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A STUDY OF LUXURY ABSORPTION OF IRON AND MANGANESE IN INSOLUBLE GLASSY FRITS BY HORTICULTURAL PLANTS

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A STUDY OF LUXURY ABSORPTION OF IRON AND MANGANESE IN INSOLUBLE GLASSY FRITS BY HORTICULTURAL PLANTS

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TABLE OF CONTENTS

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INTRODUCTION

Much is to be found scattered through literature on the effect of the addition of iron to soil on plant growth. Some references indicate very decided beneficial effects from applications of iron in one form or another, others indicate that benefits are derived from the addition of small amounts of iron and toxicity from larger applications. Literature contains still other references explaining seemingly contradictory results. Some experimenters have explained such differences in results as due to solubility of iron caused by variability in pH of the soil solution, or in the chemical composition of the soil complex. In many cases, chlorosis is considered as a symptom of lack of iron, while green color is taken as indication of satisfactory iron supply. However, a supply of iron, which may be necessary to maintain green color, may not necessarily be sufficient to result in optimum growth. This may be more especially the case where plants are grown intensively in greenhouses and hence nutrient levels of soil may be much higher than in farm soil.

There is nothing in the literature, so far as the author has been able to discover, that indubitably places a limit as to the amounts of all nutrient elements that must be available for optimum growth in horticultural plants. There is some evidence that optimum plant growth can be obtained at various nutrient levels, provided that a proper balance of various elements is maintained. One may then question what effects increasing amounts of iron and manganese will have upon plant growth if proper balance of all other essential nutrients is maintained. The presence in a plant of an amount of an element greater than that required for normal needs is called "luxury absorption" or "luxury consumption." It is difficult to ascertain at what point the absorption of a mineral element becomes luxury absorption.

In the past it has been a practical impossibility to study the effects of luxury absorption of iron and manganese because of the well-known fact that in normal agricultural soils a very small amount of the total iron is in a form available to plants.

When iron salts are applied to such soils they quickly become unavailable, so that applying iron salts directly to the soil in large amounts cannot possibly give an answer to the problem of luxury consumption of iron.

Manganese similarly is affected by composition and pH of the soil, by its interactions with other elements and more especially by its relationships with iron and calcium. For these reasons, serious difficulties are experienced in attempting to study luxury consumption.

STATEMENT OF PROBLEM

In order to determine if luxury consumption of iron is beneficial to plants, it was decided to find out what values might be obtained by the use of iron in an insoluble but available form, applied to the soil in quantities above the amounts normally found in greenhouse soils.

Iron in such insoluble form, but available to plants, is to be found in the experimental product frit, as described on page 44, at present under investigation in the Department of Botany, Michigan State College, in cooperation with the Ferro Enamel Corporation of Cleveland, Ohio. Experimental work already completed, Wynd (128, 129) shows to what extent plant roots can obtain iron from glassy frit without iron becoming soluble in nutrient solutions.

The object of the present work is to determine whether (1) plant roots can obtain iron from frit when this material is mixed with soil and (2) whether additional amounts of such iron added to the soil will produce better plant growth.

In general, the problem is to detect to what extent luxury absorption of iron and manganese affects plants. It is impossible to study luxury absorption by using soluble compounds, because of the fact that iron commonly is soluble in soil, or available to plants in relatively small amounts, although large amounts of iron may be present in insoluble or unavailable forms. Joffe and McLean (60), Monnier and Kuczraski (89), Morison and Doyne (91) and Wynd (128) concluded that iron is relatively insoluble in normal soil solution. The use of frit offers a means of supply of luxury amounts, without involving soil reactions. Preliminary experiments by Wynd and Bowden (130) with Antirrhinum and by the same authors (131) with blueberries, and by Wynd and Stromme (132) with beans, suggest the value of applying this principle to commercial production of plants.

Experimental work previously completed by Wynd (128, 129) showed the availability of iron contained in frit, but nothing is known as to the rates of application or the physiology of luxury absorption.

REVIEW OF LITERATURE

Function of iron

It has long been known that green plants cannot produce normal growth if deprived of iron. As early as 1844, Gris (39) noted that plants normally do not produce chlorophyll if deprived of iron. Other investigators, Crawford (21), Hopkins (48), Haas (41) and Olsen (94), have reported similarly.

While Willstatter and Stoll (126) proved that iron does not enter into the composition of chlorophyll, it seems to be generally accepted that it does have some function in the formation of chlorophyll.

Wolff (127) thought that iron acts as a catalyzer in plants.

Warburg (123) suggested that the iron in the plant acts as the oxygen-carrying component of the respiration ferment.

Oddo and Pollacci (93) believed that iron serves as the catalytic agent in the formation of the pyrrole nucleus and therefore, if the pyrrole nucleus is present, iron is no longer needed to complete the formation of chlorophyll. Demidenko (27) similarly found that the magnesium salt of alpha-pyrrolecarboxylic acid failed to replace iron functionally in corn seedlings. Deuber (29), Aronoff and MacKinney (3), and others, have been unable to confirm the theory that pyrrole derivatives may replace iron in the synthesis of chlorophyll.

Hopkins (48) thought that iron plays an important role in the cellular processes involving biological oxidation.

Oskerkowsky (96) found that a specific kind of iron, designated as "active iron" is concerned in chlorophyll formation. It is usual to consider "active iron" as being reduced iron, ferrous iron or mobile iron. Whatever the details may be as regards the function of iron on chlorophyll formation, either directly or indirectly, the reaction results in oxidation of the iron. This would indicate a release of kinetic energy in the change of the iron from the ferrous to the ferric form. In the latter form, the iron is inactive or immobile and is not translocated to other parts of the plant. Perhaps the energy released is utilized in and necessary to the formation of chlorophyll.

Forms of iron

Investigators have reported variously on the form of iron required by plants.

Jones (66) noted that given forms of iron in fixed small amounts are not equally efficient for plant growth.

Kliman (75) asserted that plants absorb and utilize iron only as ferrous cations. Ferric iron must first be reduced before absorption by the plant. This may be accomplished variously (1) by decomposition of soil organic matter, (2) by micro-organisms, (3) by reducing substances in the epidermis of the plant roots. This is in general agreement with present day thought on the subject. However, in this connection attention should be directed to the findings of various investigators (54, 86) on the effect of various organic acids in preventing oxidation of iron or perhaps in causing the reduction of iron. Other investigators (6, 45, 114) have demonstrated the effect of certain organic acids in inhibiting fixation of phosphorus by iron or other cations. It is well-known that some plants can obtain iron from the soil when other plants growing in the same soil show iron deficiency. Whether such plants can take in iron in ferric form, or whether such plants are more active in giving off carbon dioxide or other reducing substance that will convert ferric iron to ferrous iron, or perhaps are better able to absorb the iron through contact absorption, seems to be an unsettled matter. Possibly reduction of iron occurs in the rhizosphere as a result of biologic activity. It has been pointed out by some investigators that the rhizosphere carries a large concentration of micro-organisms, or at least a more active microflora than the body of the soil. The suggestion has been made that this population of microflora, utilizing in part waste products or excretions of the roots, may make available to the plants difficultly available compounds.

Demidenko (27) in a study of iron nutrition of sunflower and oats, concluded that higher plants assimilate iron sulfate and ferric and ferrous iron in equal measure. There seems, however, to be little proof anywhere that iron in the ferric form is assimilated by higher plants. It is more probable that ferric iron is reduced in some manner, possibly in the rhizosphere, through biologic activity, or chemical reaction under the influence of organic matter, organic acids, salts of organic acids, respiration of roots with release of carbon dioxide, or excretion of other organic substances.

Ignatieff (55) found that ferrous iron is strongly adsorbed by soil and that, therefore, reduction of iron has not been a major cause of its downward movement in podzol soils. Regardless, it seems to be generally accepted that under conditions of ample rainfall eventually all soluble soil materials must pass downward through the soil.

Hopkins and Wann (52, 53) studied the effect of H-ion on availability of iron for Chlorella sp. Ferric citrate seemed to be the most favorable source of iron generally. If calcium is omitted and sodium citrate added, iron can be maintained in available form for growth of Chlorella in alkaline solutions. Hopkins and Wann (54) believed that iron is active in growth only in ionized form.

Bastisse (6) found that activity of iron is favorably affected by traces of other elements, particularly manganese and that ferrous iron appeared more reactive than ferric iron.

Amount of iron

Regarding the amount of iron necessary for plant growth, Miller (88) states "All the directions for nutrient solutions stated that only a trace of iron was necessary and that it mattered little in what form it was presented to the plant, provided it was soluble in water. Quite recently, however, much work has been done on the question of iron nutrition which shows that not only the quantity of iron available but the form in which it is presented to the plant, can exert a marked influence upon plant growth and development. These two factors in turn are dependent upon the composition of the medium or nutrient solution—its hydrogen-ion concentration, the nature of the general environment—and to some extent upon the kind of plant under consideration. There is at the present time no criterion by which to determine whether a plant is receiving sufficient iron except by its general appearance of health and vigor."

That the amount of iron found in plants varies greatly, has been noted by many investigators.

Stiebeling (113) noted great variation in iron content of plants as between different kinds of plants.

Crawford (21) noted that only a small amount of magnesium and iron are necessary to produce a green color of leaves and that lack of iron in the plant is generally produced in so-called calcareous soils.

Gile and Carrero (37) noted that a slight deficiency of iron may diminish yield of rice without affecting the appearance of the plant. Rice plants grown in acid solution contained highest percentages of iron, while plants grown in neutral solutions had higher concentrations than those grown in alkaline solutions when some forms of iron were used, but contained equal percentages when other forms were used. Variations of iron found by Gile and Carrero in the plant ash were in all probability due to variations in availability of the iron in the various culture solutions. At least certain investigators believe this to be the case. Barnette (4) noted that higher average yields in different solution cultures were probably due to higher availability of iron.

Jones and Shive (68), in a study of the influence of iron as ferric phosphate and as ferrous sulfate on growth of wheat in nutrient solutions, found that dry weight of plants increased with increase in amount of available iron up to 2 mg. per liter, although in the highest amounts (5 mg. per liter), the ferrous sulfate was somewhat toxic to plants. Further, these experiments show that ferrous sulfate increased dry weight more than did ferric phosphate.

Shive (108, 109) noted that concentrations of iron in the solution, slightly in excess of that required for normal plant growth, may cause a chlorotic condition characteristic of iron deficiency.

Marsh and Shive (85) found large, healthy plants of soybean, were produced when there was a continuous supply of available iron. They suggested that the supply of soluble iron (in the cultural solution) must be kept at as low a concentration as possible without inducing chlorosis from lack of available iron.

Olsen (95) obtained optimum growth of maize grown in modified Knopf solution pH 4.0, when small amounts of iron were added, while larger amounts acted toxically. On the other hand, at pH 7.0, optimum growth was obtained with the larger amounts of iron.

Deuber (30) grew soybeans and Spiradella polyrhiza using potassium ferrocyanide and ferric ferrocyanide as sources of iron. He found that the higher concentrations of iron produced retarded growth.

Fuschini (34) believed that application of iron sulfate to the soil before planting may prevent rusts through increased vigor of the plants.

Kinzerskaya (73) found beneficial effects on the yield of grain from additions of ferric sulfate and fresh manure, whereas fresh manure alone was injurious.

Korolev (76) found that yields were halved when iron and aluminum phosphates were used, instead of superphosphate or precipitate.

Leclercq (78) undertook plot experiments to determine the fertilizing value of iron sulfate. It was found that 250 kilograms of iron sulfate per hectare produced an effect on oats as great as was produced by 150 kilograms of nitrate of soda.

The belief of many investigators (68, 85, 95, 108, 109) that concentrations of iron greater than that required for normal green color may be toxic, is based on solution culture for the most part. However, some investigators have found beneficial effects from relatively large applications of iron in soil culture. This may be due to the different culture media, to differences in availability of the iron, to differences in nutrient levels, or to differences in response of different kinds of plants to greater concentrations of iron.

Effect of calcium on iron

Crawford (21) has noted that lack of iron in plants is produced by peculiar soil conditions which make iron unavailable. This condition is most frequently found in calcareous soils, although such soils may contain just as much iron as do normal soils, but iron is kept insoluble by the large amount of lime present. Many investigators have noted chlorosis in plants growing in calcareous soils and have generally ascribed the chlorosis to the fact that nutritive elements, more particularly iron, have become unassimilable. Dauthenay (24) has so explained a chlorosis of fruit trees in calcareous soils.

Demetriados (26) grew Dolichos sinensis, Vitis vinifera and Evonymus pulchellus in pots in a silico-calcareous soil to which excessive amounts of iron were added and decided that excess of iron under these conditions does not cause chlorosis. Various toxic effects were observed and there was increased iron in the tissues.

Dennis (28) studied chlorosis in fruit trees and found iron chlorosis most serious in soils where faulty irrigation methods prevail and in soils having accumulations of lime and chlorides. However, possibly Dennis misinterpreted the symptoms for iron chlorosis. The chlorosis may very well have been due to toxic amounts of nitrites, chlorides or calcium or these may have accentuated iron chlorosis symptoms. The possibility of phosphate or sulfate deficiency should also be considered.

Clapp (17) noted that roses, growing in alkaline soils at pH 8.5, exhibited chlorosis which could be temporarily corrected by spraying at four to six week intervals with ferrous sulfate. The condition was permanently overcome by neutralizing the soil with sulfur or with aluminum sulfate.

Coste-Floret (20) claimed that favorable results with sulfate of iron have always been obtained on calcareous soils.

Monnier and Kuczynski (90) found that addition of a small quantity of "calcium carbonate of magnesia" precipitated the compounds of soluble iron in silicious calcium-free soil of Angers, France. Monnier and Kuczraski (89) reporting on later work, concluded that iron normally present in soils is insoluble and that this explains the marked effect of adding small amounts of iron compounds to the soil.

Gile and Carrero (37) believed that lime-induced chlorosis is caused by lack of iron and the only action of calcium carbonate is in diminishing availability of iron.

Hiltner (46) found that spraying lupine plants grown in lime soils with iron sulfate, was decidedly beneficial, as was the case for peas and vetches. When these plants were afterwards sprayed with milk of lime, they became chlorotic again. In a later report (47), he concluded that sensitiveness of lupines to lime is due to an injurious effect of lime on the nodule bacteria.

Milad (87) observed that the susceptibility of pears, apples, white lupines and rice, to chlorosis on calcareous soils, was related to the comparatively slow rate of carbon dioxide production from their roots. Those plants which did not develop chlorosis, showed a much higher rate of carbon dioxide production. That solubility of iron in calcareous soils was affected by carbon dioxide was shown by analysis; by supplying carbon dioxide to the root system it was found possible to prevent chlorosis in white lupine.

Scholz (104) studied the chlorosis of Hydrangea. He believed that the most common cause of such chlorosis was excess calcium oxide which makes iron unavailable to the plant. Addition of an iron salt to the soil may prevent chlorosis without being of benefit to the plant growth. He reached the same conclusions in further experiments (105) with Primula obconica, Hance.

Vyunov (122) found chlorosis in plants growing in soils with high calcium carbonate content, was due to change of iron into insoluble, unassimilable compounds. Raising alkalinity of the soil aggravates the condition, while greater acidity relieves it. Further, he noted that plants having acid root secretions were immune to chlorosis.

White (124) in a study of factors affecting iron chlorosis in Gardenias, found that the foliage became green when treated with iron compounds. The corrective effect of iron applied to the soil was very slow; sulfur applied to the soil prevented chlorosis; supplementary light failed to correct the trouble; low temperatures resulted in chlorosis and nematodes and stem cankers accentuated the chlorosis. However, Demidenko (27) found that plants absorbing iron through the leaves or stems, gave lower yields than those absorbing it through the roots.

Lindner and Harley (82) thought that calcium-induced chlorosis is probably brought about by a complex of causes not yet fully established.

Bennett (8) concluded that chlorosis is a disturbance of nitrogen metabolism as well as of iron metabolism and the two are intimately related.

Gile and Carrero (36) grew rice in nutrient solutions. They concluded from observations on cultures of rice and of pineapples that iron after once being transported to the leaves becomes immobile.

It is apparent that raising the alkalinity of a soil somewhat above neutrality, or increasing the calcium content, may result in a chlorosis of the leaves of plants. This chlorosis may be due to lack of iron in the leaves, which in turn is due to the lack of assimilable iron in the soil. Excess calcium or high alkalinity, results in the oxidation of the iron. Not all plants, however, are similarly affected. Some plants, in some manner or under some conditions, are able to obtain sufficient iron for normal green color. Chlorosis of plant foliage may result from other causes such as disturbance of nitrogen metabolism, or of manganese metabolism, or of deficiencies in the availability of nutrient elements, or from other causes. Excesses of absorbed elements more commonly cause necrosis, although slight excesses may affect growth only, while moderate excesses may result in varying degrees of chlorosis. Further, the outward manifestation of chlorosis varies with the cause and may vary as between different kinds of plants.

Effect of pH of the solution on solubility of iron

Jones (66) substituted ammonium sulfate for potassium nitrate in Tottingham solution and observed this resulted in greater acidity of the solution and growth of wheat plants that were not chlorotic, as compared to chlorotic wheat plants grown in Tottingham solution with potassium nitrate. He noted that in the latter case ferric phosphate was insoluble while in the former case, one-half the amount of ferric phosphate was sufficient to prevent chlorosis. Substitution of ferrous sulfate for ferric phosphate in Tottingham solution gave non-chlorotic growth, but in modified solution the same amount of ferrous sulfate was toxic.

Jones and Shive (67) showed that ammonium sulfate increased H-ion of Tottingham solution when substituted for potassium nitrate and that iron in ferric phosphate form was sufficiently available for plant needs in modified Tottingham solution.

Deuber (30) noted that ferric ferrocyanide was a satisfactory source of iron when the solution had a reaction of pH 5.0; but when more alkaline, chlorophyll development was restricted.

Barnette and Shive (5) believed that availability of iron is determined mainly by H-ion concentration of the solution.

Halvorson and Starkey (42) concluded that at pH values above 5.0, very small concentrations of ferrous iron and still smaller concentrations of ferric iron appear to be soluble in solutions under atmospheric conditions.

Sideris, Young and Krauss (110) studied effect of iron on growth of pineapple, *Ananas comosus* (L.) Merr. They found precipitation of iron and decrease of its availability to plants was caused by rising pH values.

Davis (25) studied the effect of iron and aluminum chlorides on retention of phosphorus in a virgin Hammond very fine sandy loam and concluded that formation of iron and aluminum phosphates is not the major form of fixation at soil reactions above pH 4.5. It is the author's opinion that at least in some soils and at pH values above 6, phosphates increasingly appear as calcium phosphates, while at pH values below 6 the phosphates combine with such mineral elements as iron, aluminum and manganese.

Franceschi (33) found in Toa silt loam of Puerto Rico, that solubilities of iron and manganese were increased by additions of acid, manganese more so than iron.

The effect of pH of the solution on solubility is probably due to oxidation-reduction reactions. It is well established that decrease in pH has a reducing effect and iron is changed to the reduced or ferrous form. Increase in pH results in oxidation of the iron to the ferric form, which may be precipitated and is inactive or unavailable. In general, the same reactions occur with certain other mineral elements, as manganese and aluminum. However, it should again be pointed out that under certain conditions, even at high pH, iron or at least some of the iron, may be inhibited or retarded from changing to the ferric form.

Effect of organic acids

That organic ions influence the state of mineral elements in the soil is evident. It is well known that in very acid soils iron and phosphate ions combine to form iron phosphate.

A number of investigators have demonstrated the action of organic matter in inhibiting precipitation of iron as iron phosphate.

Lafon (77) has found a prepared citro-iron sulfate effective in combating chlorosis.

Tottingham and Rankin (119) investigated solubility of ferric citrate, ferric phosphate, ferric sulfate and ferrous sulfate in Tottingham's solution at pH 4.2 and 6.0. They found that ferric citrate was the most favorable form of iron used under conditions of the experiment.

Gile and Carrero (37) reported, as judged by growth of plants, ferrous sulfate, ferric citrate and ferric tartrate afforded sufficient iron when used in proper quantities in acid and neutral solutions. Ferric tartrate was the only form of iron (among those used) which furnished sufficient amounts of that element for nutrition of rice plants in alkaline solutions.

Reed and Haas (102) found that the addition of certain organic compounds, such as sodium and potassium salts of organic acids (citrates and tartrates) and starch and sugars to alkaline nutrient solutions, increased soluble iron.

Hopkins and Wann (54) observed that iron was unavailable to _Chlorella_ in alkaline nutrient solutions, but that the addition of a sufficient amount of sodium citrate kept the iron soluble at alkaline reactions for an indefinite period.

Iyengar _et al_. (58) found that the addition of fermentable organic matter brought considerable ferrous iron into solution in acid peaty soil and neutral laterite soil, but small amounts only became soluble in alkaline soils.

Joffe and McLean (62) concluded that normal soil solutions preclude the presence of iron and aluminum in solution. Iron is made available to plants probably through the solvent action of organic solvents. Morison and Doyne (91) and Wynd (128) similarly believed that the existence of ferrous iron in normal soil solution is improbable.

Prozorovskaya (100) noted increases in iron content of plants grown in sand cultures to which humic acid or its preparations were added.

Burk *et al*. (12) noted that a function of the iron content of organic material seems to be a stimulation of growth of *Azotobacter*.

Masoni (86) found as a result of experiments on the cause of chlorosis of plants growing in limestone soils, that dilute citric acid dissolved considerable iron and that tartaric and malic acids, relatively less.

Swenson, Cole and Sieling (115) showed that certain organic acids are able to prevent fixation of phosphate by iron and aluminum and other organic acids may possess the same chemical ability.

Struthers and Sieling (114) have demonstrated the effect of various organic acids, all of which are to be found in the humic acid complex, in preventing precipitation of phosphate by iron or aluminum. Further, they have demonstrated that there are organic anions at any pH within the entire range of values, for agricultural soils, that are markedly effective in preventing precipitation of phosphate by iron or aluminum. It is known that certain of these acids, namely citric, tartaric and oxalic, form stable, soluble complexes with iron and aluminum.

Ghani and Aleem (35) found that unavailability of phosphorus under acid conditions is due to the formation of iron and aluminum phosphates and the accumulation of organic phosphorus.

Hester and Shelton (45) studied soil organic matter in coastal plain soils. They believed that organic matter delayed absorption of phosphorus by iron and aluminum.

Organic acids and their salts seem to be more or less effective in preventing oxidation of iron. Since these are found in the humic acid complex, it follows that the presence of organic matter in the soil likewise prevents oxidation of iron.

Action of iron on phosphate

Kirsanov (74) grew barley in pots on podzols and concluded that phosphorus in the form of acid phosphate immobilizes iron and the addition of lime accomplished the same result and increases the pH.

Harper and Daniel (43) examined thousands of soils, only a few of which contained appreciable amounts of iron soluble in 0.2N H_2SO_4. In these latter soils soluble phosphate fertilizers were changed into a form not readily available to plants.

Byers, Anderson and Bradfield (16) noted that soils hold phosphates in unavailable form when soil colloids are high in content of iron oxide. This is probably due to the insolubility of iron phosphate.

Hester and Shelton (45) grew lima beans in coastal plain soils and found a marked increase in yield from additions of superphosphate, but with the addition of organic matter, only one-third as much superphosphate was required. They thought that organic matter delayed precipitation of iron and aluminum phosphate and so kept it available to plants.

Iyengar (57) found that in water-logged soils ferric iron is dissolved by organic acids and reduced to ferrous iron. The latter is reprecipitated as oxide, carbonate, phosphate and sulfide. Soil phosphates, thus removed, need to be replenished by the addition of phosphate fertilizer.

King and Perkins (72) found that large amounts of iron in the soil reduced the phosphorus content of wheat plants.

Coleman (18) found that phosphorus fixation by both coarse and fine clays, depends upon reaction and exchangeable cations only when there are free iron and aluminum oxides present.

Olsen (95) believed that iron may be precipitated as iron phosphate in the vascular bundles of the plant and so become unavailable at pH 6.0 - 7.0. The result on the plant is chlorosis, even though there may be an abundance of iron present. However, iron will remain available if furnished in complex organic form as citrate, or with other organic acids. It should be pointed out that Olsen's conclusions do not entirely agree with known chemical reactions. It is more probable that at the pH noted, the phosphate combines with calcium and the iron is oxidized to the ferric form, perhaps as ferric sulfate and as such is immobile.

