Nitric Oxide Project

Report for the Period
December 1, 1953-March 1, 1954
Contract ONR 1322(00)

Abstract

During the period indicated above we have made a large number of yield measurements for the formation of nitric oxide in an electric discharge. We have tested thoroughly the simple analytical method selected as most suitable for our purposes. So far we have been able to obtain steadily increasing degrees of conversion and yields of nitric oxide per KWH of power consumed in the discharge. As a matter of fact, using a gas mixture of equal volumes of nitrogen and oxygen, we have obtained a reactor exhaust containing about 16 volume per cent of nitric oxide at a power yield of 50 grams of nitric acid per KWH consumed. A beginning has been made towards a kinetic analysis of the reactions taking place and determination of their rates as functions of power input, average pressure, gas flow rate, gas composition and other variables. As a general summary the results obtained so far indicate definitely that the higher the flow rate and the power input, the higher the degree of conversion and the yield of nitric oxide. With varying pressure a fairly flat maximum yield seems to be indicated at a pressure of about 120 to 140 mm Hg.

Experimental Procedure

All measurements, except those carried out for the study of the kinetics of the reactions taking place in the discharge, were obtained using a water-cooled reactor with a center tube having an inner diameter of 6 mm and a length of 16 inches. The hot electrode was made of solid brass and provided with four heavy circular cooling fins. It was machined to fit vacuum tight a 29/42 standard taper joint. The 45° angle V-tip of the electrode ended about half an inch above the center of the reactor's center tube. The flowing gas mixture was admitted through a center hole in the hot electrode. This hole ended however about half an inch away from the V-tip and an opening was provided by drilling another hole at right angle to the main axis of the electrode and ending at the center. In this manner turbulent flow of the gas stream was obtained as it entered the reactor.

At the opposite end of the reactor it widened out to an inner diameter of about 35 mm in order to accommodate the water-cooled ground electrode. This was made of thin-walled copper tubing and ended in a slightly rounded V-tip a few millimeters away from the outlet end of the center tube of the reactor. To be able to handle larger gas flows the reactor was provided with a standard Pyrex 1-1/2 inch pipe joint and was coupled to a Pyrex pipe tee which furnished mounting for the ground electrode and connection with the vacuum line. Side outlets to the reactor were provided for pressure readings and sampling of the gas stream. Pressures were measured using Wallace and Tiernan absolute manometers having an accuracy better than one millimeter mercury.

All gas flows were measured with simple, capillary-type glass flow meters using i-butyl phthalate as manometer liquid. A series of these flow meters were mounted on a panel board with appropriate needle valves and pressure regulators. Their outlets were joined to a manifold making it possible to produce a flowing gas mixture containing up to six different gases, all accurately controlled individually. A number of interchangeable flow tips calibrated with a precision wet test meter provided a series of overlapping flow ranges for the gases to be employed.

To obtain a sample of the gas stream as it had passed through the discharge main, a small portion was led through the side outlet in the reactor provided for the purpose into a manifold for six separate gas sampling bottles of standard type and size. The outlets of the gas sampling bottles were connected with another manifold leading to a small vacuum pump provided for their evacuation. To take a gas sample from the reactor a slow stream was first allowed to pass through the evacuated sample bottle to be used during a period of two minutes after a steady discharge state had been reached. After closing the outlet stopcock in the sample bottle the corresponding needle valve in the inlet manifold was fully opened slowly, the reactor outlet pressure noted, and the inlet stopcock of the sample bottle closed.

The output from the R-38 DC power supply used as current source was controlled employing a Machlett type ML-3668 triode power tube and a 400 watt variable bias resistor. The carefully filtered power output was continuously variable to give a maximum of about 1800 watts over short periods of time. This latter output necessitated, however, forced cooling of the hot reactor electrode and only a rough adjustment of the current could be made. Current and voltage were measured using calibrated instruments.

Experimental Results

Some of the data obtained are summarized in Tables I, II and III. The formation of nitric oxide in electric discharges has been studied extensively during the last seventy years and it would seem that every possible angle already had been covered. However, a large amount of the available material is contradictory or obtained under widely different conditions, making a comparison of the data published difficult or impossible. However, as far as we have been able to proceed up to the present time our results seem to coincide fairly well with the recent data of S. S. Vasil'ev (Kinetic Analysis of Chemical Processes in Electric Discharges, Vestnik Moskov. Univ. 6, No. 8, Ser. Fiz.-Mat. i Estestven. Nauk, No. 5, 79-96, 1951; Chem. Abstr. 46, 3876, 1952). In Table I, Part I are given some data obtained using air at a constant flow rate of 4.0 liters per minute, varying pressure and discharge maintained somewhat above minimum sustaining energy. These data have been plotted in Figure 1 and seem to indicate that a fairly flat maximum power yield is obtained in the pressure range of about 120-140 mm mercury.

In Part II of Table I are given various data obtained at the same flow rate but with a mixture of equal volumes of pure oxygen and nitrogen at approximately the same average pressure and varying power input. As shown in Figure II, these date suggest the possibility that the yield of nitric oxide increases linearly with the power input. Part III of Table I summarizes some data which seem to show that mixing the air stream with a large volume of water vapor has a negligible influence on the yield at low power inputs, while at higher ones the yield is decreased considerably. A few measurements not given here have shown that addition of helium gas appeared to have a pure dilution effect decreasing the yield in the ratio to the amount added.

