



---

## Uploaded to the VFC Website

▶▶ ▶▶ **May 2014** ◀◀ ◀◀

---

This Document has been provided to you courtesy of Veterans-For-Change!

Feel free to pass to any veteran who might be able to use this information!

For thousands more files like this and hundreds of links to useful information, and hundreds of "Frequently Asked Questions, please go to:

[Veterans-For-Change](http://www.veteransforchange.org)

---

*Veterans-For-Change is a A 501(c)(3) Non-Profit Organization  
Tax ID #27-3820181  
CA Incorporation ID #3340400  
CA Dept. of Charities ID #: CT-0190794*

### ***If Veterans don't help Veterans, who will?***

We appreciate all donations to continue to provide information and services to Veterans and their families.

[https://www.paypal.com/cgi-bin/webscr?cmd=\\_s-xclick&hosted\\_button\\_id=WGT2M5UTB9A78](https://www.paypal.com/cgi-bin/webscr?cmd=_s-xclick&hosted_button_id=WGT2M5UTB9A78)

---

### **Note:**

VFC is not liable for source information in this document, it is merely provided as a courtesy to our members & subscribers.



**Item ID Number** 04741  **Not Scanned**

**Author** Tremearne, T. H.

**Corporate Author**

**Report/Article Title** Arsenic in Natural Phosphates and Phosphate Fertilizers

**Journal/Book Title** Technical Bulletin No. 781

**Year** 1941

**Month/Day** November

**Color**

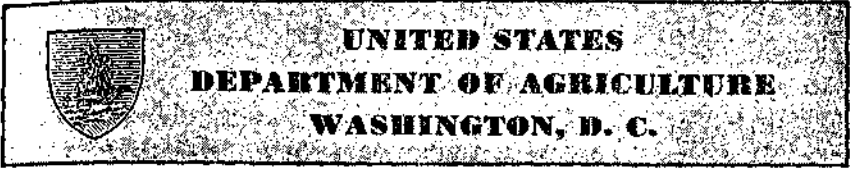
**Number of Images** 40

**Description Notes** Alvin L. Young filed these documents together under the label, "Arsenic/Cacodylic Acid and Herbicide Blue". A copy of this report is available in the NAL collection, call no.: 1 Ag84Te no.781.

TREMEARNE, T. H. & K. D. JACOB. 1941.

ARSENICAL

Technical Bulletin No. 781 • November 1941



# Arsenic in Natural Phosphates and Phosphate Fertilizers<sup>1</sup>

By T. H. TREMEARNE, junior chemist, and K. D. JACOB, senior chemist, Division of Fertilizer Research, Bureau of Plant Industry<sup>2</sup>

## CONTENTS

	Page		Page
Introduction.....		Arsenic in calcined, sintered, nodulized, and defluorinated phosphate rocks.....	19
Method of analysis.....	1	Arsenic in superphosphates and phosphoric acid.....	21
Reagents and glassware.....	2	Arsenic in ammonium phosphate, bone, and miscellaneous phosphate fertilizers.....	25
Separation of arsenic from the sample.....	2	Effect of arsenic on plants and soil organisms.....	27
Procedure used.....	3	Arsenic supplied to soil by superphosphate.....	28
Arsenic in mineral phosphates.....	5	Summary and conclusions.....	29
Arsenic-bearing constituents.....	6	Literature cited.....	31
Primary and secondary deposits.....	13		
Geologic age and arsenic content.....	16		
Phosphates compared with other rocks, minerals, coals, soils, sediments, and waters.....	17		

## INTRODUCTION

Arsenic is widely distributed in nature, though usually in "trace" quantities (100, pp. 9-13).<sup>3</sup> According to Clarke and Washington (22, pp. 20-21), arsenic occupies the thirty-eighth position in the order of abundance of the elements in the igneous rocks of the world, and its concentration therein, like that of molybdenum, rubidium, tin, and bromine, falls within the range  $1 \times 10^{-6}$  to  $9 \times 10^{-6}$  percent. Not only is arsenic a common constituent of rocks, minerals, coals, soils, sediments, and waters (see table 13), but it is nearly always present in vegetation (2a, 46, 52, 54, 59, 86, 146), particularly marine growths (18, 43, 85, 146); in the tissues of mammals, fish, and crustaceans (12, 13, 18, 45, 46, 52, 54, 59); and in atmospheric dusts, especially those of industrial districts and large cities (36, 49).

Inasmuch as crude sulfuric acid manufactured from pyrite and other sulfide ores, especially by the chamber process, usually contains an appreciable quantity of arsenic (1, 16, 28, 58, 88, 127, 130; 149, pp. 337-338), products made either directly or indirectly with such acid often contain notable amounts of this element (1, 15, 16, 39, 40, 44, 57, 76, 88, 108, 109, 127, 147). The presence of arsenic in superphosphate was pointed out by Davy (28) in 1859, and subsequently a few scattered results for this element in fertilizers and

<sup>1</sup> Submitted for publication December 1940.  
<sup>2</sup> The authors are indebted to W. L. Hill, Division of Fertilizer Research, for many helpful suggestions during the course of this work; to H. L. Marshall and D. S. Reynolds, Division of Fertilizer Research, for a portion of the supplementary analytical data; to J. A. Schriker, formerly of the Division of Soil Fertility Investigations, for valuable advice on the construction of the photoelectric colorimeter; and to a number of phosphate mining companies and fertilizer manufacturers for many of the samples.  
<sup>3</sup> Italic numbers in parentheses refer to Literature Cited, p. 31.

fertilizer materials have appeared in the literature (2a, 5, 42, 48, 49, 56, 58, 59, 67, 68, 73, 81, 89, 94, 104, 120, 130, 131, 151).

Results are given in this publication for arsenic in 210 samples of mineral phosphates from various deposits of the world, 16 samples of calcined, sintered, nodulized, and defluorinated phosphates, 30 samples of commercial superphosphates, 6 samples of crude phosphoric acid produced by the sulfuric acid process, and 19 samples of other phosphatic materials. The results for arsenic in natural phosphates represent an extension of the studies of this Division on the composition of phosphate rock (60, 61, 64, 65, 66, 68, 69, 80, 81, 82, 97, 98, 110, 111, 118).

### METHOD OF ANALYSIS

The method used for the determination of arsenic is substantially the one developed by Deemer and Schrieker (30) for the analysis of plant materials, with the inclusion of certain improvements suggested by Schrieker and Dawson (123). The method comprises the digestion of the sample with a mixture of sulfuric and nitric acids, the distillation of the arsenic as the trichloride, essentially by Taber's procedure (133), and its determination by the molybdenum-blue colorimetric method proposed by Denigès (31, 32). Denigès' original procedure has been modified and improved by Truog and Meyer (138) and Zinzadze (152, 153), as well as by Schrieker and coworkers (30, 123).

The authors' application of the method to the determination of arsenic in phosphates can be conveniently presented under the subjects: (1) Reagents and glassware, (2) separation of arsenic from the sample, and (3) procedure used.