Swenson, Cole and Sieling (115) studied fixation of phosphates by iron and aluminum. Their experiments have a direct bearing on the matter of iron precipitation. They found that maximum precipitation of basic iron phosphate occurs at pH value of 2.5 to 3.5, and for aluminum phosphate at a pH value of 3.5 to 4.0. At this range phosphorus predominates as

$H_2PO_4^-$ and there is little HPO_4^{--} and virtually no PO_4^{---}. This agrees with known facts regarding phosphorus-calcium relationships. One iron- or one aluminum-ion combined with one phosphate-ion ($H_2PO_4^-$) and in no case, regardless of amount of phosphate present, was the ratio of iron or aluminum to phosphate greater than unity. Hydrous oxides of aluminum and iron combine chemically with $H_2PO_4^-$ at low pH values because the stability of basic metal phosphate is greater than that of hydrous oxide at lower pH. When, however, pH value of soil is increased, there is a change toward greater stability of hydrous oxide and release of phosphate. Several organic anions, humus and lignin, are effective in preventing phosphate from combining with aluminum and iron or in replacing the chemically combined phosphate and thus release the latter to the soil solution.

Manganese and iron

The relationship of manganese and iron in soil and in plants has been noted by some investigators.

In 1913, Pugliese (101) reported on his investigations regarding antagonism between iron and manganese that "such antagonism exists." Johnson (63) found that pineapple plants recover from the toxic effects of manganese when supplied with iron through the leaves by means of sprays. Rippel (103) similarly noted that chlorosis, caused by the addition of manganese sulfate to water cultures of barley, could be remedied by administration of iron. He found that the iron content of normal and chlorotic plants is the same and therefore it is not iron assimilation that is restrained, but rather that its action in leaf tissues is unfavorably affected by manganese. On the other hand, Johnson (64) thought his investigations on pineapple indicated that chlorosis is due to depression of assimilation of iron by the plant. Manganese dioxide in the soil oxidizes iron into the ferric form which is assimilated with difficulty by the plant. Bishop (9) claimed that the manganese effect is not due to reduction of iron absorption by plants, but is rather related to chlorophyll formation.

Hopkins (49, 50) reported that both manganese and iron were essential to growth of Chlorella and found that no other element can replace manganese in nutrition of Chlorella. Haas (41) investigated injurious effects of manganese and iron on growth of Citrus. He noted that excessive concentrations of manganese brought about chlorosis even though iron was added in similarly large amounts.

Kapp (71) suggested that the control of soil reaction in such a manner as to regulate the amount of calcium in solution, or possibly the relationship between iron and manganese, or both, with calcium and nitrogen, appears to be partially the solution of the rice problem.

A study of the literature as cited above allows one to make certain generalizations.

1. Manganese is an essential element for plant growth.

2. The amount of manganese required is very small (less than a pound per acre may sometimes be sufficient). This indicates that the ultimate role of manganese may be as a catalyzer of certain reactions and since green color of the plant is absent when there is no manganese available, it is probable that it has some role in chlorophyll synthesis.

3. Manganese is a reducing-oxidizing agent and as such is variously affected by factors such as temperature, presence of other ions, and moisture, as well as being affected by its concentration and the concentrations of other ions. Likewise, it can variously affect other ions both in the soil and in the plant.

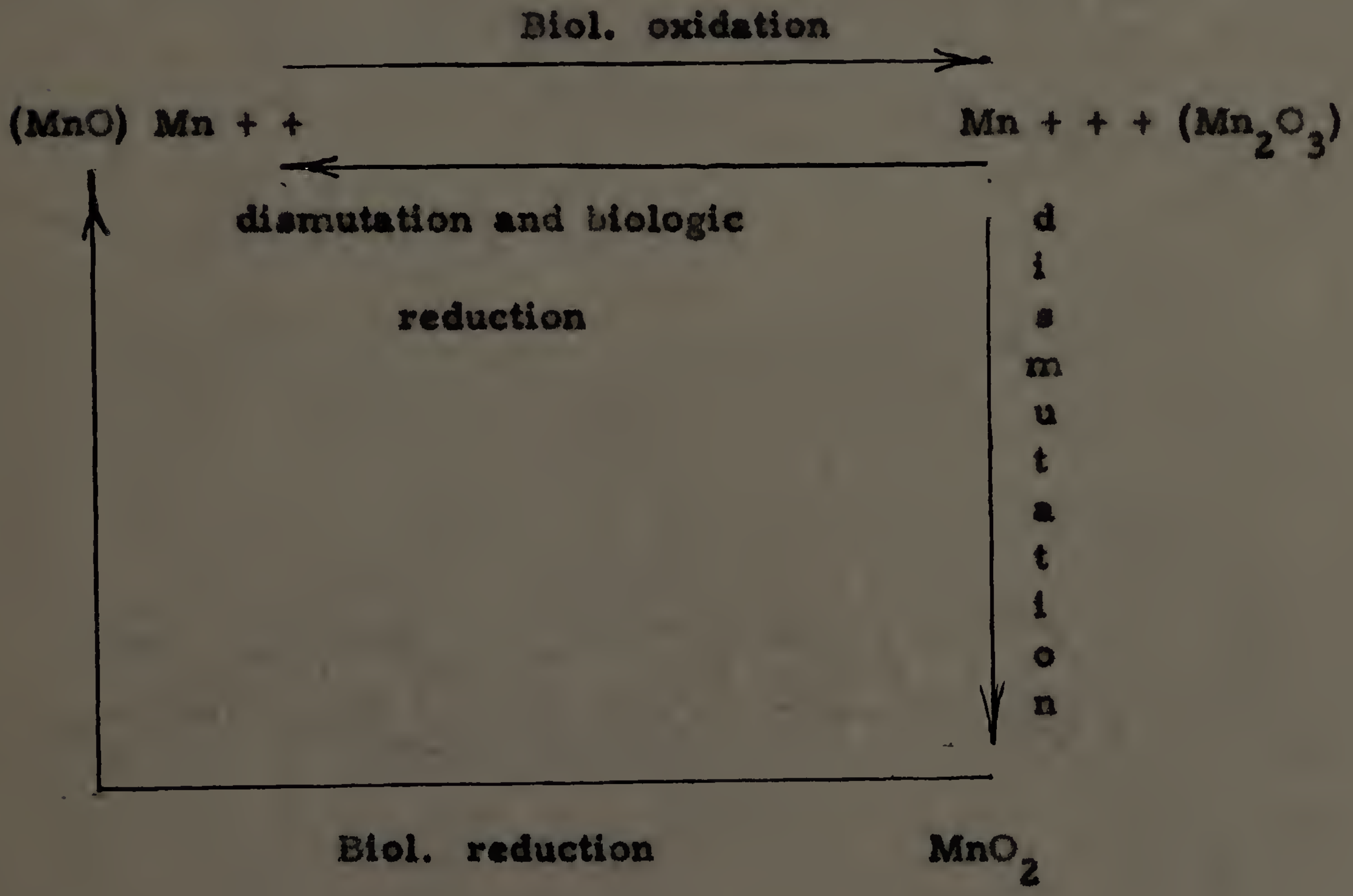
4. While a very few investigators have pointed to the possibility of a more or less definite ratio between manganese

and iron as being necessary, the work of many investigators would seem to point to such a necessary balance.

Pugliese (101) seems to have been the first to suggest a definite ratio. He stated that "optimum ratio for these two elements (Mn and Fe) seems to be in the neighborhood of 1:2.5." Johnson (63) seems to have reached a similar conclusion without specifically mentioning a definite ratio. He thought the indications were that chlorosis of pineapple in soils with excessive manganese is due to manganese dioxide in the soil changing iron to ferric form. Therefore, chlorosis was due to the unavailability of iron. Spraying plants with iron would supply iron in sufficient amounts temporarily, but permanent benefit must necessarily be accomplished by supplying sufficient ferrous iron to the soil to overbalance the effect of manganese dioxide on changing iron to ferric form. The amount of iron that would have to be applied would depend on the amount of manganese and its form. As long as reducible manganese was present in the soil, ferrous iron would be quickly oxidized to ferric iron. The problem is further complicated by biologic oxidation of manganese in the soil. Mann and Quastel (84) stated that manganese undergoes a metabolic cycle in soils, the kinetics of which is determined by the nature of microorganisms and organic matter present. The first product of biological oxidation of MnO is Mn_2O_3 which undergoes a dismutation to MnO and MnO_2.

$$Mn_2O_3 \text{ ---------- } MnO - MnO_2$$

The velocity of this reaction decreases rapidly with decrease in H-ion concentration and ceases almost completely at a pH of 8.0.



Bishop (9) suggested that since manganese concentrations in plants are found in regions of most active chemical change, this indicates that it is essential to plant development, but that manganese concentration must be carefully controlled. Hopkins (49) found that sufficient manganese must be present in solution for growth of Chlorella to insure reoxidation of iron after its reduction by the organism. A large amount of manganese either results in too high a concentration of ferric ions or prevents its reduction by Chlorella. Haas (41) found that small concentrations gave quick response in growth of Citrus cuttings, but excessive concentrations caused chlorosis even though iron was added in similarly large amounts. It would seem that he had an indication of a more or less definite ratio of amounts of iron and manganese, in which iron would be required in greater amount than manganese.

Scharrer and Schropp (106) conducted water and sand culture experiments with manganese, using it in various proportions with iron. They found that root growth was better with 5 Fe : 3 Mn than with 8 Fe : 0 Mn and that maximum growth was obtained with 7 Fe : 1 Mn. As manganese was used in greater proportion there was a progressive decrease of growth.

Hopkins and Silva (51) found that in soils in Puerto Rico, chlorosis, necrosis, sunscald and decreased growth of plants are strikingly associated with low iron and high manganese, while normal growth and recovery from chlorosis are markedly associated with low manganese and high iron. They reported that tops are more affected than roots by differences in iron-manganese relationship. They found a 20 manganese : 2 iron ratio prevented phototropic movement of the seed leaves of bean. This led them to suggest that iron acts as a protective agent against light and that interaction of iron, manganese and light are important determinants controlling the oxidation potential of green plants. When there is proper balance of iron, manganese and light, a normal range of oxidation potential results; but when not in proper balance, oxidation is too high or too low and toxicity appears.

Sherman and Harmer (107) in a study of the role of manganese in crop production, stated that ability of the soil to supply available manganous manganese is determined by the state of oxidation of the manganous-manganic system in the soil. Manganese plays an important role in plants by maintaining the oxidation-reduction level necessary for proper activation of iron for its function in synthesis of chlorophyll.

Kakehi and Baba (70) found that manganous sulfate has a stimulating effect on the growth of wheat.

Cook and Millar (19) stated that manganese deficiency usually occurs in alkaline soils.

Johnson (65) reported on fertilizer experiments with rice in nutrient solutions. With very low amounts of iron, manganous oxide and manganous sulfate caused depression of growth. As the amounts of iron were increased, the injurious effects of the manganese were overcome.

Lynd and Turk (83) found that overliming injury on an acid, sandy soil can be partially, although not completely, prevented by the application of phosphorus and manganese.

Somers, Gilbert and Shive (111) grew soybeans in a study of iron and manganese ratios. They concluded that normal plants were produced only when the iron-manganese ratio in the substrate was between 1.5 and 2.5. Somers and Shive (112), working with soybeans in nutrient solution at three different levels of iron at each of which manganese concentrations were varied, noted that the symptoms of excessive iron were the same as those from deficiency of manganese. Good growth was obtained within a narrow range around 2 for the iron-manganese ratio, regardless of total concentration.

Mulder (92) states "there are two main problems to consider in manganese nutrition of plants. The relation (antagonism) between manganese and other elements, particularly iron, and function of manganese-nitrate reduction and photosynthesis. The importance of a certain iron-manganese ratio has been emphasized by some investigators."

Pearse (97) studied iron and manganese in culture solutions using Physalis peruvina, L. and Fragaria vesca, L. He found that these plants could be grown free from either manganese or iron deficiency symptoms at widely different levels of manganese and iron, provided correct balance between the two is maintained. He suggested that in the absence of manganese, iron may be present in toxic amounts, but when there is sufficient manganese present, ferrous iron is oxidized and becomes physiologically inactive. If there is enough manganese present, all iron may be oxidized and there is then not enough ferrous iron for growth.

Relation of manganese to nitrogen nutrition

Investigators have reported variously on the effects of manganese on nitrification, ammonification and nitrate assimilation.

Leoncini (80) reported that amounts of manganese beyond 0.184% retarded nitrification. Brown and Minges (11) reported that applications of 100 lbs. of manganous sulfate per acre appreciably increased ammonification and nitrification. Addition of manganous sulfate at rates of 100 to 2,000 lbs. per acre, increased ammonification to a lesser extent, and caused no significant change in nitrification. Applications of 2,000 lbs. or more of manganous sulfate per acre inhibited nitrification and ammonification. He concluded that benefits from the application of small amounts of manganese to soil may in part be due to the effect on ammonification and nitrification.

Burstrom (13, 14, 15) concluded that there can be no assimilation of nitrate or ammonia in the absence of iron and manganese. Bertrand (7) believed that manganous sulfate improved assimilation of soil nitrogen by plants and had some effect on translocation of nitrogen within the plant.

Therond (117) found that manganese stimulates the assimilation of nitrogen in the soil and the migration of nitrogenous substances within the plant.

Pichard (98) found that manganese favored absorption of nitrogen by crops.

Vlasyuk (120) reported that manganese increased decomposition of organic matter through stimulation of microbial activity and increased the water soluble forms of nitrogen, phosphorus and potash. Within the plant manganese governs activation of nitrogen, phosphorus and potash, accelerates photosynthesis and improves nitrogen metabolism. In a later report, Vlasyuk (121) concluded that manganese regulated decomposition and synthesis of carbohydrates within the plant.

Leeper (79) found that marked manganese deficiency symptoms were related to accumulation of nitrates.

Alberts-Dietert (1) grew Chlorella in nutrient solutions and found that iron had no effect on nitrate assimilation, but that manganese was important as a catalyst for nitrate assimilation.

Leeper (79) and Whitehead and Olson (125) found that nitrates accumulate in the plant when the culture medium is low in manganese.

Jones et al. (69) found that when oxygen supply of the nutrient solution was low, nitrates were converted to nitrites, but that manganese prevented this reaction. They concluded that this indicated that manganese acted as a catalyst in nitrate assimilation particularly in the nitrite reduction phase.

Summary of investigations on iron nutrition

In summing up the findings of investigators, it can be stated that plants vary in their ability to obtain iron from the soil. Iron may be present in the soil as undecomposed silicates, sulfates or phosphates, adsorbed on clay colloids or organic matter, as hydrated or anhydrous oxides, or in soluble or insoluble compounds. It may be obtained by plants from the soil solution, from soil colloids or organic matter as an exchange phenomenon or directly from soil or rock particles through contact exchange, without necessarily passing through a soluble phase. Commonly, iron may be in the form of ferrous iron or of ferric iron in the soil. The amount of iron in ferrous form may be commonly very small, since ferrous iron may quickly be oxidized to ferric form. In ferrous form, iron is said to be soluble, available or "active," while the reverse is true of ferric iron. In very acid soil conditions, iron is likely to be soluble in relatively large amounts, but in the presence of phosphate it quickly combines to form iron phosphate. This may result in either iron deficiency or phosphate deficiency symptoms in the plant, depending upon which is in lesser amount. On the other hand, organic acids or organic matter inhibit the precipitation of iron phosphates.

In alkaline soils, iron is oxidized to unavailable ferric form and as a result plants may show symptoms of iron deficiency, depending very largely upon the kind of plant, since some plants seem to be able to obtain sufficient iron to maintain green color, even in alkaline soils. This is thought to be due perhaps to the greater production of carbon dioxide from the roots of some plants, which results in reduction of ferric to ferrous iron, in the immediate vicinity of the root. Further, organic acids and organic matter, tend to inhibit the complete oxidation of ferrous iron, or reduce ferric iron, even in alkaline soils and under some conditions at least, there may be sufficient available iron for immediate needs of the plant. Within the plant iron seems to become immobile, at least after its function has been performed. This has led some investigators to advance the hypothesis that ferrous iron acts somehow as a regulator of chlorophyll formation and in the process is oxidized to ferric iron. In that form it is immobile and cannot be moved to other parts of the plant.

There seems also to be some relationship between iron and manganese. At high iron and low manganese content there is normal green growth, while at low iron and high manganese content, chlorosis may occur in the plant. Such chlorosis may be iron deficiency or manganese toxicity. On the other hand, when manganese is deficient, even though there is an ample supply of iron present, chlorosis results, which may be identified as manganese deficiency, but could logically perhaps be noted as iron toxicity. It is generally thought that if there is sufficient manganese present, all the iron may be oxidized and therefore unassimilable. The relationship between manganese and iron has lead some investigators to theorize on the possibility that manganese within the plant regulates or controls iron in its function in chlorophyll formation. (Perhaps manganese is oxidized to manganic form and reused by iron in its change to the ferric form, thereby reducing manganese. Thus manganese might be used over again. Such reaction might explain the fact that iron is immobile within the plant.)

Manganese also affects the action of other elements. It seems to inhibit formation of nitrites from nitrates and may have some effect on nitrate assimilation.

Both manganese and iron may be biologically oxidized or reduced. Under certain conditions biological competition may be so great as to cause a deficiency of these elements for assimilation by higher plants. Such biologic activity has been found to be the cause sometimes of non-pathogenic plant disease. The grey-speck disease of oats and perhaps frenching of tobacco are examples. Manganese may also be reduced without the aid of micro-organisms.

Contact exchange

According to Mulder (92), nutrient elements may occur in the soil (a) in aqueous solution, (b) adsorbed on organic or inorganic soil colloids, (c) in the form of an insoluble inorganic compound, and (d) as a constituent of organic compounds, either as a residue of plants or animals, or in living organisms.

Many investigators have believed that plants obtained their nutrients mainly or entirely from the soil solution. Pierre (99) states that "it is generally accepted that before phosphorus and other nutrients can be taken up by the plant roots, they have to be dissolved in the water of the soil, or the soil solution." In recent years this theory has been challenged by some investigators.

Jenney and Cowan (59) in 1933 suggested that inasmuch as plants can feed on adsorbed ions, the significance of the soil solution has been overestimated. The solubility concept does not entirely account for plant growth under all conditions. In 1939, Jenny and Overstreet (60) found that certain exchangeable cations can be absorbed by roots without necessarily passing through a soluble phase. Jenny, Overstreet and Ayer (61) further developed this theory and pointed out that metallic ions may also be absorbed from the roots by the exchange material. Albrecht and McCalla (2) showed that surface migration of cations between soil particles could take place and this must necessarily take place, if the contact theory is to be accepted.

Guest (40), in sand culture experiments under neutral and alkaline conditions, found that plants made excellent growth when iron was supplied as finely ground magnetite mixed into the sand, but when the magnetite was less finely ground, there was comparatively little growth.

Wynd, et al. (129, 130, 131, 132) using nutrient solutions and fused silicates impregnated with iron and manganese oxides, have demonstrated that roots of plants can obtain sufficient of these elements for normal growth, entirely through contact exchange.

EXPERIMENTAL MATERIALS

The Frits

Glassy frits of various silicates fused at a temperature of 2,500° F and impregnated with oxides of iron and manganese during fusing, are made by the Ferro Enamel Corporation. Such frits contain iron and manganese in an insoluble form. Wynd (128, 129) has tested these frits in hydroponic culture. They contain from 5.0 to 7.5 percent iron, calculated as ferric oxide. The iron was found to be only about one-half as soluble in water as was the iron in glass of a commercial soft drink bottle.

The frits are obtainable in different sizes. Those used in work by Wynd (128, 129) were of a size of 1/8 to 1/16 inch, whereas frits used in the present experiments with soils were of 325 mesh. The exposed surface is thus tremendously increased and consequently the solubility of impregnated elements is increased insofar as they are at exposed surfaces of the particles.

Two frits were used by the author in these experiments. AB frit, containing 7.5% ferric oxide and 3% manganese trioxide;

AC frit, containing 7.5% ferric oxide. Both frits contain a trace of phosphate. The glassy material is mostly calcium and sodium silicates.

<u>Experimental soil</u>

The basic soil selected was a greenhouse soil classified as clay loam. This soil was tested by Dr. R. L. Cook of the Soils Department, Michigan State College. The Spurway System of quick tests was the method employed. The results of the test in parts per million are as follows:

Ca^{---}	20	Mg^{---}	—	P^{---}	0.5
SO_4^{--}	—	Fe^{---}	—	K^{---}	1
Cl^{---}	10	NO_2^{---}	—	pH^{--}	6.8
Mn^{---}	—	NO_3^{---}	15		

Where no figure is given there was no indication of the presence of the element in the test. This is due to the inadequacy of the test and indicates that if the element is present, the quantity in parts per million is very small and not detectable by the tests used.

Preparation of soil

The soil was screened through a 1/4 inch mesh screen and to it was added a Greenwood peat having a pH of 4.5 to 5.0, at the rate of 1 part peat to 5 parts of soil. To each pot of soil mixture was added one level teaspoonful of 0-20-0 superphosphate and the amount of frit required by the treatment. Each pot of soil was then thoroughly mixed using a hand operated mechanical mixer to distribute the peat, superphosphate and frit uniformly through the soil.

In order to obtain some information as to the optimum amounts of iron-containing frit and iron and manganese-containing frit, it was decided to use the frits at the rates of 15 grams, 30 grams, 60 grams and 90 grams per 6-inch standard pot.

The decision to use five plants in 6-inch standard pots for each treatment was made after consultation with Dr. C. Hamner and Dr. F. L. Wynd.

Plants used

A list of the plants used in the experiments follows:

Nicotiana Tabacum, *Linn.*

Cineraria cruenta, *Mass* (*Senecio cruentus DC*) "Kremer"

Lobelia Erinus, *Linn*.

Primula malacoides, *Franch*.

Iberis amara, *Linn*.

Antirrhinum majus, *Linn*. Hybrid HT x RPS

Antirrhinum majus, *Linn*. "Margaret"

Phaseolus vulgaris, *Linn*.

Calendula officinalis, *Linn*. "Ball's Orange"

Impatiens Holstii, *Engler* and *Warb*.

Tagetes patula, *Linn*. "Butterball"

Tagetes patula, *Linn*. "Naughty Marietta"

Begonia semperflorens, *Link and Otto*. "Ball's Rose"

Phlox Drummondi, *Hook*.

EXPERIMENTAL PROCEDURE

Each kind of plant was planted in the greenhouse soil to which was added superphosphate and the frit in four different amounts. Two frits were used, one containing iron, AC frit, the other containing iron and manganese, AB frit, as explained on page 44. Nine treatments were designed for each of the various kinds of plants used—four treatments with the AB frit and four treatments with the AC frit and one treatment without frit, designated as a control. In each treatment there were five plants, each plant in a separate 6-inch pot. This made a total of forty-five plants, five each in each of nine treatments. Eighteen plants were used as buffer plants along the sides and ends of the benches.

The plants were grown in several greenhouses with night temperatures generally in the vicinity of 60° F.

Plants were given nutrients in solution after the first six weeks, on the average of once a month with exceptions in the case of slow growing plants. Each plant was given the same volume of solution at each feeding. Ammonium sulfate was used at the rate of 0.2 gram per plant. At alternate feedings, an additional 0.1 gram of potassium sulfate was supplied to each plant. In the case of Nicotiana the frequency of fertilizer applications had to be increased to once a week as the plants approached maturity. Ten to five days previous to harvesting the tobacco plants received a total of 1.0 gram of ammonium sulfate and 0.4 gram of potassium sulfate. In all other plants the frequency of fertilizer application in the last month of growth was increased to once a week.

The plants were grown to some determined point of maturity for the most rapid growing plants in the test. This determined point of maturity varied for different plants and is noted in the discussion of the different plants. Then, all plants of a given kind were cut and fresh weights taken immediately.

If plants showed marked growth differences due to their genetic diversity, those plants that showed a marked deviation from the average were discarded. Wherever this was done, it is so noted in the discussion of the different plants. This practice has been followed after consultation with Dr. W. D. Baten, Experiment Station statistician at Michigan State College and Dr. F. L. Wynd. It is well known that irregularity in growth of many horticultural plants is often due to their genetic variability. It is presumed, therefore, that the most uniform plants represent the average. A dwarf plant, or an overly large plant, may be manifesting a factor found in its genetic constitution. Inclusion of such genetically variable plants would alter results and often make it impossible to determine results of an experiment with any degree of accuracy. The horticulturist commonly discards these "off" plants, as they appear during the course of the growing season.

Other factors of environment or accident of culture may result in uneven growth, even though the greatest care has been exercised. Among such factors are uneven uptake of moisture due to accidental injury to roots caused by a pathogen or due to accidental breaking of roots at planting time.

The cut plants selected were placed in paper bags for drying. The plants were first dried in a dehydrator at 140° F and then cooled to room temperature at 72° F. They were then weighed to obtain dry weights.

The dried plant material was finely ground preparatory to determining iron and manganese content.