Table II, Part I summarizes a number of measurements using air at different flow rates and fairly high power inputs. Inspection of the data shows immediately a steady increase in all cases of the yield of nitric oxide with power input and flow rate up to the limits within which we were able to operate. Part II of Table II gives some corresponding measurements using air enriched with oxygen to give a gas mixture containing equal volumes of oxygen and nitrogen. At equal flow rates, power inputs and pressures oxygen-enriched air gives considerably higher yields than ordinary air, which is in agreement with a number of older observations.

Table III gives some data obtained with a tapped reactor designed for kinetic analysis of the processes taking place in the discharge. This reactor had seven equidistant outlets from the center tube and which were joined together outside the cooling mantel to form a manifold for sampling purposes. Each outlet had a stopcock inserted and thus individual samples could be withdrawn from every one of them. The inner diameter of the center tube was 6 mm and the outlets were placed at a distance of three inches from center to center. Both hot and ground electrodes employed were the same ones as those used for the reactor described above.

Plotting the amount of nitric oxide formed per liter of NTP gas it is found, as shown in Figure III, that its concentration increases steadily as the gas stream passes through the reactor. On the other hand, as illustrated in Figure IV, the yield of nitric oxide per KWH shows a fairly well defined maximum when the gas has traversed about one-third of the total length of the reactor. No detailed calculations have been made as yet with regard to the significance of the data presented, but they do indicate an extremely high rate of formation of the nitric oxide, which increases rapidly with the power input while the rate of decomposition must be considerably lower, which is in agreement with the data of Vasil'ev quoted above.

Future Work

The main object of our project was to find out what influence the presence of carbon monoxide in relatively large quantities would have on the yield of nitric oxide in an electric discharge. To do this it was considered necessary first to lay a solid foundation of yield data in the absence of carbon monoxide. Thus we are going to continue the type of measurements we have been doing up to the present time, with the main idea in mind to improve the yield still further and to continue the study of the kinetics of the reactions taking place. To obtain increased yields we will change over from a glass to a quarz reactor and, at the same time, make it somewhat shorter and give it a larger bore. The center tube will be split at right angle near the hot electrode and the gas mixture will be introduced near the opposite end using a side inlet to the mantel. In this manner the gas will be strongly preheated before it enters the discharge which should reduce the power consumption somewhat. Shortening and widening the center tube will decrease the space velocity and lengthen the contact time at the same time the power required to sustain the discharge decreases. Lengthening the contact time should also, as strongly indicated in Figure III, increase the yield of nitric oxide per KWH.

Table I, Part I. Yield of nitric acid per KWH using a DC discharge, an air flow of 4.0 liters per minute at various pressures and close to niminum sustaining energy.

Voltage	Current	Power	Pressure in mm Hg			Yield of HNO_3
KV	MA	watts	inlet	outlet	average	gram / KWH
6.8	47	320	40	24	32	4.6
8.0	44	352	50	37	43	4.4
8.1	54	437	60	47	53	5.0
8.3	64	531	70	57	63	5.0
8.8	81	713	80	66	73	5.7
8.1	98	794	90	76	83	8.8
7.4	128	947	100	84	93	9.7
7.6	142	1079	110	95	103	10.8
7.8	152	1185	120	105	113	17.0
8.0	161	1288	130	116	123	17.1
8.0	175	1400	142	128	135	17.8
8.2	191	1566	156	144	150	14.0

Table I, Part II. Yield of nitric acid per KWH using a DC discharge, a gas mixture containing equal volumes of nitrogen & oxygen flowing at a total rate of 4.0 liters per minute at approximately constant average pressure.

Voltage	Current	Power	Pressure in mm Hg			Yield of HNO_3
KV	MA	watts	inlet	outlet	average	gram/KWH
7.6	102	775	92	80	86	6.8
7.5	112	840	90	76	83	7.7
7.2	131	943	90	76	83	9.0
6.8	150	1020	90	74	82	10.9
6.4	190	1216	90	71	80	10.5
5.9	230	1357	90	69	79	13.8
5.4	285	1540	90	65	77	16.8

Table I, Part III. Yield of nitric acid per KWH using a DC discharge, air as such or saturated with water vapor at ordinary temperatures at the total pressures indicated.

A. Measurements with air as such

Flow lit./min.	Voltage KV	Current MA	Power watts	Pressure in mm Hg inlet	outlet	average	Yield of HNO_3 gr./KWH
4.0	6.1	89	543	53	33	43	11.3
4.0	4.9	154	755	53	23	38	11.9
4.0	4.7	171	804	53	20	36	13.2
4.0	4.3	200	860	53	11	32	14.8
4.0	6.1	91	555	53	33	43	11.6
6.0	7.3	109	796	80	47	63	8.9
6.0	6.4	148	947	80	38	59	13.1

B. Measurements with air saturated with water vapor at reactor inlet pressure by bubbling it through a porous plate immersed in water.

Flow lit./min.	Voltage KV	Current MA	Power watts	Pressure in mm Hg inlet	outlet	average	Yield of HNO_3 gr./KWH
4.0	6.6	77	508	53	31	42	6.8
4.0	5.8	111	644	53	26	40	8.1
4.0	5.0	155	775	53	16	35	9.5
4.0	4.8	182	874	55	3	29	13.6
4.0	4.7	210	987	58	3	30	17.1
6.0	7.5	112	840	80	50	65	6.2
6.0	6.5	155	1008	80	41	60	7.9
6.0	6.3	169	1065	80	37	58	7.8
6.0	5.8	200	1160	80	28	54	7.7
6.0	5.5	220	1210	81	9	45	6.3
6.0	8.3	138	1145	108	80	94	8.6
6.0	7.9	165	1303	108	79	93	11.7

Table II, Part I. Yield of nitric acid per KWH using a DC discharge at various air flow rates in liters per minute, pressures & power inputs.