### REAGENTS AND GLASSWARE

On account of the relatively large quantity of reagents required for the determination of the small quantities of arsenic involved (usually less than 50 parts per million), special attention had to be given to the arsenic content of the reagents. Sodium carbonate, beta-dinitrophenol, molybdenum trioxide, and molybdenum metal are used in such small quantities that they are not likely to introduce significant amounts of arsenic. Hydrochloric, nitric, and sulfuric acids, ammonium oxalate, and potassium bromide of reagent grade, and sodium chloride that had been purified for biological work were very satisfactory. Cuprous chloride that meets the American Chemical Society's specifications for analytical reagent chemicals (10) is not suitable because of the relatively high arsenic tolerance (50 p. p. m.). Cuprous chloride that contains not more than 0.5 p. p. m. of arsenic can, however, be obtained from certain manufacturers of laboratory chemicals.

In 1935, Lockemann (92, 93) pointed out that hot, concentrated sulfuric acid dissolves appreciable quantities of arsenic from Jena glass, and he expressed the opinion that disregard of this factor has caused serious error in many of the older determinations of arsenic. Deckert (29) said the quantity of arsenic dissolved from the glass during the analysis can be greatly decreased by first boiling concentrated sulfuric acid in the flask for at least 2 hours; also, he stated

that arsenic-free Jena glassware made prior to about tenths of 1 percent of arsenic since that time show less.

Confirming Deckert's experience with previously used flasks was as for low-arsenic glass (6) blank was significantly higher had not been used previous materials, however, the quantity of high-arsenic glass was low-arsenic glass. As percentage of fluorine (81, 82, 98, 111) constituent of superphosphatic fertilizers,<sup>5</sup> such material contains little or no arsenic that the use of boron-coated determination of boron in fluorine-bearing materials storage of superphosphatic fluorine compounds may sample with arsenic from

TABLE 1.—Derivation of arsenic

Material	Derivation of arsenic
Reagents alone	.....
Do	.....
Reagents+0.1 gm. fluorspar	.....
Reagents+0.1 gm. sodium fluoride	.....
Reagents+1 gm. phosphate rock <sup>3</sup>	.....

<sup>1</sup> 500-ml. Kjeldahl flasks of Pyrex glass.  
<sup>2</sup> New flasks, not previously used; 20 of times.  
<sup>3</sup> Florida land pebble, standard source percent of fluorine (73).

By careful selection of glassware, the reagent blank throughout this investigation

### SEPARATION

The authors' recovery results alone and in the presence of Schrieker (30).

<sup>4</sup> Also, SILETTERLY, F. F. Private communication.  
<sup>5</sup> For example, the materials listed in 2.35, 2.63, 2.41, 1.26, 3.96, 0.83, and 2.04.

42, 48, 49, 56,  
10 samples of  
16 samples of  
osphates, 30  
crude phos-  
19 samples of  
e in natural  
s Division on  
8, 69, 80, 81,

substantially  
ie analysis of  
nts suggested  
the digestion  
he distillation  
s procedure  
colorimetric  
al procedure  
er (138) and  
ers (30, 123).  
mination of  
d under the  
arsenic from

ents required  
nic involved  
on had to be  
n carbonate,  
lenum metal  
to introduce  
and sulfuric  
agent grade,  
al work were  
rican Chemi-  
icals (10) is  
(50 p. p. m.).  
m. of arsenic  
ers of labo-

concentrated  
e from Jena  
is factor has  
is of arsenic.  
m the glass  
iling concen-  
so, he stated

that arsenic-free Jena glass is manufactured. Pyrex chemical glass-ware made prior to about the middle of the year 1934 contained a few tenths of 1 percent of arsenic, but analyses of the glass manufactured since that time show less than 0.3 p. p. m. of arsenic (134, 143).<sup>4</sup>

Confirming Deckert's results (29), the reagent blank obtained with previously used flasks was practically the same for high-arsenic glass as for low-arsenic glass (table 1). It will be noted that the reagent blank was significantly higher with new flasks of low-arsenic glass that had not been used previously. In the presence of fluorine-bearing materials, however, the quantity of arsenic obtained with flasks made of high-arsenic glass was 1.6 to 9.2 times that found with flasks of low-arsenic glass. As phosphate rock usually contains 3 to 4 percent of fluorine (81, 82, 98, 118) and this element is also an important constituent of superphosphates (63, 82), as well as of certain other phosphatic fertilizers,<sup>5</sup> such materials should be digested in glassware that contains little or no arsenic. Likewise, Rader and Hill (111) found that the use of boron-containing glassware causes large errors in the determination of boron in phosphate rock, superphosphate, and other fluorine-bearing materials. Furthermore, the use of bottles for the storage of superphosphates and other materials that contain active fluorine compounds may also result in serious contamination of the sample with arsenic from the glass (p. 25).

TABLE 1.—Derivation of arsenic from glassware in the analysis of fluorine-bearing materials

Material analyzed	Arsenic found by digestion in—	
	Low-arsenic glass <sup>1</sup>	High-arsenic glass <sup>1</sup>
	Milligrams	Milligrams
Reagents alone.....	0.0678	
Do.....		
Reagents+0.1 gm. fluorspar.....	.0050	0.0048
Reagents+0.1 gm. sodium fluoride.....	.0104	.0832
Reagents+1 gm. phosphate rock <sup>2</sup> .....	.0096	.0588
	.0188	.0290

<sup>1</sup> 500-ml. Kjeldahl flasks of Pyrex glass.  
<sup>2</sup> New flasks, not previously used; all other digestions were made in flasks that had been used a number of times.  
<sup>3</sup> Florida land pebble, standard sample No. 120 of the National Bureau of Standards, contained 3.76 percent of fluorine (73).

By careful selection of the chemicals and the use of low-arsenic glassware, the reagent blanks were kept below 0.006 mg. of arsenic throughout this investigation.

SEPARATION OF ARSENIC FROM THE SAMPLE

The authors' recovery of arsenic from monopotassium arsenate, alone and in the presence of phosphate rock, is shown in table 2. The results are in good agreement with those reported by Deemer and Schricker (30).

<sup>4</sup> Also, SHETTERLY, F. F. Private communication. Corning Glass Works, Corning, N. Y.  
<sup>5</sup> For example, the materials listed in table 17 as Nos. 1885, 1849, 1901, 1902, 1921, 1538, and 1172 contain 3.35, 2.63, 2.41, 1.25, 3.96, 0.83, and 2.06 percent of fluorine, respectively.

TABLE 2.—Recovery of arsenic from monopotassium arsenate by digestion and distillation

Material or mixture	Arsenic from monopotassium arsenate		
	Present	Recovered	
	Milligrams	Milligrams	Percent
Monopotassium arsenate (KH <sub>2</sub> AsO <sub>4</sub> )	0.005	0.0030	100.0
	.005	.0050	100.0
	.025	.0255	102.0
	.100	.0248	99.2
	.100	.1017	101.7
KH <sub>2</sub> AsO <sub>4</sub> +1 gm. phosphate rock <sup>1</sup>	.100	.1006	100.6
	.025	.0246	98.4
	.025	.0247	98.8

<sup>1</sup> Distillate was made up to a volume of 100 ml., and 25-ml. aliquots were used for development of the molybdenum-blue color.