Iron and manganese determinations were made according to standard methods (see appendix) and iron-manganese ratios computed. Data are recorded in tables.

RESULTS OF TESTS

Nicotiana Tabacum, Linn.

Seeds of Nicotiana "Common Havana" were obtained from Professor C. V. Kightlinger, Department of Agronomy, University of Massachusetts, through Dr. Linus H. Jones of the Department of Botany, University of Massachusetts. These seeds were sown in early October, 1950, and the young plants potted into 6-inch pots containing the soil mixtures, in late November, 1950.

The Nicotiana plants were harvested February 25, 1951, by cutting the stalk at ground level. Each plant was then weighed and placed in a bag and dried. Average height, fresh weights, dry weights, iron and manganese analyses and Mn/Fe ratio for each treatment, are shown in Table I. Iron and manganese analyses (see appendix) of leaves and stems were made in duplicate.

It is to be noted that the frit containing iron and manganese (AB frit), produced growth of greater weight for each level used than the frit containing iron alone (AC frit), weights increasing with increased amounts of frit (Figure 2). The

TABLE I

AVERAGE FRESH WEIGHT, HEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *NICOTIANA TABACUM*, *LINN*. FOR EACH TREATMENT

Type of frit	Frit per 6 in. pot (gr.)	Av. ht. (in.)	Av. fresh wt. (gr.)	Av. dry wt. (gr.)	Iron content p.p.m.		Manganese content p.p.m.		Fe/Mn	
					Leaf	Stem	Leaf	Stem	Leaf	Stem
	15	12.30	171.34	15.40	627	141	21	0	29.6	
5%	30	14.93	212.08	19.35	298	123	20	0	14.6	
Fe_2O_3	60	16.30	216.94	20.55	359	90	66	0	5.5	
	90	20.87	271.30	27.07	301	93	70	0	4.3	
5%	15	14.53	223.16	22.52	335	129	54	0	6.2	
Fe_2O_3	30	16.44	220.18	22.60	402	112	34	0	11.8	
2%	60	18.60	248.08	23.63	783	124	47	0	16.7	
MnO_2	90	26.00	302.28	33.47	443	105	34	0	13.0	
Control		15.13	212.12	20.22	1170	120	35	0	33.6	

same generally holds true for heights of plants (Figures 1 and 3), although there was no important difference in average heights between control and plants grown in soil with 15 grams of AB frit. The AC frit containing iron alone, gave an average fresh weight of 171.34 grams at 15 gram level whereas that of the control was 212.12 grams. Treatment with 30 grams AC frit was not markedly different from the control. However, at the 60 gram level there was some increase and there was a great increase in fresh weight at the 90 gram level (Figure 2).

The depression of growth when 15 grams AC frit was used is interesting and is perhaps due to low solubility of manganese occurring in the soil. This is perhaps due to the fact that the soil was high in phosphate; manganese in the soil may have combined to some extent with phosphate. Analysis for manganese in these plants (Table I) showed a relatively low amount of manganese present and a very high value, 29.6, for the ratio of iron to manganese. The lowered supply of available manganese was sufficient to prevent chlorosis, but it may not have been sufficient for best growth in spite of an abundant supply of iron. Despite the possible limiting effect of low

Figure 1. Nicotiana Tabacum, Linn. Showing response of plants to increasing amounts of frit as compared to control. From left—15, 30, 60, 90 grams AC frit; control; 90, 60, 30, 15 grams AB frit.

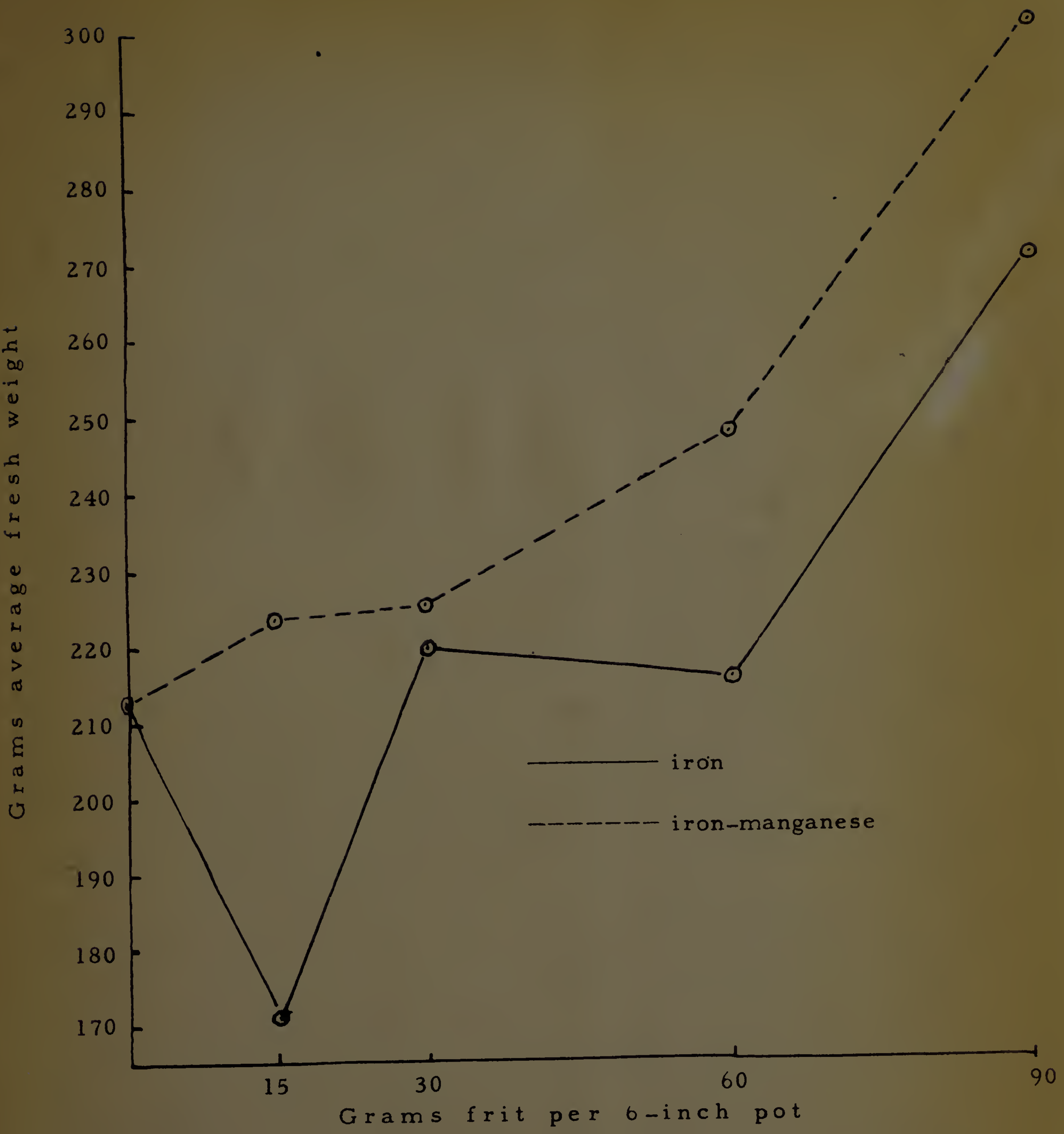


Figure 2. Effects of frits on fresh weight of Nicotiana Tabacum, Linn.

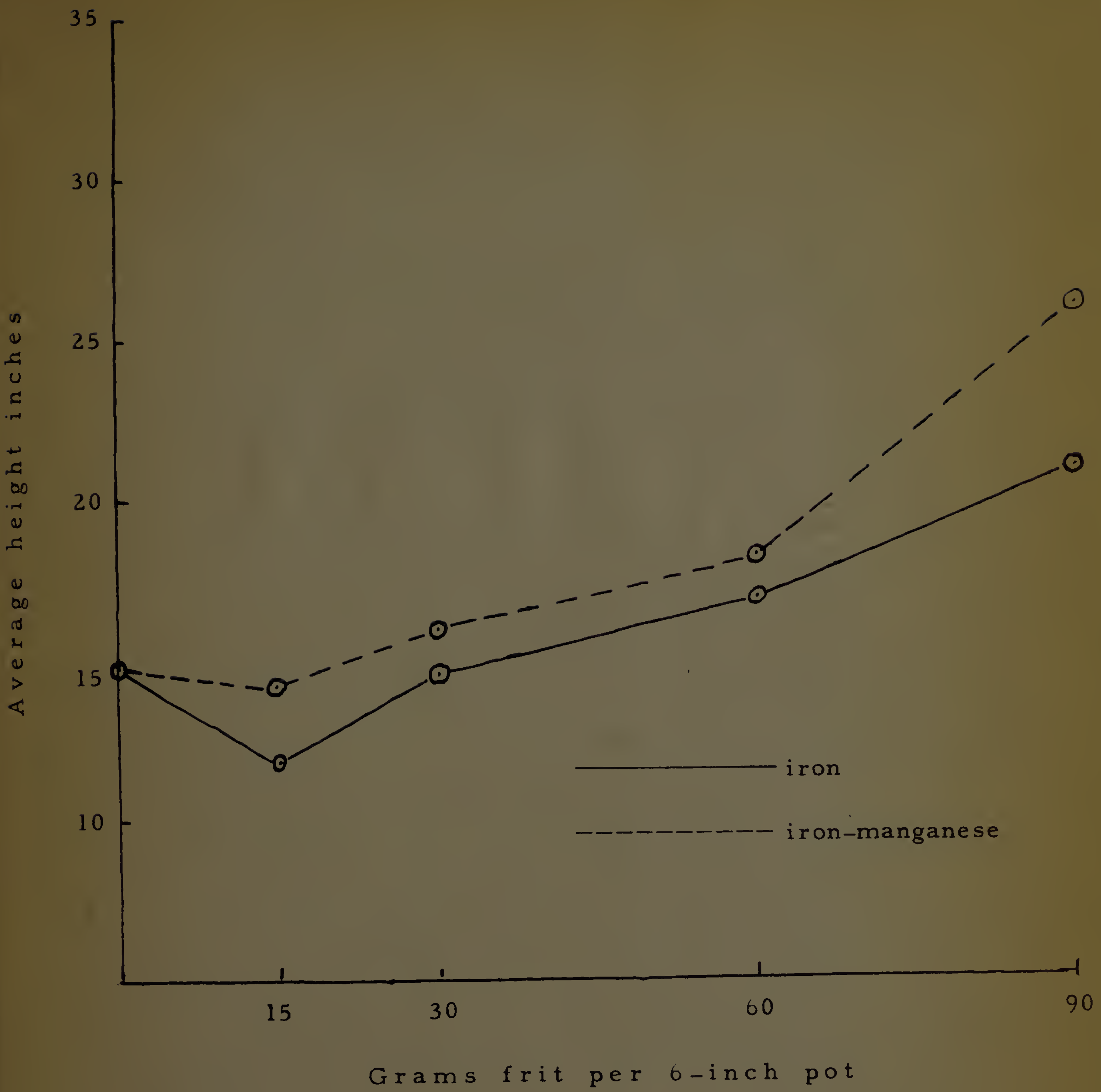


Figure 3. Effects of frits on height of plants of Nicotiana Tabacum, Linn.

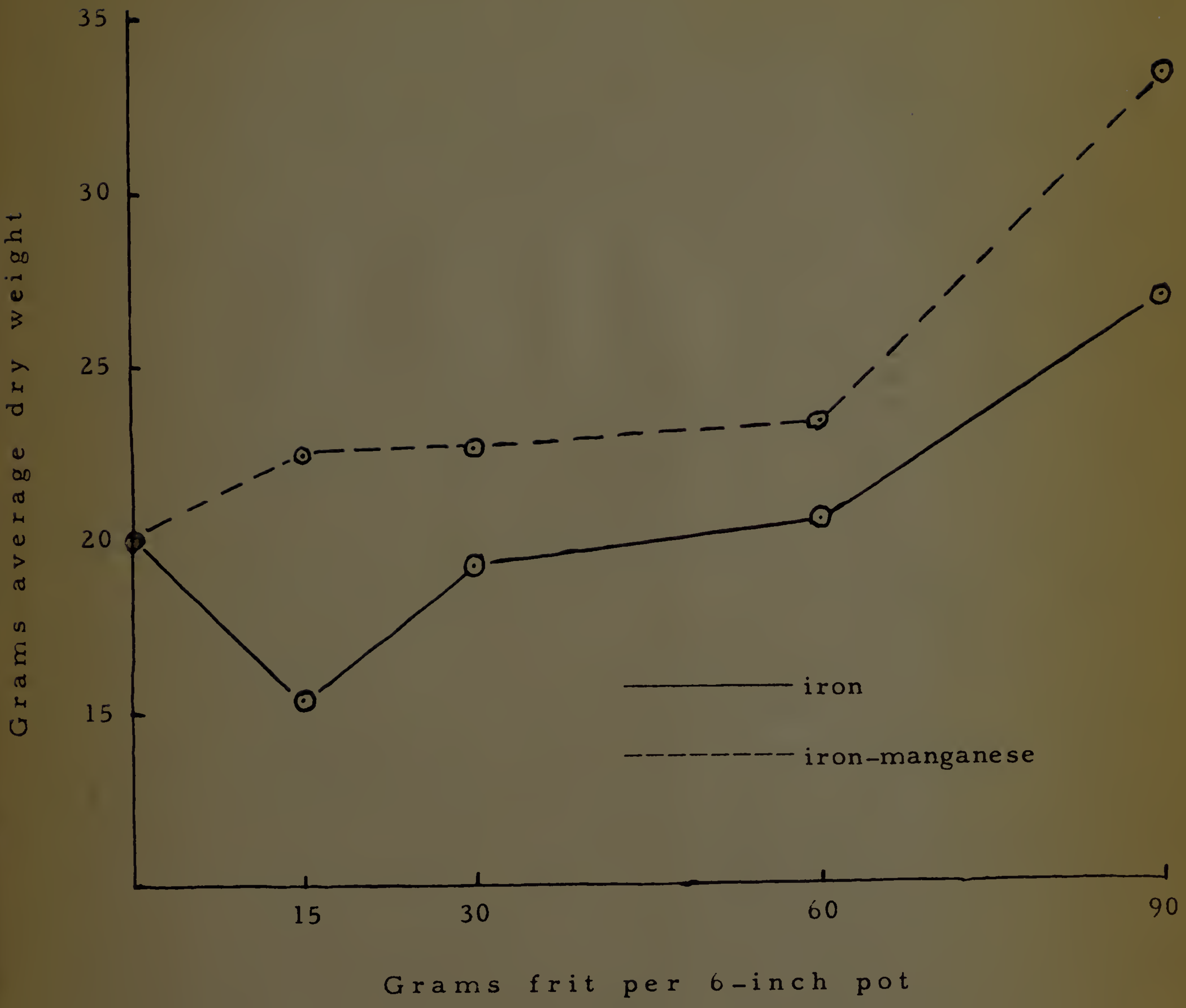


Figure 4. Effects of frit on dry weight of Nicotiana Tabacum, Linn.

manganese, increased amounts of AC frit improved growth and at the highest level (90 grams) was much better than the control.

Figure 1 shows (a) that frits had an effect on plant growth, (b) that iron-manganese frit was of greater benefit in promoting growth of Nicotiana than was iron frit, (c) that increased amounts of either frit caused increased growth.

Figure 3 shows the effect of various frits on growth as measured by heights of plants. Plants were measured from ground level to terminal bud. Heights and fresh weights are closely correlated. While the difference in heights does not appear to be statistically significant, there is a small positive trend for the AC treatments.

The treatments with iron frits showed an increasing amount of manganese present in the tissues with increased amount of frits used. The best growth with this frit was obtained at the 90 gram level. Analysis of plants in this treatment gave the lowest iron-manganese ratio value. There is no correlation apparent in the treatments using iron-manganese frit, except as already noted, as between fresh weights, iron and manganese analyses and ratio values. The analyses of plants in all treatments do not show luxury absorption of iron. However, four of the treatments, namely the 60 and 90 gram treatments with iron frit and the 15 and 60 gram treatments with the iron-manganese frit, produced plants with much higher manganese content than did the control. This might be construed as being evidence of luxury absorption of manganese. It is noted that these treatments with the exception of the 60 gram iron-manganese treatment, showed the lowest iron-manganese ratio value. There was increased growth with increase in the amount of the frits used. Any explanation of the cause of increased growth with increased amounts of frit used is difficult. Since the analyses do not show increased uptake of iron in the frit treatments, it may well be that some unnoted factor is responsible.

Statistical analysis of fresh weights of Nicotiana Tabacum, Linn. was calculated in the following manner.

Analysis of variance was used to determine the significance of results on advice of Dr. W. D. Baten, Statistician, Michigan Agricultural Experiment Station. However, it must be pointed out that the treatments were not randomized. Therefore, the differences in treatments are not as reliable as they would have been had they been randomized. On the other hand, examination of the detail data pertaining to position shows no trends of effects from environmental factors and there is no evidence in the observed values that they were not representative replications.

Treatments

15AB	30AB	60AB	90AB	Check	90AC	60 AC	30 AC	15 AC
220.0	240.8	240.0	252.3	173.1	245.9	231.0	200.6	159.0
220.6	170.1	246.0	334.7	221.1	272.1	217.7	230.3	162.3
201.7	217.6	246.6	324.1	241.8	296.1	192.9	212.1	164.2
250.4	218.8	256.0	320.1	212.6	246.3	201.2	208.3	156.1
223.1	253.6	251.8	280.2	212.0	296.1	241.9	209.1	215.1
*223.16	220.18	248.08	302.28	212.12	271.30	216.94	212.08	171.34

The following analysis pertains to these data.

Analysis of variance of the data on tobacco

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F
Total	44	78039.4		
Between replications averages	4	2748.71		
Between treatment averages	8	58231.78	7,278.97	13.654
Error	32	17058.91	533.09	

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* Average. AB designates iron-manganese frit. AC designates iron frit. Numbers refer to grams of respective frits.

After computing a t-value, it was found that the difference necessary for significance for the 5% probability point is 36.6 grams. By examining the treatment averages, it is seen that the average 90 gram AB and 90 gram AC is significantly greater than the averages for all other treatments, including the control.

The 15 gram AC treatment is significantly less than all other treatments including the control. The 60 gram AB treatment is very close to being significant. A statistical test for linearity of AB averages was then calculated; its analysis follows.

Analysis of variance for testing linearity of AB means

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	3	21682.90		
Linear or regression	1	19668.36	19668.36	37.79
Deviation from regression level	2	2014.54		
Error			533.09	

There is, therefore, a significant positive and linear trend for the AB treatment averages.

Analysis of variance for testing linearity of AC means

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Total	3	965513		
Linear or regression	1	22757	22757	42.689
Deviation from regression level	2	942756		
Error			533.09	

There is, for the AC means, a significant positive and linear trend.

Cineraria cruenta, Mass.

The Cineraria of the florist was developed originally as a hybrid between Senecio cruentus and Senecio tussilaginis. Various so-called races of Cineraria have been produced. Among these are dwarf, large-flowered types with broad florets and tall, small-flowered types with narrow florets. "Kremer's" type Cineraria has been developed by selection from original crosses between a dwarf, large-flowered type and a tall, small-flowered type. This variety seldom shows complete uniformity in habit of growth.

Forty-five plants from four-inch pots of "Kremer's" Strain of Cineraria were selected for uniformity, from one hundred plants available for this experiment. The soil was carefully washed from the roots and the plants were potted in 6-inch standard pots in the soil mixtures in late November, 1950. The plants were harvested February 24, 1951, by cutting the stalks at ground level.

Fresh weights were recorded, the plants dried and dry weights recorded (Table II) in the same manner as for Nicotiana Tabacum.

Data were gathered from all plants and are included here. However, it is the writer's opinion from years of experience in the culture of horticultural plants, that more accurate results are obtainable in nutrition experiments, if data from plants that are widely different, due to genetic variation, are omitted. Reference to Figures 5 and 6 will illustrate the point. Figure 5 shows a curve that includes the data from five plants in each treatment. Figure 6 shows the effect of the treatments when irregular plants are removed. The removal of the irregular plants has removed a source of error. This is illustrated in Figure 7, which shows representative plants from all treatments.

TABLE II

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF CINERARIA CRUENTA, MASS. FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	121.48	11.80	489	32	15.3
	30	161.78	17.70	479	34	14.1
	60	150.12	16.60	417	33	12.8
	90	140.28	15.10	476	33	14.6
5% Fe_2O_3 2% MnO_2	15	137.44	13.10	489	44	11.1
	30	133.44	12.70	564	92	6.2
	60	164.74	16.80	456	136	3.4
	90	171.70	19.50	406	144	2.8
Control		153.30	14.80	550	80	6.0

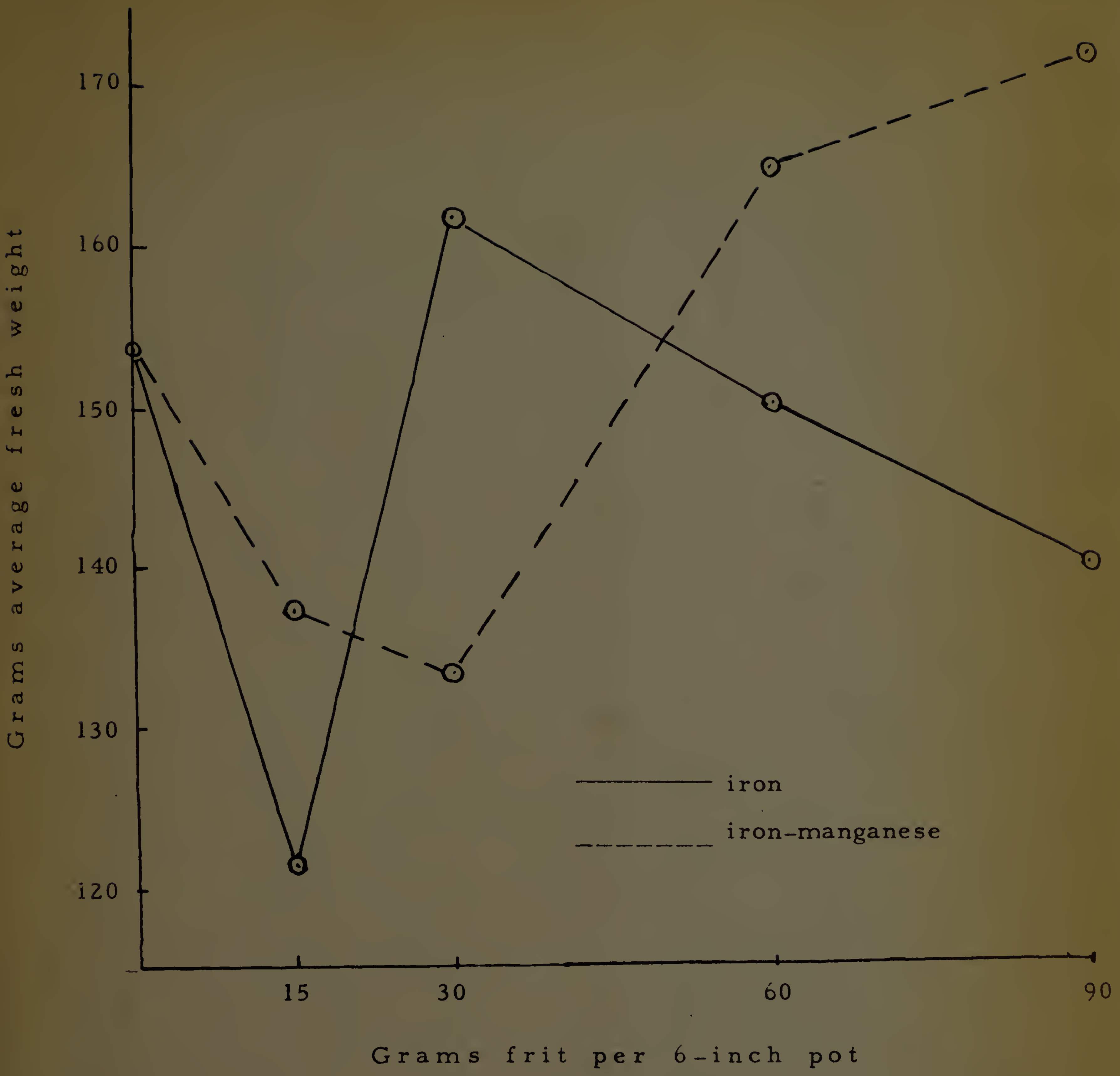

Figure 5. Effects of frits on fresh weight of *Cineraria cruenta*, *Mass*.

