of effective radiation varying from 1.9 (6500 Å.) to 3.4 v. It was shown by Dymond[5] that gaseous iodine is dissociated into atoms only on absorption of radiation of shorter wave length than 5000 Å. (2.48 v.), a normal and an excited atom resulting.

To suggest a similar behavior of the tri-iodide ion, the light-absorbing system in the reaction studied seems to be unjustified. On the other hand, the heat of dissociation of iodine into two normal atoms is only 36,000 cal. (1.5 v.), so that evidently the reaction mechanisms (1) $I_3^- + h\nu \longrightarrow I_3^-$ (activated); I_3^- (activated) $+ Fe^{++} \longrightarrow Fe^{+++} + 2I^- + I$; $I + Fe^{++} \longrightarrow Fe^{+++} + I^-$; and (2) $I_3^- + h\nu \longrightarrow I^- + 2I$; $I + Fe^{++} \longrightarrow Fe^{+++} + I^-$ are both possible.

We will not go into a detailed discussion of the probable cause of the wrong observations made by Rideal and Williams. A weak transmission of the light filters used and the large reaction vessel leading to very small changes in the iodine titer may account for them.

Summary

The reaction $2Fe^{++} + I_3^- \longrightarrow 2Fe^{+++} + 3I^-$ has been shown to be sensitive to the following lines in the mercury spectrum: $\lambda = 5460$, 4360 and 3660 Å. This is contrary to earlier results of Rideal and Williams, who found a maximum of sensitivity in the region 6500−5000 Å. and no reaction in the region 4000–5000 Å.

An approximate determination of the quantum yield at the three wave lengths indicates a reaction of one molecule per quantum in each case.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, BUREAU OF SOILS]

THE GASOMETRIC DETERMINATION OF NITRIC OXIDE, WITH SPECIAL REFERENCE TO ABSORPTION BY FERROUS CHLORIDE

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During the course of certain experiments involving the use of nitric oxide, the desirability of having available a satisfactory method for the rapid determination of this gas became evident. A search of the literature revealed that the analysis of mixtures of the oxides of nitrogen has been the subject of rather careful investigation and considerable controversy, but the same does not appear to apply to the case of nitric oxide alone.

Various methods for the latter gas, however, have been suggested. Among these are included reduction by glowing copper, oxidation by potassium bromate, hydrogen peroxide, potassium permanganate and

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[5] Dymond, *Z. Physik*, **34**, 553 (1925).

potassium dichromate, absorption by solid potassium hydroxide and absorption by solutions of sodium sulfite and of ferrous sulfate.

The most feasible method for a rapid determination appeared to be that involving absorption of the gas by a solution. In addition to sodium sulfite and ferrous sulfate, various other salts have been observed to form compounds with nitric oxide. Notable among these are certain cupric, ferric, nickelous, manganous and cobaltous salts, and the ferrous halides.[1] The possibility of using solutions of these salts for analytical purposes seemed to be sufficient to justify at least one trial with each.

Disadvantages in the use of both sodium sulfite and ferrous sulfate have been recorded in the literature. While Divers,[2] who first proposed its use, considered a solution of sodium sulfite to be quite satisfactory, Moser[3] has found the complete absorption of nitric oxide by such a solution to occur only after long shaking. With a solution of ferrous sulfate, Moser claimed satisfactory results. His conclusion was not supported by Klemenc and Bunzl[4] nor by Webb.[5] The latter author dwells considerably upon the fact that, in the case of ferrous sulfate and similar salts, "—an equilibrium is ultimately established of the type $FeR_2 + NO \rightleftharpoons FeR_2.NO$." As a consequence of this equilibrium, the absorption of nitric oxide by such solutions in the ordinary type of apparatus leads to inaccurate analytical results.

Experimental Part

Apparatus.—The initial problem involved the selection of an apparatus capable of avoiding the difficulties just discussed. During the course of an earlier investigation, the author had found an absorption buret to be highly satisfactory for the determination of carbon monoxide by means of a solution of cuprous chloride. An attempt to use a similar apparatus in the present case seemed to be justifiable in view of the similarity in the two absorption processes involved.

The apparatus finally adopted is shown in Fig. 1. It is in principle allied to the Morehead absorption apparatus,[6] and also resembles one part of the Illinois gas apparatus,[7] but has been subjected to certain modifications tending towards simplicity and ease of operation.[8] When making a

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[1] Manchot, *Ann.*, **375**, 308 (1910). Besson, *Compt. rend.*, **108**, 1012 (1889). Hüfner, *Z. physik. Chem.*, **59**, 416 (1907). Thomas, *Bull. soc. chim.*, **19**, 343, 419 (1898); *Ann. chim. phys.*, [7] **13**, 145 (1897).

