REDUCTION OF NITRO COMPOUNDS WITH METAL REDUCING COLUMNS IN GLACIAL ACETIC ACID

Thesis for the Degree of M. S.

MICHIGAN STATE UNIVERSITY

Harry Elmer Keller

1959

REDUCTION OF NITRO COMPOUNDS WITH METAL REDUCING COUPLES IN GLACIAL ACETIC ACID

By

Harry Elmer Koller

A THESIS

Submitted to the College of Science and Arts of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

1959

ACKNOWLEDGEMENTS

The author is deeply indebted to Dr. Kenneth G. Stone for his guidance and his help throughout the entire investigation and preparation of this thesis.

Acknowledgment is also extended to Dr. Andrew Tirnick for his helpful suggestions in the use of the high frequency apparatus.

****

VITA

Name: Harry Elmer Keller

Born: May 20, 1930 in Reed City, Michigan

Academic Career: Reed City High School, Reed City, Michigan (1944-1948)

University of Michigan, Ann Arbor, Michigan (1948-1952)

Michigan State University, East Lansing, Michigan (1957-)

Degrees Held: B. S. in Chemistry, University of Michigan (1952)

REDUCTION OF NITRO COMPOUNDS WITH METAL REDUCING AGENTS IN CHEMICAL ASSAY WORK

By

Henry Elmer Keller

An ABSTRACT

Submitted to the College of Science and Arts of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

Year 1939

Approved K. G. Stone

ABSTRACT

A metal reductor consisting of a column packed either with amalgamated zinc (2% mercury, 30 mesh granular zinc) or with amalgamated lead (2% mercury, 30 mesh granular lead) was used to reduce several aromatic nitro compounds. When the samples were dissolved in 0.1 M perchloric acid in acetic acid the nitro compounds were reduced quantitatively to the amino. The amines were then determined by bromination.

The amount of zinc used was greater than the amount required by the nitro compound, since amalgamated zinc reduces hydrogen ion and oxygen dissolved in the solvent.

If the sample was deaerated before reduction, the amount of lead liberated, as determined by lead chromate precipitation, was equivalent to the amount of nitro compound. Thus this method could be used to determine the nitro compound.

Oxygen is more soluble in acetic acid than in water and was reduced by the columns with the liberation of an equivalent amount of metal ion. The solubility of oxygen in acetic acid determined in this manner was found to be 0.16 millimoles per 100 ml. of solvent. The acetic acid was saturated with oxygen in contact with air at 750 millimeters.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Peré (9) and Loubonets (3,4,5,6,7,8) individually and together (10,11,12) determined several aromatic nitro compounds by reduction of the nitro group to the amino group with a liquid amalgam reductor in aqueous solution, bromination of the amine with potassium bromide-potassium bromate, addition of potassium iodide and back titration with sodium thiosulfate. These investigators used an aqueous sulfuric or hydrochloric acid solution as the reaction medium.

Schribner and Reilley (13) determined several nitro compounds indirectly by following essentially the same procedure for the reduction of the nitro group, and then titrating the zinc ion liberated by the reduction with EDTA.

The use of metallic reducing columns has been reviewed by Stegemann (14). The determination of the nitro group has been reviewed by Becker and Shaefer(1).

If the nitro group could be reduced by an amalgam reducing column in glacial acetic acid solvent, the products would be the corresponding amine and the metal acetate. Both these products should be basic in the solvent. The object of this investigation is to determine nitro compounds by reduction with a metal amalgam reducing column to form the amine and metal acetate, and then to titrate the amine and metal acetate as bases with standard perchloric acid in acetic acid solvent.

II. EXPERIMENTAL

A. Chemicals

The chemicals used in this investigation were not repurified unless otherwise stated. Repurification of the nitro compounds was not considered necessary since the purity of the compounds could be checked by the determination of other functional groups in the compound, or by reduction of the aromatic nitro compounds to the amine and quantitatively brominating the aromatic ring.

The compounds titrated, labeled purity and source are:

Meta-nitrobenzoic acid, Eastman, C.P.

Ortho-nitrobenzoic acid, Eastman, C.P.

Ortho-nitrophenol, Eastman, C.P.

Para-Nitrophenol, Eastman, C.P.

Nitroethane, Eastman, C.P.

Nitrobenzene, Eastman, recrystallized

Meta aminobenzoic acid, Eastman, C.P.

Sodium acetate trihydrate, Bakers analyzed

Potassium acetate, Bakers analyzed

Lead acetate trihydrate, Bakers analyzed

Sulfuric acid, Dupont reagent

Zinc oxide, Bakers analyzed

Perchloric acid, Merck 70% reagent

(Ethylenedinitrilo)-Tetraacetic acid (EDTA), Hach Chemical Company, reagent

Other chemicals used were:

Primary standards--

Potassium acid phthalate, Bakers analyzed primary standard, oven-dried for two hours at 105°.

Potassium dichromate, Merck reagent, oven-dried for two hours at 105°.

Potassium bromate, Mallinckrodt, analytical reagent, oven-dried for two hours at 105°.

Other chemicals:

Potassium bromide, Fisher reagent grade

Potassium iodide, Bakers analyzed

Lead, Mallinckrodt, analytical reagent

Zinc, Bakers analyzed

Barium perchlorate, G. Frederick Smith

Mercuric acetate, Bakers analyzed

Acetic anhydride, Eastman C.P.

Solvent:

Acetic acid, Bakers analyzed and Dupont reagent grade

B. Standard Solutions

Standard perchloric acid in acetic acid was prepared by diluting 8.5 ml. of 70% perchloric acid with 900 ml. of acetic acid and then adding 20 ml. of acetic anhydride while the solution was being swirled. The solution was then diluted to one liter with acetic acid. The solution was standardized by titrating weighed portions of potassium acid phthalate with this solution either to a visual end-point using crystal

violet indicator (five drops of a 1% solution in acetic acid) or potentiometrically.

Standard sodium and potassium acetate solutions were prepared by dissolving the salts in acetic acid. Sodium acetate trihydrate was used, and acetic anhydride was added to react with the water. Anhydrous potassium acetate was used, so acetic anhydride was not added. The solutions were standardized by titration of an aliquot portion with standard perchloric acid either to a visual end-point using crystal violet indicator or potentiometrically.

Standard potassium dichromate solution was prepared by dissolving a weighed portion of the salt and diluting to volume in a volumetric flask.

Standard potassium bromate-potassium bromide solution was prepared by dissolving 5.2450 grams of potassium bromate and 75 grams of potassium bromide in water and diluting to two liters in a volumetric flask.

Standard sodium thiosulfate was prepared by dissolving 12.5 grams of sodium thiosulfate pentahydrate in one liter of water in which 0.5 gram of sodium carbonate had been dissolved. This solution was standardized by adding potassium iodide and dilute (1:4) sulfuric acid to an aliquot portion of the potassium bromide-potassium bromate solution and titrating the iodine liberated with the sodium thiosulfate solution to a starch end-point.

A 0.1 N solution of sulfuric acid in acetic acid was prepared by diluting 2.7 ml. of concentrated sulfuric acid with one liter of acetic

acid. The solution was standardized by potentiometric titration of a weighed portion of potassium acid phthalate dissolved in acetic acid. It was found that powdered barium perchlorate had to be added to the potassium acid phthalate solution to obtain a suitable break.

Standard zinc acetate solution was prepared by dissolving 2.4394 grams of zinc oxide in water containing a slight excess of acetic acid and diluting to one liter with water. This solution contained two milligrams of zinc per ml.

Standard EDTA solution was prepared by dissolving 12 grams of disodium dihydrogen ethylenediaminetetraacetate dihydrate in about 800 ml. of water. This solution was standardized by titrating a 25 ml. aliquot of the standard zinc solution to which 10 ml. of pH 10 ammonia-ammonium chloride buffer had been added to the point where the red color of the eriochrome black T indicator could no longer be seen. The EDTA solution was then diluted to such an extent that by following the same titration procedure a 25.0 ml. aliquot of the zinc solution required 25.0 ml. of the EDTA solution to reach the end-point.

C. Apparatus

A Beckman model M pH meter, equipped with a glass electrode and a sleeve-type saturated calomel electrode, was used for the potentiometric titrations.

High frequency titrations were conducted with a modified high frequency titration apparatus designed and constructed by Fleck (15). The apparatus was operated at 1148.5 megacycles. The current measuring

component of the Sargent Model XXI polarograph was used to measure the change in grid current, which is the response of the high frequency apparatus.

The reduction columns were prepared in typical Jones reductor columns. Glass wool plugs were placed in the bottom of the column above the stopcock to retain the amalgam.

In preparing the zinc amalgam, 150 grams of the zinc metal was agitated with 4.8 grams of mercuric acetate dissolved in acetic acid. It was found that solid zinc acetate was formed by the reaction, and several washings by decantation were required to remove the zinc acetate. When perchloric acid was added to the reaction mixture the zinc acetate dissolved. The amalgam was transferred to the column and packed by tapping the side of the column with a glass stirring rod.