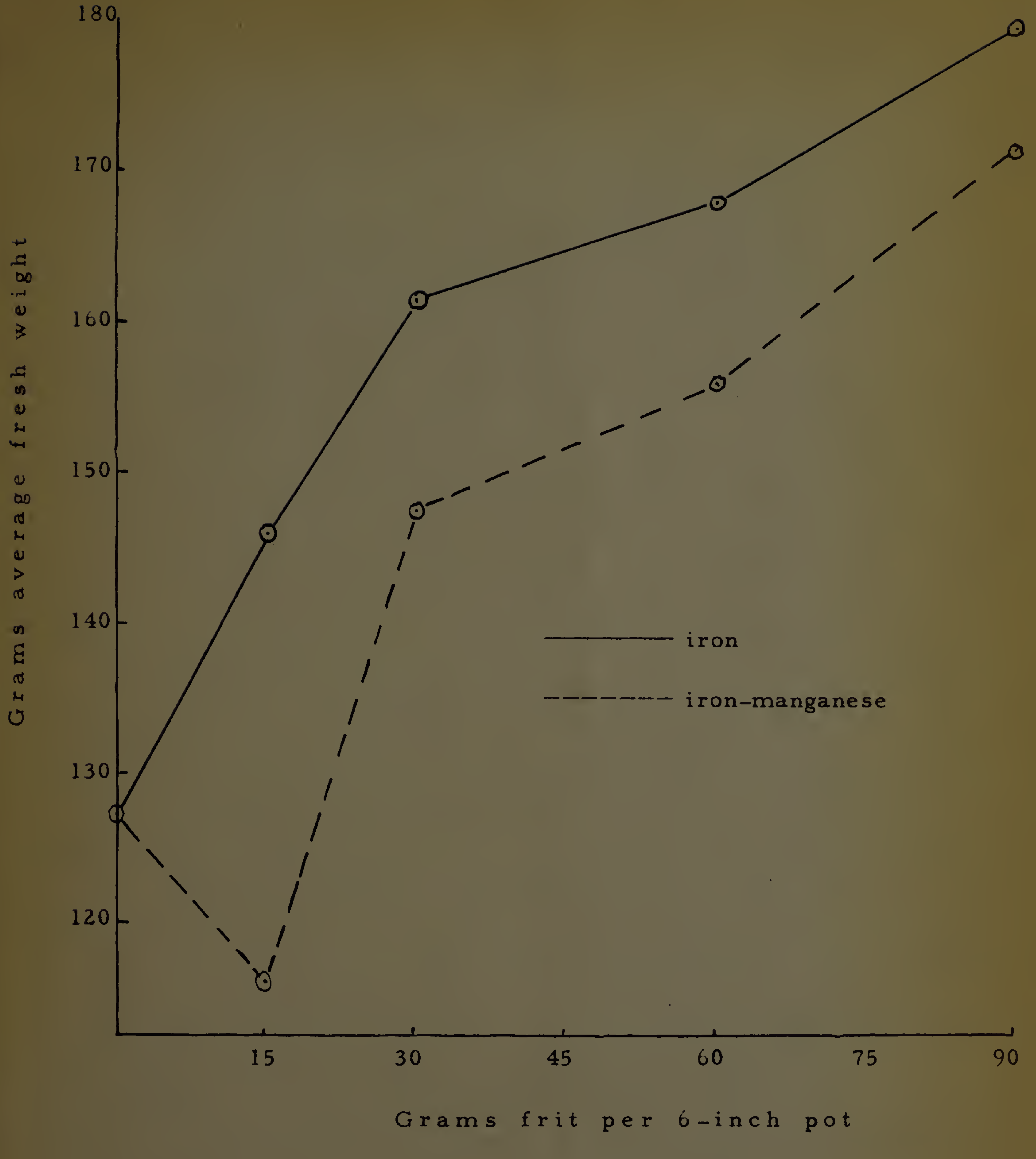

Figure 6. Effects of frits on fresh weight of Cineraria cruenta, Mass. when irregular plants are not included.

Figure 7. Cineraria cruenta, Mass. Left to right—15, 30, 60, 90 grams AC frit; control; 90, 60, 30, 15 grams AB frit. Variations in flowering and growth habit are noticeable, even when some selection is practiced. The AC treatments seem to indicate a trend toward increased growth with increased frit. The trend is less apparent with the AB frits.

Statistical analysis of the data on fresh weights was computed in the same manner as for Nicotiana. There were no significant differences between the treatment means. This was due to the great variability of the plants in the given treatment and can be attributed to genetic variability in the author's opinion.

While a statistical analysis was not computed for data as presented in Figure 6, the curves show a significant trend that is positive for the treatments, except for the 15 grams AB treatment.

Analyses for iron and manganese were carried out in duplicate. Results are recorded in Table II. Iron-manganese ratio values were computed and recorded in the table. Greatest growth as measured by fresh weights occurred in the soil receiving 90 grams of iron-manganese frit. There seems to be little correlation between iron in parts per million in the plant tissue and amount of growth in the various treatments. There does seem to be a relation between absorption of manganese and fresh weights. The treatment with 90 grams of iron-manganese frit gave the greatest fresh weight and the lowest iron-manganese ratio value. There was more manganese in parts per million with this treatment than with any other treatment.

The differences in ratio values, iron-manganese, in the treatments indicates that manganese was obtained from the frits. Where iron frits alone were used, the ratio values are much higher than where the iron-manganese frits were used. There is no evidence from the iron analysis of the plants that iron was obtained from the frits or that luxury absorption occurred. Luxury absorption of manganese seems to have occurred in the two high levels of the iron-manganese frit treatments. However, the excess manganese was not toxic since these treatments resulted in greatest fresh weights.

Lobelia Erinus, Linn.

Cuttings were made in late September, 1950, from a single plant. Forty-five of these plants were selected for uniformity and potted in soil mixtures in 6-inch standard pots in late November, 1950.

The bedding *Lobelia* is a much-branched, tender perennial. Branches are slender ascending and root abundantly at the nodes. Since the habit of the plant makes it difficult to assay differences in growth by observation, no pictures were obtained of this plant. Plants were harvested February 17, 1951, by severing plants at ground level and then cutting off the roots along the stems at the juncture of stem and roots. Data obtained are given in Table III. Figure 8 shows graphically the effects of treatments on growth as measured by fresh weights. Best growth was obtained where 15 grams of iron-manganese frit was used per 6-inch pot. With higher amounts of iron-manganese frit there was a proportional decrease in amount of growth, as measured by fresh weights. All treatments with iron-manganese frit gave better growth as measured by fresh weights than did the control.

The iron frit gave best growth as measured by fresh weight, with treatment using 60 grams. The fresh weight was about the same as obtained with the treatment using 60 grams of iron-manganese frit. Aside from this, iron frit gave lower average fresh weights in all cases than did iron-manganese frit. Treatments using 15 grams and 90 grams of iron frit respectively showed lower average fresh weights than did the control. From these experiments, basing conclusions upon fresh weights, it appears that growth of Lobelia was increased approximately 25% by addition to the soil of 15 grams of iron-manganese frit, but that larger amounts were proportionally less beneficial.

TABLE III

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF LOBELIA ERINUS, LINN. FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
	15	64.33	6.55	588	47	12.5
5%	30	83.13	7.25	304	52	5.8
Fe_2O_3	60	90.65	8.62	457	47	9.7
	90	76.20	6.95			
5%	15	99.18	8.80	417	66	6.3
Fe_2O_3	30	92.60	8.20	450	80	5.6
2%	60	89.70	6.92		130	
MnO_2	90	84.63	7.75	520	137	3.8
Control		78.83	6.55	394	102	3.9

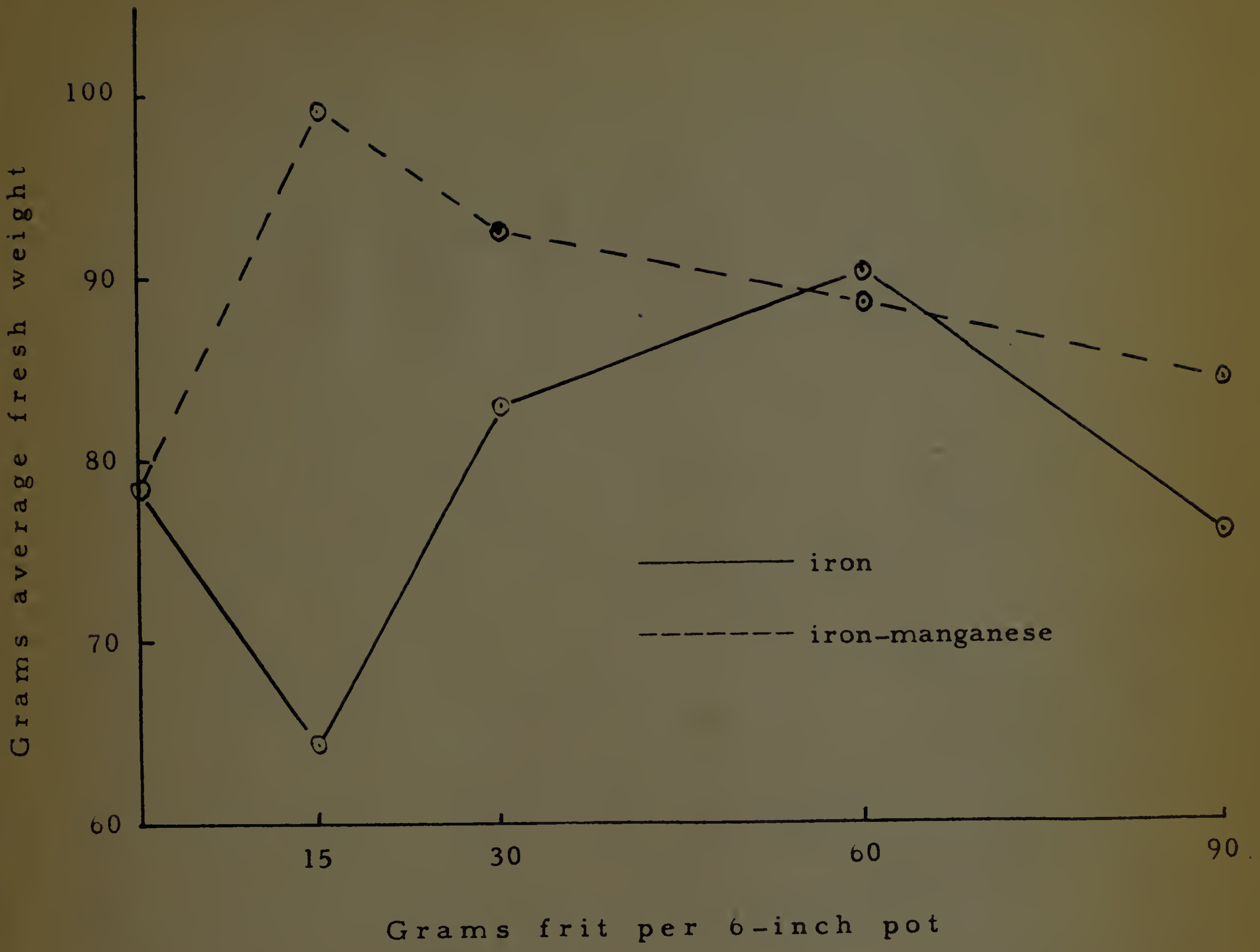

Figure 8. Effects of frits on fresh weight of Lobelia Erinus, Linn.

A statistical analysis of the data, however, shows no significant differences between the treatment averages.

There was no correlation between fresh weights and iron content. In the treatments with the iron-manganese frit there seems to be an inverse relationship between manganese content and fresh weight. In general, decreased average weights were obtained with increased amounts of frit and the manganese content of the plant increased with increased amounts of the iron-manganese frit. This seems to indicate that these plants obtained manganese from the frits.

Plants from all treatments, except the 30 gram iron frit treatment, analyzed higher iron content than the control. This may indicate luxury absorption of iron although there is no correlation as to amount of iron and grams fresh weight between the treatments.

The treatments with iron-manganese frit at the 60 and 90 gram levels resulted in plants with much higher manganese content than control. This may be luxury absorption.

Primula malacoides, Franch.

Forty-five plants of _Primula_ _malacoides_ "Erickson's White" in 3-inch pots were selected for uniformity. The soil was carefully washed off the roots and the plants were then potted in the experimental soil mixtures in 6-inch standard pots in late November, 1950. The plants were harvested February 26, 1951, by cutting off all growth above the ground level. The plants were in full flower at this time.

Table IV shows the data that were collected. Figure 9 graphically compares fresh weights. No pictures were taken since there was little detectable difference in the appearance of plants.

An analysis of variance showed no statistical significance between treatment means.

The greatest average fresh weight, 131.45 grams, was obtained with the use of 60 grams of iron frit per plant, while the next highest weight was for plants grown at 90 gram level of iron-manganese frit.

The varying results in average fresh weights here are difficult to explain. They may have to do with complicated relationships between iron, manganese, phosphate, calcium and aluminum.

Iron and manganese analyses are recorded in Table IV.

There is very little relationship between the fresh weights and iron and manganese in the plant. There is some indication

TABLE IV

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *PRIMULA MALACOIDES, FRANCH*, FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	106.65	8.78	927	61	15.3
	30	117.20	9.43	888	30	29.3
	60	131.45	10.25	935	21	44.0
	90	111.70	8.78	782	23	34.0
5% Fe_2O_3 2% MnO_2	15	113.00	9.10	882	50	17.6
	30	104.00	8.93	776	31	25.0
	60	100.50	8.43	915	33	28.1
	90	125.60	8.98	927	32	29.0
Control		110.20	8.70	876	21	41.3

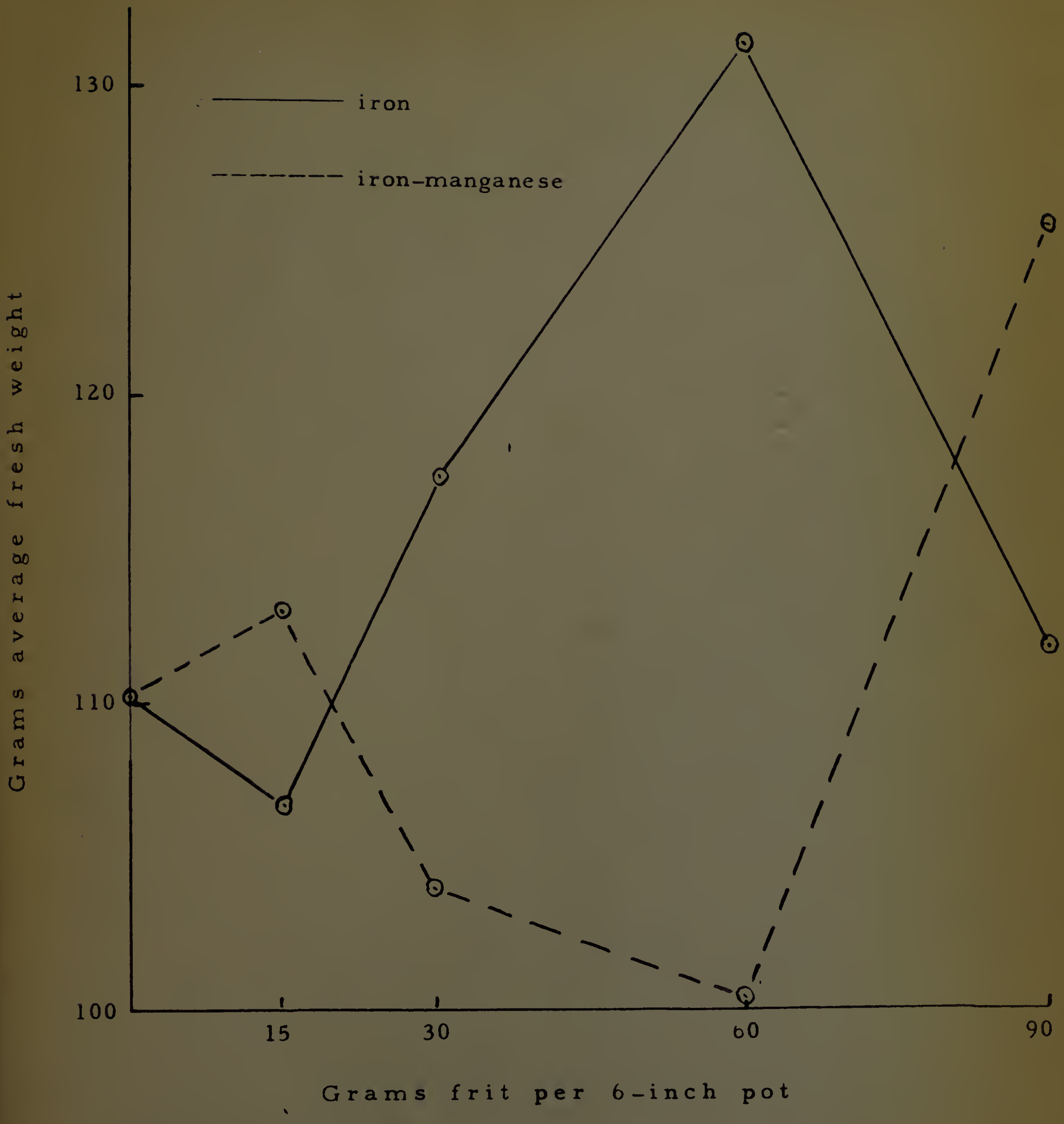

Figure 9. Effects of frits on fresh weight of Primula malacoides, Franch.

that the greater the ratio value of iron to manganese, the greater the fresh weight. The highest ratio value was found in the plants grown with 60 grams of iron frit and this treatment showed the highest fresh weights. There is no evidence from the analysis that iron was absorbed in luxury amounts or that iron was obtained from the frits. Treatments with the iron-manganese frits produced plants with higher manganese content than did the control. This may be luxury absorption of manganese.

Iberis amara, Linn.

This plant is a member of the Family Cruciferae, members of which family have occasionally been found to be distinctive in response to soil nutrients. It is well known that plants in this family require sulfur as a nutrient to a greater extent than plants in many other families. That these plants differ from many other plants in uptake of nutrients may be deduced from the fact that plants of this family never have mycorrhiza formations. Most higher plants are known to possess such formations, at least under certain conditions. It has been suggested that plants with rapid transpiration or plants with relatively great root respiration (87) can absorb mineral food efficiently. Conversely, plants that are weak in transpiration as well as plants that do not respire freely from the absorbing roots, do not absorb mineral elements freely and consequently may require the assistance of symbiotic fungi in order to obtain a sufficient supply of minerals. Since such fungi have not been found, to the writer's knowledge, in association with the roots of members of the Family Cruciferae, it may be inferred that these plants are especially efficient in their uptake of nutrients. It follows that high concentrations of minerals in solution or available in the soil would more quickly affect plant growth. The more rapid transpiration of such plants would be likely to result in higher concentrations of such elements in the plant tissues. Such higher concentrations could cause symptoms of toxicity. It is possible, under conditions of high pH, that there would be an insufficient supply of sulfur available. On the other hand, at low pH there may be a deficiency of calcium, which could result in either calcium deficiency or perhaps sulfur toxicity symptoms in the plant.

Eisenmenger and Kucinski (32) made a study of magnesium needs of seed plants. They concluded that resistance to magnesium deficiency increases as one goes up the scale of evolutionary development. However, the members of the Solanaceae and Cucurbitaceae do not fit into this scheme. They noted that it is significant that the more highly developed seed plants, because of their greater sturdiness, are far more resistant to abnormal agencies such as disease conditions, extremes of temperature, and high or low concentrations of elements.

Lewis and Eisenmenger (81) studied potassium uptake as related to the evolutionary development of plants. They thought that the fact that the lower seed plants are more efficient than the higher species in obtaining their ions from what might be called unavailable sources, indicates that their direct ancestors lived in an environment where frugality and slow growth were a necessity. Statistically the percentage gain of potassium from both soluble and insoluble sources tended to decrease as the plants ascend from the lower to the higher order of development. Plants of the lower orders showed deficiency symptoms earlier than those of higher order.

This investigator believes that the difference in uptake of plants is related to the evolutionary age of the plant as pointed out by Eisenmenger et al. (31, 32, 81), but possibly the differences have evolved through evolution of cell walls and protoplasm from simpler more easily permeable condition in lower plants to more complex, less permeable condition of the higher plants. The symbiotic relationship in plants, with no such relationships in lower plants and common in higher plants, seems also related to uptake of moisture and mineral elements.

Seeds of the variety "White Rocket" were sown November 24, 1950. Sixty-three young plants were selected and potted in the soils December 20, 1950. Eighteen of these plants were used as buffer plants in the outside rows, on either side of the bench.

Iberis was harvested February 18, 1951, by cutting plants off at the ground level. At this time the more advanced plants were in flower. All data are recorded in Table V. On the basis of average fresh weights, all treatments with iron-manganese frit depressed growth. No satisfactory explanation is possible. Perhaps this plant is intolerant of manganese, except in smallest amounts, or possibly the iron-manganese ratio was out of proportion to the needs of the plant.

TABLE V

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF IBERIS AMARA, LINN. FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	16.40	1.93	249	34	7.3
	30	14.30	1.60	212	36	5.8
	60	14.84	1.63	171	23	7.3
	90	14.90	1.78	165	21	7.8
5% Fe_2O_3 2% MnO_2	15	13.83	1.50	171	20	8.4
	30	11.32	1.40	136	29	4.7
	60	11.43	1.18	149	11	14.1
	90	13.76	1.83	387	80	4.8
Control		13.90	1.88	147	30	4.9

According to Shive (108) there is no longer any doubt concerning the interdependence of iron and manganese in their effects on plant growth. That there is a definite ratio within the plant necessary to maintain a proper balance between these two elements has been determined by investigators. Shive (109) maintains that the ratio of Fe/Mn should be within the range of 1.5 to 2.5 for the species investigated, but that it is not to be expected that the same range of values would be effective with all species either within the plant or in nutrient substrate.

This plant seems quite different in its reaction to soil nutrients. This was demonstrated by growth of plants in a parallel series, using frits in the same amounts in a very acid soil, over 60 per cent of which was organic matter. Plants of Iberis in this soil often showed distinct symptoms of manganese toxicity, the plants being slightly to greatly stunted and in the more severely stunted plants there was a total loss of green color of leaves, with silver-colored drying of the furthermost leaf margins. Doubtless in this very acid soil, pH 4.5 to 5.0, some of the manganese and iron contained in the frits became soluble. This, added to amounts already highly soluble in the very acid soil, with its high content of organic matter which probably inhibited precipitation of both iron and manganese, appeared to cause toxicity to plants. To determine whether the depressive effect is due to excess iron, manganese, aluminum, sulfur or phosphate, or perhaps a deficit of calcium, would require a new set of experiments, limiting each of these factors separately and in combination. It would seem to the investigator that this plant would be a very good subject for study of manganese-iron-aluminum-phosphorus-calcium-H-ion relationships in soils. The fact that healthy as well as stunted plants appeared in the control in this very acid soil is further confusing.

Figure 10 shows graphically the variations in average fresh weight in different treatments.

A statistical analysis of the fresh weights was calculated in the same manner as for Nicotiana Tabacum. There was no significant difference between treatment means.

