that with neutral potassium iodide and with indigo have current quantitative application. The reaction of ozone with potassium iodide was first studied quantitatively by Andrews, who with Tait made volumetric studies on the gas phase decomposition of ozone, however they did not deduce the O₃ formulae which was first proposed in an undergraduate textbook, by Odling. Modern spectroscopic determinations owe their origin to Hartley's pioneering studies of 1881.

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References

1. Van Marum M (1786) Beschreibung einer Electriciermaschine. Schwickert, Leipzig
2. Scoutetten H (1856) L'Ozone.... Masson, Paris
3. Royal Society of London, Catalogue of Scientific Papers (1800–1863)
4. Kahlbaum GWA (ed), Darbshire FV, Sidgwick NV (trans) The Letters of Jons Jakob Berzelius and Christian Friedrich Schönbein, 1836–1847. Williams and Norgate, London (900), 4 a, p 39; 4 b, p 45; 4 c, p 54; 4 d, p 59; 4 e, p 67; 4 f, p 69; 4 g, p 76; 4 h, p 97; 4 i, p 99; 4 j, p 106; 4 k, p 48

5. Kahlbaum GWA, Darbishire FV (eds) (1899) *The Letters of Faraday and Schoenbein, 1836–1862*. Swabe, Bale, Williams and Norgate, London, 5 a, p 304; 5 b, p 302; 5 c, pp 130, 136, 139 and 140; 5 d, pp 314 and 318, 5 e, pp 269, 273 and 284; 5 f, p 323; 5 g, p 318 et seq.; 5 h, p 257
6. Fox CB (1873) *Ozone and Antozone, their history and nature...* Churchill, London
7. Oesper RE (1929) Christian Friedrich Schönbein Part I Life and Character. *J Chem Education* 6:432
8. Oesper RE (1929) Christian Friedrich Schönbein Part II Experimental Labor. *J Chem Education* 6:677
9. *The Scientific Papers of the late Thomas Andrews (1899)*, with a memoir by P. G. Tait and A. Crum Brown. Macmillan, London
10. Andrews T (1856) On the constitution and properties of ozone *Phil Trans* 146:1
11. Andrews T, Tait PG (1857) Note on the density of ozone. *Proc Roy Soc* 7:498
12. Andrews T, Tait PG (1859) Second note on ozone. *Proc Roy Soc* 9:606
13. Andrews T, Tait PG (1860) On the volumetric relations of ozone and the action of the electrical discharge on oxygen and other gases. *Phil Trans* 150:113
14. Odling W (1861) *A manual of chemistry, descriptive and theoretical, Part I*. Longman, Green, Longman and Roberts, London, p 93
15. Andrews T (1867) On the identity of the body in the atmosphere which decomposes iodide of potassium with ozone. *Proc Roy Soc* 16:63
16. Soret JL (1866) Recherches sur la densité de l'ozone. *Ann Chim Phys* 7:113 [see also (1866) *Phil Mag*, 31 (4 series):82]
17. Soret JL (1868) Recherches sur la densité de l'ozone, Seconde Partie. *Ann Chim Phys* 13:257. [see also (1867) *Phil Mag* 34 (4th series):26; (1867) *Compt Rend* 64:904]
18. Brodie BC (1872) An experimental enquiry on the action of electricity on gases – I On the action of electricity on oxygen. *Phil Trans* 162:435
19. Brodie BC (1862) On the oxidation and dissociation effected by the alkaline peroxides. *Phil Trans* 152:837
20. Wilder HM (1885) *Lists of Tests (Reagents)*, P. W. Bedford, New York
21. Budavari S, O'Neil MJ, Smith A, Heckelman P (eds) (1989) *The Merck Index*, 11th edn. Merck, Rahway, 21 a, p 4457
22. Mohr F (1862) *Lehrbuch der Chemische-Analytischen Titrimethode*, 2nd edn. Vieweg und Sohn, Braunschweig
23. Ladenburg A, Quasig R (1901) Quantitative Bestimmung des Ozons. *Ber* 34:1184