<sup>2</sup> Florida land pebble, standard sample No. 120 of the National Bureau of Standards.

Experiments by Hoffman and Lundell (74) indicate that boron, germanium, mercury, rhenium, antimony, selenium, and tin, if present in the digested sample, may follow the arsenic, completely or in part, into the distillate. Extensive determinations of these elements in mineral phosphates have been made only in the case of selenium (110) and boron (111). Small quantities of selenium, such as those present in soils and phosphate rocks, do not interfere in the determination of arsenic by the molybdenum-blue method (126). Little or no interference by boron is indicated by the small effect of fluoride additions on determinations made in low-arsenic glass, in comparison with the effect of such additions on those made in high-arsenic glass (table 1), although considerable boron is doubtless dissolved from both kinds of glass in the presence of fluorine.

Small quantities of tin have been reported in double superphosphate and bonemeal (42) and in phosphate rocks from Florida, Tennessee, and Maxville, Mont. (42, 73, 106). Hill, Marshall, and Jacob state that samples of Florida land pebble, Tennessee blue rock, and Idaho phosphates were tested for molybdenum with negative results (68). However, neither of these elements would be expected to interfere in the determination of arsenic. Spectrochemical analyses by Scribner (73) showed no antimony in one sample each of Florida land pebble and Tennessee brown rock; so far as the authors know, these are the only tests that have been made for antimony in natural phosphates. According to Byers and Robinson,<sup>6</sup> small quantities of antimony do not interfere in the determination of arsenic by distillation with hydrobromic acid at 126° C. and subsequent analysis of the distillate by the molybdenum-blue method.

Apparently no tests for rhenium in natural phosphates have been made, and, so far as the authors know, only two samples of phosphate rock have been examined for mercury, both with negative results (73). Likewise, spectrochemical analyses showed no germanium in Florida land pebble, Tennessee brown rock, and Maxville, Mont., phosphates (73, 106). The authors' experiments indicated little or no interference by added germanium in the determination of arsenic.

Silica interferes slightly when the quantity in the final solution exceeds 1 mg. per milliliter (123). In the analysis of fluorine-bearing materials, silica may be present in the solution as a result of volatiliza-

<sup>6</sup> BYERS, H. G., and ROBINSON, W. O. Private communication. Bureau of Plant Industry.

tion in combination with volatilization occurs only by the fact that distillate (3.56 percent fluorine). Furthermore, there was itself.

Phosphorus interferes for arsenic (123). Hoffmann and Lundell (74) reported the presence of heating phosphates with than 150°. In the distillate in the distillation of phosphorus in the distillate.

Total arsenic, as determined by direct digestion of phosphate rocks by fusion with a mixture of sodium carbonate prior to the acid digestion, increase in the recovery.

Add 10 ml. of concentrated sulfuric acid to the sample and dilute to a volume of 100 ml. in a free glass. (Concentrated sulfuric acid for at least 1 hour before use in strong fuming sets in the room temperature. Add contents of the flask by rinsing the walls of the flask with 25 ml. of water; if necessary, add oxalate, and repeat the procedure.)

Add to the cold digestate a few drops of cuprous chloride solution. Add concentrated hydrochloric acid and a rubber stopper carrying a glass tube inside diameter, consistent with the exit). Allow the digestate to settle at the bottom of a 100-ml. beaker. Add distilled water and is immediately and control the rate of distillation obtained in about 10 minutes. electrically heated by a power source for the distillation.

After the distillation is complete, add acid to the solution and dilute to a 150-ml. beaker.

<sup>7</sup> Although larger samples may be analyzed, a blue color is developed only when the

tion in combination with fluorine during the distillation. That such volatilization occurs only to a negligible extent, if at all, is indicated by the fact that distillates from 1-gm. samples of phosphate rock (3.56 percent fluorine) contained no more than 0.1 mg. of fluorine. Furthermore, there was no evidence of interference by the fluorine itself.

Phosphorus interferes quantitatively in the molybdenum-blue test for arsenic (123). Hoffman and Lundell (74) found that some phosphorus is volatilized when phosphates are heated at 200° to 220° C. with mixtures of hydrochloric or hydrobromic and sulfuric or perchloric acids in a moderate stream of dry carbon dioxide, and Reynolds (116) reported the presence of phosphorus in certain distillates obtained by heating phosphates with perchloric acid at temperatures not higher than 150°. In the determination of arsenic, the maximum temperature in the distillation mixture is approximately 125°, and the presence of phosphorus in the distillate has not been observed.

Total arsenic, as distinguished from acid-soluble arsenic obtained by direct digestion of the sample, was determined in a few typical phosphate rocks by fusing the sample with 2.2 times its weight of a mixture of sodium carbonate (1 part) and sodium nitrate (0.1 part) prior to the acid digestion (70, p. 209). The results showed little or no increase in the recovered arsenic as a result of fusion of the sample.

PROCEDURE USED

Add 10 ml. of concentrated nitric acid and 30 ml. of concentrated sulfuric acid to the sample, preferably of such weight that the arsenic content is 0.005 to 0.040 mg.,<sup>7</sup> in a 500-ml. Kjeldahl flask of arsenic-free glass. (Concentrated sulfuric acid should be boiled in new flasks for at least 1 hour before they are placed in use.) Heat the flask until strong fuming sets in, boil the contents for 30 minutes, and then cool to room temperature. Add 20 ml. of distilled water, and mix the contents of the flask by gentle swirling, add 2 gm. of ammonium oxalate, rinse the walls of the flask with 2 to 3 ml. of water, and boil the contents for 30 minutes. Cool the flask, and dilute the contents with 25 ml. of water; if nitrous fumes are evolved add more ammonium oxalate, and repeat the digestion.

Add to the cold digestion mixture 30 gm. of sodium chloride, 2 gm. of cuprous chloride, 0.5 gm. of potassium bromide, and 25 ml. of concentrated hydrochloric acid, and immediately close the flask with a rubber stopper carrying a Hopkins trap fused to a delivery tube (3 mm. inside diameter, constricted to about 1 mm. inside diameter at the exit). Allow the delivery tube to extend within 2 to 3 mm. of the bottom of a 100-ml. graduated cylinder that contains 70 ml. of distilled water and is immersed in an ice bath. Heat the Kjeldahl flask and control the rate of distillation so that 25 ml. of distillate are obtained in about 30 minutes. A resistance unit of the type used in electrically heated Kjeldahl outfits is a very convenient source of heat for the distillation.

After the distillation is completed, add 10 ml. of concentrated nitric acid to the solution in the graduated cylinder, transfer the contents to a 150-ml. beaker, and evaporate on a steam bath or hot plate to a

<sup>7</sup> Although larger samples can be used, the quantity of arsenic in the solution at the time the molybdenum-blue color is developed should fall within these limits.