Analyses of iron (Table V) show less iron in the control plants than in any of the treatments except the 30 grams AB frit treatment. However, increased iron absorption with increased amounts of frit does not occur. The lowest average fresh weight was obtained in the treatment with 30 grams

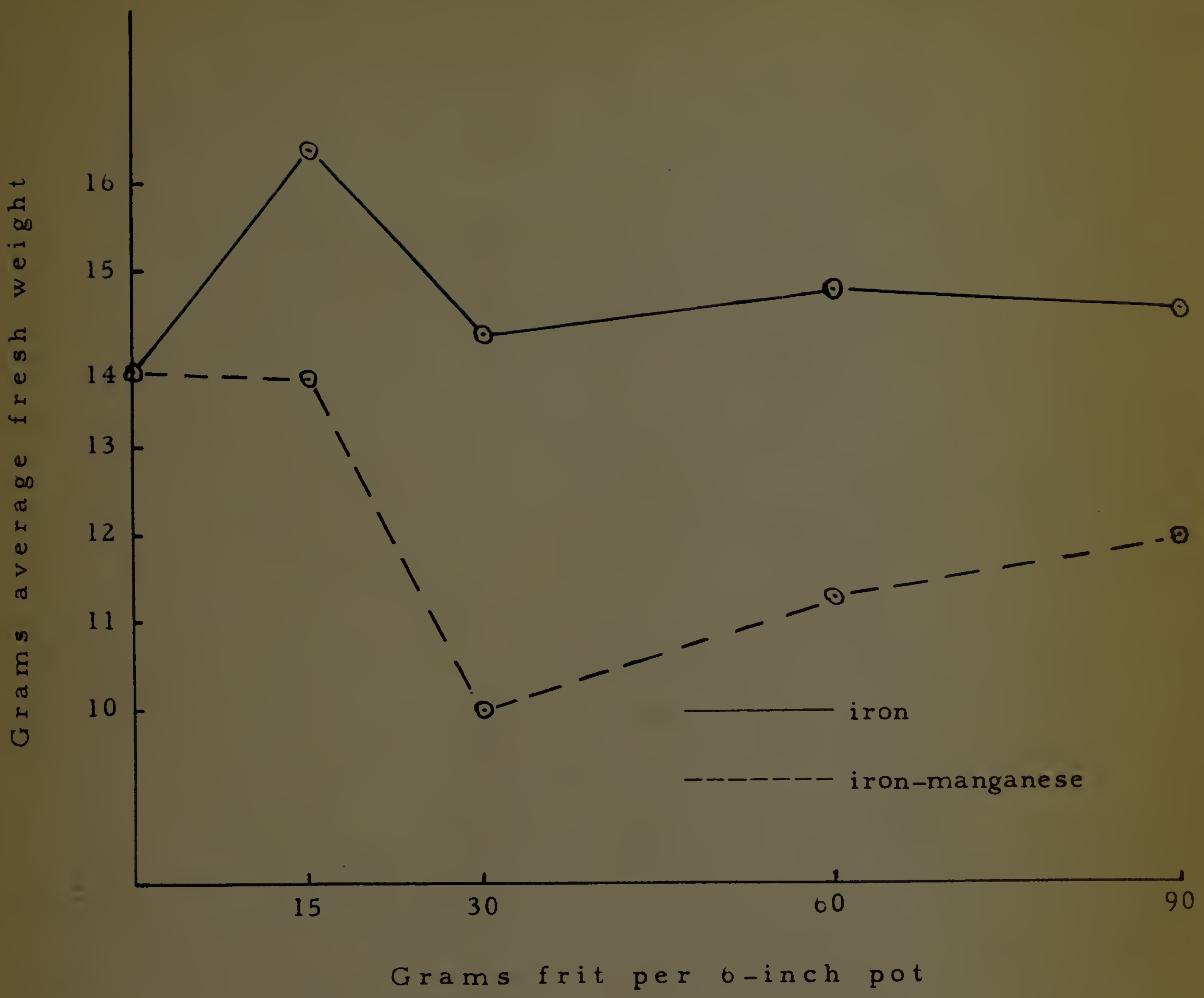

Figure 10. Effects of frits on fresh weight of Iberis amara, Linn.

iron-manganese frit and these plants also contained the least iron and the lowest ratio value of iron to manganese. There is no relationship between growth and either iron or manganese absorption. Strangely, the AC frit treatments show less iron in the plants as more of the frit was used in the treatments.

All treatments, except the 30 gram level with iron-manganese frit, produced plants with higher iron content than the control and several treatments produced plants with higher manganese content. There is no evidence that luxury absorption in any of the treatments recorded in Table V were toxic.

Antirrhinum majus, Linn. var. HT x RPS

One hundred and fifty plants of hybrid snapdragon were obtained from Dr. Judd Haney of the Department of Horticulture, Michigan State College. These were in 3-inch pots and had been pinched twice. They were an especially uniform hybrid F_1 generation, designated as HT x RPS. Forty-five plants were selected for uniformity and the soil was removed from their roots by washing. They were planted in the soils in 6-inch standard pots in late November. They were harvested March 5, 1951, when the most advanced plants had opened the last flowers.

The height and weight of the plants were taken as they were cut and the data recorded in Table VI. The plants were then dried in a dehydrator at a temperature ascending from 100° F to 140° F for six days, then cooled to room temperature and the total dry weights recorded.

Plants grown in soil containing 15 grams of AC frit per 6-inch pot, were the only plants with average fresh weights greater than the control (Table VI). When more than 15 grams of iron-frit were used, the growth as measured by fresh weights was decreased more or less proportionately to the amount of frit used.

The iron-manganese frit in each case resulted in lower average fresh weights than was the case with iron frits (Figure 13). By comparison on the basis of average fresh weights, it seems evident that for snapdragon there was a sufficient amount of manganese available in the soil for normal growth and that there was nearly enough iron available. Additional amounts of manganese added in the frit depressed growth in proportion to the amount used. The same depression occurred also when more than 15 grams of iron frit were used (Figure 11).

TABLE VI

AVERAGE HEIGHT, FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *ANTIRRHINUM MAJUS, LINN.*, HT x RPS. FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average height (inches)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
	15	46.72	70.86	14.28	183	0	
5%	30	44.66	68.10	12.66	131	11	12.4
Fe_2O_3	60	43.30	56.72	10.30	167	14	12.2
	90	42.74	58.64	9.48	209	14	15.3
5%	15	43.58	80.76	14.28	136	11	12.9
Fe_2O_3	30	43.88	68.50	11.20	178	19	9.4
2%	60	40.24	63.50	9.76	127	14	9.3
MnO_2	90	40.98	60.08	9.73	160	43	3.7
Control		47.18	73.34	11.70	144	0	

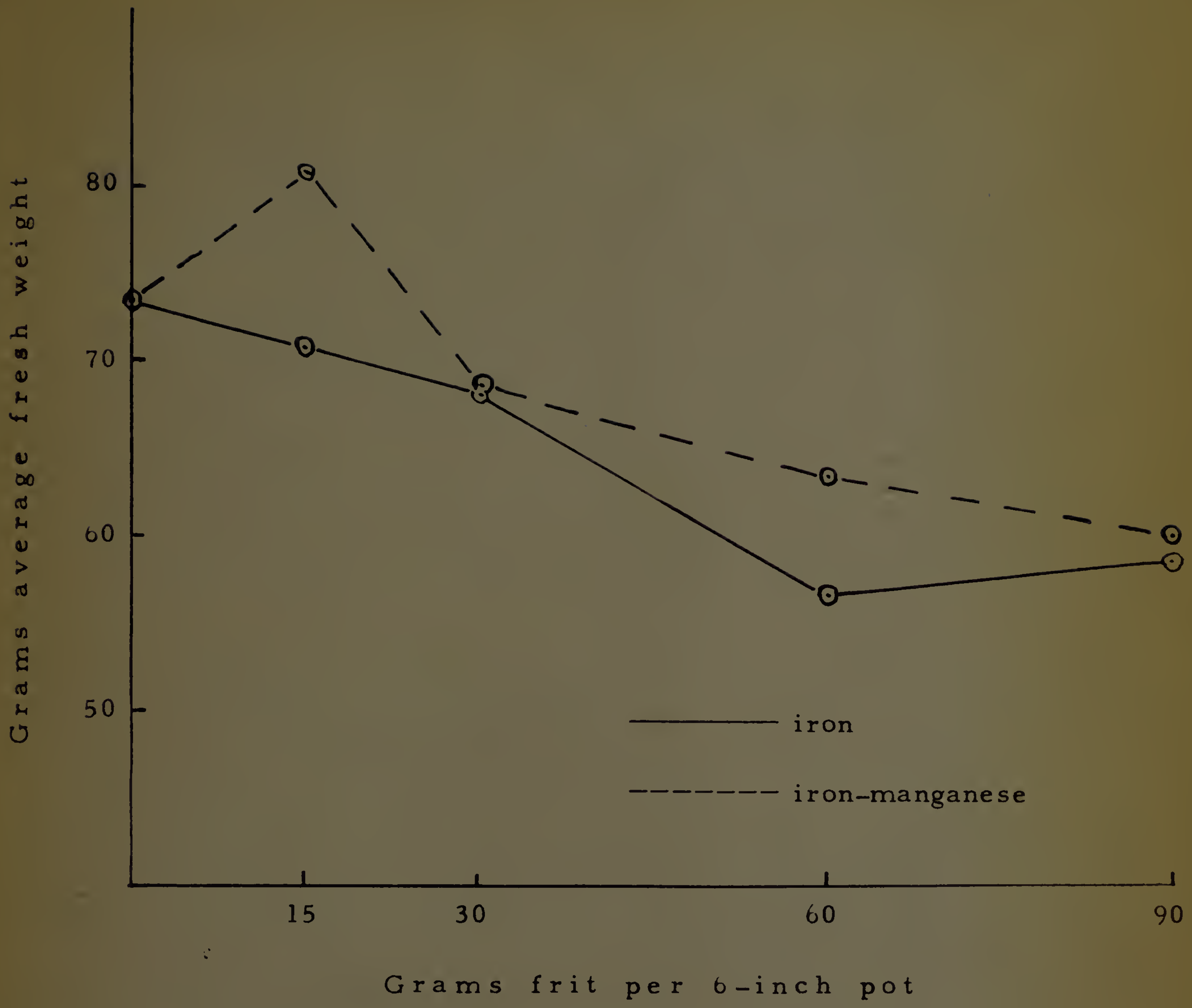

Figure 11. Effects of frits on fresh weight of <u>Antirrhinum majus</u>, <u>Linn</u>. var. HT x RPS.

These results differ from those obtained by Wynd and Bowden (130). They found a positive response to the use of iron-manganese frit. This may possibly be explained by the different types of soil used.

Generally the plants growing in the iron-manganese frit reached full flowering previous to those growing in the iron frit.

An analysis of variance was carried out on the data on fresh weights (Table VI), from nine treatments and five replications.

After computing a t-value, it was found that the difference between any two treatments for significance at the 5 per cent probability point is 13.12 grams.

Examination of the treatment averages shows that the treatments 60 grams AB and 90 grams AB have average fresh weights significantly lower than the check. The treatment 15 grams AC average is significantly larger than the average of treatments 60 grams AC, 90 grams AC, 15 grams AB, 30 grams AB, 60 grams AB and 90 grams AB. The 90 grams AB and the 90 grams AC treatment averages are significantly lower than the check.

A statistical test for linearity of AB averages was then calculated. This shows no statistically significant trend. Reference to Figure 11, however, appears to show a negative trend for the curves for both frits.

A statistical analysis of average heights shows no significant trend for the AB means. The analysis of the AC means does show a statistically significant trend (Figure 12).

Analysis for iron, Table VI, showed no relationship between growth and amounts of the mineral absorbed. However, the control and the treatment with 15 grams of iron frit resulted in tallest growth and analysis for manganese gave no determinable manganese. It also appears likely that manganese was absorbed from the AB frit, since the amounts found in the plant are generally higher for plants grown in the iron-manganese frit than for plants grown in the iron frit. There is no indication of luxury absorption of iron, but there is some indication of absorption of manganese in excess of the needs of the plant and a depressing influence on plant growth as a result.

There is further some indication that manganese exerts a depressing (antagonistic?) effect upon iron absorption. The treatments with 15 grams and 90 grams of iron frit showed

Figure 12. Effects of frits on heights of plants of _Antirrhinum majus_, _Linn_. var. HT x RPS.

Figure 13. Antirrhinum majus, Linn. F_1 hybrid designated as HT x RPS. A vigorous rose-pink flowered hybrid. From left—15, 30, 60, 90 grams AC frit; control; 15, 30, 60, 90 grams AB frit. The picture shows the depression of growth in the frit treatments. The depression of growth appears greater for plants in the AB treatments.

greatest amounts of iron absorbed. The 15 gram treatment showed no absorption of manganese. The 30 gram and 60 gram treatments resulted in growth with lower iron content and considerable manganese content. In the 90 gram treatment the iron content increased approximately 21 per cent over the 60 gram treatment. It would appear, therefore, that depressing effect of manganese on iron absorption depended on the amount of manganese present and that the amount of iron available for plants in this treatment exceeded the maximum amount that could be affected by the manganese naturally present in the soil. If the theory is accepted that the iron is absorbed directly from the frit, it is difficult to understand just how the manganese of the soil solution can affect the absorption of iron from the frit. It is possible that the effect of the manganese occurs within the absorbing cells of the roots or perhaps the manganese has an effect on permeability. It appears that either iron or manganese may have a depressing effect on growth of Antirrhinum when present in luxury amounts and that the two elements are closely interrelated in their effects on growth of Antirrhinum.

A further possibility is that manganese absorbed by the roots may immobilize iron in the root cells, thus reducing the amount of iron to reach the green plant. The amount of iron so immobilized would be proportional to the amount of oxygen that could be given up by the manganese, i.e., by the amount of manganese present.

It is also possible that manganese replaces iron in the frit. The iron so replaced is immediately oxidized and is inactive or unavailable to the plant.

Antirrhinum majus, Linn., variety "Margaret"

One hundred small plants of Antirrhinum majus, "Margaret" in 2-1/2 inch pots were obtained December 20, 1950. Forty-five of these plants were selected, each having two sets of leaves above the seed leaves. The soil was washed from the roots and the plants planted in soil in the 6-inch standard pots. The plants were grown until all were in flower and harvested by cutting at ground level April 7th, 1951. Heights of plants and fresh weights were recorded and the plants dried in the same manner as described for other plants. Data are recorded in Table VII. The average fresh weights for the treatments are graphically shown in Figure 14. The growth obtained from the addition of 15 grams of iron-manganese frit is greater than that obtained from any other treatment and is statistically

TABLE VII

AVERAGE HEIGHT, FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF ANTIRRHINUM MAJUS, LINN., VARIETY "MARGARET," FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average height (inches)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
	15	32.67	40.54	5.76	101	29	3.5
5%	30	30.15	34.54	4.78	161	36	4.4
Fe_2O_3	60	33.67	44.76	5.90	163	23	7.1
	90	32.50	35.30	4.76	175	26	6.8
5%	15	33.00	49.68	6.62	82	29	2.8
Fe_2O_3	30	32.03	39.62	5.12	96	39	2.4
2%	60	33.15	39.48	5.32	97	44	2.2
MnO_2	90	32.20	33.70	4.68	149	41	3.6
Control		33.15	42.66	5.62	107	23	4.7

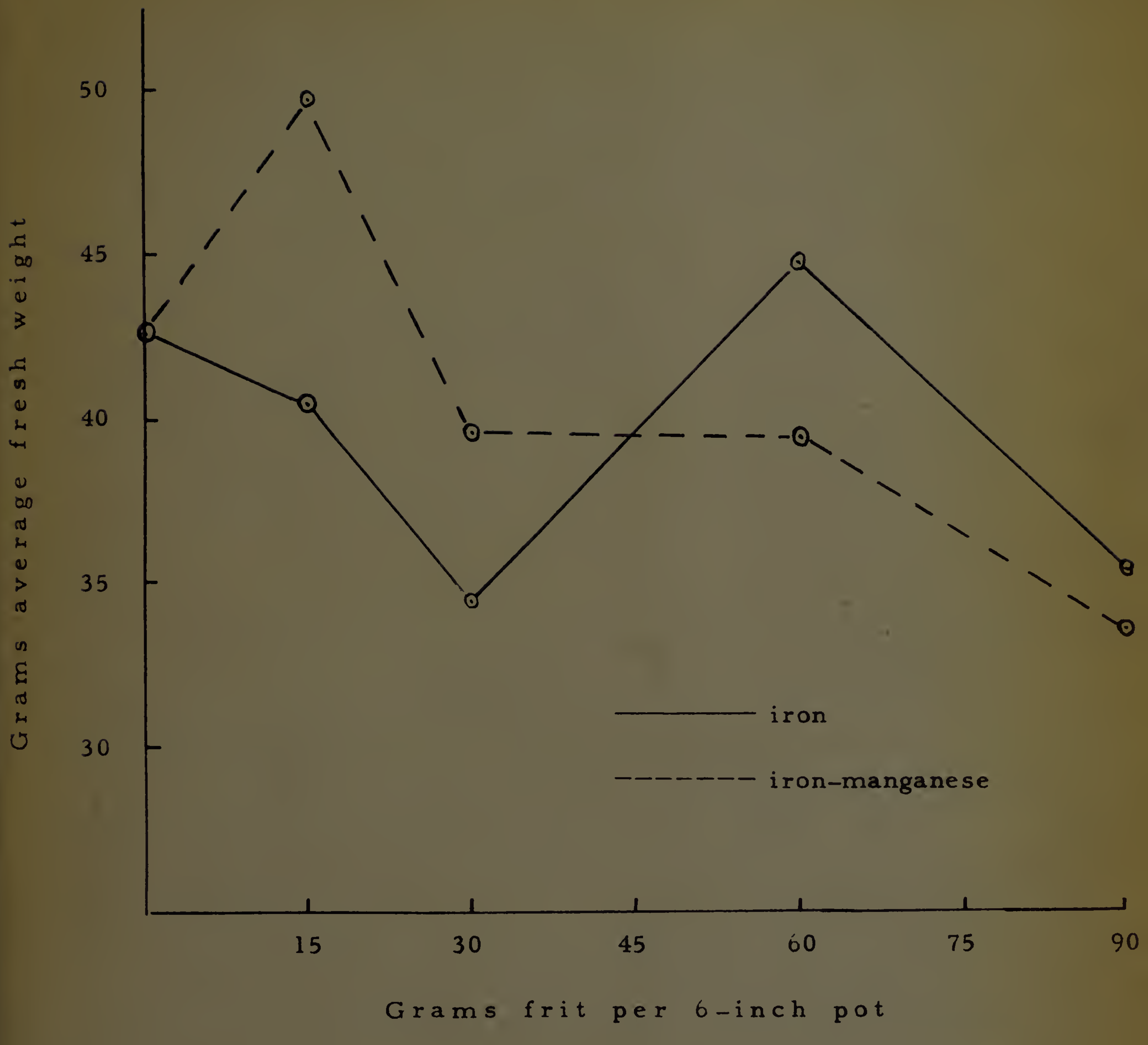

Figure 14. Effects of frits on fresh weight of Antirrhinum majus, Linn. var. "Margaret."

significant from all treatment growth averages except the one with the 60 grams iron-manganese frit. The average heights of plants in all treatments was less than the control (Figure 15).

An analysis of the variance was carried out on the data on fresh weights (Table VII), from nine treatments and five replications.

After computing a t-value, it was found that the differences between any two treatments for significance at the 5 per cent probability point is 7.6 grams.

Examination of the treatment averages shows that the average for 15 grams AB is significantly greater than the averages for 30 grams AB, 60 grams AB, 90 grams AB, 90 grams AC and 30 grams AC. Test for linearity of AB averages was then calculated. There is a significant negative and linear trend for the AB treatment averages. This means that when the frit is increased, the fresh weight decreases.

A similar analysis for the AC means shows no significant trend, although the 30 grams AC frit is significantly less than the check.

Iron absorption is generally less and manganese absorption more than for Antirrhinum HT x RPS. This results in

Figure 15. Effects of frits on heights of plants of *Antirrhinum majus*, *Linn*. var. "Margaret."

lower ratio values iron to manganese. This variety is not as vigorous in growth as HT x RPS. Is this due to lower iron-manganese ratio values? Is manganese toxic in the quantities absorbed? Does this variety absorb more manganese and less iron than the HT x RPS variety? Is this the reason for the less vigorous growth of this variety? The highest average fresh weight was obtained with the 15 grams AB frit. The plants of this treatment had the lowest iron content. This same treatment resulted in greatest fresh weight in HT x RSP variety. The highest iron content of plants in the iron-manganese treatments was obtained at the 90 gram level and these plants had the lowest fresh weight. The highest iron content in the iron frit treatment was obtained in the plants grown in the 90 gram treatment and these plants had the lowest dry weight. There seems to be an inverse relationship between growth and iron content in the plants grown in the AB frit treatments. In these treatments the greater the quantity of iron-manganese frit in the treatment, the greater the amount of iron content in the plant and the less the average fresh weight. This indicates a possible toxicity of iron and, therefore, luxury absorption.

Treatments with the AC frits resulted in increased iron absorption with increased amounts of the frit as was the case with the AB frits. There is no relationship between growth and treatments or iron content of the plants. Some treatments produced plants with evidence of luxury absorption of manganese.

Phaseolus vulgaris, Linn.

Seeds of Phaseolus, red kidney bean, were planted directly into 6-inch pots in mid December, 1950. The plants were harvested by cutting off at ground level March 10, 1951. Data are recorded in Table VIII.

Only plants grown in soil with 90 grams of iron-manganese frit showed fresh weights greater than the control (Table VIII). In all other treatments the average fresh weights were less than those of the control. In general, the average fresh weights of plants grown in the iron-manganese frits were somewhat greater than those grown in the iron frit.

Figure 16 shows graphically the average fresh weights of the treatments. While the plants were growing, slight differences in growth between treatments could be noted (Figure 17).

TABLE VIII

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *PHASEOLUS VULGARIS*, *LINN*. FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	15.85	3.35	196	32	6.2
	30	17.10	3.65	168	23	7.4
	60	14.70	3.40	169	23	7.4
	90	19.15	3.82	236	23	10.4
5% Fe_2O_3 2% MnO_2	15	17.45	4.30	144	52	2.8
	30	18.22	4.05	165	46	3.6
	60	14.15	2.45	292	41	7.5
	90	23.22	4.92	139	49	2.8
Control		19.42	3.68	186	46	4.1

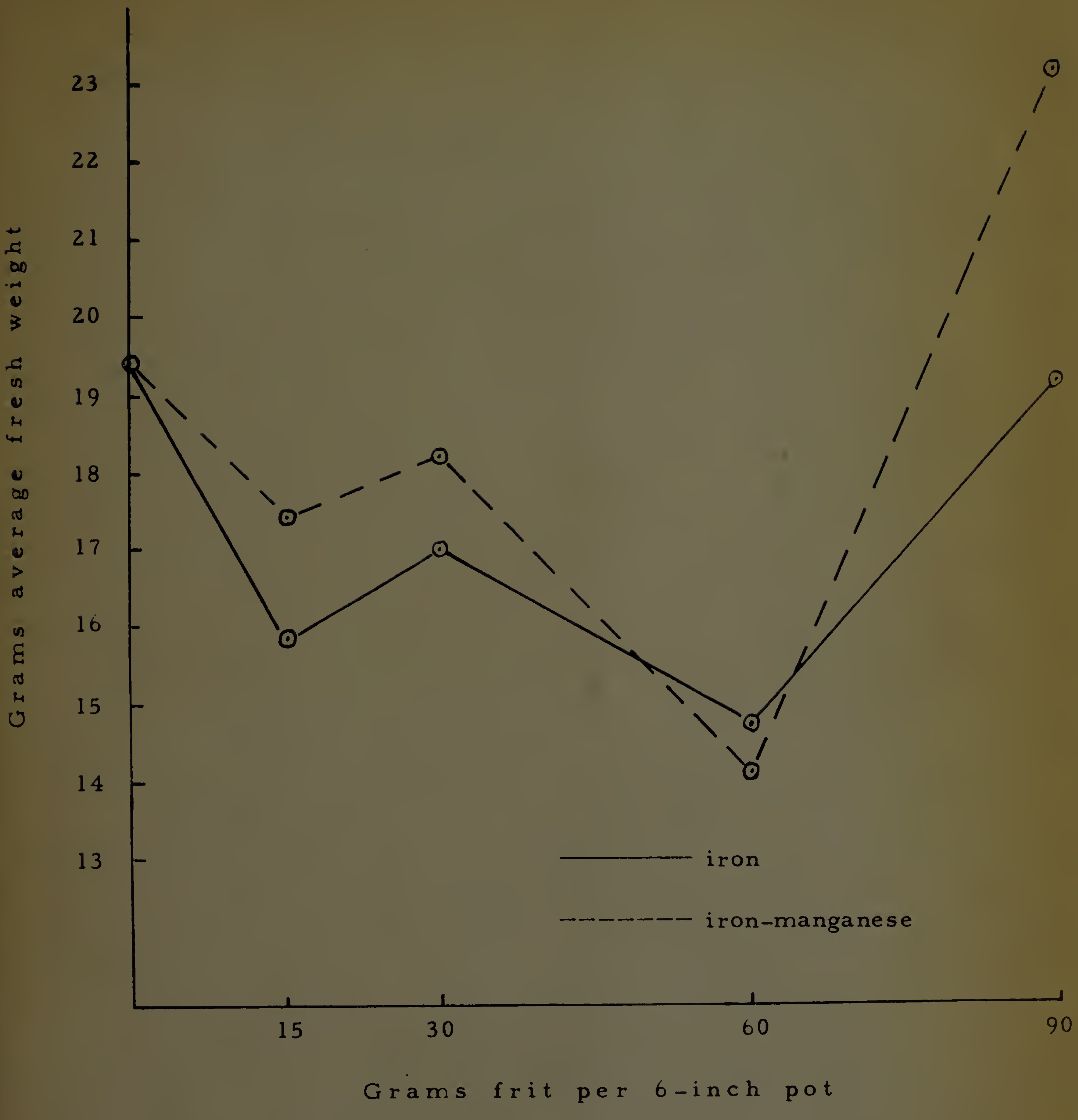

Figure 16. Effects of frits on fresh weight of <u>Phaseolus vulgaris</u>, <u>Linn</u>.