[2] Divers, *J. Chem. Soc.*, **75**, 82 (1899).

[3] Moser, *Z. anal. Chem.*, **50**, 401 (1911).

[4] Klemenc and Bunzl, *Z. anorg. allgem. Chem.*, **122**, 315 (1922).

[5] Webb, "Absorption of Nitrous Gases," Edw. Arnold and Co., London, **1923**, p. 12.

[6] Morehead, U. S. pat. 824,999 (1906).

[7] "The Analysis of Fuel Gases," *Univ. Illinois Bull.*, **22**, No. 8 (1924).

[8] An ordinary 100cc. buret could be used in the construction of a similar apparatus.

determination, the apparatus was filled with water up to the ground-glass joint B, and a sample of gas of any desired volume was collected by connecting a source of supply either at B or at D (preferably at D) and lowering the leveling bulb C. It was found that a 50cc. sample of nitric oxide, if introduced slowly, could stand in the buret for an hour without being absorbed to the extent of 0.1 cc., even when the leveling system contained nothing but pure water. L served as a reservoir for artificially prepared mixtures. The absorbing solution, placed in A, was allowed to trickle down the inside of the buret and into the vessel J. When absorption was complete, and the level of the absorbing solution had dropped to B, some water was sent through to ensure that the final and original conditions of the meniscus, walls of the buret, etc., were the same. The automatic siphoning arrangement, K, was so placed that the liquid in J never dropped to a low enough level to permit air to enter through H. Fresh solutions were used for each determination. The water jacket G served to lessen temperature changes.[9]

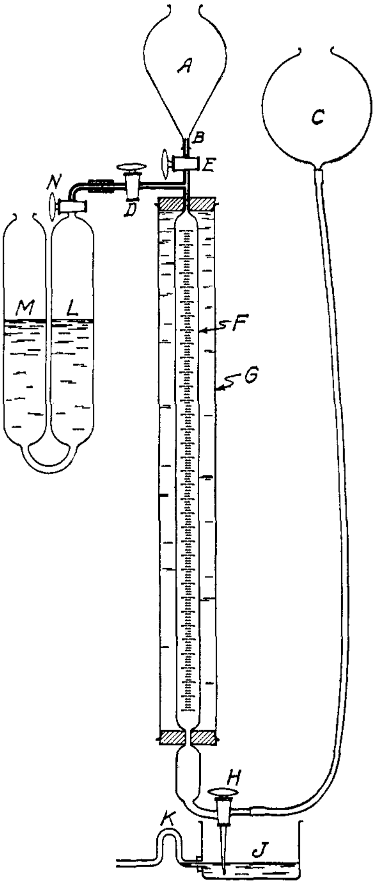

Fig. 1.—Apparatus for the determination of nitric oxide by absorption.

This type of apparatus has certain advantages for the analysis of nitric oxide, as well as various other gases. It allows a continuous change of the liquid film in contact with the gas, which probably accounts for the fact that in general the method has been found experimentally to be more rapid than other methods. Since the gas is stationary and no shaking is required, the apparatus does not require the constant attention demanded by other types. The use of the apparatus is particularly advantageous in cases where, as with nitric oxide and many of its absorbing solutions, there is a tendency towards an equilibrium condition involving incomplete absorption. In any apparatus in which the solution is not being continually replenished,

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[9] Since the absorption of nitric oxide is not accompanied by significant thermal effects and the room temperature did not vary by more than 1°, no temperature regulation, other than that maintained by the water jacket, was considered necessary in the present work.

such a tendency undoubtedly introduces errors, which occur to a much less extent in the apparatus shown.

The apparatus is particularly applicable to the determination of nitric oxide in mixtures with gases which are but slightly soluble in water. The possibility of using it with mixtures of nitric oxide with more soluble gases is to be investigated later. When using the apparatus for certain other absorptions, such as that of ethylene by sulfuric acid, there was added a thermometer inside the water jacket and a bubbling arrangement to keep the water stirred. For more accurate work the use of a compensometer[9a] in connection with the absorption buret has been contemplated.

Materials.—Nitric oxide was prepared from sodium nitrite and sulfuric acid by the method of Noyes.[10] As indicated by the results shown below, the purity of a sample which had been stored over water for two months was 97.5%. Analyses by a method similar to that of Gaillard[11] gave a slightly lower value, 97.4%.

Twenty per cent. solutions (on the basis of the anhydrous material) were prepared from the best salts available, and served as stock solutions for the experiments. Since Ehrenfeld[12] has observed that an excess of alkali prevents oxidation, the sodium sulfite solution was also made about 2% with respect to sodium hydroxide. To overcome the tendency towards difficultly soluble basic salts,[13] 5 cc. of concd. sulfuric acid was added to each 100 cc. of ferrous sulfate solution.