When the granular lead was amalgamated by treatment with mercuric acetate dissolved in acetic acid, it was found that the lead particles adherred to one another, thus forming lead balls. These balls varied in diameter, most of them being too large to fit into the Jones reductor column. To overcome this difficulty the dry granular lead was placed in the column and a solution of mercuric acetate was sucked quickly through the column into a 500 ml. suction flask attached to a water pump. The mercuric acetate solution was passed several times through the column so that complete reaction between the lead and mercuric acetate could be attained. It was assumed that the rapid passage of the mercuric solution through the column would give as uniform a coat

of mercury as possible. Sufficient mercuric acetate was used to form an amalgam containing 2% mercury.

D. Reduction Procedures

Although the procedures used for passing the samples through the reducing columns varied slightly from sample to sample, only three basic procedures were used.

In one procedure a 25 or 50 ml. aliquot of the sample dissolved in either acetic acid or standard perchloric acid in acetic acid was pipeted into the storage bulb of the column. The sample was then passed through the column into a receiving vessel, the rate of flow being controlled with the stopcock. When the level of the liquid in the bulb approached the level of the amalgam, acetic acid was used to rinse down the sides of the storage bulb and to elute all of the sample from the column. A 50 ml. portion of acetic acid was found to be sufficient to elute all of the sample from the column.

In a second procedure, a larger sample dissolved in acetic acid or in standard perchloric acid in acetic acid was used. The sample was added to the storage bulb in 50 ml. portions. The first 50 ml. of eluent from the column was discarded, aliquots being taken from the solution being eluted after that.

When samples were to be deaerated a third procedure was employed. The sample, dissolved in acetic acid or standard perchloric acid in acetic acid was placed in a 500 ml. separatory funnel. A dispersion tube connected to a carbon dioxide cylinder was immersed in the solution.

A stream of carbon dioxide was allowed to flow through the dispersion tube and sample solution for 15 minutes. A two-hole rubber stopper was used to stopper the top of the reducing column. Two pieces of glass tubing extended from one inch above the stopper to one inch below the stopper. Before the sample solution was introduced into the storage bulb of the column, the storage bulb was flushed with carbon dioxide to displace the air. The delivery tube of the separatory funnel containing the deaerated sample was attached to one of the glass tubes extending through the rubber stopper by means of a rubber tube connection. The deaerated sample solution was then introduced into the storage bulb at such a rate that the level of liquid in the bulb remained fairly constant while the solution was being eluted. The solution passing through the column was saturated with carbon dioxide, and carbon dioxide was liberated while the solution was in contact with the amalgam as evidenced by the formation of bubbles. Thus no further effort was made to maintain the oxygen free atmosphere over the solution. The first 50 ml. of eluent was discarded and aliquots taken from the succeeding portion of the eluent.

E. Titration Procedures

1. Potentiometric Titrations

The standardisation control of the pH meter was adjusted to zero volts with the selector knob in the standardise position. The sample was placed in a 250 ml. beaker and stirred with a magnetic stirrer continuously during the titrations. The selector knob was turned to

the 0-800 millivolt scale and titrant was added in 1.0 ml. increments, except near the end-point where the increments were reduced to 0.1 ml. Readings of potential were taken after each increment.

2. High Frequency Titrations

The high frequency titration apparatus and the polarograph were allowed to warm up at least 10 minutes prior to titrations. The samples were introduced into the titration vessel and the volume adjusted to 150 ml. with acetic acid.

Polarograph adjustments were made so that the recorder indicator assumed some desirable initial value. This was accomplished by selecting a 1.0 volt span, a 20% bridge setting and a sensitivity of 0.06 microamperes per millimeter. The upscale or downscale compensation was used for the final adjustment.

The tip of the buret extended below the surface of the solution being titrated. Reagent was added in measured 0.5 or 1.0 ml. portions. Instrument readings were made when the indicator became steady after each portion of the titrant had been added.

3. Bromination Procedures

The bromination procedure was used extensively to determine the amount of amine formed from a weighed sample of certain aromatic nitro compounds. After the solution of the nitro compound had been passed through the column, an aliquot was pipeted into a 500 ml. iodine flask. An aliquot of the standard potassium bromide-potassium bromate solution

was also pipeted into the flask and sufficient water was added to double the volume. A 10 ml. portion of 1:4 sulfuric acid was then added, and the flask was stoppered and shaken. The mixture was then allowed to stand until the color of bromine could be detected in the solution or longer, although longer standing had no effect on results.

Solid potassium iodide was then placed in the cup of the iodine flask, and water was added to dissolve the potassium iodide. The potassium iodide solution was then allowed to enter the flask by raising the stopper, and the flask was swirled. The solution was then titrated with standard sodium thiosulfate solution to the point where the iodine color was faint. Starch indicator was then added and the titration continued until the blue color of the starch-iodine complex could no longer be seen.

When the lead column was used for the reduction, lead bromide precipitated when the sample solution and the potassium bromide-potassium bromate solutions were mixed. When the potassium iodide was added, the precipitate changed to the yellow lead iodide. This yellow color made it quite difficult to determine when the titration of the iodine was nearly complete, but when the starch was added, the end-point was quite sharp.

4. Determination of Lead by the Chromate Procedure

To determine the amount of lead in the eluent from the column, an aliquot was pipeted into a 400 ml. beaker and diluted to about 250 ml. with water. Standard potassium dichromate solution was then added from

a pipet while the solution was being stirred constantly. When the aliquot of potassium dichromate had been added, the mixture was allowed to stand for 10 minutes. The lead chromate precipitate was then filtered under suction through a 30 ml. medium porosity sintered glass crucible, and the filtrate caught in a 500 ml. suction flask. The precipitate was washed five times with water.

Potassium iodide and 10 ml. of 1:4 sulfuric acid were added to the filtrate and the liberated iodine was titrated with standard sodium thiosulfate to a starch end-point as in the bromination procedure.

Certain of the amines appeared to be reoxidized by the potassium dichromate, and this method could not be used in these cases.

5. Determination of Zinc by the EDTA Method

The zinc in the column eluent was determined by evaporating the acetic acid from the solution under reduced pressure and titrating the zinc acetate remaining with EDTA.

An aliquot was pipeted into a 500 ml. suction flask and a few boiling chips added. The flask was then stoppered with a rubber stopper and a thick walled rubber hose was attached to the side arm of the flask and to a suction pump. The flask was then partially immersed in hot (90° C.) water and the suction applied until the acetic acid had evaporated.

The solid remaining in the flask was dissolved in water, 10 ml. of pH 10 ammonia-ammonium chloride buffer and six drops of eriochrome black T indicator solution were added, and the solution was titrated with

standard EDTA solution to the point where the red color of the indicator could no longer be detected.

III. DISCUSSION OF RESULTS

A. Operations with the Zinc Column

1. Initial Work

Samples of ortho- and meta-nitro phenol dissolved in acetic acid were run through the column. Titrations of the eluent with perchloric acid using crystal violet indicator were attempted. It was found that the indicator changed color over a range of approximately 15 ml. of 0.1 N perchloric acid.

Samples of ortho- and meta-nitrophenol were dissolved in 0.1 N perchloric acid and passed through the column. Titration of the excess acid in the eluent was attempted with standard sodium acetate using crystal violet indicator, but again the indicator changed color over approximately 15 ml. of the 0.1 N sodium acetate.

A solution was prepared by dissolving zinc oxide and meta-amino-benzoic acid in excess 0.1 N perchloric acid. This solution approximated the theoretical eluent from the column. This solution was titrated potentiometrically with standard sodium acetate. Figure 1 shows the titration curve for this sample. Two slight breaks can be observed in the curve, one corresponding roughly to the excess perchloric acid and the second to the zinc perchlorate acting as an acid. During the course of this titration zinc acetate precipitated from the solution. Neither of the breaks are sufficiently distinct to be useful analytically.