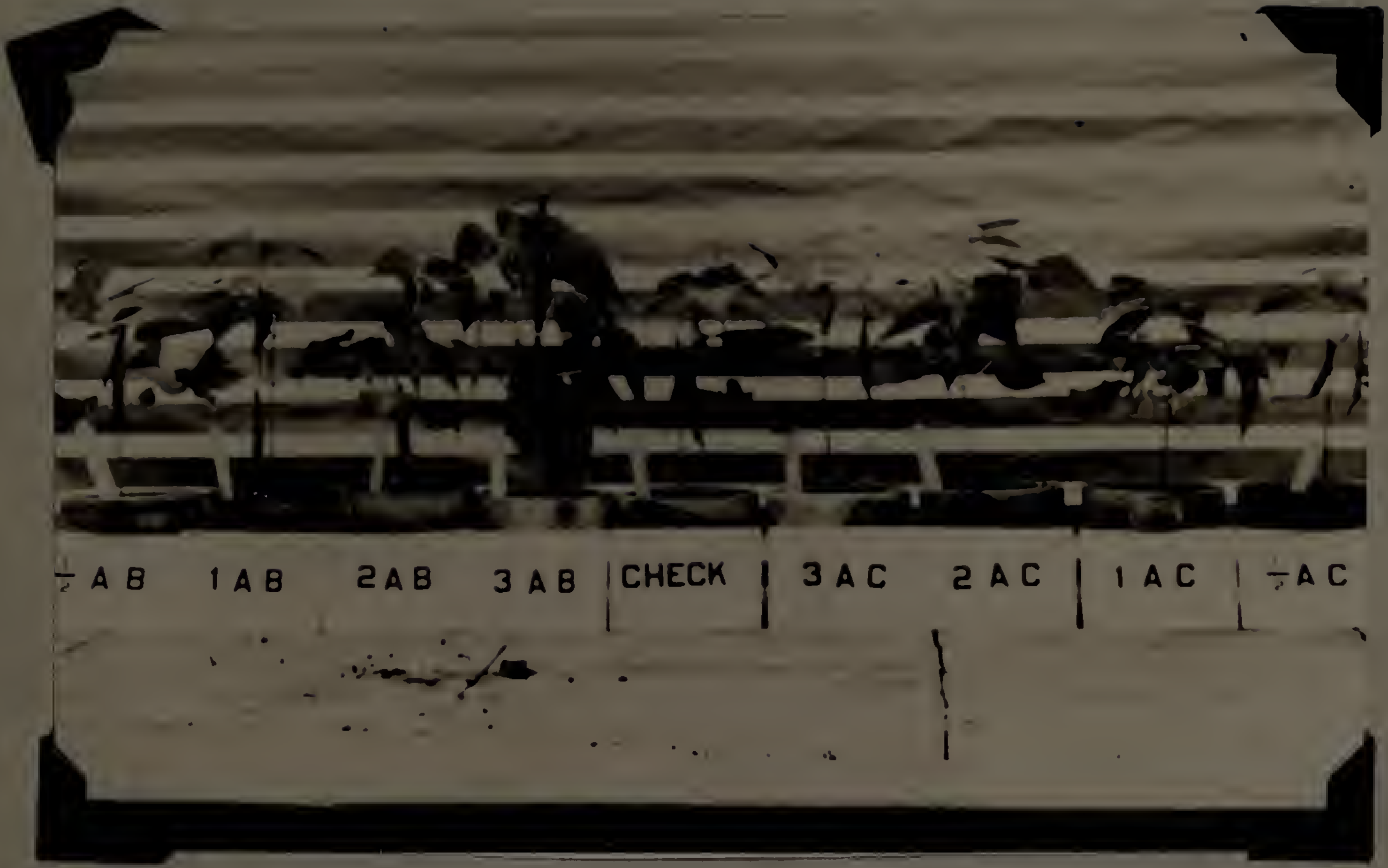

Figure 17. *Phaseolus vulgaris, Linn.* From left—15, 30, 60, 90 grams AB frit; control; 90, 60, 30, 15 grams AC frit. Very slight differences between treatments apparent.

A statistical analysis of the data showed no significant differences between the treatment means.

There seems to be no relationship between growth and iron and manganese content or ratio. Plants grown in AB frits generally show higher manganese content than the plants grown in the AC frits, but not significantly different from control plants. Since the only difference between the control and the treatments with the AC frit was the amounts of frit, data should show manganese absorption about the same in plants from all AC treatments and control. However, manganese absorption is less in all of the treatments than in the control. It must be assumed that this lower manganese absorption is due to some quality of the frit. Either some of the soil manganese is directly absorbed by the frit, or the frit exchanges some of the iron ions for manganese ions. Such exchange of ions probably would result in oxidation of the ferrous ions to ferric ions which would be unavailable to plant roots. When the amount of iron frit is increased above a certain point at which no more manganese of the soil solution could be exchanged for iron of the frit, the remaining iron would then be available for absorption by the plant. Such a possibility is indicated by the fact that the treatment with 90 grams of AC frit resulted in plant growth with higher iron content than in the control, while all other AC treatments had plants with iron contents comparable to the control. It is apparent (Table VIII) that there has been a depression of manganese absorption by the plants in the iron frit treatments. This depression is increased with increased amounts of the iron frit.

There is no clear evidence of luxury absorption of iron except in the treatments with 60 grams AB frit and 90 grams AC frit. There is also no positive evidence of luxury absorption of manganese in any treatment, although the 15 and 90 gram levels of AB frits produced plants with slightly higher manganese content than the control.

Calendula officinalis, Linn.

Seeds of the variety "Ball's Orange" were sown October 1, 1950, and selected plants were potted in the soil mixtures in 6-inch standard pots in late November, 1950.

Plants of Calendula were harvested March 4, 1951, in the same manner as Nicotiana and Cineraria. The data collected are recorded in Table IX. Figure 18 shows graphically the effect of treatments on growth as measured by average fresh

TABLE IX

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *CALENDULA OFFICINALIS*, *LINN*. FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	135.18	12.82	359	0	
	30	134.88	10.95	410	30	13.5
	60	162.10	14.15	417	0	
	90	156.05	13.82	468	52	9.1
5% Fe_2O_3 2% MnO_2	15	173.43	14.70	354	53	6.7
	30	120.85	11.57	645	105	6.2
	60	149.90	13.65	643	144	4.5
	90	143.03	13.40	473	133	3.5
Control		145.25	13.20	527	55	9.7

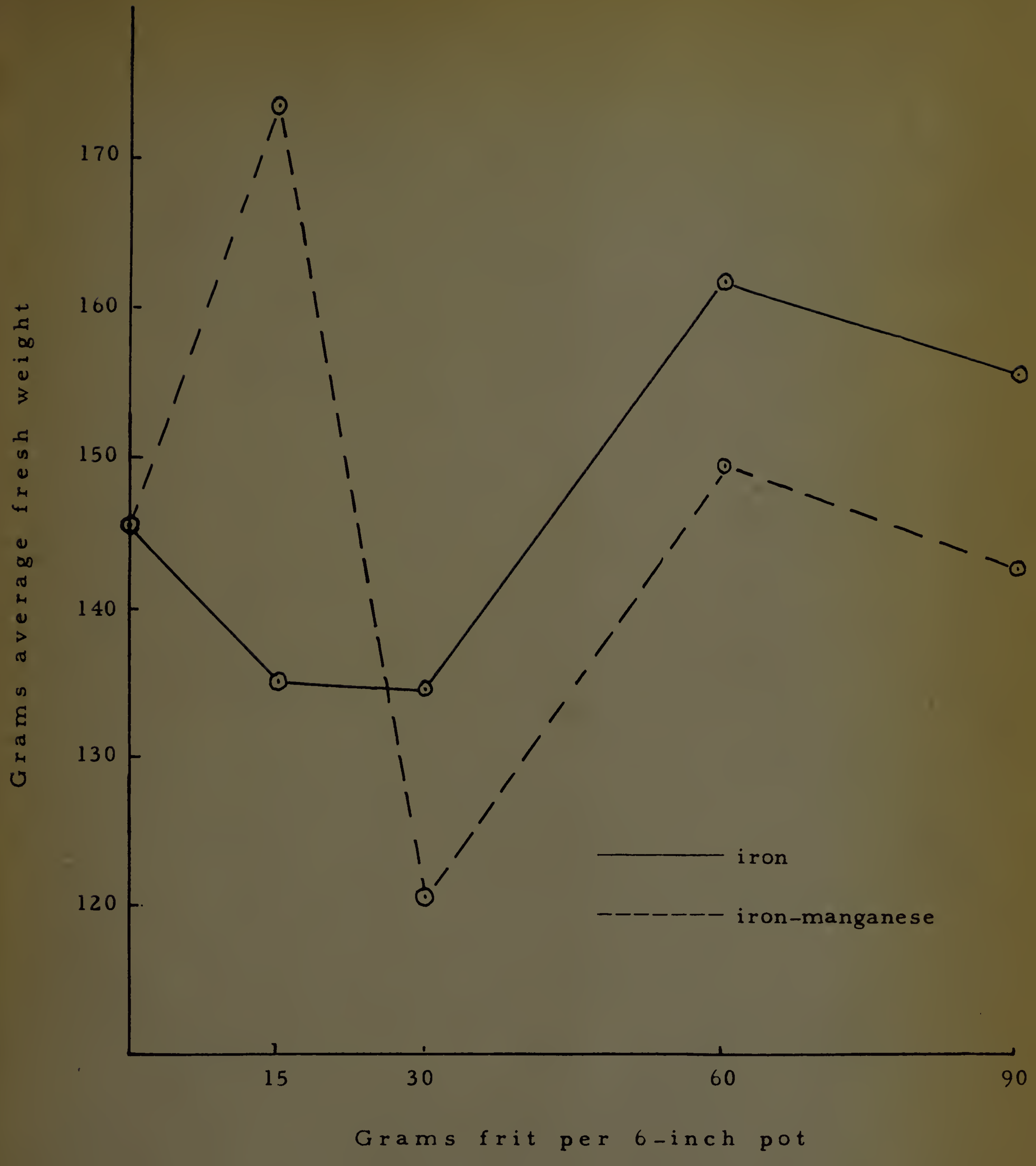

Figure 18. Effects of frits on fresh weight of Calendula officinalis, Linn.

weights. The plants receiving 15 grams of iron-manganese frit made the greatest growth as expressed in average fresh weights. Variations between treatments may be explained on the basis of iron-manganese ratio. When 15 grams of iron-manganese frit were used, the ratio between iron and manganese would be greater than in any other treatment, if iron and manganese already in the soil are added to that provided from the frit. In all other treatments, manganese seems to have a depressing effect on growth as measured by fresh weights and as compared to treatments using iron frit.

A statistical analysis showed no significant differences between the treatment means.

Analyses of iron and manganese in the plants in the different treatments show no relationship of iron or manganese content or ratio to growth (Table IX). It is interesting to note that while increased amounts of the AC frit resulted in increased amounts of iron in the plants, in no case did the iron content approach that of the plants grown in the control. It is assumed that soil manganese in some way immobilizes part of the iron in the frit. The complex interrelationship between iron and manganese in the soil and in the plant as well as the inaccuracies of any method of determining iron content, especially in small amounts, may well account for the difficulty in establishing relationships between growth and manganese and iron in soil and in plant.

Luxury absorption of iron occurred in the treatments with 30 and 60 grams of AB frit. Luxury absorption of manganese was obtained in plants produced by all levels of the AB frit except the 15 gram treatment.

Impatiens Holstii, Engler and Warb.

A single large plant of Impatiens Holstii, growing in the garden, was selected and several hundred cuttings were made. In late November, 1950, forty-five of these plants were selected for uniformity and planted in the treated soils in 6-inch standard pots. This plant had a varied branching habit, often being much branched, sometimes exhibiting little branching (Figure 21). They were harvested March 19, 1951, by cutting off at ground level, weighed, dried, dry weights taken, ground and prepared for analysis, in the same manner as for all other plants. Data are recorded in Table X.

A statistical analysis showed no significant differences between treatment means of fresh weights.

TABLE X

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *IMPATIENS HOLSTII, ENGLER AND WARB.*, FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	90.70	6.55	150	44	3.4
	30	124.10	8.78	141	35	4.1
	60	101.75	5.33	151	30	5.0
	90	66.73	4.75	198	35	5.7
5% Fe_2O_3 2% MnO_2	15	143.18	11.05	243	58	4.2
	30	143.35	10.60	193	68	2.8
	60	137.15	10.23	141	74	1.9
	90	121.75	8.58	193	73	2.7
Control		144.58	10.98	210	56	3.7

Reference to Figures 19 and 20 shows an effect that although not significant, is interesting. Addition of both frits caused a depression of growth, more or less proportionate to the amount of frit in the soil. The iron frit caused greater depression than the iron-manganese frit and this was clearly noticeable in the growing plants.

This plant exhibits rapid transpiration. It is a very succulent plant and with an ample supply of moisture and nutrients grows rapidly. Evidently it takes up water and nutrients easily under normal soil conditions. With rapid transpiration the uptake of an element freely available, such as the iron in the frit, could be so great as to cause a concentration of the element in the tissues, far beyond the needs of the plant. However, analysis of iron does not indicate luxury absorption of this element. Analysis for manganese indicates possible luxury absorption of this element.

Analyses of iron and manganese (Table X) show no relationship between these elements and growth. However, manganese and iron in plants grown in the AC frits is less than in the control. Again the only explanation is that soil manganese has become absorbed by the frit and in the process iron

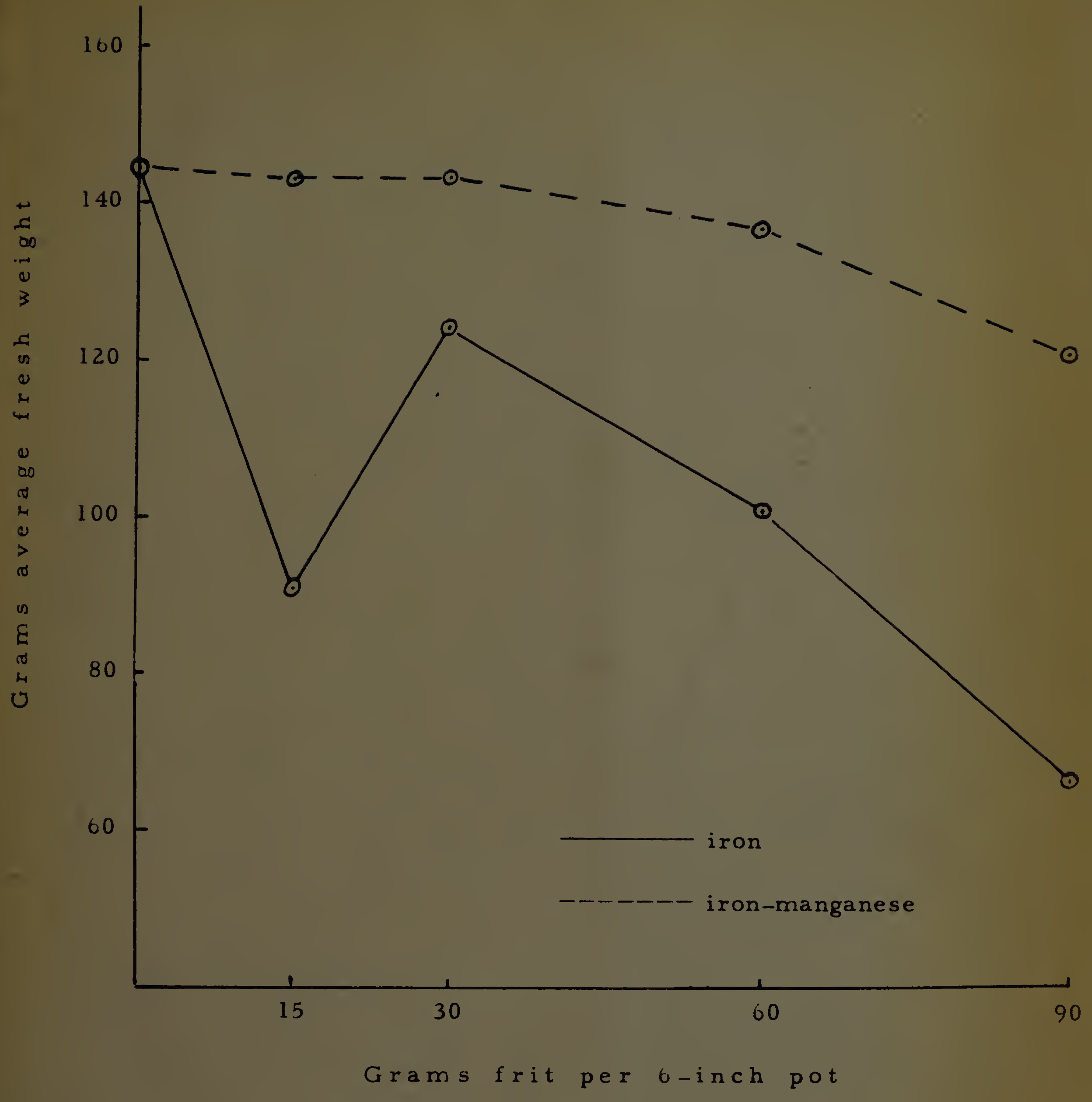

Figure 19. Effects of frits on fresh weights of Impatiens Holstii, Engler and Warb.

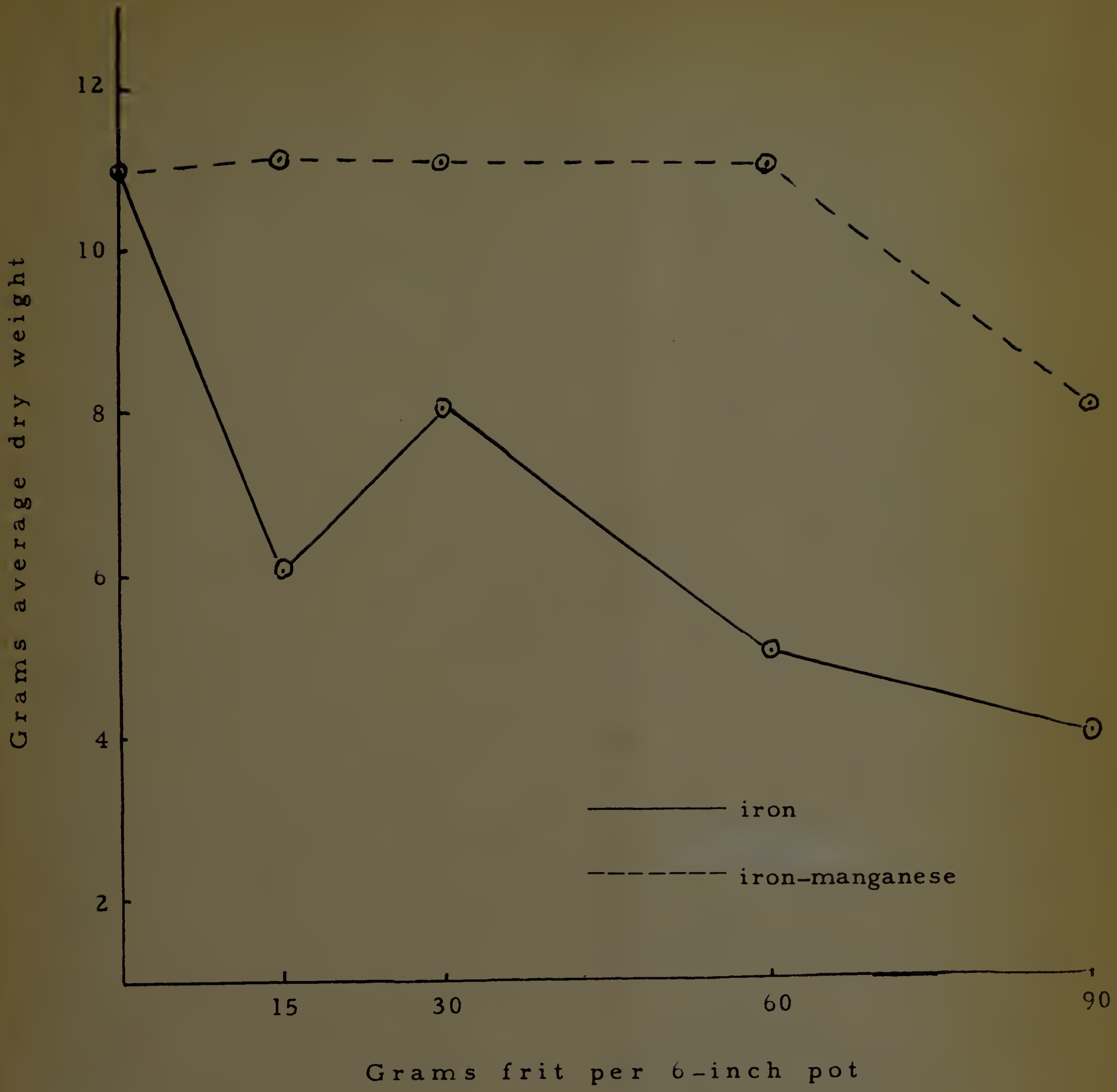

Figure 20. Effects of frits on dry weight of Impatiens Holstii, Engler and Warb.

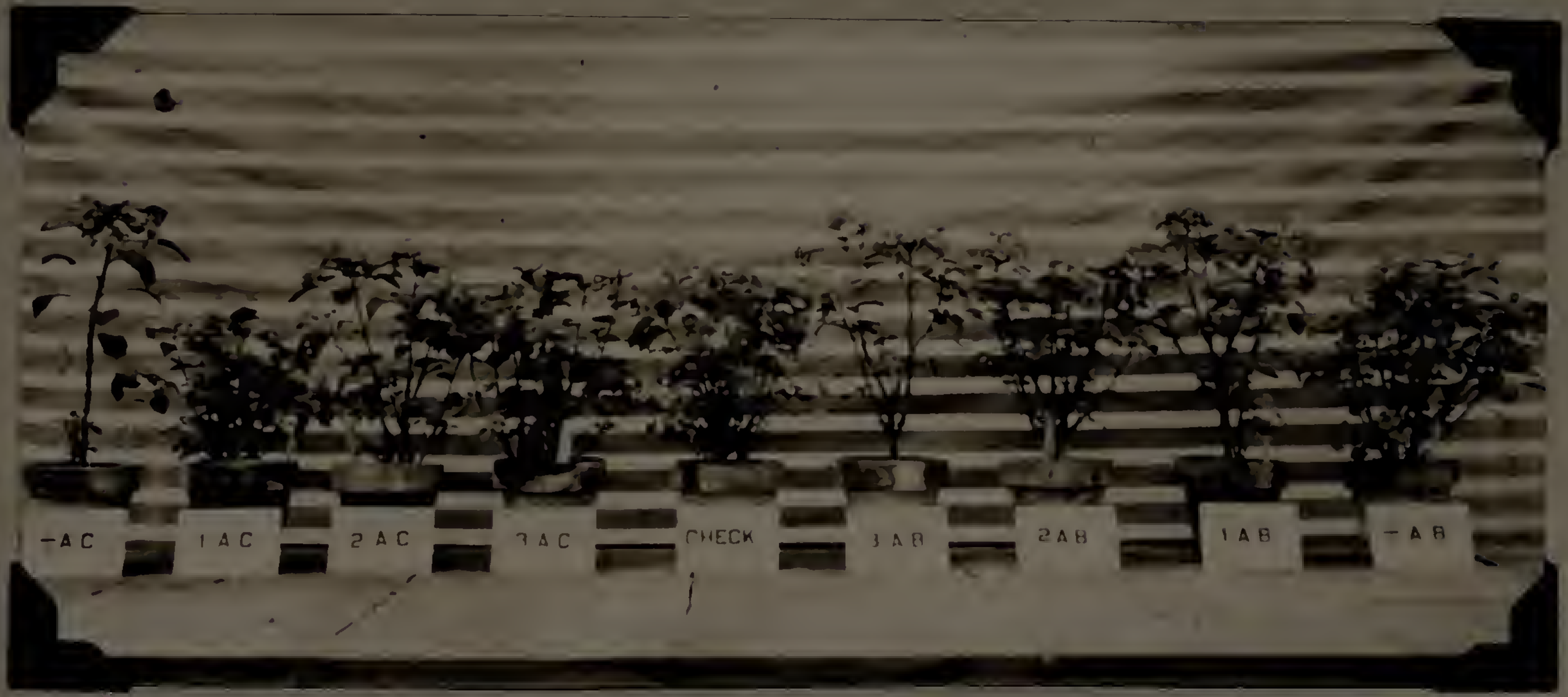

Figure 21. Impatiens Holstii, Engler and Warb. From left—15, 30, 60, 90 grams AC frit; control; 90, 60, 30, 15 grams AB frit. The branching habit of this plant makes it difficult to detect difference by simple observation.

has been released and immobilized through oxidation in the soil solution.