TURE

tion and dis-

assium arsenate

recovered

mg	Percent
150	100.0
150	100.0
255	102.0
243	99.2
117	101.7
106	100.6
94	98.4
47	98.8

development of the

that boron, if present or in part, elements in sodium (110) are present combination of no inter-additions with the (table 1), the kinds of

phosphate Tennessee, Michigan state and Idaho salts (68). interfere in Scribner and pebble are the phosphates. tion with distillate

have been phosphate salts (73). a Florida phosphates no inter-

l solution e-bearing volatiliza-ry.

volume of approximately 10 ml. with the occasional addition of 1 to 2 ml. of concentrated nitric acid, if necessary, to insure complete elimination of chlorine from the solution. Evaporate the colorless solution to dryness on a steam bath, add 1 to 2 ml. of concentrated nitric acid, and again evaporate to dryness. Finally, add 1 ml. of a 1-percent solution of sulfuric acid and evaporate on the steam bath to the consistency of a thick sirup.

Dissolve the sirupy solution in 7 to 10 ml. of hot water, and transfer it to a 50-ml. volumetric flask, taking care that the total volume of the solution is slightly below 40 ml. Add 1 drop of a saturated aqueous solution of beta-dinitrophenol, make slightly alkaline with a 0.36 N aqueous solution of sodium carbonate, and carefully neutralize with 1-percent sulfuric acid solution. Then add exactly 0.5 ml. of molybdenum-blue reagent,<sup>8</sup> rinse the neck of the flask with a small quantity of distilled water, adjust the volume of the solution to approximately 40 ml., and heat the flask on a steam bath for 1 hour with occasional swirling of the contents. Cool the solution, dilute it with distilled water to a volume of 50 ml., and immediately compare the color with that of similarly treated standard arsenic solutions by means of either a visual or a photoelectric colorimeter. As pointed out by Deemer and Schrieker (30), further dilution of the solution after the volume has been adjusted to 50 ml. is not permissible.

A photoelectric colorimeter<sup>9</sup> is preferable to a visual instrument. Its use not only affords greater precision but also eliminates the personal equation from the matching of the colors and the necessity for the continual preparation of fresh standards. According to Schrieker and Dawson (123), the precision of the molybdenum-blue method is approximately 0.001 mg. of arsenic in 50 ml. of solution when the color intensity is measured with a photoelectric colorimeter.

With samples of phosphates containing up to 100 p. p. m. of arsenic, the difference between duplicate determinations seldom exceeded 0.5 p. p. m. and was usually less than 0.3 p. p. m. of arsenic. With larger quantities of arsenic the differences were frequently somewhat greater.

### ARSENIC IN MINERAL PHOSPHATES

Results for acid-soluble arsenic in mineral phosphates are given in tables 3, 4, 5, 6, and 7 and are summarized in table 8. Values for phosphorus pentoxide content are also given in these and later tables for purposes of comparison. Except as otherwise indicated, the analytical data in these and other tables are reported on the moisture-free basis (105° C.). For individual samples of all types and sources of phosphate, the results range from 0.4 p. p. m. in a Florida soft phosphate (No. 1091, table 3) to 188.2 p. p. m. in an Arkansas phosphate (No. 1712, table 5). The arsenic contents of the South Carolina river rock (average 68.4 p. p. m.), Arkansas phosphate (average 61.0

<sup>8</sup> Heat a quantity of molybdenum trioxide in an electric muffle furnace at approximately 500° C. for 1 hour, and dissolve 48 gm. of the cold, ignited trioxide in 1 liter of hot, concentrated sulfuric acid, stirring frequently (solution 1). Dissolve 4.8 gm. of the ignited trioxide and 0.7 gm. of pure molybdenum metal powder in 100 ml. of hot, concentrated sulfuric acid, stirring frequently (solution 2). Cool the solutions, and prepare the reagent solution by diluting 100 ml. of solution 2 to 1 liter with solution 1.

<sup>9</sup> Practically all of the results for arsenic given in this publication were obtained with the aid of a photoelectric colorimeter that was copied, with slight modification, from an instrument constructed by John A. Schrieker of this Bureau (private communication). The general principle of the colorimeter is similar to that of the instruments described by Zinzadze (154) and Barton and Yoe (9).

p. p. m.), and Montana phosphate, general, considerably higher than the other extreme are Florida averages of 5.4 and 5.5 p. p. m. and Tennessee brown rock and phosphates, average 11.9 and

TABLE 3

Sample No.	Location of deposit	As, p. p. m.	P <sub>2</sub> O <sub>5</sub> , %
1448	Bartow.....	28.21	30.41
1853	do.....	30.51	30.51
618	Pierce.....	30.51	30.51
617	Brewster.....	30.51	30.51
619	Nichols.....	31.00	31.00
910	Mulberry.....	31.28	31.28
947	Brewster.....	31.60	31.60
780	Not known.....	32.17	32.17
1879	do.....	32.17	32.17
1857	do.....	32.17	32.17
1893	do.....	32.17	32.17
1895	do.....	32.17	32.17
439	Mulberry.....	31.00	31.00
1882	Not known.....	31.00	31.00
622	Nichols.....	34.00	34.00
1875	Bartow.....	31.00	31.00

771	Not known.....	31.00	31.00
590	Benotls.....	31.00	31.00
691	Inverness.....	31.00	31.00
689	Floral City.....	31.00	31.00

1091	Bartow.....	0.4	30.41
680	Not known.....	0.4	30.41
1359	Hardee County <sup>10</sup>	0.4	30.41

581	Not known.....	15.00	30.41
828	Felicia.....	15.00	30.41
727	Dunclon.....	21.00	30.41
726	Felicia.....	21.00	30.41

1946	Liverpool <sup>11</sup> .....	77.71	30.41
------	-------------------------------	-------	-------

- <sup>1</sup> Dust recovered from exit gases of blast furnace.
- <sup>2</sup> Sample representative of large shipment.
- <sup>3</sup> Analysis reported by Jacoby, H. G.
- <sup>4</sup> Concentrated by froth flotation.
- <sup>5</sup> Concentrated by oiling and tabling.
- <sup>6</sup> Standard sample number of the Bureau.
- <sup>7</sup> 13.6 p. p. m. of As in this sample.
- <sup>8</sup> Contains much aluminum phosphate.
- <sup>9</sup> Contains principally aluminum phosphate.
- <sup>10</sup> Deposit east of Peace River, De Soto County.
- <sup>11</sup> Commercial material as furnished by De Soto County.



p. p. m.), and Montana phosphate (average 47.6 p. p. m.) are, in general, considerably higher than those of the other phosphates. At the other extreme are Florida hard rock and Virginia apatite, with averages of 5.4 and 5.5 p. p. m., respectively. Florida land pebble and Tennessee brown rock, the most widely used of the domestic phosphates, average 11.9 and 14.6 p. p. m. of arsenic, respectively.