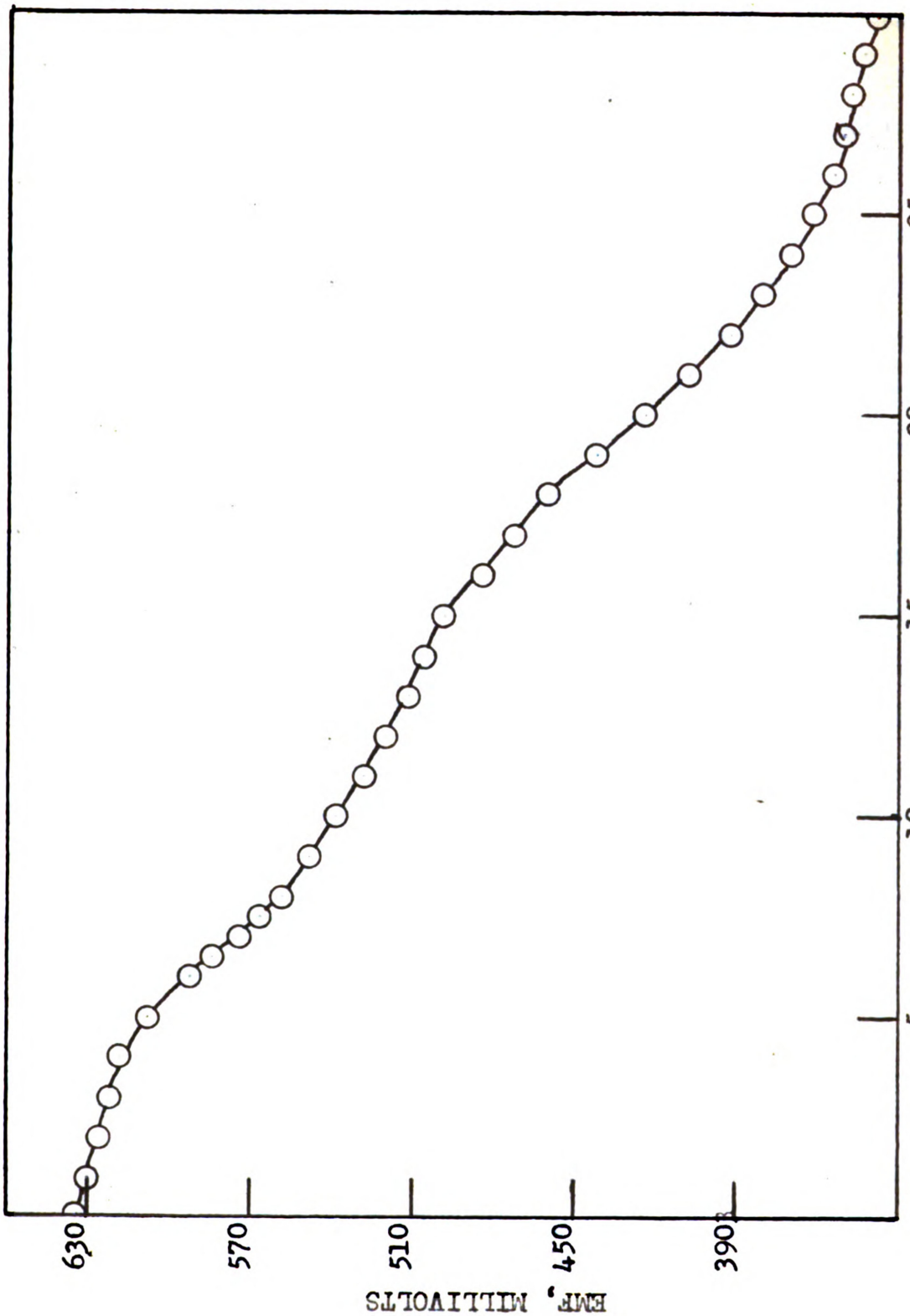

Figure 1. Potentiometric titration of theoretical column eluent

This sample was also titrated by the high frequency titration procedure. Figure 2 shows the titration curve for this titration. Thus the excess acid can be determined quite easily by the high frequency titration in the theoretical column eluent.

A sample of meta-nitro benzoic acid was dissolved in standard perchloric acid and passed through the column. According to the theoretical stoichiometry of the reduction there should have been a slight excess of perchloric acid in the sample after the reduction. High frequency titration of the eluent with sodium acetate gave no end point, however, the plot of instrument response versus ml. of titrant being a straight line. Thus the amount of base in the eluent is not equivalent to the amount of nitro compound passed through the column.

In order to see if the zinc column would reduce the perchlorate ion in acetic acid, a portion of 0.1 N perchloric acid was passed through the column and the eluent diluted with water. Silver nitrate test solution was added to the solution, but no precipitate of silver chloride was observed. Since it is harder to reduce perchlorate than any other oxidation state of chlorine and since no chloride ion was found, it was assumed that the zinc amalgam would not reduce perchlorate ion.

2. Reduction of Nitro Compounds with the Zinc Column

To check the efficiency of the column in the reduction of the nitro compounds, several samples of ortho- and meta-nitrobenzoic acid and nitrobenzene were run through the column under various conditions and

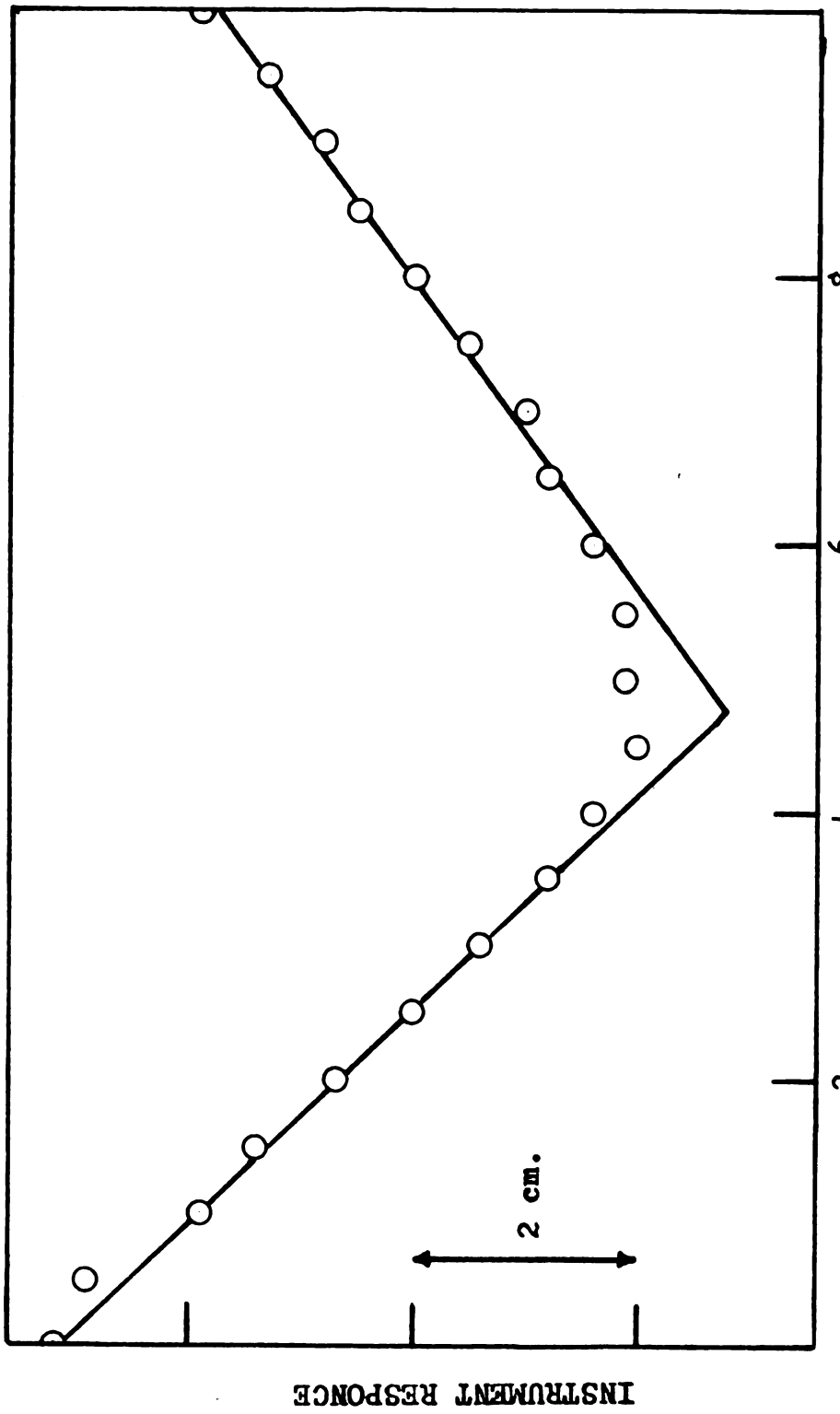

Figure 2. High frequency titration of theoretical column eluent

the amount of amine in the eluent determined by the bromination procedure. Tables I and II show the results of these determinations.

The column reduced the nitro compounds with 100.0 ± .6% efficiency as determined by the bromination method if the proper conditions were maintained.

Perchloric acid must be present in the solution passing through the column in order that there be complete reduction, but part of the hydrogen for the reduction can be supplied by the acetic acid. Figure 3 shows how the extent of reduction varies with the concentration of the perchloric acid present in the solvent. The sample size used in the samples represented in Figure 3 should have required approximately 0.24 N perchloric acid if the perchloric acid alone were to supply the hydrogen for the reduction, but the reduction appears complete when the concentration is greater than about 0.06 N.

When acetic acid was used as a solvent consistently, zinc acetate accumulated in the column, and the reduction efficiency decreased as the zinc acetate accumulated. Samples numbered 24 to 32 in Table II are samples which were run consecutively through the column to illustrate this point.

The rate of passage of the sample through the column and the surface area of the amalgam available affect the reduction efficiency of the column. A column packed with amalgamated 10 mesh granular zinc was first prepared. Most of the samples run through this column were not completely reduced. The samples in Table I were run using this column.