Tagetes patula, Linn.

Tagetes patula, Linn., variety "Spry" was sowed in late October, 1950. Another variety, "Naughty Marietta," was sowed November 25, 1950. Forty-five plants of each variety were selected and planted in the treated soils, the former in late November, 1950, and the latter in December, 1950.

Both varieties were harvested April 15, 1951, in the same way as the other plants. Data are recorded in Tables XI and XII.

Statistical analysis showed no significant differences between the treatments for either variety.

Figure 22 shows the uniform growth of *Tagetes patula, Linn.*, variety "Naughty Marietta." Reference to Figures 23 and 24 graphically shows very slight differences.

Tagetes is a member of the Compositae. This family is known to have many species that have a symbiotic relation with micro-organisms of the soil. This might imply that, under certain soil conditions, the plant would be less effective in uptake of mineral elements. The fact that the plant treatments

TABLE XI

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *TAGETES PATULA, LINN.*, VARIETY "SPRY" FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	32.54	4.58	358	52	6.9
	30	47.20	6.40	354	38	9.3
	60	38.70	5.58	431	39	10.9
	90	32.76	4.82	387	61	6.4
5% Fe_2O_3 2% MnO_2	15	33.46	4.88	548	64	8.6
	30	39.96	5.56	338	77	4.4
	60	41.08	5.48	419	142	2.9
	90	34.72	4.60	348	235	1.5
Control		36.04	5.04	562	106	5.3

TABLE XII

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *TAGETES PATULA, LINN.*, VARIETY "NAUGHTY MARIETTA" FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	59.56	8.50	257	71	3.6
	30	50.96	6.80	325	71	4.6
	60	53.98	7.36	325	61	5.4
	90	61.98	8.28	256	38	6.7
5% Fe_2O_3 2% MnO_2	15	53.34	7.28	348	83	4.2
	30	53.06	7.16	387	83	4.6
	60	49.82	6.86	359	102	3.5
	90	54.80	7.56	361	114	3.2
Control		62.98	8.44	332	94	3.5

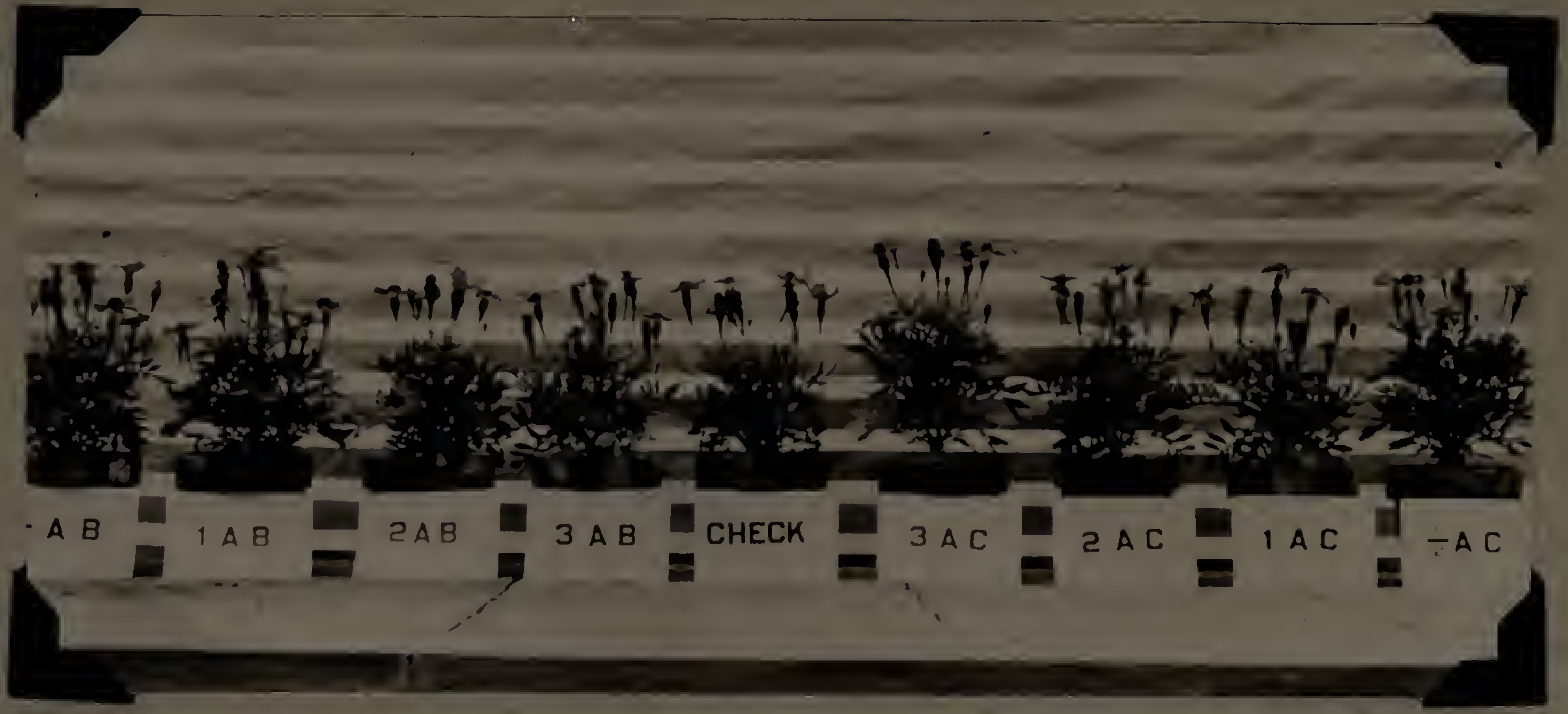

Figure 22. <u>Tagetes</u> <u>patula</u>, <u>Linn</u>., variety "Naughty Marietta." From left—15, 30 60, 90 grams AB frit; control; 90, 60, 30, 15 grams AC frit. This plant is very uniform in its growth habit. The growth seems not to have been affected by treatments.

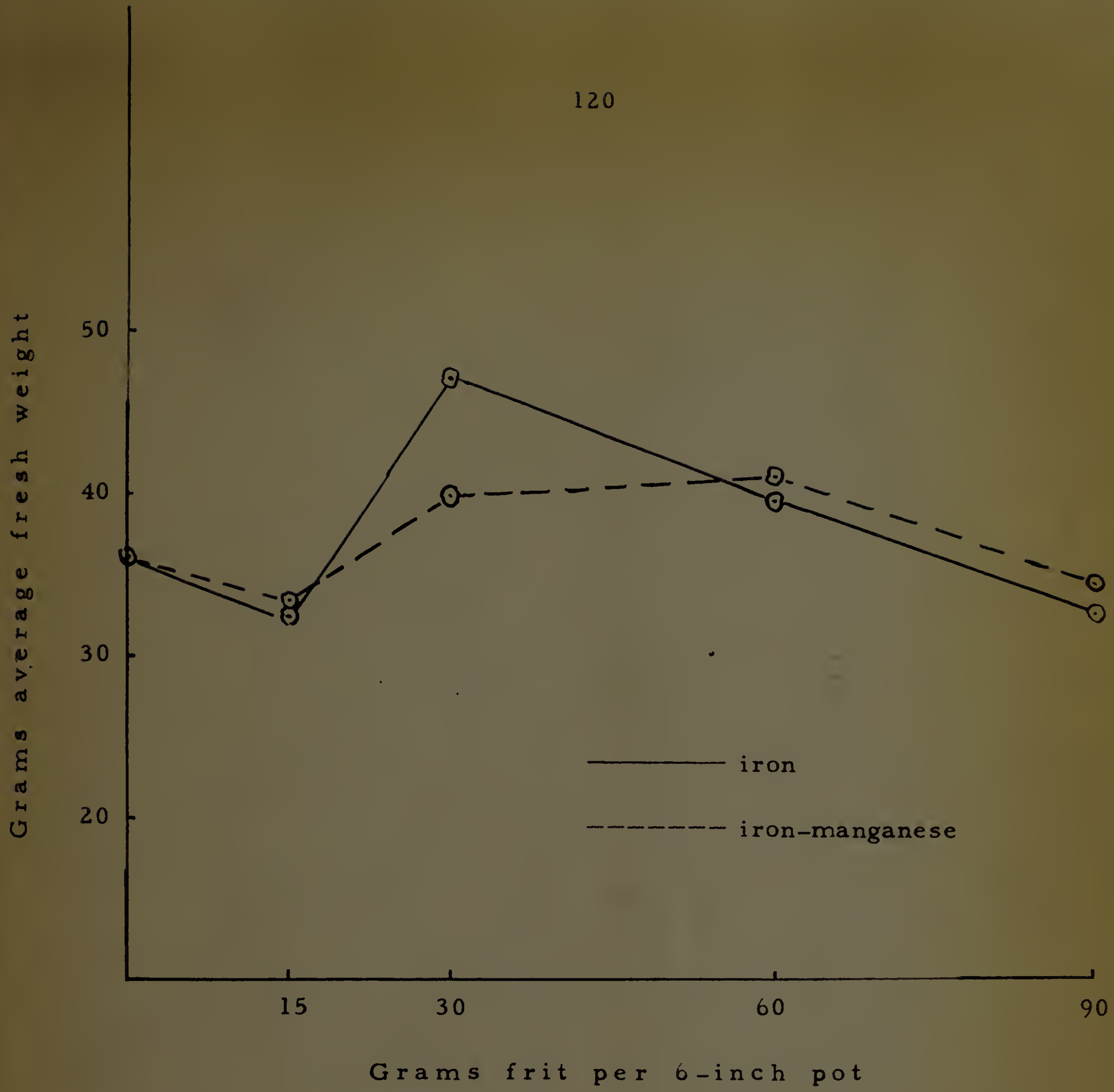

Figure 23. Effects of frits on fresh weight of <u>Tagetes</u> <u>patula</u>, <u>Linn</u>. var. "Spry."

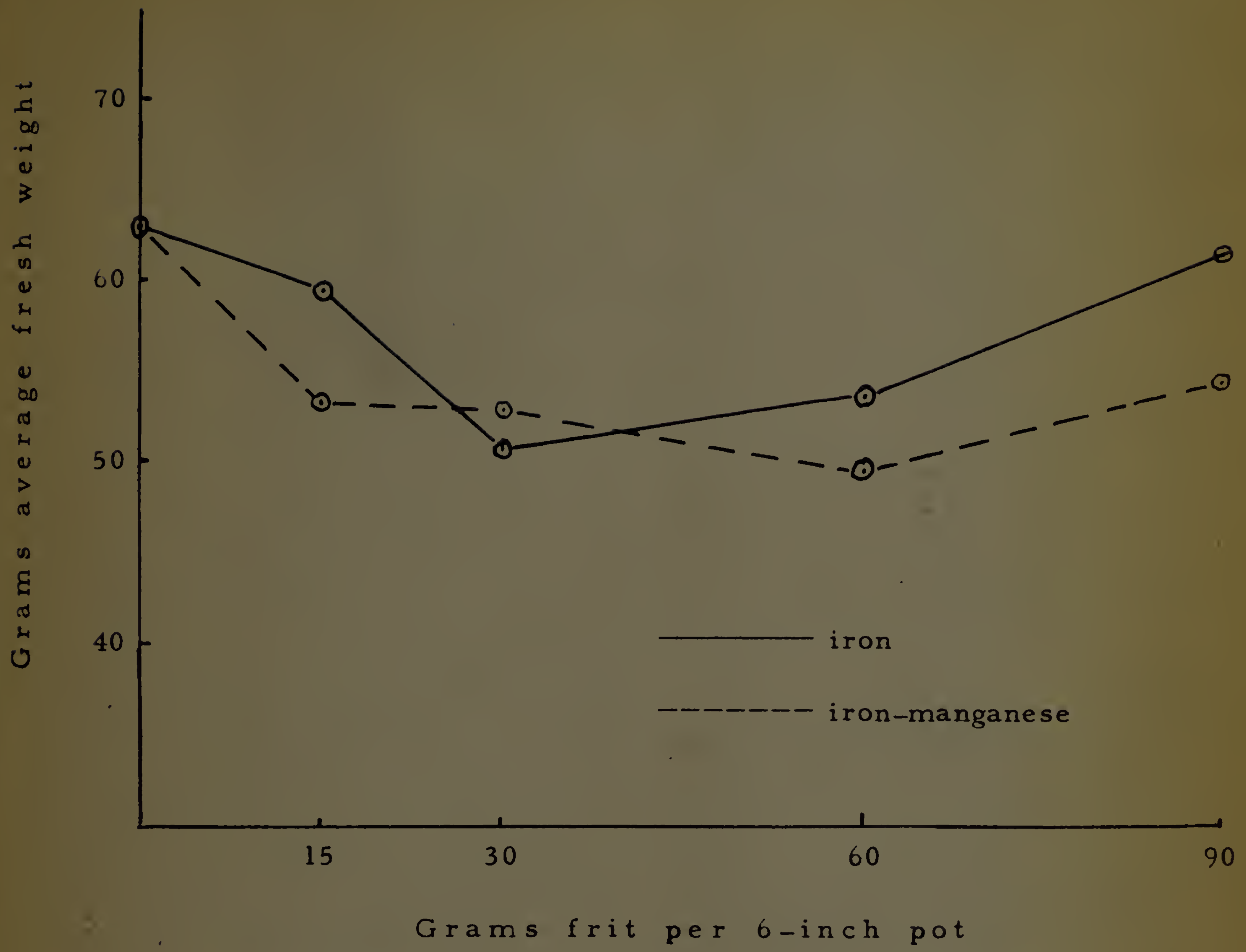

Figure 24. Effects of frits on fresh weight of _Tagetes_ _patula_, _Linn_. var. "Naughty Marietta."

showed no significant differences, might indicate that iron or iron and manganese, was not absorbed into the roots in luxury amounts and, therefore, additional amounts of available iron and manganese in the soil had no effect on plant growth.

A study of the analyses for iron and manganese in the tests with both varieties of Tagetes (Tables XI and XII) reveals no relation between growth and amounts of frits used, iron content, manganese content, or iron-manganese ratio. Plants of both varieties grown in the AC treatments showed less manganese and iron content than the control. The same conclusion regarding exchange of iron of the frit with manganese of the soil, as in previous cases (Impatiens, Phaseolus) seems to apply equally well. The analyses of the AB treatments show slightly greater amounts of iron than the control for the variety "Naughty Marietta" and less for the variety "Spry."

Luxury absorption of manganese is indicated for the AB frit treatments at the 60 gram and 90 gram levels for both varieties.

Begonia semperflorens, Link and Otto.

Forty-five seedlings of Ball's Rose Begonia one inch high were selected and planted in the treated soils in early

December, 1950. The plants were harvested April 15, 1951, in the usual manner. Data are recorded in Table XIII.

An analysis of variance was carried out on the data on fresh weights from nine treatments and five replications. The difference between the averages of any two treatments, for significance at the 5 per cent probability point, is 39.2 grams. On examining the above averages, it is seen that the 90 grams AB average is significantly larger than the average for check, the 60 grams AC average, the 30 grams AC average and the 15 grams AC average.

There is no evidence of a linear trend for the AB averages or for the AC averages. There is a linear trend for the AC averages with the 15 grams AC data omitted (Figure 25).

There seemed to be considerable genetical variability in this lot of plants, as several of the plants produced white flowers and there was considerable color variation even in those with rose-colored flowers. Some plants carried distinctly rose-scarlet flowers.

It is to be noted that plants of Begonia in soils to which AC frit was added were very slow in growth and that this is

TABLE XIII

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF *BEGONIA SEMPERFLORENS*, *LINK*. AND *OTTO*, FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	102.24	3.76	510	50	10.2
	30	80.14	4.10	346	44	7.9
	60	93.38	4.20	390	59	6.6
	90	118.76	5.48	373	32	11.7
5% Fe_2O_3 2% MnO_2	15	111.84	6.76	376	53	7.1
	30	138.98	6.56	401	68	5.9
	60	120.44	5.62	475	97	4.9
	90	148.02	6.66	332	92	3.6
Control		108.48	5.02	381	55	7.0

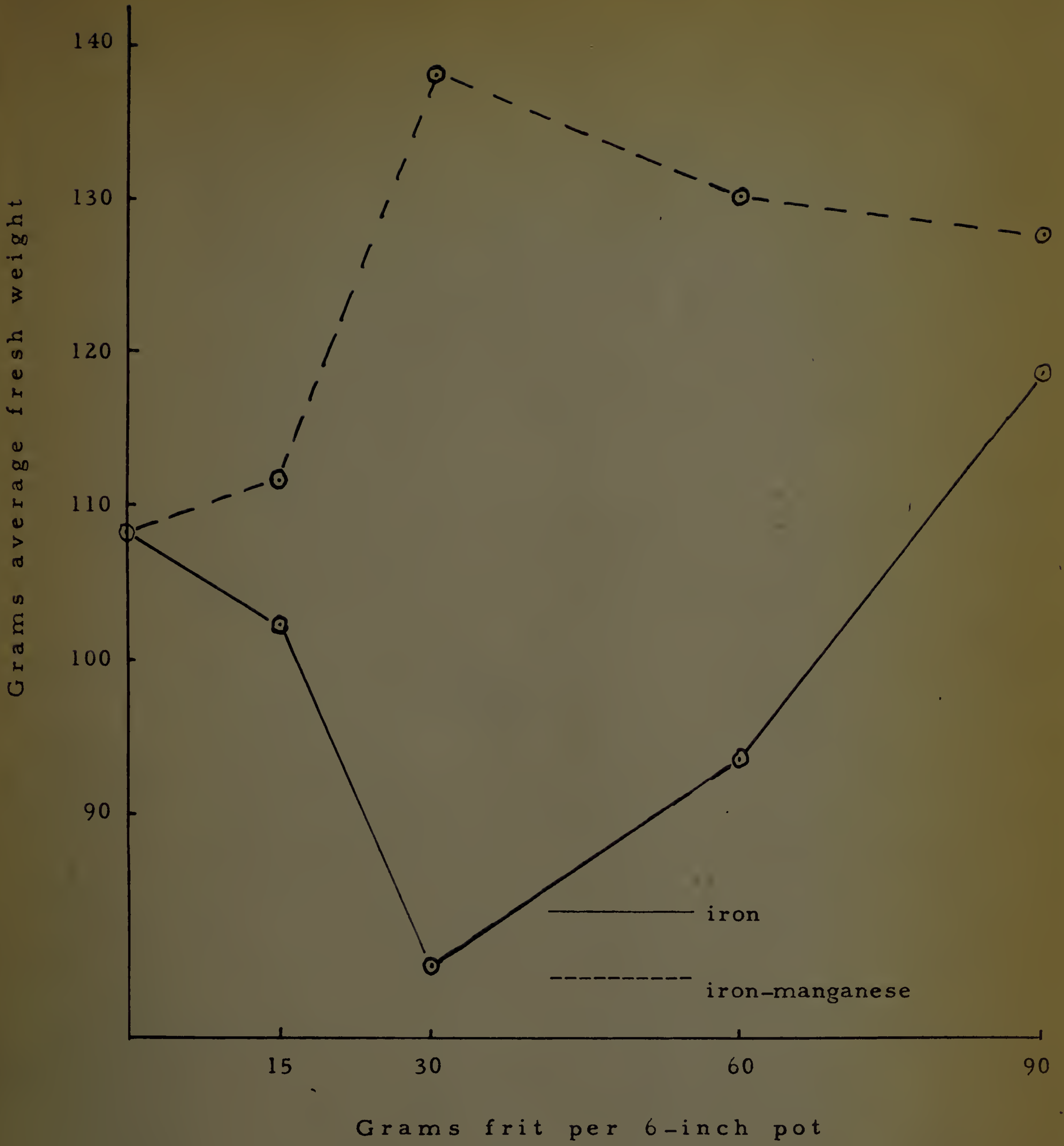

Figure 25. Effects of frits on fresh weight of *Begonia semperflorens*, *Link* and *Otto*.

reflected in the fresh weights. The slow growth probably was due to nutritional disturbance. It may have been iron toxicity due to excess iron or to improper iron-manganese ratio. It is doubtful that the slow growth could have been caused by phosphate deficiency, first, because of the quantity of superphosphate added to the soil; second, because the pH rising from approximately 5.5 was not favorable to precipitation of phosphorus by iron; and third, because the amount of organic matter in the soil would have a tendency to inhibit phosphate precipitation. The possibility of calcium deficiency must be eliminated due to the high lime content of the irrigation water. All plants received the same amounts of potassium sulfate and ammonium sulfate. That sulfates were not in excess must also be eliminated as a possibility since all plants received equal amounts.

Manganese content of plants is generally lower for the iron frits and higher for the iron manganese frits than control plants.

There is no constant relationship between iron or manganese content and growth as represented by fresh weights or dry weights.

Greatest fresh weight showed lowest iron-manganese ratio. This was obtained in plants grown in the 90 gram iron-manganese treatment. In this treatment the iron content was the lowest of any treatment including the control.

There is apparent luxury absorption of iron in the 15 grams treatment with iron frit and in all treatments with the iron-manganese frit except the 15 grams treatment. There is luxury absorption of manganese in all treatments of the iron-manganese frit except the 15 grams treatment.

Phlox Drummondii, Hook.

Seed of *Phlox Drummondii gigantea* were sowed December 1, 1950. The seedlings were transplanted into the treated soils in 6-inch pots December 26, 1950. A total of forty-five plants, five in each treatment, were grown. The plants were harvested May 1, 1951. Average fresh weights, average dry weights, iron and manganese content and iron-manganese ratio are recorded in Table XIV.

Maximum growth of plants grown in the soils with iron-manganese frit was obtained at the 90 gram level, while with the soils with iron frit maximum growth occurred at the 15 gram level. Average fresh weights for each treatment are graphically shown in Figure 26.

TABLE XIV

AVERAGE FRESH WEIGHT, DRY WEIGHT, IRON AND MANGANESE CONTENT OF PHLOX DRUMMONDII, HOOK., FOR EACH TREATMENT

Type of frit	Frit per 6 inch pot (grams)	Average fresh weight (grams)	Average dry weight (grams)	Iron p.p.m.	Manganese p.p.m.	Fe/Mn
5% Fe_2O_3	15	44.60	4.14	408	38	10.8
	30	30.40	3.00	489	35	14.1
	60	26.30	3.04	372	38	9.8
	90	34.55	3.60	682	38	18.0
5% Fe_2O_3 2% MnO_2	15	42.28	5.30	550	38	14.5
	30	37.90	4.23	431	44	9.8
	60	21.73	2.17	583	59	9.9
	90	44.70	4.80	623	58	10.8
Control		34.46	3.58	489	50	9.8

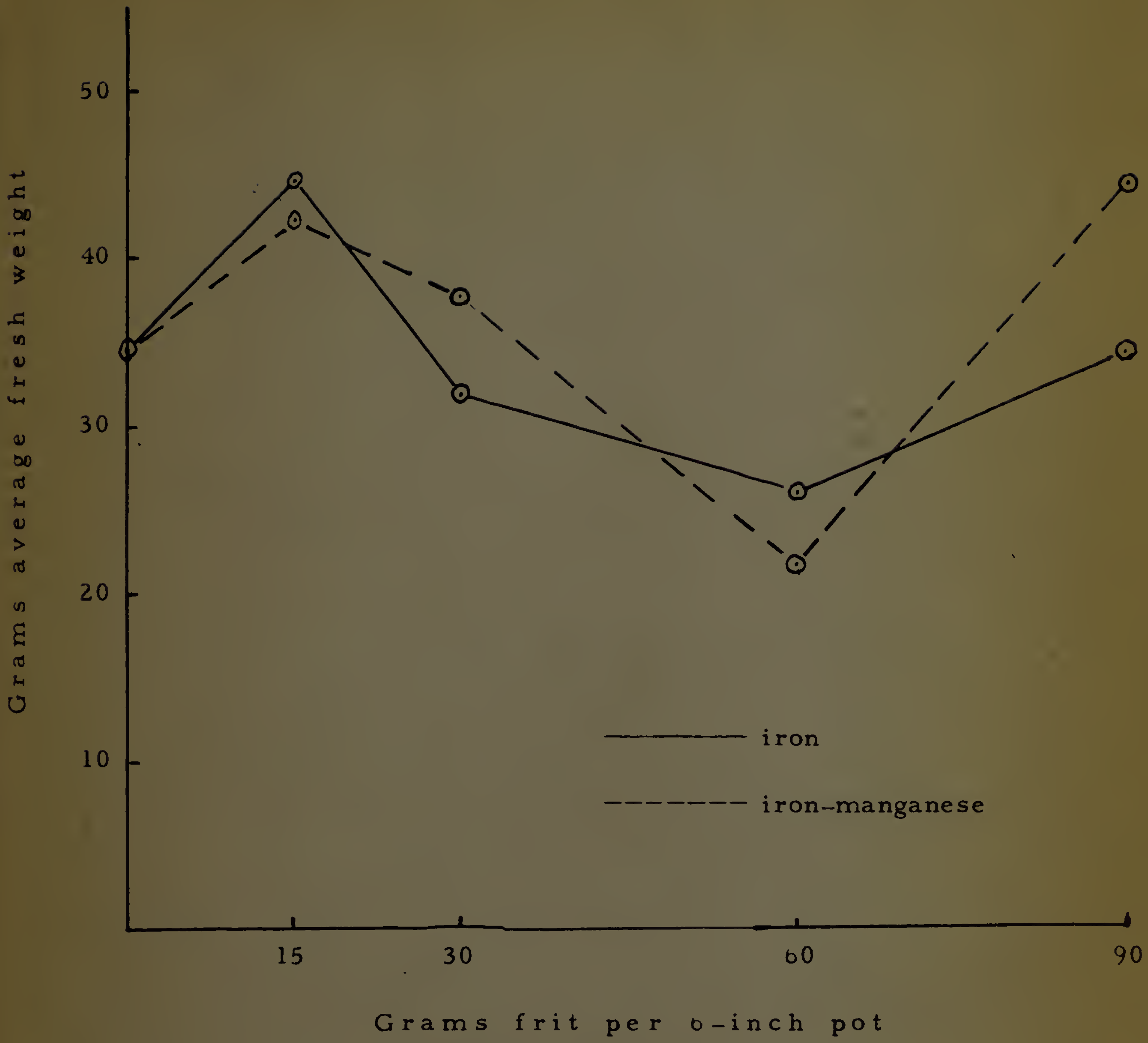

Figure 26. Effects of frits on fresh weight of Phlox Drummondii, Hook.