TABLE 3.—Arsenic in Florida phosphates

LAND-PEBBLE PHOSPHATE							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As	Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As
		Percent	P. p. m.			Percent	P. p. m.
1448	Bartow.....	28.23	18.5	627	Lakeland.....	33.70	13.4
1853	do.....	30.37	10.5	1891	Not known.....	33.80	8.5
618	Pierce.....	30.53	18.2	1873	do.....	34.03	12.1
617	Brewster.....	30.70	19.7	1884	do.....	34.12	15.4
619	Nichols.....	30.98	11.6	1855	do.....	34.41	7.6
916	Mulberry.....	31.09	21.2	1310	Mulberry.....	34.44	14.2
947	Brewster.....	31.28	17.3	1851	Bartow.....	34.88	8.4
790	Not known.....	31.40	12.3	1447	do.....	35.11	11.4
1879	do.....	32.32	16.3	1445	Pembroke.....	35.16	8.3
1857	do.....	32.35	15.4	1302	Mulberry.....	35.18	18.3
1893	do.....	32.82	9.8	912	do.....	35.37	10.6
1895	do.....	33.02	12.3	1850	Not known.....	35.38	3.6
439	Mulberry.....	33.22	9.8	120	Mulberry.....	35.40	12.9
1882	Not known.....	33.47	8.3	1867	Not known.....	35.47	4.3
622	Nichols.....	33.56	5.4	898	Lakeland.....	35.53	5.5
1875	Bartow.....	33.59	9.9				

HARD-ROCK PHOSPHATE							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As	Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As
		Percent	P. p. m.			Percent	P. p. m.
771	Not known.....	31.25	3.0	434	Dunnellon.....	35.33	1.4
590	Benotis.....	33.52	6.8	588	Floral City.....	35.70	2.8
591	Inverness.....	33.52	8.7	623	Hernando.....	35.74	4.6
589	Floral City.....	34.68	7.1	932	Dunnellon.....	35.99	9.1

SOFT PHOSPHATE							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As	Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As
		Percent	P. p. m.			Percent	P. p. m.
1091	Bartow.....	25.47	0.4	728	Juliette.....	31.90	5.9
580	Not known.....	29.49	18.6	1450	Rital.....	32.78	5.5
1359	Hardee County <sup>o</sup> .....	30.32	13.3	443	Gilchrist County.....	34.94	1.3

WASTE-POND PHOSPHATE							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As	Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As
		Percent	P. p. m.			Percent	P. p. m.
581	Not known.....	18.18	7.1	915	Dunnellon.....	23.63	5.3
628	Felicia.....	19.33	9.5	1459	Felicia.....	25.11	12.1
727	Dunnellon.....	21.63	9.2	725	Juliette.....	25.31	8.0
726	Felicia.....	23.48	10.4	1455	Hernando.....	32.80	10.4

RIVER-PEBBLE PHOSPHATE							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As	Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As
		Percent	P. p. m.			Percent	P. p. m.
1946	Liverpool <sup>u</sup> .....	27.77	21.2				

<sup>1</sup> Dust recovered from exit gases of dryers and kilns.  
<sup>2</sup> Sample representative of large shipment.  
<sup>3</sup> Analysis reported by Jacob, Hill, Marshall, and Reynolds (81, p. 30).  
<sup>4</sup> Concentrated by froth flotation.  
<sup>5</sup> Concentrated by oiling and tabling.  
<sup>6</sup> Standard sample number of the National Bureau of Standards. Hoffman and Lundell (73) reported 13.6 p. p. m. of As in this sample.  
<sup>7</sup> Contains much aluminum phosphate.  
<sup>8</sup> Contains principally aluminum phosphate.  
<sup>9</sup> Deposit east of Peace River, near Wauchula.  
<sup>o</sup> Commercial material as formerly produced.  
<sup>u</sup> De Soto County.

TABLE 4.—Arsenic in Tennessee phosphates  
BROWN-ROCK PHOSPHATE

Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>		Sample No.	Location of deposit	As	
		Percent	P. p. m.			Percent	P. p. m.
1321	Franklin.....	19.46	9.2	762	Mount Pleasant.....	33.73	7.9
1922	Columbia.....	22.85	56.1	906	Wales.....	34.39	24.2
1913	Franklin.....	22.95	7.4	1861	Not known.....	34.40	6.6
1916	Mount Pleasant.....	23.38	7.6	908	Mount Pleasant.....	34.44	13.0
1482	Match.....	28.67	12.3	1863	Not known.....	34.52	11.9
587	Wales.....	30.17	25.9	1871	do.....	34.53	5.1
56	Not known.....	31.28	28.9	1899	do.....	34.84	6.6
1340	Centerville.....	32.07	22.6	1893	Wales.....	34.92	13.1
1926	Mount Pleasant.....	32.08	13.4	1897	do.....	34.96	7.7
664	Wales.....	32.85	17.9	1342	Mount Pleasant.....	35.77	10.5
586a	Mount Pleasant.....	32.94	14.2	1317	Not known.....	36.52	14.8
1924	do.....	33.53	7.2	1401	Wales.....	36.74	13.8
1889	Siglo.....		6.4				

BLUE-ROCK PHOSPHATE							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>		Sample No.	Location of deposit	As	
		Percent	P. p. m.			Percent	P. p. m.
571	Gordonsburg.....	27.90	16.6	576	Gordonsburg.....	31.22	21.4
572	do.....	29.16	19.8	448	do.....	32.03	21.4
772	Glover.....	30.45	17.4	449	do.....	33.65	8.4
980	Gordonsburg.....	30.97	37.7				

WHITE-ROCK PHOSPHATE							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>		Sample No.	Location of deposit	As	
		Percent	P. p. m.			Percent	P. p. m.
1483	Perry County.....	28.41	21.7	1031	Godwin.....	35.80	4.8
1048	Toms creek.....	30.20	5.2				

PHOSPHATIC LIMESTONE							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>		Sample No.	Location of deposit	As	
		Percent	P. p. m.			Percent	P. p. m.
446	Gordonsburg.....	10.16	13.9	447	Mount Pleasant.....	14.04	11.4
916	Mount Pleasant.....	11.22	6.9	770	Not known.....	19.13	23.5
917	Gordonsburg.....	11.68	17.3				

OTHER PHOSPHATES							
Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>		Sample No.	Location of deposit	As	
		Percent	P. p. m.			Percent	P. p. m.
1516	Mountain City.....	29.26	8.6	1049	Boma.....	31.22	8.9

<sup>1</sup> Matrix.

<sup>2</sup> Mixture of matrix and washed phosphate sand; used for production of sinter for electric furnace smelting.

<sup>3</sup> Analysis reported by Jacob, Hill, Marshall, and Reynolds (81, p. 29).

<sup>4</sup> Standard sample number of the National Bureau of Standards. Hoffman and Landell (73) reported 15.9 p. p. m. of As in this sample.

<sup>5</sup> Concentrated by froth flotation.

<sup>6</sup> Sample representative of large shipment.

<sup>7</sup> Johnson County.

<sup>8</sup> Kidney phosphate.

<sup>9</sup> Putnam County.

TABLE 5.—Arsenic in Arkansas

Sample No.	Location of deposit	As
1708	Independence County	
1710	do	
1712	do	
1705	do	
1235	Wallace	
1245	do	
1714	Pontotoc County	
1242	Cotton County	
SOUTH CAROLINA		
405	Not known	
1139	Johns Island	
SOUTH CAROLINA		
1646	Broad River	
1645	Cosaw River	
1136	Piney River	
<sup>1</sup> Prospect sample. <sup>2</sup> Lafferty Creek area. <sup>3</sup> Selected material. <sup>4</sup> Sample from an abandoned mine. <sup>5</sup> Ground material formerly used for fertilizer. <sup>6</sup> Musonza sample. <sup>7</sup> Commercial material as later reported. <sup>8</sup> Lamb's mine. <sup>9</sup> Bulow mines. <sup>10</sup> Analysis reported by Jacob, Hill, Marshall, and Reynolds (81, p. 29). <sup>11</sup> Mouth of White Branch. <sup>12</sup> Brickyard Point. <sup>13</sup> Mouth of Bull River. <sup>14</sup> Fluorapatite concentrate obtained from the same source.		