TABLE I

NITRO COMPOUNDS REDUCED BY ZINC (10 MESH) AMALGAM; BROMINATION PROCEDURE

Sample	$HClO_4$ Concn.	Mg. Sample	ml. $Na_2S_2O_3$ Blank	ml. $Na_2S_2O_3$ Sample	N $Na_2S_2O_3$	Percent Recovered
Meta-nitrobenzoic acid						
1	0.1	103.1	43.59	9.45	0.1081	99.6
2	0.1	103.1	43.59	9.65	0.1081	99.1
3	0.1	103.1	43.59	15.05	0.1081	83.3
4	0.1	104.4	43.59	27.05	0.1081	47.7
5	0.1	104.4	43.59	13.00	0.1081	88.2
6	0.1	104.4	43.59	12.50	0.1081	89.7
7	0.1	104.4	43.59	20.25	0.1081	67.3
8	0.1	103.1	43.59	10.52	0.1081	96.6
9	0.1	103.1	43.59	10.62	0.1081	96.3
10	0.1	103.1	43.59	10.58	0.1081	96.4
11	0	102.1	43.59	19.84	0.1081	70.0
12	0	102.1	43.59	25.64	0.1081	52.9
13	0.1	102.4	43.59	13.40	0.1081	88.7
14	0.1	102.4	43.59	11.60	0.1081	94.0
15	0.1	102.4	43.59	14.58	0.1081	95.3
16	0.1	102.4	43.59	10.62	0.1081	96.9
17	0.1	102.4	43.59	28.10	0.1081	45.5
18	0.1	102.4	43.59	30.80	0.1081	37.6
19	0.1	102.4	43.59	32.30	0.1081	33.2
20	0.1	104.6	43.59	9.78	0.1081	97.3
21	0.1	104.6	43.59	10.25	0.1081	95.9
Ortho-nitrobenzoic acid						
22	0.1	102.6	48.10	10.96	0.09806	99.4
23	0.1	102.6	48.10	10.60	0.09806	99.8
24	0.1	102.6	48.10	10.76	0.09806	99.4

TABLE II

NITRO COMPOUNDS REDUCED BY ZINC (30 MESH) AMALGAM; BROMINATION PROCEDURE

Sample	$HClO_4$ Concn.	Mg. Sample	Ml. $Na_2S_2O_3$ Blank	Ml. $Na_2S_2O_3$ Sample	N $Na_2S_2O_3$	Percent Recovered
Ortho-nitrobenzoic acid						
1	0.1	102.6	48.10	10.96	0.09806	98.9
2	0.1	102.6	48.10	10.60	0.09806	99.8
3	0.1	102.6	48.10	10.76	0.09806	99.4
4	0.1	102.6	48.10	10.54	0.09806	99.9
5	0.1	102.6	48.10	10.60	0.09806	99.8
Meta-nitrobenzoic acid						
6	0.1	101.8	48.10	10.70	0.09806	100.3
7	0.1	101.8	48.10	10.78	0.09806	100.1
8	0.1	101.8	48.10	10.79	0.09806	100.1
9	0.1	101.8	48.10	10.84	0.09806	100.1
10	0	101.2	48.10	12.54	0.09806	96.0
11	0	101.2	48.10	12.44	0.09806	96.2
12	0.0167	101.3	48.10	11.82	0.09806	97.8
13	0.0167	101.3	48.10	11.64	0.09806	98.3
14	0.0333	101.3	48.10	11.26	0.09806	99.3
15	0.0333	101.3	48.10	11.10	0.09806	99.8
16	0.0500	101.3	48.10	11.54	0.09806	99.6
17	0.0500	101.3	48.10	11.48	0.09806	99.7
18	0.0667	101.3	48.10	11.44	0.09806	99.8
19	0.0667	101.3	48.10	11.37	0.09806	100.0
20	0.0833	101.3	48.10	11.36	0.09806	100.0
21	0.0833	101.3	48.10	11.30	0.09806	100.2
Nitrobenzene						
22	0.05	73.81	47.80	12.23	0.09806	97.0
23	0.05	73.81	47.80	10.68	0.09806	101.2
24	0.0	73.81	47.80	17.22	0.09806	83.4
25	0.0	73.81	47.80	10.70	0.09806	101.1
26	0.0	74.70	47.80	17.98	0.09806	80.3
27	0.0	74.70	47.80	18.70	0.09806	78.4
28	0.0	74.70	47.80	27.85	0.09806	53.7
29	0.0	74.70	47.80	29.65	0.09806	48.9
30	0.0	74.70	47.80	39.70	0.09806	21.9
31	0.1	74.71	47.80	10.68	0.09806	100.0
32	0.1	74.95	47.80	10.50	0.09806	100.1

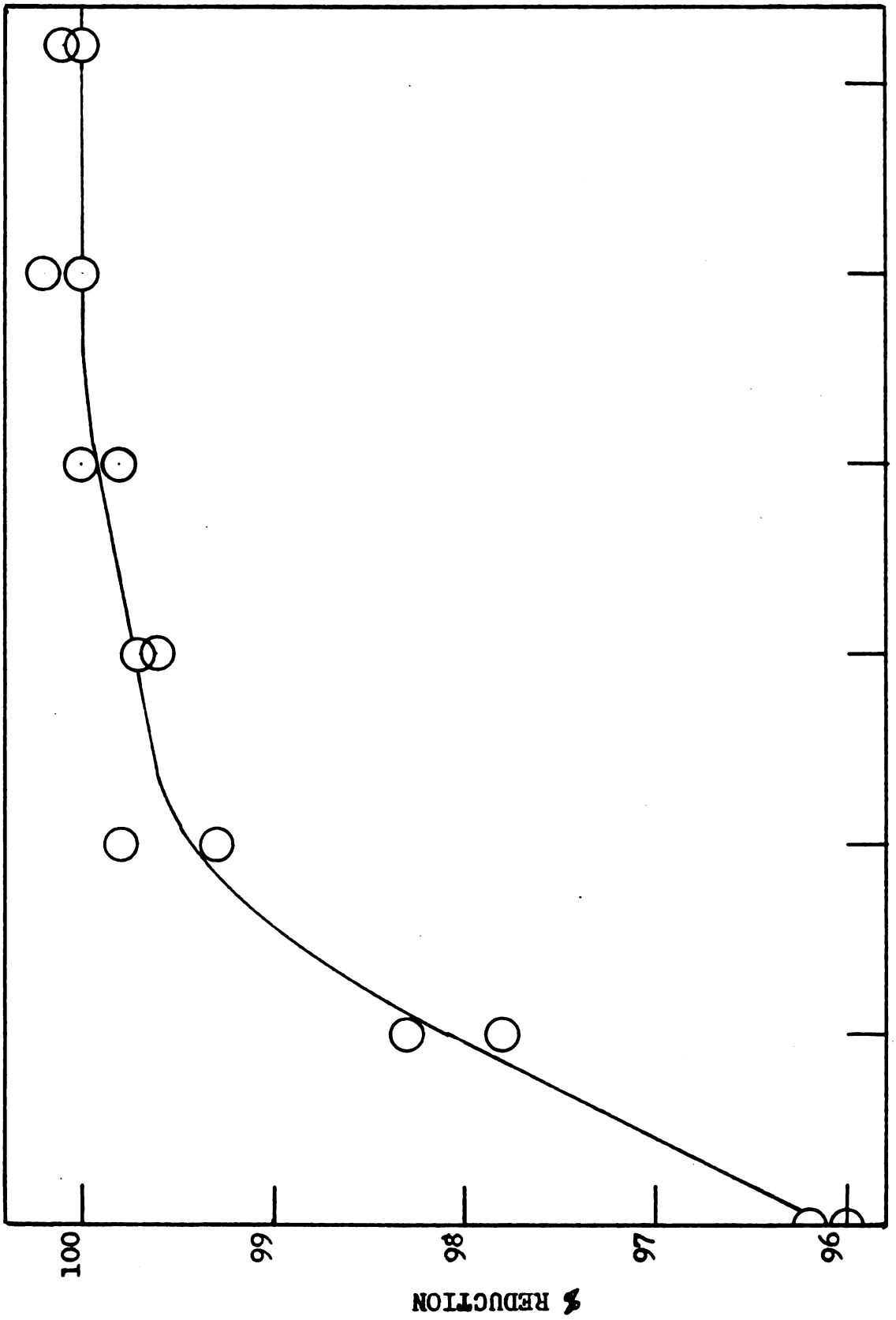

Figure 3. Effect of perchloric acid on the extent of reduction

A column packed with amalgamated 30 mesh zinc was then prepared. Using this column 100.0 ±0.6% of the theoretical amount of amine was found by the bromination method for most samples of ortho- and meta-nitrobenzoic acid and nitrobenzene when perchloric acid was used as the solvent. The samples run using this column are in Table II.