Flow	Voltage KV	Current MA	Power watts	Pressure mm Hg inlet	outlet	average	Yield of HNO_3 gr./KWH
3.0	6.8	67	455	52	49	46	6.9
3.0	6.4	80	512	52	40	46	9.4
3.0	5.6	120	672	53	39	46	9.8
3.0	5.2	156	811	53	38	45	8.6
3.0	5.4	130	702	53	38	45	11.3
4.0	5.8	105	609	51	27	39	11.9
4.0	5.0	165	825	54	21	38	11.9
4.0	5.1	220	1122	67	35	51	17.3
4.0	6.7	210	1407	100	82	91	17.8
5.0	5.3	248	1314	81	39	60	24.3
5.0	5.9	230	1357	90	57	74	20.8
5.0	6.6	210	1386	100	73	87	23.9
6.0	5.7	240	1368	90	40	65	24.4
6.0	6.7	200	1340	100	65	83	24.1
7.0	6.8	175	1190	97	58	78	19.3
7.0	6.1	232	1414	100	51	70	19.1
7.0	6.7	220	1474	110	70	90	25.5
7.0	7.2	205	1476	122	84	103	30.1
7.0	7.6	202	1535	131	98	114	27.5
8.0	5.9	280	1652	111	45	78	27.7
8.0	6.3	272	1714	120	65	92	28.2
8.0	6.9	250	1725	130	83	106	36.2
9.0	6.3	265	1670	120	45	82	30.3
9.0	7.0	250	1750	130	71	100	33.8
10.0	6.4	255	1632	120	39	79	30.1
10.0	6.8	245	1666	125	60	92	37.2
10.0	6.8	260	1768	131	68	99	35.7
11.0	6.3	310	1953	135	33	84	35.0
11.0	6.6	290	1914	138	60	99	42.6

Table II, Part II. Yield of nitric acid per KWH using a DC discharge with oxygen-enriched air containing equal volumes of oxygen & nitrogen at various flow rates in liters per minute, pressures & power inputs.

Flow	Voltage KV	Current MA	Power watts	Pressure mm Hg inlet	outlet	average	Yield of HNO_3 gr./KWH
8.0	6.5	185	1203	94	40	67	19.6
8.0	7.0	175	1225	100	54	77	24.2
8.0	6.8	210	1428	109	61	85	31.6
8.0	6.2	265	1643	110	54	82	34.4
8.0	6.8	245	1666	121	75	98	36.3
8.0	7.1	250	1775	131	90	110	41.6
8.0	6.4	275	1750	120	68	94	39.6
10.0	6.4	260	1664	119	39	79	37.1
10.0	6.6	255	1683	122	50	86	37.4
10.0	6.4	280	1792	125	53	89	40.5
10.0	6.6	270	1782	127	59	93	42.9
10.0	6.8	265	1802	131	67	99	50.0
11.0	6.6	275	1815	131	35	83	43.7
11.0	6.6	280	1848	132	45	88	46.8
11.0	6.8	270	1836	134	60	97	46.4

Table III. Yield of nitric acid per KWH using a tapped reactor, a DC discharge & an air flow of 4.0 liters per minute. Yield at a given outlet of the reactor computed assuming linear variation of potential drop.

Outlet number	Dist. to hot electr.	Voltage KV	Current MA	Press. in mm Hg		g./lit. gas $HNO_3 \times 10^3$	Yield HNO_3 g./KWH
				inlet	outlet		
			A. Average total power input 612 watts				
1	5"	8.5	72	51	47	7.3	13.8
2	8	8.5	72	51	44	12.1	14.1
3	11	8.4	73	51	40	13.1	11.2
4	14	8.4	73	51	37	14.7	9.9
5	17	8.4	73	51	33	16.3	9.0
6	20	8.4	73	51	30	17.3	8.2
7	23	8.6	71	51	26	21.3	8.7
			B. Average total power input 830 watts				
1	5	6.8	122	54	49	14.6	20.5
2	8	6.8	122	54	44	22.6	19.6
3	11	6.8	122	54	40	26.4	16.5
4	14	6.9	120	54	35	31.5	15.6
5	17	6.9	121	54	29	40.5	16.5
6	20	6.9	119	54	23	41.1	14.2
7	23	7.0	118	54	13	49.1	14.8
			C. Average total power input 1184 watts				
1	5	7.4	160	67	62	16.4	16.0
2	8	7.4	160	67	58	33.9	20.7
3	11	7.3	160	67	53	35.7	15.8
4	14	7.4	160	67	48	48.7	16.9
5	17	7.4	160	67	43	56.2	16.1
6	20	7.4	160	67	38	55.4	13.5
7	23	7.4	160	67	33	58.0	12.3

The Determination of the Amount of Nitric Oxide Formed in an Electric discharge

by Wilbur Simon

Introduction. Many reagents are available for the colorimetric determination of nitrates. The reagents most commonly used are diphenylamine and phenoldisulfonic acid. In addition to these ferrous sulfate, strychnine, methyl umbelliferone and brucine have been employed. Each reagent has its drawbacks; phenoldisulfonic acid must be prepared fresh and can be used only in the absence of water. Diphenylamine is an oxidation-reduction indicator and is sensitive to other oxidizing agents. Ferrous sulfate is an unstable reagent being easily oxidized to ferric iron by contact with air. Strychnine is the most sensitive of these reagents but requires freshly prepared solutions each time. Methyl umbelliferone was not as soluble as stated in the literature and the procedure given did not yield the expected results when followed.