Results

Table I gives the results of a preliminary study of the absorption of nitric

TABLE I

THE RELATIVE DEGREE OF ABSORPTION OF NITRIC OXIDE BY SOLUTIONS OF VARIOUS SALTS

Purity of nitric oxide used, 97.5%

Soln. used	Vol. of soln., cc.	Vol. of gas, cc.	Vol. absorbed, cc.	Absorption, %
$MnSO_4$	100	100	0.9	0.9
$Ni(NO_3)_2$	100	100	1.8	1.8
$CuSO_4$	100	50	1.1	2.3
$Co(NO_3)_2$	100	100	3.1	3.2
H_2O only	100	100	9.7	9.9
Fe_2Cl_6	100	50	10.2	20.9
$Na_2Cr_2O_7$	100	50	15.3	31.4
Na_2SO_3	100	100	75.9	77.8
$FeSO_4$	60	100	97.6	100
$FeCl_2$	40	100	97.5	100

[9a] Tour, *Chem. Met. Eng.*, **23**, 1104 (1920).

[10] Noyes, THIS JOURNAL, **47**, 2170 (1925).

[11] Gaillard, *J. Ind. Eng. Chem.*, **11**, 745 (1919).

[12] Ehrenfeld, *Z. anorg. Chem.*, **59**, 161 (1908).

[13] See Moser and Herzner, *Z. anal. Chem.*, **64**, 81 (1924).

oxide by the various stock solutions. The procedure consisted in collecting a sample of the gas, sending an absorbing solution through the buret very slowly (about ten minutes was allowed, unless absorption was complete in less time), and measuring the volume of the gas remaining.

The above results show that, of the nine salts tried, only ferrous chloride, ferrous sulfate and sodium sulfite gave promise of being of service for rapid analyses. A study was then undertaken to determine the most favorable concentrations of these salts from the standpoints not only of economy in material but also in the time required for absorption. The volumes of solutions and the time requirements recorded do not represent exact determinations of the minima in each case. They do, rather, give indication of what may be expected in a satisfactory operation carried out as rapidly as a careful observation of the progress of the absorption appears to justify. The use of a buret allowing a more even flow of the absorbing solutions than did the one employed would probably lead to slightly better results. The higher solubility of ferrous chloride permitted trials with more concentrated solutions than was the case with the other salts. A saturated solution of ferrous chloride contains about 40% of the salt. Typical results are shown in Table II.

TABLE II

THE ABSORPTION OF NITRIC OXIDE BY SOLUTIONS OF FERROUS CHLORIDE, SODIUM SULFITE AND FERROUS SULFATE

Concn. of soln., %	Vol. of soln. used			Time for absorption			Reduction in vol. of 100cc. sample		
	$FeCl_2$, cc.	Na_2SO_3, cc.	$FeSO_4$, cc.	$FeCl_2$, sec.	Na_2SO_3, min.	$FeSO_4$, min.	$FeCl_2$, cc.	Na_2SO_3, cc.	$FeSO_4$, cc.
Satd.	25	...	...	55	..	...	97.6	..	..
20	45	350	75	70	25	4.5	97.7	97.6	97.4
10	60	300	150	105	23	5	97.4	97.7	97.6
5	90	200	200	160	20	9	97.3	97.5	97.6
2.5	110	275	325	330	27	9.5	97.5	97.3	97.3

The average of the values shown in the last three columns is exactly 97.5, which figure, considered as a percentage, was taken as the value expressing the purity of the gaseous sample. The remaining 2.5% was undoubtedly largely nitrogen. It was not anticipated that the various salt solutions, prepared from water already saturated with air, would dissolve any appreciable quantity of nitrogen. Several blank runs were made, however, the buret being filled with nitrogen only. In no case was there any observable decrease in the volume of this gas.

A study of the results shown in Table II indicates that solutions of ferrous chloride, which have previously received no recognition for the purpose of analytical absorptions, are the most satisfactory of the various solutions tried. This is true with respect to the volume of solution, as well as to the time required for an absorption. Of the different solutions of ferrous chloride, the more concentrated are to be preferred. While not so economical in the use of the salt itself, they allow more rapid analyses, and probably more accurate ones, since the tendency is to stop short of complete absorption when the rate of absorption is slow.

The results shown above confirm an earlier observation of Moser and Herzner[13] to the effect that the more concentrated solutions of sodium sulfite are not the most satisfactory for absorption. With ferrous sulfate, however, the rate of absorption appears to increase with concentration. A consideration of the results shown in Table II led to the selection of 20% solutions of the ferrous salts and a 5% solution of sodium sulfite for subsequent work (see Table III).