3. Determination of the Blank

The zinc in the column eluent was determined as previously described by the EDTA method. It was found that in all cases where the zinc was determined it was not present in an amount equivalent to the nitro compound. For example, when 0.307 millimoles of meta-nitrobenzoic in 0.1 M perchloric acid was passed through the column 1.57 millimoles of zinc was found in the eluent instead of the 0.92 millimoles expected. Whenever 0.1 M perchloric acid was used as a solvent, there was more zinc in the eluent than could be accounted for as having taken part in the reduction of the nitro group. By running samples of acetic acid, and of perchloric acid through the column it was found that this extra zinc arose from two sources. Oxygen is quite soluble in acetic acid, and when the solvent with the dissolved oxygen is passed through the column, the oxygen is reduced with the liberation of an equivalent amount of zinc. When the acetic acid was deoxygenated with carbon dioxide prior to passage through the column, the amount of zinc in the eluent was reduced greatly.

The second source of the extra zinc is from the perchloric acid. Amalgamated zinc is a strong enough reductant that it will reduce

hydrogen from a solution of perchloric acid in acetic acid. Samples of various concentrations of perchloric acid were deaerated and passed through the column. Zinc was determined in the eluent by the EDTA method. The results are shown in Figure 4. The amount of zinc found in the eluent and thus the amount of reaction between the zinc amalgam and the perchloric acid is directly proportional to the concentration of the perchloric acid. Figure 4 also shows the very slight reaction between deaerated acetic acid and the amalgam.

Since zinc acetate precipitated during the titration of solutions containing zinc perchlorate with sodium acetate, formed during the preparation of the zinc amalgam, and formed in the column itself during reductions if excess perchloric acid were not present, the solubility of zinc acetate in acetic acid was determined. Zinc metal was heated with acetic acid to effect reaction. The solution was then cooled nearly to room temperature, during which time zinc acetate began to crystallize from the solution. The mixture was then placed in a constant temperature bath at 25° for several days to allow the equilibrium to be established. The solid zinc acetate was then removed from the supernatant liquid by filtration through a fine porosity sintered glass crucible and the zinc in the filtrate determined in the usual way with versene. A value of 0.74 grams of zinc acetate per liter of solution was obtained, which compares quite poorly with the value of 0.055 grams per liter reported by Davidson and McAllister (2).

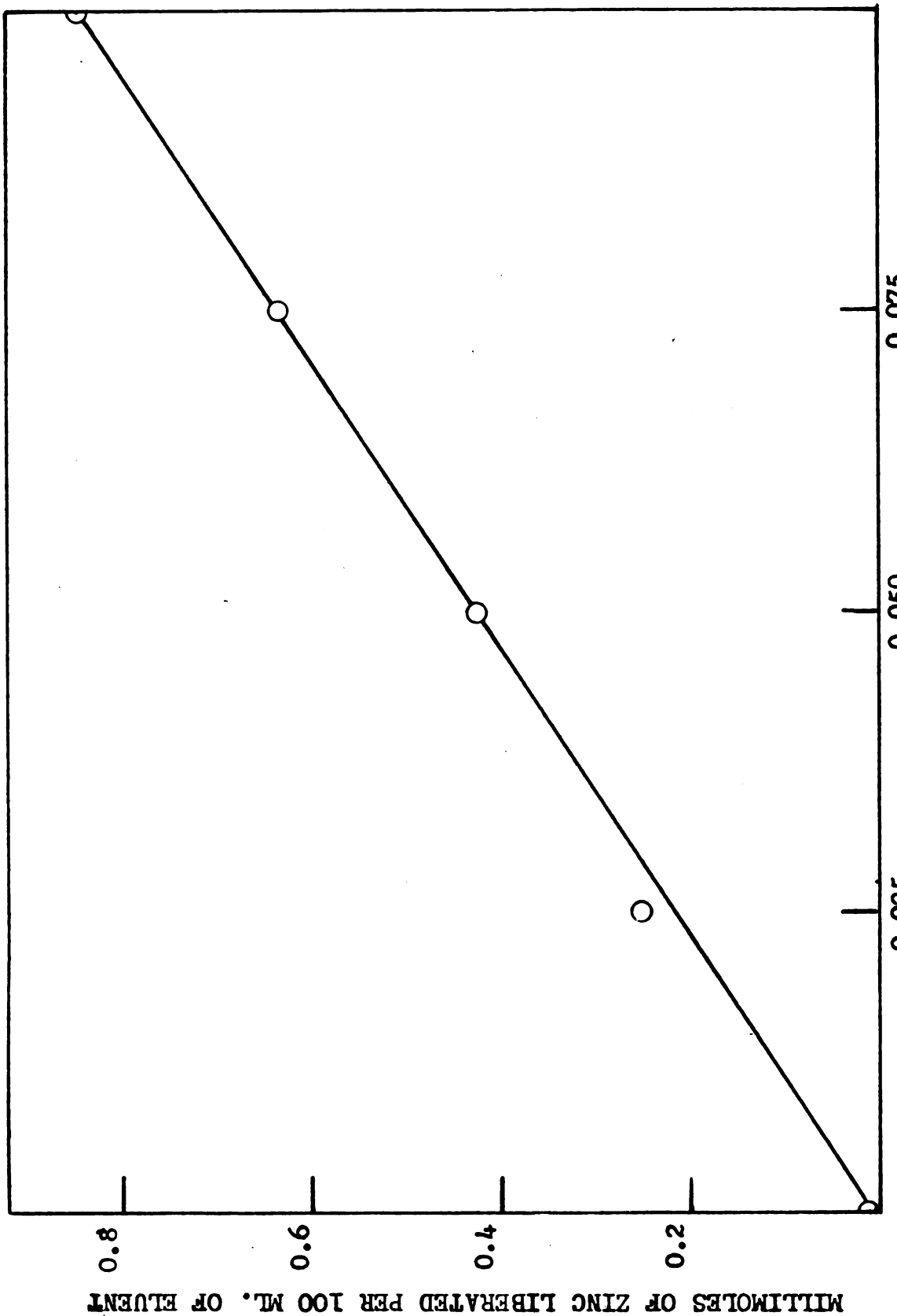

Figure 4. Effect of perchloric acid on the blank for the zinc column

B. Operations with the Lead Column

1. Reductions of Nitro Compounds

Since lead acetate is soluble in acetic acid and since lead is a fairly good reducing agent, a column was constructed using amalgamated granular lead.

An attempt was made to titrate a solution of lead acetate in acetic acid with perchloric acid potentiometrically. No break could be observed in the potential versus ml. of perchloric acid plot.

Sulfuric acid is not a strong acid in acetic acid. However, since lead sulfate is insoluble in acetic acid, sulfuric acid should be a fairly strong acid during that part of the titration where lead sulfate is precipitating. A sample of meta-nitrobenzoic acid dissolved in acetic acid was passed through the column and the eluent titrated potentiometrically with 0.1 N sulfuric acid. Figure 5 shows the rather poorly defined break obtained for this titration.

An attempt was made to standardize the sulfuric acid by titrating a weighed portion of potassium acid phthalate with the sulfuric acid potentiometrically. No break could be detected in the potential versus ml. sulfuric acid for the titration. When powdered barium perchlorate was added to the solution being titrated, an end-point was detectable, although rather poorly defined. Figure 6 shows such a titration curve.

A solution of lead acetate in acetic acid was prepared and standardized by the dichromate method. The sulfuric acid was then