Analyses for iron and manganese content show no relationship with growth nor is there any relationship between iron-manganese ratio and growth. Two treatments, the 90 gram and 60 gram treatments with the iron-manganese frits, showed evidence of luxury absorption of both iron and manganese. The 15 gram level of the iron-manganese frit and the 90 gram level of the iron frit showed luxury absorption of iron alone. Only in the case of the plants grown in the 60 gram level of iron-manganese frits was there any possible toxicity and the much depressed growth here must be due to some complicated relationship or some unknown factor, since even higher iron content and higher as well as lower ratio values had no such effect in other treatments. The highest manganese content was obtained in these plants, but the manganese content was not significantly higher than in the 90 gram treatment which resulted in highest fresh weight.

There is luxury absorption of iron in the 90 grams iron frit treatment and in all treatments with the iron-manganese frit except the 15 grams treatment. There is luxury absorption of manganese in the 60 grams and 90 grams treatments with the iron-manganese frit.

DISCUSSION

It is common knowledge that different kinds of plants, grown under the same conditions, differ in their elemental composition. It is also well-known that plants differ in their power of taking up some cations from the soil, or in their power of transferring them into their aerial portions. The relationship between nutrient absorption and plant growth is complex.

Rate of uptake of moisture may determine the amount of mineral elements absorbed by roots. The amount of moisture in the soil may influence the rate at which plants absorb moisture from the soil. Slight variations in soil moisture content may cause variations in leaf turgidity. Such slight differences of turgidity as between plants may cause variations in rates of photosynthesis which in turn affect growth rates. Thoday (118) found a great difference in photosynthesis of *Helianthus annuus* as between turgid and wilted leaves. Iljin (56) found photosynthesis of leaves of *Bidens tripartita* and *Phlomis pungens* much reduced when water content was reduced. Brilliant (10) obtained similar results with *Hedera helix* and *Impatiens* parviflora. Dastur (23) and Heinicke and Childers (44) found water content of apple leaves related to the process of photosynthesis.

The carbon dioxide respiration of plant roots aids the plant in obtaining phosphorus, iron, manganese and other elements, by increasing acidity in the vicinity of absorbing surfaces. Some plants may excrete organic acids that similarly result in making these elements available. Jenney *et al*. (60, 61) have demonstrated that direct exchange of excreted hydrogen ions with cations held by mineral particles is another possible mechanism by which plants are able to obtain mineral elements from the soil. Finally, biological reactions may make available to plant roots elements such as manganese and iron which otherwise would be unavailable. The fact that these reactions must take place in the immediate rhizosphere of the root hairs greatly complicates the study of the mechanism of intake of mineral elements. Further, the permeability of cell walls and protoplasm is affected by many factors not the least of which may be the constituency and concentration of the soil solution. Changes in permeability may greatly affect the kind and amount of the ions absorbed, as well as the rate of absorption. The plant may seem to exhibit a choice of ions, which is in reality the varied manifestations of response to the many and complex factors governing plant growth processes.

Under normal conditions of oxygen supply, carbon dioxide alone is excreted by roots. When the supply of oxygen is limited, there is incomplete decomposition or oxidation and as a result, excretory products of respiration consist of organic acids.

The respiration of root systems may vary with the extent, activity, and kind of root system. Plants with long, thick tap roots and few fibrous roots may excrete carbon dioxide in small amounts. Under certain conditions wherein the soil has a high pH, such plants may be unable to obtain sufficient amounts of some elements for good green growth. Milad (87) reported that the lupine is inefficient in production of carbon dioxide from the roots. The root system of the lupine is typified by a long tap root. Plants with an active much-branched fibrous root system are likely to be more efficient in obtaining mineral elements from the soil under adverse soil conditions.

Czapek (22) found that absorption of potassium and phosphorus varied as between different kinds of plants. This variation was correlated directly with differences in carbon dioxide excretion. Others have reported similarly on the solvent action of excreted carbon dioxide on soil nutrients.

It is a well-known fact that plants respond favorably to an increasing amount of a nutrient in the soil, provided this nutrient was not originally present in an amount sufficient for maximum growth. Beyond a certain limit the plant does not respond to an increasing amount, but may continue to absorb an increasing amount from the soil. Most plants absorb a greater quantity of inorganic salts than is necessary for their maximum growth, if there is an abundance of these in the soil.

The occurrence in a plant of a greater quantity of an element than is required for its needs is called "luxury consumption." The point at which absorption of mineral elements becomes luxury absorption is difficult to determine. Luxury absorption may result in toxic effects on plant growth. Accumulation of mineral elements within plant tissues, when absorption is greater than utilization, may reach a concentration that becomes toxic to plant tissues. Excesses of elements in the soil solution such that the osmotic pressure of the soil solution becomes more than a negligible factor, may cause movement of moisture and possibly nutrients from plant to soil. It is known that under certain conditions, at least some plants may lose ions to the soil. Cereals are known to lose potassium to the soil towards the end of the growing season. Soils high in certain elements may also extract ions of other elements from plants. Moreover, soils deficient in certain elements may cause movement of those elements from roots to soil. Yet if aeration conditions are adequate, roots can hold their ions against diffusion into the soil. Excesses of an element in the soil may result in deficiency of some other element. Excess calcium, for example, may result in deficiency of potash in plants growing in such soil. Potassium deficiency may affect nitrogen utilization. Similarly excess calcium may result in deficiency of other elements such as iron, aluminum, manganese and phosphorus. Excesses or deficiencies of mineral elements within the plant may result in lowered growth rate or may show other toxic symptoms such as chlorosis and necrosis of plant tissues. Adding an element to the soil does not always result in absorption of that element by the plant. At least some elements may be adsorbed by the soil colloids so strongly that the plant is unable to obtain sufficient amounts of these elements for normal growth. Furthermore, other elements may combine with the added element forming an insoluble compound that is either precipitated or held in suspension in the soil solution and in either case may be unavailable to the plant.

Even in hydroponics there is great difficulty in analyzing results of nutritional experiments because of complex factors that cannot entirely be controlled. There has been much nutritional work reported using one or two plants in a treatment. While much valuable information has been revealed by such work, the fact remains that the greatest care must be exercised in interpreting results. Relations between yield and absorption of a given element often may be determined by differences in the amounts of elements absorbed by plants in different treatments, or between different plants of the same treatment. The time required for absorption and the time elapse for the absorbed elements to function in growth as between different plants, may similarly affect growth and yield.

The glassy frits, manufactured by the Ferro Enamel Corporation, may be prepared with various minor elements impregnated within the frit and they can be furnished in any size particle that may be required for hydroponic or soil culture. This material offers a new field for the study of contact absorption of mineral elements by plant roots. The experiments described herein were designed to show only that roots of plants growing in normal soil can obtain minor elements sufficient for plant growth, or even in luxury amounts, by contact absorption. The effects of luxury absorption are further demonstrated.

In each of the experiments reported, it seems evident that the insoluble iron and manganese contained within the frit have had an apparent effect on plant growth, even though these elements are contained in the soil used in sufficient amount for normal green growth of plants.

The experiments with Nicotiana showed this most clearly. This plant showed almost a direct proportional increased growth with increased amounts of iron and manganese available in insoluble form. Except for a depression of growth when the smallest amount of iron-containing frit was used, there was an increase in growth for the iron-containing frit. However, for the equivalent amount used, there was greater growth when manganese was furnished with the iron in a ratio value of approximately 2.0. This closely agrees with the findings of Shive (109) and Somers, Gilbert and Shive (111), who found that the ratio Fe/Mn was between 1.5 and 2.5 for optimum growth for species investigated. That this proportion may not be correct for all plants is indicated in experiments with other plants reported herein. Takeuchi (116) found that different species were not equally stimulated by manganese.

Some plants seemed to show increased growth with iron frit, while others seemed to benefit more from the iron-manganese frit. Among the kinds of plants that seemed to have better growth with the iron frit than with the iron-manganese frit were Iberis, Antirrhinum and Cineraria. This may indicate that these plants require a higher iron-manganese ratio value. Among the plants that seemed to show better response to the iron-manganese frit were Nicotiana, Lobelia, Phaseolus, Begonia and Impatiens. Plants that gave varied response were Primula and Calendula. Tagetes showed very little effect on growth due to either frit in any of the treatments.

Plants varied as to the treatment that gave the greatest growth response (Table XV).

Both frits seemed to have a toxic effect on the growth of Impatiens and Antirrhinum.

TABLE XV

TREATMENT THAT RESULTED IN MAXIMUM AVERAGE GROWTH FOR EACH PLANT

Type of Frit	5% Fe_2O_3, MnO_2				Check	5% Fe_2O_3			
Grams of Frit	15	30	60	90		90	60	30	15
Antirrhinum HT x RPS									x
Antirrhinum "Margaret"	x								
Begonia		x							
Calendula	x								
Cineraria				x					
Iberis									x
Impatiens					x				
Lobelia	x								
Nicotiana				x					
Phaseolus				x					
Phlox						x			
Primula							x		
Tagetes "Spry"					x				
Tagetes "Naughty Marietta"					x				

The varied response of different plants to the treatments may indicate different levels of iron and manganese required for growth in different plants. Some plants seem to require small amounts of available iron and manganese or are especially efficient in absorbing these elements. Other plants seem to be benefited by luxury amounts. Such plants either require additional amounts or are less efficient in obtaining these elements from the soil.

Three conclusions can be drawn from the tests. The first is that plants can obtain iron and manganese that are contained in the soil in relatively insoluble, but available form. Differences in growth in different treatments seemed to indicate this condition in all plants except _Tagetes_. While many of the differences in growth are not statistically significant, differences could be noted while the plants were growing. The second conclusion that seems important is that, in some cases at least, increased amounts of iron and manganese in proper ratio in the soil can result in increased growth. This is especially demonstrated in _Nicotiana Tabacum_. A second experiment with this plant showed generally the same response to treatments as described herein. Further, it seems to the author that these plants might show further increased growth with iron-manganese frit in still larger amounts than the 90 gram treatments described. A third point is that plants differ in their requirements for iron and manganese or abilities to absorb iron and manganese.

Results of the manganese analyses for the different plants are recorded in Table XVI. It is evident that something approaching luxury absorption, if not luxury absorption, has taken place in many plants grown in the iron-manganese treated soils. This is noted in comparison with controls in all iron-manganese treatments for Primula and Antirrhinum "Margaret," and in all except the 15 gram levels for Cineraria, Calendula and Impatiens. In Lobelia and Tagetes the two highest levels of the AB frit show manganese absorption in excess of the control. In all plants except Nicotiana, Primula, Iberis, Antirrhinum, plants grown in the AC frit treatments gave lower manganese content than the control. It was expected that plants grown in the AC frits would contain approximately the same amounts of manganese as the control. That they did not do so and generally absorbed considerably less manganese than the control is evidence of the complex relationship between

TABLE XVI

SUMMARY OF MANGANESE ANALYSIS

Plant	Type of Frit								Con-trol
	5% Fe_2O_3 (grams)				5% Fe_2O_3 2% MnO_2 (grams)				
	15	30	60	90	15	30	60	90	
Nicotiana leaf*	21	20	66	70	54	34	47	34	35
Cineraria	32	34	33	33	44	92	136	144	80
Lobelia	47	52	47	--	66	80	130	137	102
Primula	61	30	21	23	50	31	33	32	21
Iberis	34	36	23	21	20	29	11	80	30
Antirrhinum HT x RPS	0	11	14	14	11	19	14	43	0
Antirrhinum "Margaret"	29	36	23	26	29	39	44	41	23
Phaseolus	32	23	23	23	52	46	41	49	46
Calendula	0	30	0	52	53	105	144	133	55
Impatiens	44	35	30	35	58	68	74	73	56
Tagetes "Spry"	52	38	39	61	64	77	142	235	106
Tagetes "Marietta"	71	71	61	38	83	83	102	114	94
Begonia	50	44	59	32	53	68	97	92	55
Phlox	38	35	38	38	38	44	59	58	50

* Leaf tissue only. Figures in p.p.m.

iron and manganese existing in the soil as well as within the plant.

Godden and Grimmett (38) were of the opinion that perhaps manganese is more easily taken up from the soil by the plant than is iron. The tests reported herein do not appear to support this opinion. Eisenmenger and Holland (31) thought the H-ion concentration of the soil is probably more of a factor in iron assimilation than is the amount of insoluble iron compound present. They found that manganese gave inconsistent results as to amounts in plants and that there was evidence that applications of manganese tend to increase the amount of phosphorus in the plants.

In the experiments reported herein there was much inconsistency in amounts of both iron and manganese found in the plants. It is the opinion of the investigator that a portion of the manganese in the soil has displaced some of the iron ions in the frit, these iron ions combining with the oxygen dissociated from the manganese. The oxidized iron ions become unavailable to the plants. Such reaction would explain the lower absorption of manganese and iron.

The amount of manganese found within the plant may have no direct connection with growth. If the function of manganese is to release oxygen for oxidation of the ferrous iron which in the process of oxidation furnishes energy necessary for the formation of chlorophyll, the amount of manganese required for the process might be very small since the manganese may easily be reoxidized and function repeatedly in the oxidation of iron. The more rapid the growth processes, the more frequent would be the changes in the state of the manganese, but the iron, once its function is completed, becomes immobilized and the rate of supply of the iron must be continued to replenish the immobilized iron. Additional amounts of manganese would be required for the new growth only. Therefore, within the green leaf there could be no fixed ratio between amounts of iron and manganese. Presumably ratio values in young leaves would be considerably lower than in old leaves.

Analyses of iron for all treatments for each plant are recorded in Table XVII. Such analyses show no regular relationship to growth, but there are a few facts that should be noted. The *Iberis* plants, in all treatments except the 30 grams iron-manganese frit, were found to contain larger quantities of iron than the control. The *Lobelia* plants, except those in

TABLE XVII

SUMMARY OF IRON ANALYSIS

Plant	Type of Frit								
	5% Fe_2O_3 (grams)				5% Fe_2O_3 2% MnO_2 (grams)				Control
	15	30	60	90	15	30	60	90	
Nicotiana leaf*	627	298	359	301	335	402	783	443	1170
Cineraria	489	479	417	476	489	564	456	406	550
Lobelia	588	304	457		417	450		520	394
Primula	927	888	935	782	882	776	915	927	876
Iberis	249	212	171	165	171	136	149	387	147
Antirrhinum HT x RPS	183	131	167	209	136	178	127	160	144
Antirrhinum "Margaret"	101	161	163	175	82	96	97	149	107
Phaseolus	196	168	169	236	144	165	292	139	186
Calendula	359	410	417	468	354	645	643	473	527
Impatiens	150	141	151	198	243	193	141	193	210
Tagetes "Spry"	358	354	431	387	548	338	419	348	562
Tagetes "Marietta"	358	354	431	387	548	338	419	348	562
Begonia	510	346	390	373	376	401	475	332	381
Phlox	408	489	372	682	550	431	583	623	489

* Leaf tissue only. Figures in p.p.m.

the 30 grams iron frit treatment, all analyzed higher in iron than the control. The *Primula* plants analyzed higher in iron in all treatments, except the 90 grams iron frit and the 30 grams iron-manganese frit treatments. *Antirrhinum* "Margaret" plants showed higher iron in all treatments with the iron frit except the 15 gram treatment and were also higher than the control in the 90 gram iron-manganese treatment. None of the plants of *Tagetes* "Spry" contained so much iron as the control, while the plants of *Tagetes* "Naughty Marietta" were slightly higher in iron for all treatments with iron-manganese frit. Plants of *Nicotiana* from all treatments and of *Cineraria* from all treatments except the 30 grams iron-manganese, had smaller amounts of iron than the control.

The conclusions reached are: (1) it is extremely difficult to obtain accurate iron determinations; (2) there is a complicated relationship between iron and manganese as well as other elements that results in a variable absorption of iron; (3) there is evidence of luxury absorption of iron in some cases in the tests; (4) there is some evidence of luxury absorption of manganese in some treatments; (5) manganese affects iron by displacing it in some compounds and by causing its oxidation in the soil solution.

SUMMARY

The effect upon plant growth of luxury amounts of iron and iron and manganese available to plant roots in relatively insoluble form was studied.

These minor elements were supplied to the plants in relatively insoluble form impregnated in finely ground glassy frit.

The experiments were planned to study five levels of iron and iron combined with manganese to determine (a) whether plant roots growing in soil could obtain these minor elements by contact absorption; (b) whether amounts of the two elements beyond that required for normal green growth would result in increased growth.

Fourteen kinds of plants were used in the experiments.

The growth of Nicotiana was greatly benefited by additional amounts of the iron and manganese frit, and to a lesser extent by the iron frit, almost directly proportional to the amount used up to the highest amounts.

While growth of Cineraria was benefited by additional amounts of both frits, the iron-manganese frit generally showed

slightly better results at each level, with the exception of the 60 gram treatments.

Lobelia and Calendula were benefited most by the smaller amount of iron-manganese frit.

Iberis and Antirrhinum showed some benefit from the lowest level of the iron frit, but the iron-manganese frit depressed growth in both cases.

Phaseolus showed most growth with the highest level iron-manganese frit and in general the iron-manganese frit at all levels gave better results than the iron frit.

The results of the experiments with Primula showed most growth with the iron frit at the 60 gram level and the iron-manganese frit at the 90 gram level. The fact that differences in growth occurred with differences in treatments in many plants would indicate that the plants obtained both iron and manganese by contact absorption from the frits. These differences were often not statistically significant.

In the case of Nicotiana Tabacum reference to Figure 4 leaves no doubt but that the growth of Nicotiana plants was influenced by the frits and that the iron-manganese frit was slightly more beneficial than the iron frit.

These tests show that most crops can obtain iron and manganese from the frits used.

Analysis for iron indicates that in some treatments luxury absorption occurred. Similarly there were treatments in which luxury absorption of manganese occurred. It is apparent that there is close relationship between iron and manganese and the interaction of these elements in the soil, as well as within the plant, may have a considerable effect on plant growth.

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APPENDIX

A. Determination of iron

(Hummell, F. C. and Willard, H. H. Determination of iron in biological materials. Ind. Eng. Chem. Anal. Ed. 10:13-15. 1938).

Reagents

Acetic acid. 2 N. Dilute 120 gms. of glacial acetic acid to 1 liter with distilled water.

Hydrochloric acid. 1:1.

Hydrochloric acid. 1:100.

Ammonium citrate. 1%. Dissolve 1 gm. of ammonium citrate in distilled water and dilute to 100 ml.

Bromophenol blue indicator solution. 0.4%. Grind 1 gm. of solid bromophenol blue in a mortar with 3 ml. of 0.05 N NaOH, transfer to a volumetric flask and dilute to 250 ml. with distilled water.

Buffer solutions

1. Solution of pH 3.5—Mix 6.4 ml. of 2M sodium acetate solution with 93.6 ml. of 2M acetic acid solution and dilute to 1 liter with distilled water.

2. Solution of pH 4.5—Mix 43 ml. of 2M sodium acetate solution with 57 ml. of 2M acetic acid solution and dilute to 1 liter.

Hydroquinone solution. Dissolve 1 gm. of hydroquinone in 100 ml. of a buffer solution of pH 4.5, store in a refrigerator.

O-phenanthroline solution. Dissolve 1 gm. of orthophenanthroline monohydrate in distilled water, warming if necessary to effect solution, and dilute to 400 ml.

Sodium acetate. 2M. Dissolve 272 gms. of sodium acetate ($NaAc.3H_2O$) in distilled water and dilute to 1 liter.

Iron. Standard solution. Dissolve 1 gm. of electrolytic iron in 50 ml. of 10% H_2SO_4, warming if necessary to hasten the reaction. Cool, and dilute to 1 liter with distilled water; 1 ml. contains 1 mg. of Fe.

Procedure

Pipette similar aliquots of digested ash solution into both a 25 ml. volumetric flask and a 25 ml. Erlenmeyer flask.

An aliquot is chosen which will fall in the range of the photometer (.01-.10 mgm. of iron). To the solution in the Erlenmeyer flask are added 5 drops of bromophenol blue indicator; it is then titrated with 2M sodium acetate until the color matches that of an equal volume of buffer solution of pH 3.5 containing the same quantity of indicator. Add 1 ml. of the hydroquinone solution and 2 ml. of O-phenanthroline reagent to the aliquot in the volumetric flask and adjust the pH of the contents to 3.5 by adding the same volume of sodium acetate. If a turbidity develops upon adjustment of the pH of the aliquot in the Erlenmeyer flask, add 1 ml. of ammonium citrate solution to the volumetric flask before adding the sodium acetate solution. Make to volume, mix and let stand for 1 hour to assure complete color development. Compare the color in the Coleman spectra photometer at wave lengths of 510 mu against a water blank. Make a standard curve containing .01 to .10 mgm. of Fe and develop color as above.

B. Determination of manganese

A. O. A. C. method for plant material.

(Association of Official Agricultural Chemists. Official and Tentative Methods of Analysis. Ed. 6. pp 116, 120-121. Washington, D. C. 1945).

Reagents

Nitric acid. Concentrated solution.

Potassium periodate. Salt.

Ferric nitrate. Salt.

Sulphuric acid. Concentrated solution.

Procedure

Pipette an aliquot of the silica-free solution of the plant ash into a beaker and evaporate to a volume of about 30 mls. Add from 5-10 mls. of concentrated nitric acid and continue the evaporation. Do not evaporate until dense fumes appear, otherwise ferric sulfate will become difficult to dissolve. Add water, a little at a time, and heat until the iron salts are dissolved. Dilute to about 150 mls. Add potassium periodate or its equivalent of periodic acid in small portions, until 0.3 gm. has been added. Boil a few minutes or until the color of potassium permanganate has attained its maximum intensity. Cool. Determine the transmittance or optical density in a colorimeter, using a wave length of 530 mu, and a PC-4 filter.

Standard curve

Pipette a volume of water equal to the aliquot of the unknown solution to be analyzed into a 250 ml. flask. Add 15 mls. of concentrated sulfuric acid and enough ferric nitrate to about equal the amount of iron in the sample. Add a known volume of standard 0.1 N potassium permanganate, and 0.3 gm. of potassium periodate and boil for a few minutes. Cool. Dilute to volume.

Note

The Association of Official Agricultural Chemists (Official and Tentative Methods of Analysis. Ed. 6. p 116), recommends that from 10 to 50 gms. of plant tissue be ashed in a platinum crucible freed of silica by filtration, and the filtrate made up to 200 mls. The aliquot used for the determination of manganese should represent from 0.12 to 0.5 gms. of the plant ash. This would correspond roughly to about two to five gms. of the dry plant material. Nitric acid may be present, but hydrochloric acid must be absent.

This procedure does not provide for the absence of iron, but approximately corrects the error involved by adding iron to the standard solution of potassium permanganate used to prepare the standard curve. For approximate values of manganese, the procedure is satisfactory, but in order to obtain precise data, iron should be absent.

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