Brucine in chloroform or brucine sulfate in water solutions were found to be best suited for the analysis of the gas samples withdrawn from our discharge reactors. Although the procedure worked out is very simple many precautions must be carefully observed in order to obtain a precision of 2 per cent or better.

Discussion of procedure. The nitration of brucine sulfate in dilute solutions requires a fairly high temperature of the liquid. The heat required is furnished by the heat of solution of sulfuric acid in water. Unless the brucine sulfate is dissolved before the concentrated sulfuric acid is added some nitrate may be lost as nitric acid. If the reaction is quenched before full color development has taken place the addition of distilled water will produce additional color but the heat of solution at this point is imsufficient to produce complete color development with regard to the unreacted amount of nitric acid present in the sample.

Dilution to any given volume is complicated by the expansion of the liquid due to further evolution of heat. When the solution is cooled to room temperature the volume will decrease and the addition of more water will warm the solution again. However, with some practice it is possible to gage the dilution in such a manner that the solution will come close to the desired volume when it has cooled to room temperature. When the solutions are transferred to the photometer absorption cells bubbles are formed on their walls and several minutes are required for them to come to the surface so that a valid reading can be made. In addition to the precautions just given all glass ware used must be washed with generous quantities of distilled water. If reagent-grade sulfuric acid is used no further purification is necessary provided that a suitable reagent blank is employed as reference.

A study was made of all pertinent phases of the analytical procedure. Thus it was found that the rate of addition of the sulfuric acid does not affect the results obtained. Addition times ranging from five seconds to one minute were tried and found to give negligible variations. After the addition of sulfuric acid had been completed the optical density of the solution increased steadily during the first five minutes and then it showed no further increase over a period of fifteen minutes or more. As an added precaution to get [illegible] comparable results the time of color development was standardized to a length of five minutes. In the case of brucine sulfate which is only slightly soluble in cold water a saturated solution was first prepared at room temperature and then filtered and diluted. Precipitation of brucine sulfate would affect the precision of the analysis, since the optical density of the resulting solution increases with its concentration. The same is true for the quantity of sulfuric acid employed which must be the same in all cases to get comparable results. Whether nitrites or nitrates are present they give the same analytical result.

The absorption of the oxides of nitrogen in the gas samples is accelerated by the use of an oxidizing agent. Either hydrogen peroxide or potassium permanganate may be employed for this purpose, but because both of them contain minute amounts of nitrates the solution blanks should contain these reagents in appropriate quantities. If too much permanganate is added to a sample, solution manganese dioxide may be formed which co-precipitates part of the nitric acid present as manganous nitrate. This may be remedied by analysis of the precipitate after dissolving it in a minimum quantity of hydrochloric acid.

Using the procedure to be described below, quite precise results have been obtained and about fifty determinations may be carried out per day. Several hundred analyses have already been performed and the method appears to be reliable. The precision achieved seems to be within the limitations of the instrument employed. There is some deviation from the Beer-Lambert law which is based on the use of monochromatic light. A filter photometer like the one used gives a comparatively wide band of light.

Analytical procedure. The gas samples are collected in evacuated sampling tubes as previously described. About 70 cc of 1:500 sulfuric acid containing potassium permanganate is sucked into the tube by opening the lower stopcock. After the solution has been allowed to stand over night it is drained into a 100 cc volumetric flask and the sample tube is rinsed three or four times with distilled water, the washings being added to the volumetric flask containing the sample. The sample is finally diluted to 100 cc with distilled water.

A five cc sample is then pipetted into a 25 cc Pyrex volumetric flask and six drops of an aqueous solution of brucind sulfate are added followed by 10 cc of concentrated sulfuric acid from a 50 cc burette in order to maintain sufficient accuracy. The resulting mixture is swirled gently and allowed to stand for five minutes. It is then placed in ice water and diluted to 25 cc with distilled water. The optical density of the solution is measured with a Fischer "Electrophotometer" using a suitable reagent blank and employing a 425 millimicron optical filter. The reading obtained is matched with the curve for readings previously made with a series of standard solutions of potassium nitrate following exactly the same procedure. Whenever a fresh brucine sulfate solution is prepared a new calibration curve is made up by successively pipetting off 1, 2, 3, 4 and 5 cc of a standard potassium nitrate solution containing the equivalent of 10 micrograms of nitric acid per cc. All aliquots are diluted with sufficient distilled water to bring the volume to exactly five cc. Figure V is a calibration curve drawn using data obtained by the above procedure. It shows only a minor deviation from the Beer-Lambert law.

Table I summarizes the data obtained for a representative series of samples analyzed February 20, 1954. All samples contained different amounts of nitric acid and all determinations were performed in duplicate.

In order to determine the absolute precision of the method nine samples of a standard solution of potassium nitrate containing 50 micrograms of nitric acid were analyzed. The results obtained are shown in Table II.

Table I. Some data showing precision of analytical procedure utilizing brucine sulfate for determination of nitrates.