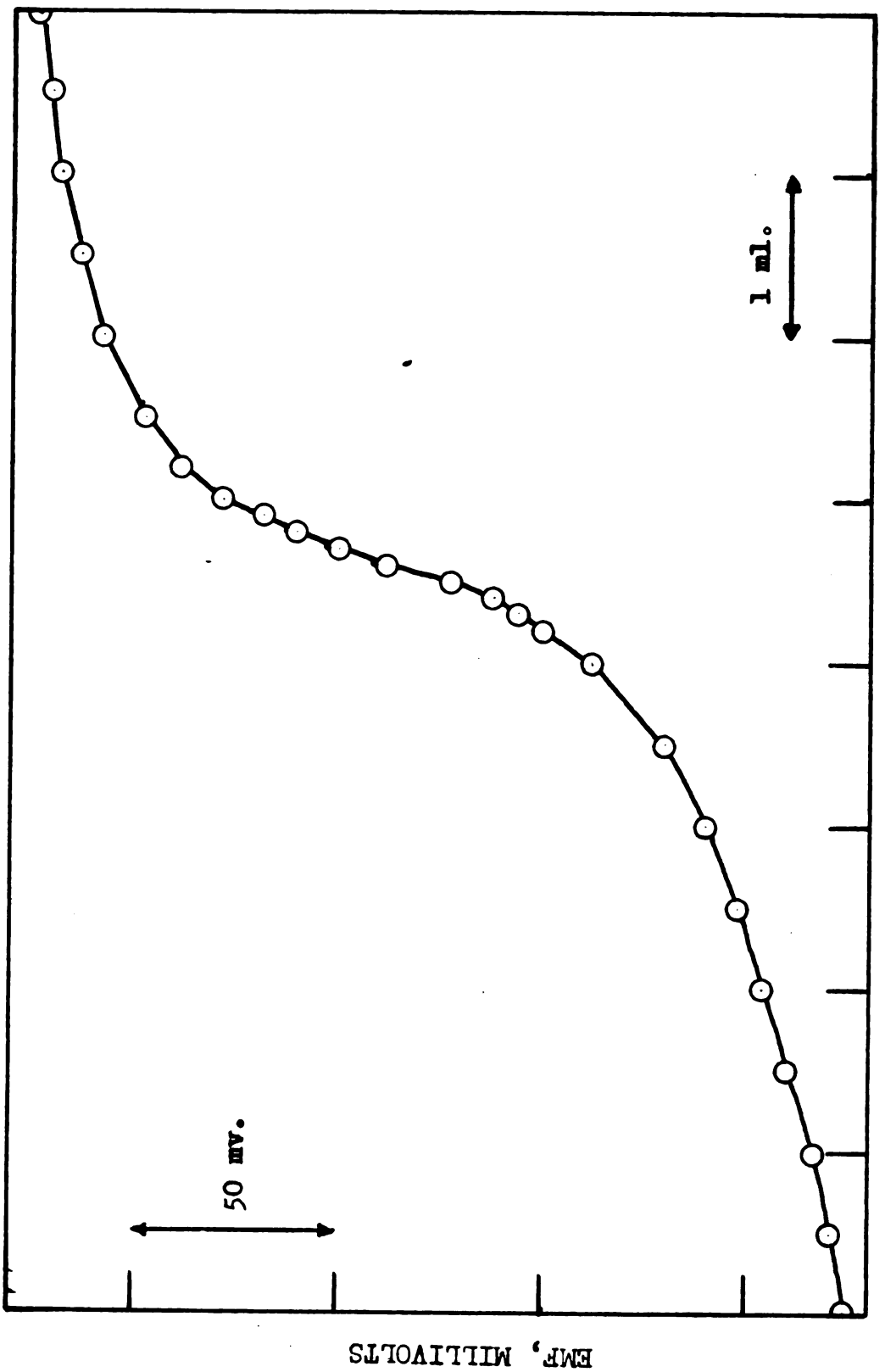

Figure 5. End-point of a titration of a sample of meta-nitrobenzoic acid reduced by the lead column and titrated with sulfuric acid

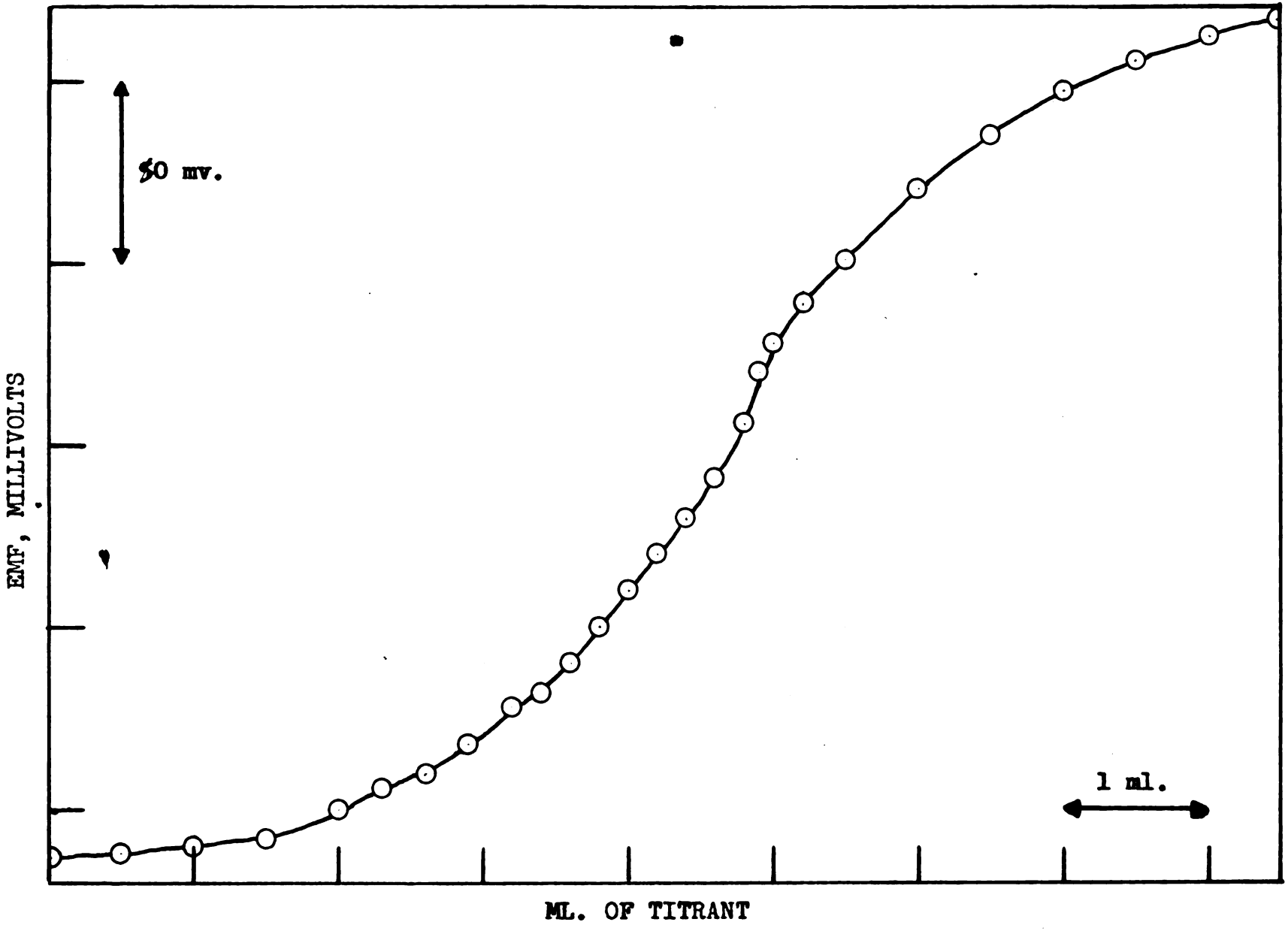

Figure 6. End-point of a titration of potassium acid phthalate plus solid barium perchlorate with sulfuric acid

standardized by titrating an aliquot of this lead acetate solution with the sulfuric acid potentiometrically. Figure 7 shows the titration curve for this titration.

Samples of meta-nitrobenzoic acid, para-nitrophenol, and nitrobenzene dissolved in acetic acid were passed through the column and the eluents were titrated potentiometrically with sulfuric acid. A blank was run along with these samples, the volume of sulfuric acid being required for the blank was subtracted from the volume required for the sample. Figure 8 shows a titration curve for the titration of the blank. Table III shows the results of titrations of the nitro compounds. The amount of sulfuric acid required per mole of nitro compound varied considerably, but in no case was the theoretical amount of acid required. This indicates that the reduction is not complete under the conditions used, and that the extent of reduction is highly dependant on conditions.

It was found that using the lead column the amount of amine formed could be determined by the bromination procedure. Using this method as a criteria, it was found that the extent of reduction was dependent upon the rate with which the solution was passed through the column and upon the concentration of perchloric acid present. It was found, however, that if a small amount of perchloric acid were added to a sample and the sample then passed through the column, no potentiometric end-point could be obtained by titration of the eluent with sulfuric acid.