TABLE 5.—Arsenic in Arkansas, Kentucky, Oklahoma, South Carolina, and Virginia phosphates

ARKANSAS PHOSPHATES

Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As	Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As
		Percent	P. p. m.			Percent	P. p. m.
1768	Independence County <sup>1</sup>	21.14	67.3	1713	Independence County <sup>2</sup>	29.02	66.6
1710	do <sup>2</sup>	22.34	44.9	1707	do <sup>2</sup>	31.51	42.8
1712	do <sup>2</sup>	23.98	188.2	1287	do <sup>1</sup>	31.98	32.6
1705	do <sup>1</sup>	27.14	36.7	1708	do <sup>2</sup>	33.73	14.6

KENTUCKY PHOSPHATES

1235	Wallace	21.19	10.3	1234	Wallace	27.89	6.7
1245	do	23.68	12.7				

OKLAHOMA PHOSPHATES

1714	Pontotoc County	12.60	17.9	1716	Craig County	27.51	19.3
1242	Cotton County	24.31	18.6				

SOUTH CAROLINA LAND-ROCK PHOSPHATE

405	Not known	16.07	9.2	1137	Charleston <sup>3</sup>	27.58	18.9
1139	Johas Island <sup>4</sup>	26.92	27.5	1138	do <sup>1</sup>	27.85	12.0

SOUTH CAROLINA RIVER-ROCK PHOSPHATE

1646	Broad River <sup>11</sup>	26.74	83.1	1617	Broad River	26.97	67.9
1645	Coosaw River <sup>12</sup>	23.91	60.7	1612	Coosaw River <sup>12</sup>	27.31	56.8

VIRGINIA PHOSPHATES<sup>13</sup>

1136	Piney River	38.12	6.6	1295	Piney River	39.50	4.3
------	-------------	-------	-----	------	-------------	-------	-----

- <sup>1</sup> Prospect sample.
- <sup>2</sup> Lafferty Creek area.
- <sup>3</sup> Selected material.
- <sup>4</sup> Sample from an abandoned mine.
- <sup>5</sup> Ground material formerly sold for direct application to the soil.
- <sup>6</sup> Museum sample.
- <sup>7</sup> Commercial material as formerly produced.
- <sup>8</sup> Lamb's mine.
- <sup>9</sup> Bulow mines.
- <sup>10</sup> Analysis reported by Jacob, Hill, Marshall, and Reynolds (*St. p. 30*).
- <sup>11</sup> Mouth of Whale Branch.
- <sup>12</sup> Brickyard Point.
- <sup>13</sup> Mouth of Bull River.
- <sup>14</sup> Fluorapatite concentrate obtained from ilmenite-apatite ore by a magnetic separation process (*36*).

306609°-41-2

TABLE 6.—Arsenic in Idaho, Montana, Utah, and Wyoming phosphates

Sample No.	Location of deposit	IDAHO PHOSPHATES	
		P <sub>2</sub> O <sub>5</sub>	As
		Percent	P. p. m.
1607	Bingham County, Wolverine Creek Canyon.....	22.19	4.5
1411	Bear Lake County, Georgetown Canyon.....	30.30	8.7
1530	Bear Lake County, Paris area.....	32.21	21.5
1609	Caribou County, Wells Canyon.....	32.21	10.3
454	Caribou County, Conda.....	32.24	15.4
1408	do.....	32.26	14.8
1253	do.....	32.36	15.1
973	do.....	32.53	17.7
1865	do.....	32.54	9.8
1008	Caribou County, Diamond Gulch.....	33.12	10.5
1617	Bear Lake County, Hot Springs.....	34.85	7.8
1616	Bear Lake County, Bloomington Canyon.....	35.15	11.3
1412	Bear Lake County, Slight Canyon.....	35.39	9.3
1613	Caribou County, Upper Deer Creek Canyon.....	35.53	25.7
1614	Caribou County, sec. 9, T. 7 S., R. 4 E.....	35.95	4.9
1606	Fort Hall Indian Reservation, SE¼ sec. 2, T. 4 S., R. 37 E.....	36.10	16.0
MONTANA PHOSPHATES			
1280	Marville.....	24.96	12.3
1011	Garrison, William Anderson mine.....	27.63	495.6
1099	do.....	31.39	106.0
1930	do.....	31.62	58.7
1017	do.....	34.92	39.7
1633	Avon, Cronin and Crowley mine.....	34.97	68.2
1252	Garrison, William Anderson mine.....	36.38	41.0
1040	do.....	37.47	18.2
1407	Avon, Cronin and Crowley mine.....	37.94	17.7
UTAH PHOSPHATES			
1041	Uintah County, Brush Creek area.....	16.74	15.3
1634	do.....	20.82	16.4
1637	do.....	26.41	13.2
1400	Morgan County, Weber Canyon.....	26.90	19.2
1681	Uintah County, Ashley Creek Gorge.....	27.62	43.2
1409	Cache County, Logan Canyon.....	31.50	18.0
1630	Rich County, Brazer Canyon.....	35.17	8.4
1620	Rich County, north end of Crawford Mountains.....	37.87	8.6
WYOMING PHOSPHATES			
1624	Hot Springs County, Bighorn River Canyon.....	17.56	7.6
1621	Fremont County, Willow Creek.....	24.12	10.8
460	Cokeville, mine of Cokeville Phosphate Co.....	26.60	18.8
1623	Fremont County, Little Pope Agie Canyon.....	27.60	10.9
1622	Fremont County, Willow Creek.....	29.06	13.8
948	Cokeville, mine of Cokeville Phosphate Co.....	30.19	11.7
1625	Lincoln County, Beckwith Hills.....	31.80	8.0
1626	Lincoln County, Raymond Canyon.....	33.98	8.8
1627	Teton County, Talbot Creek.....	37.00	17.3

- 1 Sample from outcrop of deposit.  
 2 Commercial material as formerly produced.  
 3 Float phosphate.  
 4 Commercial material.  
 5 Composite sample of shipments during the period Sept. 25, 1934, to Jan. 1, 1935.  
 6 Partially weathered material from old mine dump.  
 7 Prospect sample.  
 8 Analysts reported by Jacob, Hill, Marshall, and Rader (81, p. 30).  
 9 Sample from dump of old Bradley mine.  
 10 Sample from outcrop of upper phosphate bed.  
 11 Sample representative of large shipment.  
 12 Sample from outcrop of lower phosphate bed.