Sample number	Rel. optical density Det. I	Rel. optical density Det. II	Deviation in percent
1	14.0	14.0	0.0
2	14.1	14.1	0.0
3	39.4	38.6	1.0
4	14.4	14.0	1.4
5	7.2	7.2	0.0
6	9.0	9.0	0.0
7	14.1	13.7	1.4
8	6.6	6.6	0.0
9	9.5	9.7	1.0

Table II. The precision of the brucine sulfate procedure as given by the analysis of a solution containing 50 micrograms of nitric acid.

Sample	Reading	Sample	Reading
1	37.4	6	37.5
2	37.8	7	37.5
3	39.0	8	37.5
4	37.8	9	37.7
5	37.5		

Table III. The effect of variations in amount of sulfuric acid added upon photometer reading obtained.

H_2SO_4 cc	Det. I	Det. II
8	28.1	28.0
9	33.8	33.8
10	36.3	36.3
11	40.1	40.4

The standard deviation for the data in Table II is ±1.25 per cent. However such a precision can be obtained only with extreme care, one of the most important factors being the quantity of sulfuric acid added. Table III illustrates the importance of measuring the amount of acid added very carefully.

The variations in photometer reading shown by the data in Table III can not be accounted for by nitrates present in the sulfuric acid since a reagent blank containing 8 cc of the acid yielded results showing an optical density only 0.008 units lower than one containing 10 cc of acid. In Table IV are given some data showing the effect of time of color development upon the readings obtained.

Table IV. The effect of time elapsed before cooling upon the optical density observed.

Time elapsed in minutes	Photometer reading
5	36.1
6	36.1
7	36.1
8	36.1
10	36.1

Summary. If sufficient care is taken to control the pertinent variables, brucine sulfate may be used for the determination of nitrates in aqueous solutions. The method is simple and well within the precision which can be expected from a filter photometer.