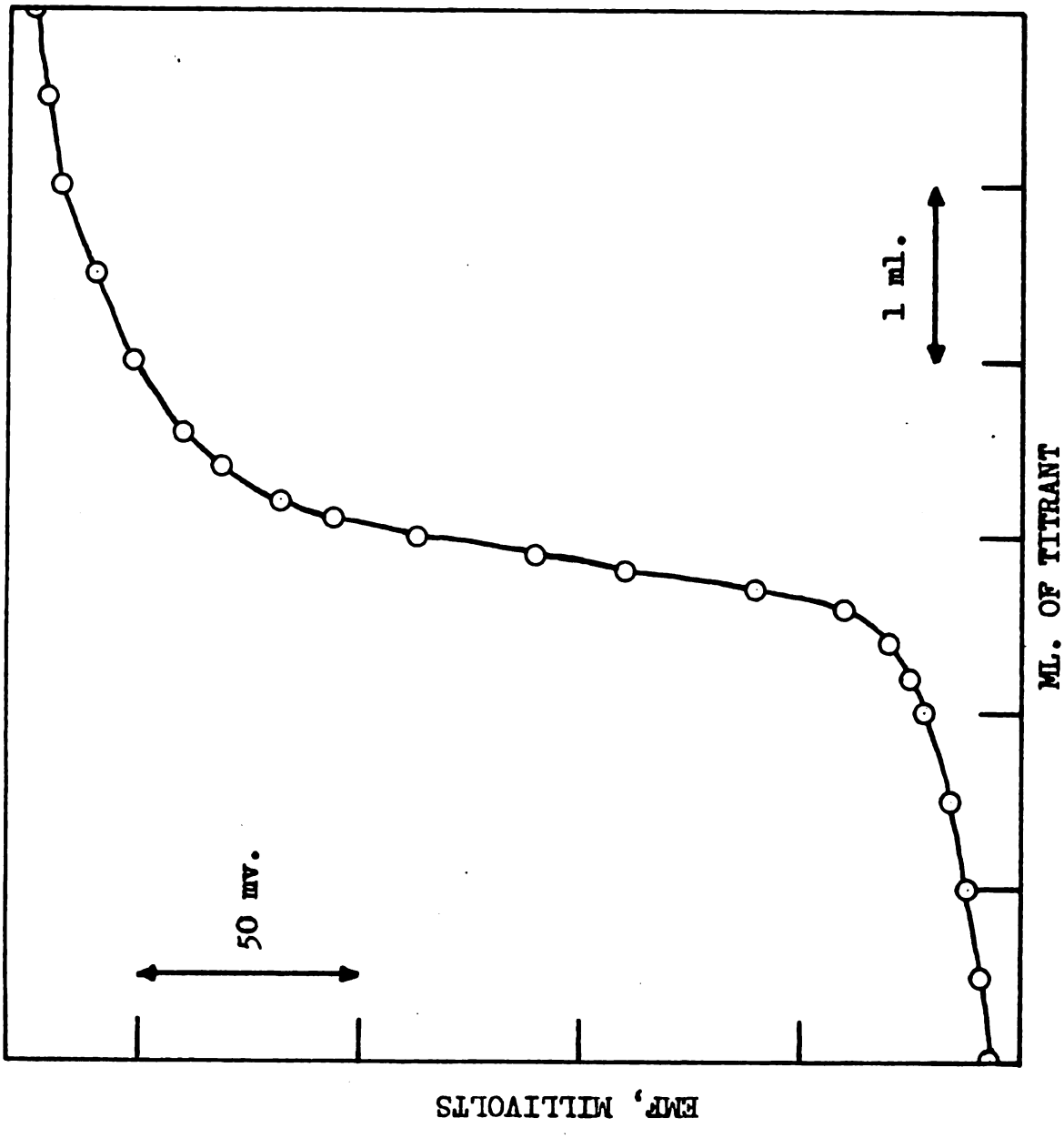

Figure 7. End-point of a titration of lead acetate with sulfuric acid

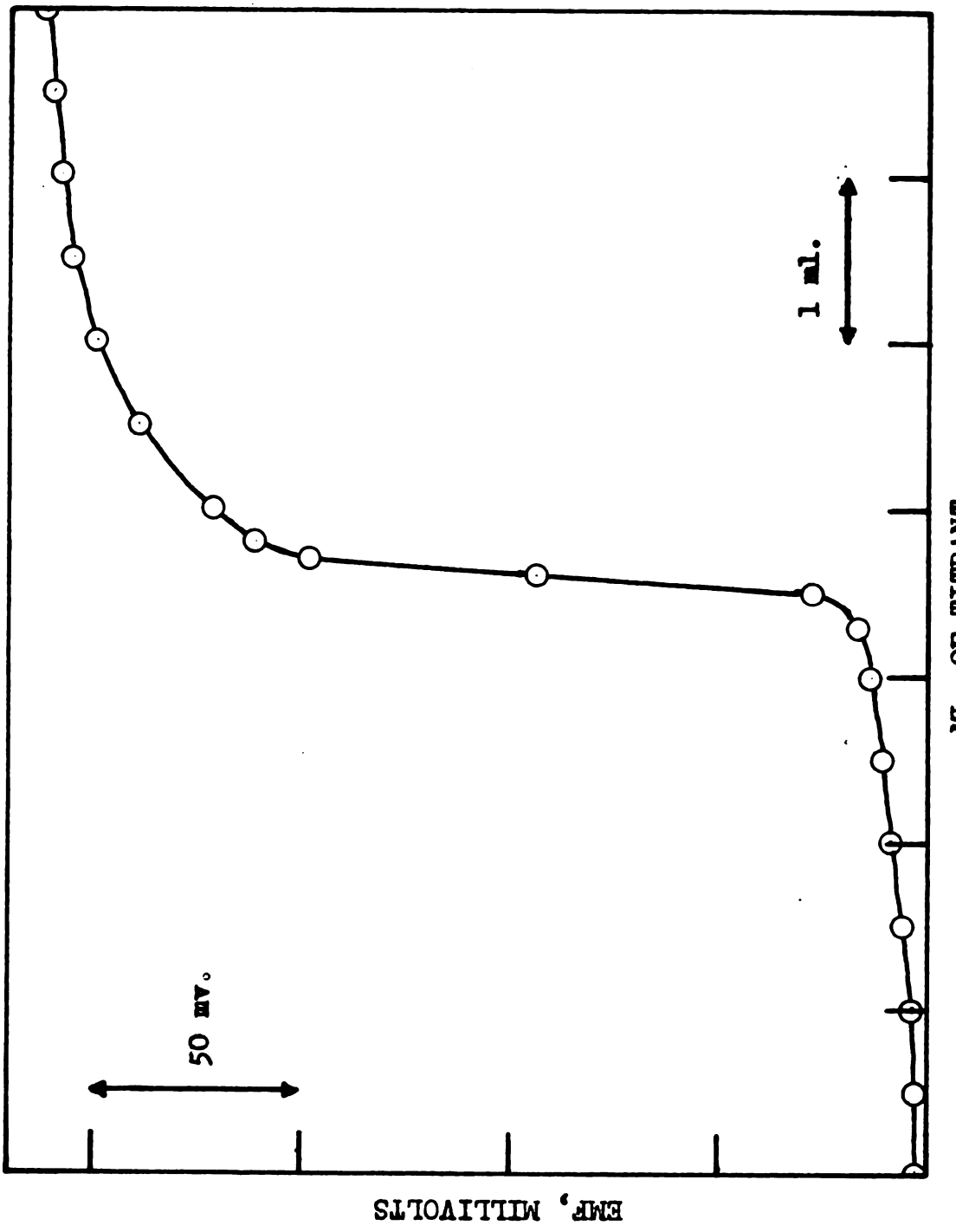

Figure 8. End-point of a titration of the blank for the lead column with sulfuric acid

TABLE III

NITRO COMPOUNDS REDUCED BY LEAD AMALGAM; H_2SO_4 TITRATION

Sample	Mg. Sample	H_2SO_4			
		Ml.	N	Meq. Blank	Meq. per Mmole NHO_3
Meta-nitrobenzoic acid					
1	104.7	38.95	0.00912	0.556	4.65
2	104.7	38.70	0.00912	0.556	4.62
3	62.04	31.50	0.00912	0.677	5.74
4	62.04	30.34	0.00912	0.677	5.43
Ortho-nitrophenol					
5	34.91	26.96	0.00912	0.588	7.02
6	51.71	37.25	0.00912	0.648	7.19
7	51.71	37.25	0.00912	0.648	7.19
Nitrobenzene					
8	36.91	30.46	0.00912	0.66	6.8

By dissolving samples in 0.1 N perchloric acid, and passing them through the column, and determining the amine formed by the bromination procedure, it was found that 100.0 ± 0.6% of the theoretical amount of amine could be recovered from the column eluent. Samples number 9 to 15 of Table IV show these results.

Determinations based on the chromate procedure for the amount of lead in the eluent were carried out both by determining the blank due to dissolved oxygen and by deaerating the solution before passage through the column. Sample number 1 of Table V shows a 0.9% deviation for the nitrobenzene when the blank was determined, but samples numbered 2 to 7 in Table V show an average of only 0.4% deviation for several samples of nitrobenzene and meta-nitrobenzoic acid when the samples were deaerated prior to passage through the column. Attempts were made to determine ortho- and para-nitrophenol by this method, but the amines were apparently oxidized by the dichromate, and the resulting mixture could not be filtered.

A sample of nitroethane was dissolved in 0.1 N perchloric acid, deaerated, and passed through the column. Lead was determined in the eluent by the dichromate method. Using the amount of lead found, only about 25% of the nitroethane was reduced.