Sample No.	Location
560	Algeria, Dyr
1558	Algeria, Djebel Kou
1459	Algeria, Djebel Kou
550	Algeria, Bordj-Bordj
1547	Egypt, Safage
1549	do
1571	Morocco, Louis-Ger
1672	Morocco, Kourigha
563	Morocco
1162	do
556	Tunisia, Kalaw-Djer
552	Tunisia, Gafsa
1531	do

1462	Austria, Fraubuch
1220	Belgium, Liège
1155	Estonia, Tallinn
1240	France, Soume
1463	Poland
1203	U. S. S. R., Souda
1261	U. S. S. R., Egnay
1262	U. S. S. R., Vyatka
1305	U. S. S. R., Krasn
1260	do

1223	Ancient Island
1207	Assumption
1480	Astley Island
1585	Cherbourg
152	do
1545	Carageo Island
985	do
943	do
1589	Datto Island
1286	Denis Island
4001	Grand Cay
1222	Iran de N
1230	Makatea
1150	do
450	Nauru Island
1567	do
1596	Ocean Island
451	do
1597	Peleiti Island
1501	Russ Island
1300	Walpole

882	Canada, Br
1906	Canada, G
1157	South Aus
1188	South Aus

- 1 Fluorapatite, calc  
 2 Fluorapatite, calc  
 3 Aluminat  
 4 Aluminat  
 5 Fluorapatite

osphates

TABLE 7.—Arsenic in foreign phosphates  
AFRICAN PHOSPHATES

Sample No.	Location of deposit	P <sub>2</sub> O <sub>5</sub>	As
		Percent	P. p. m.
560	Algeria, Dyr.....	23.39	16.3
1556	Algeria, Djebel Onk.....	27.08	14.4
1559	Algeria, Djebel Konif.....	29.99	7.6
559	Algeria, Bordj-Redir.....	32.34	30.7
1547	Egypt, Safaga.....	27.70	22.1
1549	do.....	32.79	14.1
1571	Morocco, Louis-Gentil.....	31.86	7.7
1672	Morocco, Kourigha.....	34.07	9.7
563	Morocco.....	34.30	10.4
1162	do.....	35.11	25.2
558	Tunisia, Kalaa-Djerda.....	26.91	19.1
552	Tunisia, Gafsa.....	27.55	27.6
1651	do.....	29.04	9.6

## EUROPEAN PHOSPHATES

1462	Austria, Frambachkirchen.....	27.03	15.3
1226	Belgium, Liège.....	18.13	54.8
1165	Estonia, Tallinn.....	25.68	23.0
1240	France, Soume.....	24.66	22.0
1463	Poland.....	17.51	19.5
1263	U. S. S. R., Saratov.....	18.40	15.4
1264	U. S. S. R., Egoriev.....	22.37	42.0
1262	U. S. S. R., Vyatka.....	27.86	43.2
1305	U. S. S. R., Kola Peninsula.....	31.63	7.6
1260	do.....	30.08	7.6

## INSULAR PHOSPHATES

1223	Angaur Island, Palau group.....	40.00	7.4
1287	Assumption Island, Seychelles group.....	30.40	17.3
1489	Astove Island, Seychelles group.....	34.36	21.4
1595	Christmas Island, Indian Ocean.....	39.35	8.7
452	do.....	39.46	8.0
1545	Curacao Island, Netherlands West Indies.....	30.31	12.0
985	do.....	34.39	11.8
943	do.....	40.66	7.6
1530	Daito Islands, Pacific Ocean.....	25.62	76.2
1236	Denis Island, Seychelles group.....	32.84	14.5
1904	Grand Conception Island, coast of French Guiana.....	51.53	39.5
1222	Juan de Nova Island, Mozambique Channel.....	32.29	15.1
1230	Makatea Island, French Oceania.....	37.91	10.1
1159	do.....	36.22	7.8
459	Nauru Island, Pacific Ocean.....	33.92	5.6
1507	do.....	39.25	5.1
1560	Ocean Island, Gilbert group.....	40.16	7.9
451	do.....	40.32	9.7
1697	Peleliu Island, Palau group.....	37.66	12.0
1691	Rasa Island, Pacific Ocean.....	30.03	12.7
1306	Walpole Island, New Caledonia group.....	24.28	40.4

## OTHER PHOSPHATES

562	Canada, British Columbia, Crow's Nest Pass.....	24.11	28.3
1906	Canada, Quebec Province.....	40.30	28.2
1187	South Australia, Kapunda.....	30.18	24.3
1188	South Australia, Port Clinton.....	33.53	29.3

- 1 Fluorapatite, crude lumps.  
 2 Fluorapatite, concentrated by froth flotation.  
 3 Aluminum iron phosphate.  
 4 Aluminum phosphate.  
 5 Fluorapatite.

%O <sub>2</sub>	As
Percent	P. p. m.
22.19	4.5
30.30	8.7
32.21	21.5
32.21	10.8
30.24	15.4
32.26	14.8
32.36	16.1
32.63	17.7
32.54	9.8
35.12	10.5
34.65	7.8
35.15	11.3
36.39	9.3
30.53	23.7
34.95	4.9
36.10	15.0

24.96	12.3
27.63	46.6
31.39	106.0
31.62	56.7
34.92	30.7
33.97	63.2
35.38	41.0
37.47	18.2
35.94	17.7

35.74	15.3
36.82	16.4
35.41	13.2
35.30	19.2
37.62	43.2
37.50	18.0
35.17	8.4
37.87	8.6

37.56	7.6
34.12	10.8
35.60	28.8
35.50	10.9
36.06	13.8
36.19	11.7
35.80	8.0
35.98	9.8
35.08	17.3

TABLE 8.—Summary of results for arsenic in mineral phosphates  
DOMESTIC PHOSPHATES

Type or source of phosphate	Samples analyzed	Arsenic	
		Range	Average
	Number	P. p. m.	P. p. m.
Florida land pebble.....	31	3.6-21.2	11.9
Florida river pebble.....	1		21.2
Florida hard rock.....	8	1.4-9.1	5.4
Florida soft.....	6	4-18.6	7.5
Florida waste pond.....	8	5.3-12.1	9.0
South Carolina land rock.....	4	9.2-27.5	17.1
South Carolina river rock.....	4	66.8-83.1	68.4
Fluorapatite from Virginia.....	2	4.3-8.6	6.5
Tennessee brown rock.....	25	5.1-66.1	14.6
Tennessee blue rock.....	7	8.4-37.7	20.4
Tennessee white rock.....	3	4.8-21.7	10.6
Tennessee phosphatic limestone.....	5	6.9-23.5	14.6
Other Tennessee phosphates.....	2	3.6-8.9	6.8
Kentucky.....	3	6.7-12.7	9.9
Arkansas.....	3	14.6-133.2	61.0
Oklahoma.....	3	15.6-19.3	17.8
Idaho.....	16	4.5-25.7	12.6
Montana.....	9	12.3-104.0	47.0
Utah.....	8	8.4-43.2	17.8
Wyoming.....	9	7.6-18.8	12.1
FOREIGN PHOSPHATES			
Africa.....	13	7.6-36.7	17.4
Canada.....	12	28.2-28.3	28.3
Europe.....	10	7.6-51.8	25.1
Islands.....	21	5.1-76.2	16.3
South Australia.....	2	20.3-24.3	22.3

<sup>1</sup> Kidney phosphate from Borna and phosphate rock from Mountain City.