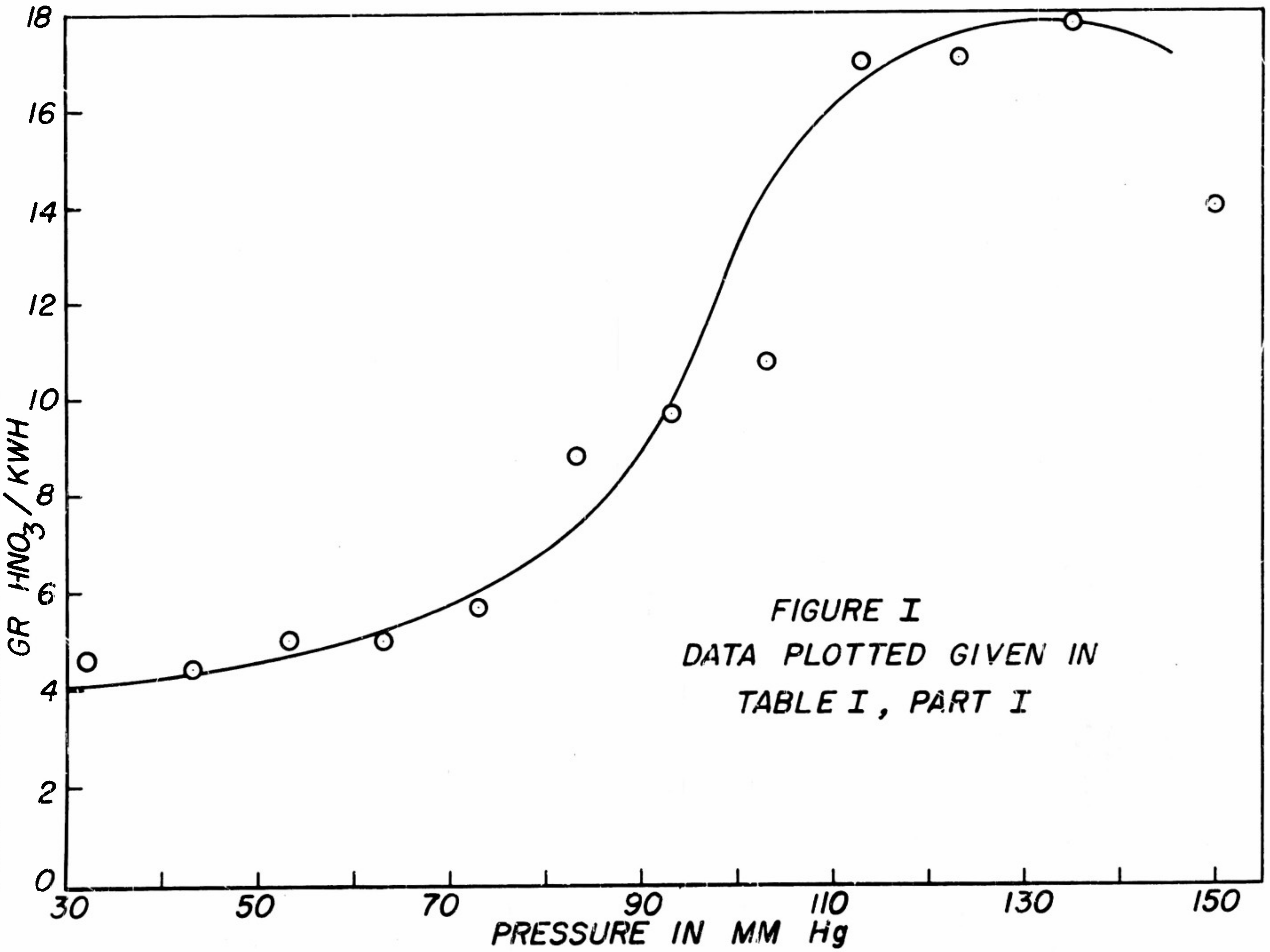

FIGURE I
DATA PLOTTED GIVEN IN
TABLE I, PART I

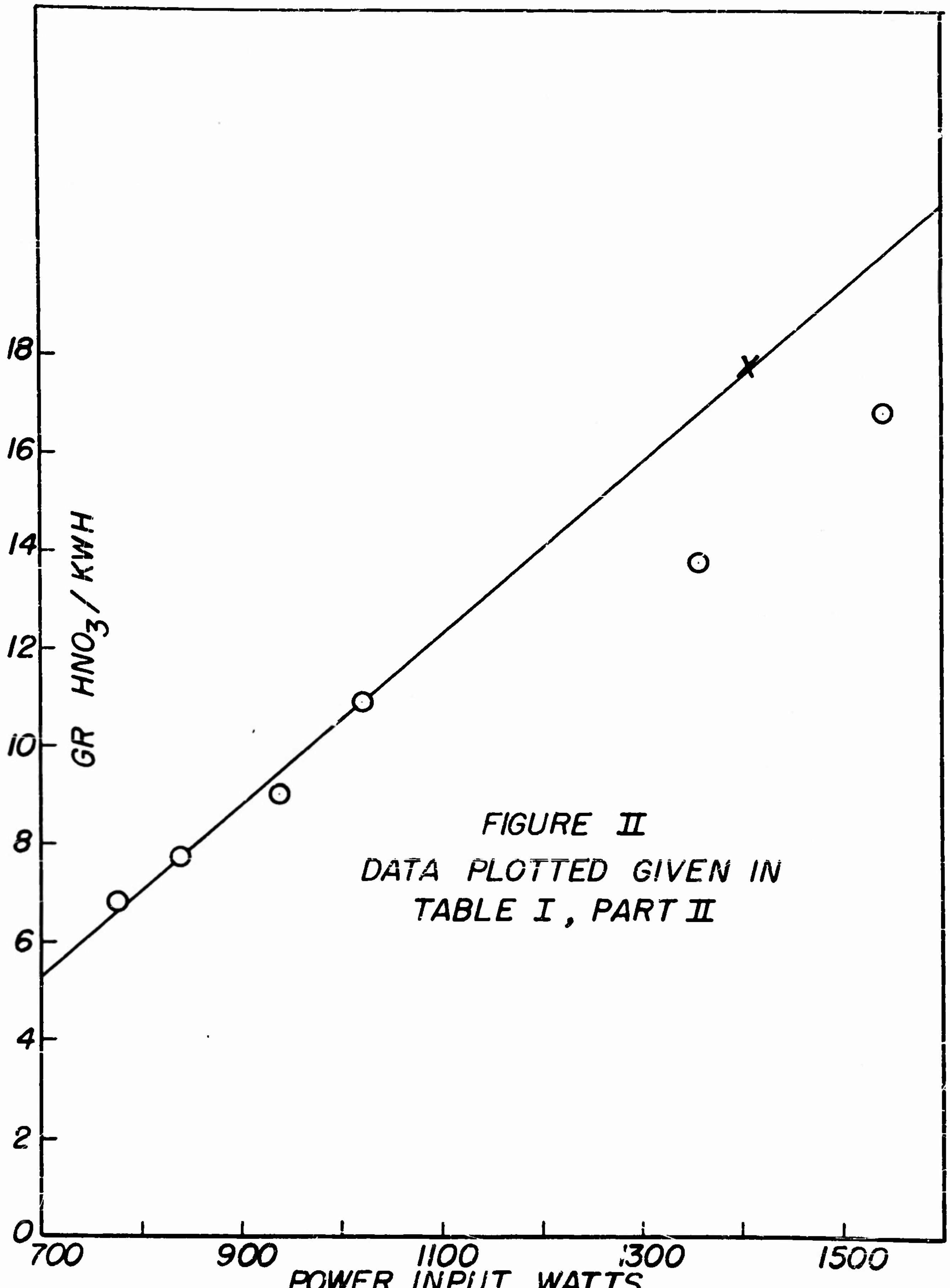

FIGURE II
DATA PLOTTED GIVEN IN