2. Determination of the Blank

Blanks due to air dissolved in the acetic acid were determined several times for the lead column by titration potentiometrically with

TABLE IV

NITRO COMPOUNDS REDUCED BY LEAD ANALGAM; BROMINATION PROCEDURE

Sample	$HClO_4$ Concn.	Mg. Sample	Ml. $Na_2S_2O_3$ Blank	Ml. $Na_2S_2O_3$ Sample	N $Na_2S_2O_3$	Percent Recovered
Nitrobenzene						
1	0.05	73.81	47.80	10.68	0.09806	99.8
2	0	73.81	47.80	13.65	0.09806	91.9
3	0	73.81	47.80	11.30	0.09806	99.3
4	0	74.80	47.80	13.71	0.09806	90.2
5	0	74.80	47.80	11.37	0.09806	98.1
6	0	74.80	47.80	19.85	0.09806	67.9
7	0	74.80	47.80	11.90	0.09806	96.7
8	0	74.80	47.80	11.65	0.09806	97.4
9	0.1	74.80	47.80	10.60	0.09806	100.2
10	0.1	74.95	47.80	10.48	0.09806	100.2
11	0.1	74.95	47.80	10.57	0.09806	100.0
12	0.1	72.37	47.80	11.40	0.09806	100.6
Meta-nitrobenzoic acid						
13	0.1	117.27	47.80	4.74	0.09806	100.3
14	0.1	96.15	47.80	12.34	0.09806	100.6
15	0.1	96.15	47.80	12.33	0.09806	100.6

TABLE V

DEAERATED NITRO COMPOUNDS REDUCED BY LEAD AMALGAM; $K_2Cr_2O_7$ PROCEDURE

Sample	Mg. Sample	Meq. $K_2Cr_2O_7$	$Na_2S_2O_3$ Ml.	$Na_2S_2O_3$ N	Percent Recovered
Nitrobenzene					
1*	74.95	7.5	7.36	0.09806	100.9
2	83.31	7.5	14.40	0.09806	100.0
3	72.37	7.5	22.85	0.09806	99.4
4	72.37	7.5	22.78	0.09806	99.5
Meta-nitrobenzoic acid					
5	117.27	7.5	12.58	0.09806	99.6
6	96.15	7.5	23.93	0.09806	99.5
7	96.15	7.5	23.62	0.09806	100.1
Nitroethane					
8	42.50	7.5	62.5	0.09806	26.9
9	42.50	7.5	64.0	0.09806	24.0
10 and 11**					

*Sample not deaerated, a blank of 1.240 meq. of $K_2Cr_2O_7$ being determined.

**Ortho- and para-nitrophenol were run, but the solution was unfilterable after $K_2Cr_2O_7$ was added.

0.1 N sulfuric acid and by the dichromate method. The results of these determinations are found in Tables VI and VII.

No precipitate of lead chromate could be detected when potassium dichromate was added to the eluent when deaerated 0.1 N perchloric acid was passed through the column. Thus the only blank is due to dissolved oxygen.

The variation in the magnitude of the blank for the various samples could be due to the change in the solubility of oxygen in the acetic acid with temperature, or due to the fact that different batches of acetic acid had more oxygen dissolved in them.

To determine if the reduction product of the oxygen was hydrogen peroxide, oxygen was bubbled through an acetic acid sample. The sample was then passed through the column into a solution of potassium iodide, starch indicator and 1:4 sulfuric acid under a carbon dioxide atmosphere. No blue color was observed. However, when hydrogen peroxide was added to the mixture, the blue color of the starch-iodine complex was observed. Thus the reduction product of the oxygen in acetic acid does not appear to be hydrogen peroxide.

To be certain that nitrobenzene was reduced to aniline, five grams of nitrobenzene dissolved in acetic acid was passed repeatedly through the column. Bromine was added to the eluent to prepare 2,4,6-tribromoaniline. The product was recrystallized from aqueous ethanol. The melting point of the recrystallized product was 120-1°, of an authentic sample 115-117°, and of a mixture 115-118°.

TABLE VI

AIR BLANK WITH THE LEAD COLUMN; H_2SO_4 TITRATION

Sample	Vol. HOAc	H_2SO_4 Ml.	H_2SO_4 N	Mmole. Pb / 100 Ml. HOAc
1	85	6.32	0.08912	0.331
2	85	6.17	0.08912	0.323
3	85	6.60	0.08912	0.346
4	100	7.60	0.08912	0.339
5	100	7.60	0.08912	0.339
6	100	7.45	0.08912	0.327
7	100	5.92	0.1085	0.321

TABLE VII

AIR BLANK WITH THE LEAD COLUMN; $K_2Cr_2O_7$ PROCEDURE

Sample	Vol. Solvent	$HClO_4$ Concn.	Meq. $K_2Cr_2O_7$	$Na_2S_2O_3$ Ml.	$Na_2S_2O_3$ N	Mmole. Pb / 100 Ml. Solvent
1	100	0.0	2.50	15.70	0.09806	0.320
2	125	0.0	3.00	17.95	0.09806	0.331
3	100	0.0	3.75	29.85	0.09806	0.274
4	100	0.0	1.50	7.00	0.09806	0.271
5	100	0.1	1.50	6.10	0.09806	0.301
6	100	0.1	1.50	7.00	0.09806	0.271
7*	100	0.1	1.50	15.78	0.09806	0.000
8*	100	0.0	1.50	15.70	0.09806	0.000

*Sample was deaerated.

IV. SUMMARY AND CONCLUSIONS

A. The Zinc Column

A metal reductor consisting of a reducing column packed with zinc amalgam containing 2% mercury prepared from 30 mesh granular zinc will reduce several aromatic nitro compounds dissolved in 0.1 N perchloric acid quantitatively to the amine. The amine can then be determined by the bromination method, thus providing a rapid, convenient and accurate method for the determination of aromatic nitro compounds. One of the main difficulties expected with this method would be in those cases where bromination is not a suitable method for the determination of the amine.

No method was found whereby the nitro compound could be measured by determining the amount of zinc in the column eluent. If there was not sufficient perchloric acid in the sample, solid zinc acetate formed in the column, and if perchloric acid is present, it will react with the amalgam to liberate zinc perchlorate and hydrogen. Acetic acid itself reacts slightly with the column to liberate zinc acetate and hydrogen.

Oxygen is considerably more soluble in acetic acid than in water, and it is reduced by the column with the liberation of an equivalent amount of zinc. If the solution is deaerated before the sample is passed through the column, oxygen is removed and thus does not liberate zinc.

B. The Lead Column

A metal reductor consisting of a reducing column packed with lead amalgam containing 2% mercury and prepared from granular lead will reduce several aromatic nitro compounds dissolved in 0.1 N perchloric acid quantitatively to the amine. The amine can then be determined by the bromination method, but the determination is less desirable than when the zinc column is used, since lead iodide precipitates and causes a slight interference with the end-point of the iodine titration. This method is subject to the same restrictions using the lead column as it was when the zinc column was used.

If the solutions of the nitro compounds in 0.1 N perchloric acid were deaerated before passage of the solution through the column, the amount of lead in the eluent was equivalent to the amount of nitro compound originally in the sample. The lead in such samples of the eluent can be determined by the dichromate method for some nitro compounds, but for other nitro compounds, the potassium dichromate apparently oxidizes the amine, and the method fails.

No method was found by which the excess acid could be determined after the reduction of the nitro compound. If no perchloric acid is added prior to passage of the sample through the column the amount of basic material formed can be determined by potentiometric titration of the eluent with 0.1 N sulfuric acid, but the reduction of the nitro compounds is not complete under these conditions.

LITERATURE CITED

1. Becker, W. W., and W. E. Shaefer, in Organic Analysis, Vol. 2, Interscience Publishers, Inc., New York, 1954, pp. 71-93.

2. Davidson and McAllister, J. Am. Chem. Soc., 52, 507 (1930).

3. Lobunets, M. M., Univ. etat Kiev, Bull. sci., Recueil chim., 2, No. 2, 69-72 (1936); through Chem. Abstracts, 31, 2969 (1937).

4. Lobunets, M. M., ibid., 2, No. 2, 81-3 (1936); through Chem. Abstracts, 31, 2966 (1937).

5. Lobunets, M. M., ibid., No. 3, 71-8 (1937); through Chem. Abstracts, 33, 2439 (1939).

6. Lobunets, M. M., ibid., No. 4, 23-6 (1939); through Chem. Abstracts, 35, 1356, (1941).

7. Lobunets, M. M., ibid., No. 4, 11-4 (1939); through Chem. Abstracts, 35, 1356 (1941).

8. Lobunets, M. M., Zavodskaya Lab., 7, 872-4 (1938); through Chem. Abstracts 33, 504 (1939).

9. Per'e, M. I., Univ. etat Kiev. Bull. sci., Recueil chim., No. 3, 37-41 (1937); through Chem. Abstracts, 33, 2439 (1939).

10. Per'e, M. I., and M. M. Lobunets, Ibid., 2, No. 2, 45-50 (1936); through Chem. Abstracts, 31, 2966 (1937).

11. Per'e, M. I., and M. M. Lobunets, Ibid., 2 No. 2, 73-9 (1936); through Chem. Abstracts, 31, 2969 (1937).

12. Per'e, M. I., and M. M. Lobunets, ibid., No. 3, 43-7 (1937); through Chem. Abstracts, 33, 2438 (1939).

13. Scribner, W. G., and C. H. Bailley, Anal. Chem., 30, 1462-62 (1958).

14. Stegemann, K., in Neuere massanalytische Methoden, Ferdinand Enke Verlag, Stuttgart, 1956, pp. 163-185.

15. Timnick, A., and L. Fleck, in "High Frequency Titration of Some Monobasic and Dibasic Acids in Nonaqueous Media." M. S. Thesis, Michigan State University.