24. Hayhurst W, Pring JN (1910) The Examination of the Atmosphere at Various Altitudes for Oxides of Nitrogen and Ozone. *J Chem Soc* 97:868
25. Thorburn Burns D, Townshend A (1992) Amplification Reactions: Origins and Definitions – Progress and Present Status. *Talanta* 39:715
26. Schmitz LR, Parry GD (1973) Stoichiometry of the ozone-iodide reaction: significance of iodate formation. *Environ Sci Technol* 7:647
27. Flamm DL, Anderson SA (1975) Iodate formation and decomposition in iodometric analysis of ozone. *Environ Sci Technol* 9:660
28. Lechner G (1911) Estimation of ozone by an alkaline solution of potassium iodide. *Z Electrochem* 17:412
29. Allen N (1930) Quantitative determination of small amounts of hydrogen peroxide and ozone. *Ind Eng Chem (Anal edn)* 2:55
30. Birdsall CM, Jenkins AC, Spadinger E (1952) Iodometric Determination of Ozone. *Anal Chem* 24:662
31. Zeplichal F, Hentrich H (1967) Determination of Ozone Content. *Gummi Asbest Kunststoffe* 20:340
32. Cohen IC, Smith AF, Wood R (1968) A field method for the determination of ozone in the presence of nitrogen dioxide. *Analyst* 93:608
33. Factory Inspectorate HM (1969) *Methods for the Detection of Toxic Substances in Air No. 18, Ozone – the Presence of Nitrous Fumes*. HMSO, London
34. Gordon G, Rakness K, Vornehm D, Wood D (1989) Limitations of the Iodometric Determination of Ozone. *J Am Water Works Assn* 81:72
35. ASTM (1989) *1989 Annual Book of ASTM Standards Volume 11.03 Atmospheric Analysis: Occupational Health and Safety*. ASTM, Philadelphia
36. Axelsson H, Edmer H, Galle B, Ragnarson P, Rudin M (1990) Differential Optical Absorption Spectroscopy (DOAS) Measurements of Ozone in the 280–290 nm Wavelength Region. *Appl Spectrosc* 44:1654
37. Mellor JW (1922) *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol 1. Longmans Green, London, p 877
38. Davy H (1813) *Elements of Agricultural Chemistry in a course of lectures for the Board of Agriculture delivered between 1802 and 1812*, 1st edn. Longman, Hurst Rees Orme and Brown, London [2nd ed. (1814); 3rd ed. (1821); 4th ed. (1827); 5th ed. (1836); 6th ed. (1839)]
39. Davy J (1829) *Miscellaneous Chemical Observations*. *Edin New Phil J* 6:128
40. Davy J (1836) Some Observations on Atmospheric Electricity. *Trans Roy Soc Edin* 440
41. Leichnitz K (1989) *Detector Tube Handbook*, 7th edn. Drägerwerk, Lübeck
42. Bergshoeff G, Lanting RW, van Ham J, Prop JMG, Reijnders HFR (1984) Spectrophotometric Determination of Ozone in Air with Indigo Disulphonate. *Analyst* 109:1165
43. Takeuchi K, Kutsuna S, Ibushki T (1990) Continuous measurement of ozone in air by chemiluminescence using indigo-5,5-disulphonate. *Anal Chim Acta* 230:183
44. Strake MR, Pacey GE, Gordon G (1984) Residual Ozone Distribution by Flow Injection Analysis. *Anal Chem* 56:1973
45. Arnold C, Mentzel C (1902) Reactions for Ozone. *Ber* 35:1324
46. Wenger PE, Duckert R, Van Nieuwenburg CJ, Gillis J (1948) *Reagents for Qualitative Inorganic Analysis*. Elsevier, Amsterdam
47. Hartley WN (1881) On the Absorption Spectrum of Ozone. *J Chem Soc* 39:57
48. Hartley WN (1881) On the absorption of Solar Rays by Atmospheric Ozone. *J Chem Soc* 39:111
49. Hartley WN (1889) On the chemistry of the solar spectrum, the blue of the sky and the fluorescence of ozone. *Nature* 39:474
50. Leh F (1976) Air pollution instruments for oxidants. *Int Lab (Sept–Oct)* 13, 14, 16, 18, 21