TABLE I, PART II

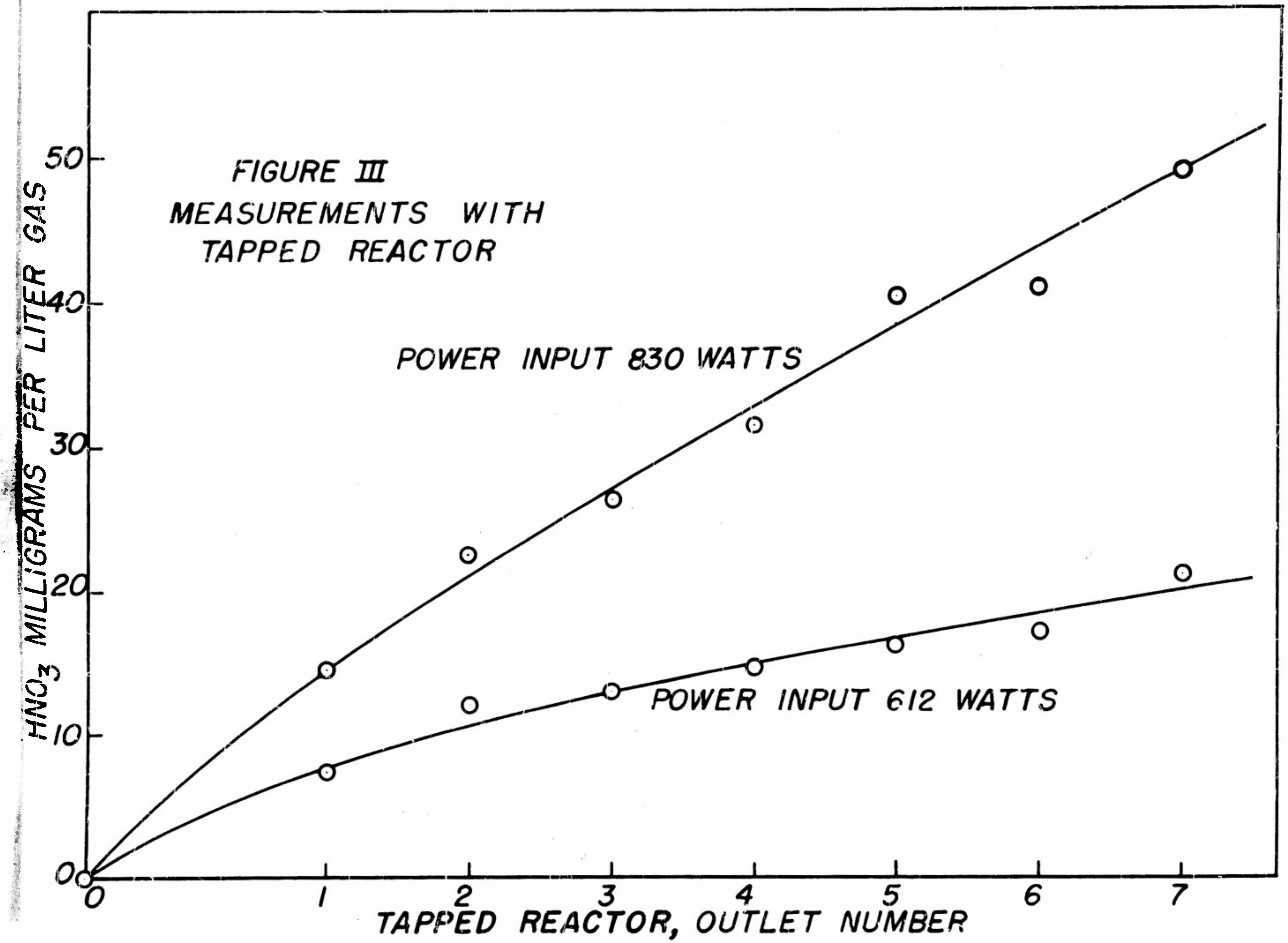

FIGURE III
MEASUREMENTS WITH
TAPPED REACTOR

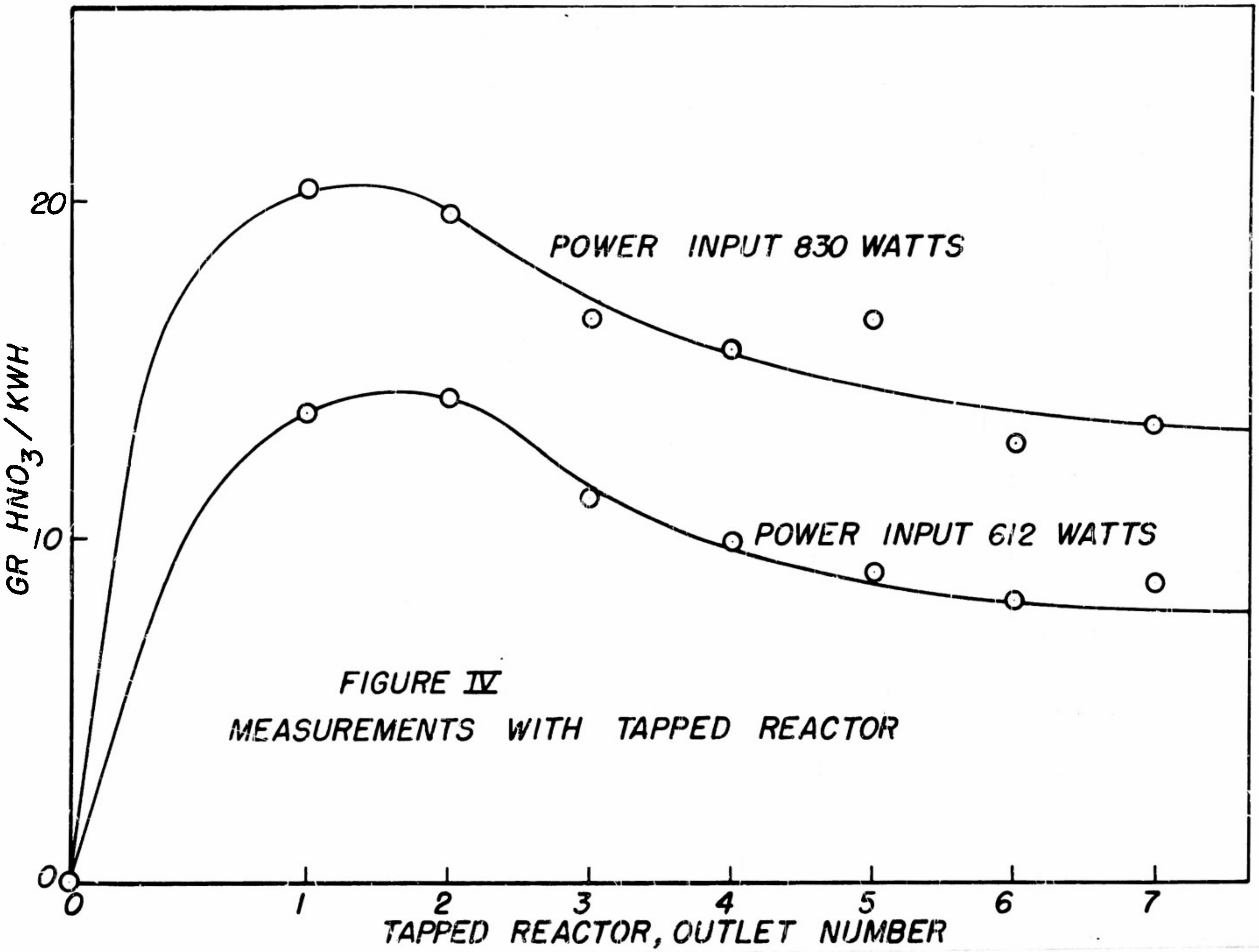