The final project involved an investigation of the determination of nitric oxide in more dilute concentrations. For this purpose mixtures of nitric oxide and nitrogen were collected in the reservoir. They were then shaken thoroughly with the confining liquid to obtain uniformity and also to lessen the subsequent tendency towards solution of the nitric oxide by the liquid. The confining liquid was a nearly saturated solution of sodium chloride, the tendency of which to absorb nitric oxide was found to be less than that of any of the solutions for which data are available in Table I.

Table III

The Determination of Nitric Oxide in Mixtures with Nitrogen

	Sample			Vol. not absorbed			% of NO in mixture		
Mixture No.	$FeCl_2$, cc.	$FeSO_4$, cc.	Na_2SO_3, cc.	$FeCl_2$, cc.	$FeSO_4$, cc.	Na_2SO_3, cc.	$FeCl_2$	$FeSO_4$	Na_2SO_3
1	99.9	99.5	99.6	36.8	36.8	36.8	63.2	63.0	63.1
2	99.5	99.6	99.8	63.0	63.2	63.2	36.7	36.5	36.7
3	99.4	99.7	99.4	90.2	90.4	90.0	9.3	9.3	9.5
4	60.1	59.8	60.9	57.0	56.6	57.7	5.2	5.4	5.3

The agreement between the values obtained by the different solutions appears to be as satisfactory as might be expected in the case of the procedure followed. Although no exact record was made of the fact, it was observed that when using the ferrous salts the dilute mixtures required practically as much time for an analysis as did the more concentrated ones. With sodium sulfite, on the other hand, considerably less time was required for the determination of the nitric oxide present in a given volume of a more dilute mixture. In the case of a 5% gas, for instance, the use of a solution of sodium sulfite is not so objectionable as is the case with a concentrated gas.

Summary

An apparatus in which the gaseous sample is continually in contact with fresh absorbing solution (so that a state of equilibrium cannot be established) has been applied successfully to the determination of nitric oxide.

Trials with solutions of various salts, which have been reported to form compounds with nitric oxide, have revealed ferrous chloride, ferrous

sulfate and sodium sulfite to be the more desirable ones for analyses by absorption. Of these three, ferrous chloride, which does not appear to have been used previously for analytical purposes, is the most satisfactory.

WASHINGTON, D. C.

NOTES

Vacuum Oven.—For drying in a vacuum at elevated temperature and for the absorption of moisture, an efficient apparatus (the Abderhalden vacuum drying tube) is on the market. This, however, allows the drying of only small samples of material, as used for combustion, etc. The Abderhalden apparatus cannot be appreciably enlarged, as great difficulty would be encountered in opening the tapered ground joint of the larger size apparatus after the drying in vacuum had been finished. This difficulty has been met by the substitution of a flange ground to fit a tubulated desiccator top as shown in Fig. 1. The apparatus is of Pyrex, is inexpensive, and maintains its vacuum well.

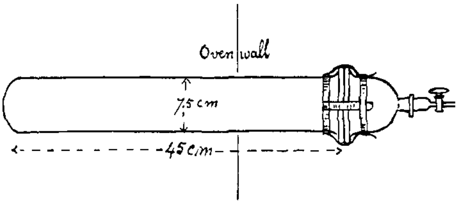

Fig. 1.—Vacuum drying tube.

The tube is allowed to project 15 cm. outside the oven, thereby preventing the heat of the oven from softening the lubricant used upon the flange as a seal, and also providing a cooler section in which the absorbent (usually sodium hydroxide in copper trays) is placed.

To prevent the cover from falling when the vacuum is released, a copper band or hoop is placed around the tube next the flange. To this are soldered four copper strips at equal intervals. These are folded over the joint and their free ends are held in place by another hoop, which is slipped over the dome of the cover. The apparatus is evacuated with an oil pump and closed by a stopcock ground into the tubulature of the cover. Two such tubes may conveniently be placed side by side in the ordinary oven. The cover is removed easily by a turning motion, especially when the oven is still warm, not necessitating, as a rule, the use of a safety razor blade as applied to sticking desiccator covers.

It would seem possible to construct an efficient apparatus of larger size, either of Pyrex or copper. If copper is used, however, it may be necessary to cool the flange by means of a water jacket or spiral tube in order to maintain the seal. Concentric grooves in the rims might also prove helpful.

Thanks are due to the Corning Glass Works for the construction of the special glass apparatus and to A. G. Sterling of the Bureau of Chemistry for making the metal parts.

Thermoregulator.—The lower part of the regulator is the ordinary