FIGURE IV
MEASUREMENTS WITH TAPPED REACTOR

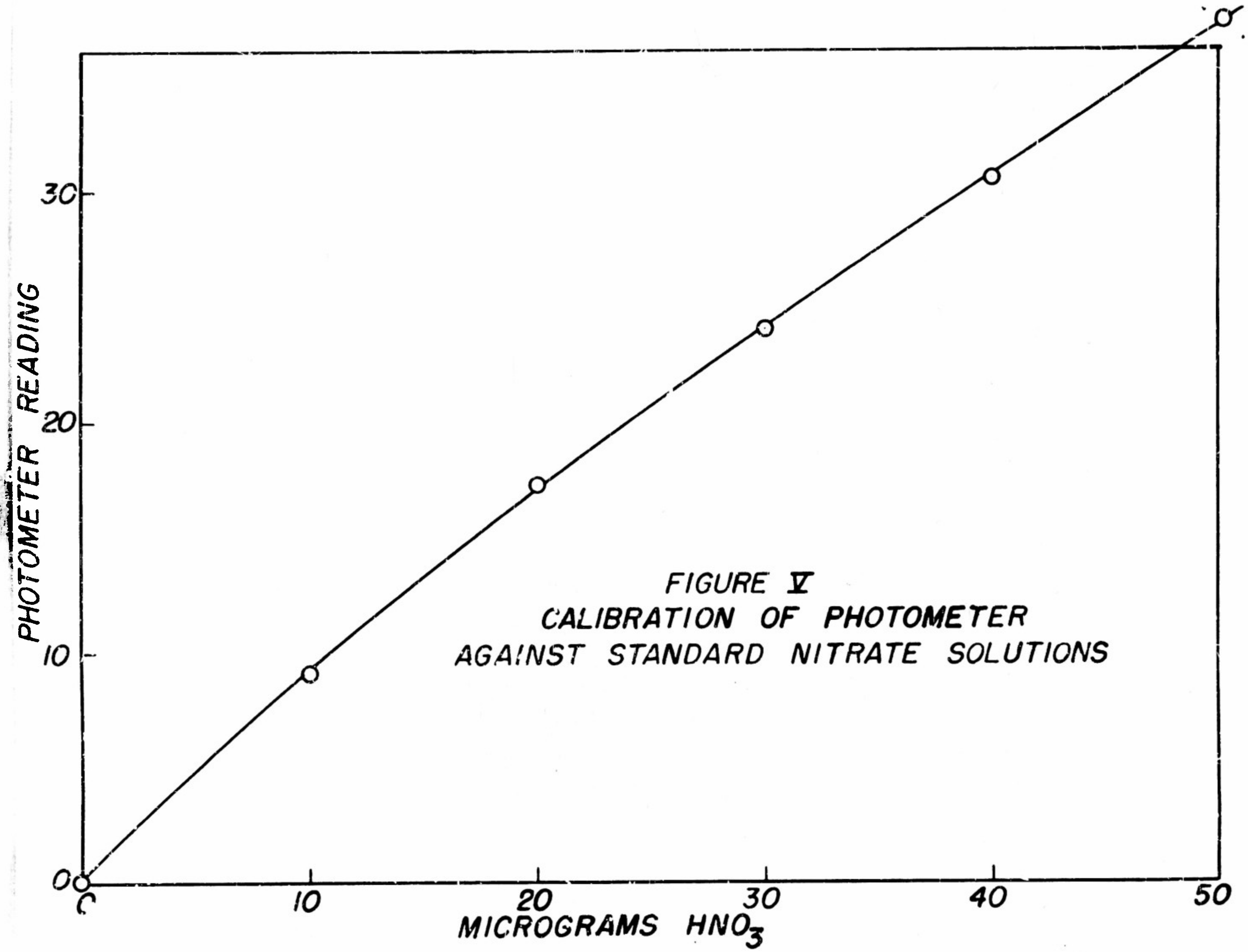

FIGURE V
CALIBRATION OF PHOTOMETER
AGAINST STANDARD NITRATE SOLUTIONS