<sup>2</sup> Including a sample of fluorapatite from Quebec Province.

<sup>3</sup> Including 2 samples of fluorapatite from Union of Soviet Socialist Republics.

<sup>4</sup> Including a sample of aluminum phosphate from Grand Comnetable Island and a sample of aluminum iron phosphate from Dalte Islands.

Aside from the results on 18 samples of domestic phosphate rocks previously reported from this Division (68, 81), very few figures for arsenic in mineral phosphates appear in the literature. Thus, the arsenic content of 9 samples of Florida phosphate rock, presumably land pebble, analyzed by Longfield-Smith (94) ranged from a trace to 29 p. p. m., which is in good agreement with the range of results for Florida land pebble given in table 3. Likewise, the figures shown in tables 3 and 4 for the National Bureau of Standards standard samples No. 120 (Florida land pebble) and 56a (Tennessee brown rock), respectively, agree closely with the results reported thereon by Hoffman and Lundell (73). Mansfield (96, p. 212) states that no arsenic was found in a sample of phosphate rock from Driggs, Idaho, or in a composite sample representing 12 individual samples of high-grade phosphate rock from different parts of the Idaho field. As reported by Williams (145), Fairchild found 13 p. p. m. of arsenic in a sample of low-grade phosphatic shale from a prospect hole just north of the mouth of Seymour Canyon, Summit County, Utah, and a sample of oolitic phosphate from an outcrop on the edge of Provo Valley, due north of Midway, Wasatch County, contained less than 6.5 p. p. m. of arsenic.

The spectrochemical results (65 to 326 p. p. m.) of Goldschmidt and Peters (49) for arsenic in Angaur Island phosphate are very much higher than the authors' figure (7.4 p. p. m.) on such material (table 7). Also the spectrochemical results (300 and 1,000 p. p. m. of arsenic)

of Noddack and Gotthard and Zint of Haberlandt (50) than the authors' Quebec (table 7), Republics (table 7) to 2.3 p. p. m., average (48) on 11 sample Peninsula, Union authors' figure (7)

The data in table 8 show arsenic and phosphate. In some samples arsenic with iron is present. Florida soft and Tennessee white and Tennessee blue rock show an increase in arsenic in others there is probable association phosphate rock can be etc.

Williams and Williams' various samples of soil which, so far as known, are arsenic. The results in the soil profile, and arsenic content relation between of which the soils were humid-area soils but low in arsenic, will be higher in arsenic.

In a study of 200 in different geological in arsenic were Grimmett and the Waiotapu Valley arsenic with iron point out that from aqueous solution the arsenic in clay adsorption by the present evidence hydrated ferric rocks. Also, adsorption has been demonstrated.

The association of iron sulfides, has been investigated to 400 p. p. m.)

Phosphates

Arsenic	
Range	Average
P. p. m.	P. p. m.
0.6-21.2	11.9
4-9.1	21.2
4-18.6	5.4
3-12.1	7.5
2-27.5	9.0
1.8-88.1	17.1
3-8.6	68.4
1-66.1	5.5
4-37.7	14.6
8-21.7	20.4
9-23.5	10.6
6-8.9	14.6
7-12.7	8.8
6-188.2	9.9
8-10.3	61.0
5-25.7	17.6
3-106.0	12.6
4-43.2	47.6
6-18.8	17.8
	12.1
0-36.7	17.4
2-28.3	28.3
6-84.8	25.1
1-76.2	16.3
3-24.3	22.3

sample of aluminum

phosphate rocks

new figures for... Thus, the... presumably... from a trace... range of results... figures shown... standard sam-... brown rock),... tion by Hoff-... at no arsenic... Idaho, or in... of high-grade... As reported... in a sample... north of the... a sample of... Valley, due... 6.5 p. p. m.

Goldschmidt... very much... material (table... of arsenic)

of Noddack and Noddack (104) on specimens of fluorapatite from St. Gotthard and Zinnwald, respectively, and those (up to 2,200 p. p. m.) of Haberlandt (56) on fluorapatite from Jumilla, Spain, are far higher than the authors' results (4.3 to 28.2 p. p. m.) on fluorapatite from Quebec (table 7), Virginia (table 5), and the Union of Soviet Socialist Republics (table 7). On the other hand, the chemical results (0.6 to 2.3 p. p. m., average 1.6 p. p. m. of arsenic) of Gileva and Melentiev (48) on 11 samples of fluorapatite from various localities in the Kola Peninsula, Union of Soviet Socialist Republics, are lower than the authors' figure (7.6 p. p. m.) on 2 samples from this region (table 7).

ARSENIC-BEARING CONSTITUENTS

The data in tables 3 to 7 reveal no uniform relationship between arsenic and phosphoric oxide in the different types and sources of phosphate. In some instances the trend is toward a decrease in arsenic with increasing phosphoric oxide (Algeria, Curaçao Island, Florida soft and land pebble, Montana (Garrison), South Carolina, and Tennessee white rock). In others, the trend seems to be toward an increase in arsenic with increasing phosphoric oxide (Morocco, Tennessee blue rock, and Union of Soviet Socialist Republics), whereas in others there is no trend in either direction. Indications of the probable associations of arsenic with the other constituents of phosphate rock can be obtained from the available data on soils, minerals, etc.

Williams and Whetstone (146) recently reported analyses of numerous samples of soils from localities throughout the United States, which, so far as known, had never been artificially contaminated with arsenic. The results showed no uniformity of distribution of arsenic in the soil profile, no observable relation between climatic conditions and arsenic content of soil groups, and no clearly defined, systematic relation between arsenic content and the geological formations from which the soils were developed. In general, however, sandy soils and humid-area soils having high silica-sesquioxide ratios were relatively low in arsenic, whereas soils of subhumid and arid regions tended to be higher in arsenic.

In a study of 20 samples of Italian soils taken from different depths in different geological formations, Zuccàri (155) found that soils high in arsenic were also high in iron. Likewise, the investigation by Grimmett and coworkers of the arsenical muds, soils, and waters of the Waiotapu Valley, New Zealand, indicates a definite association of arsenic with iron in this area (52, 53). Goldschmidt and Peters (49) point out that freshly precipitated ferric hydroxide removes arsenic from aqueous solutions by adsorption. They express the opinion that the arsenic in clayey sediments is likely present as the result of its adsorption by the hydrated ferric oxide in such sediments, and they present evidence to show that the arsenic is associated with the hydrated ferric oxide, as well as with the iron sulfide, in sedimentary rocks. Also, adsorption of arsenious acid by hydrous aluminum oxide has been demonstrated by Yoe (150).

The association of arsenic with sulfur in sulfide ores, especially the iron sulfides, has long been known and has been the subject of numerous investigations. Dunn and Bloxam (36) attribute the arsenic (50 to 400 p. p. m.) in the atmospheric dusts of English industrial cities

to its presence in the pyrite that occurs in the coal burned in these cities. In this connection, Abel's report (2a) of 424.1 p. p. m. of arsenic in a sample of ground coal brasses (pyrite separated from coal) from an unstated course is of interest. On the other hand, Goldschmidt and Peters (49) conclude that the arsenic in coal was derived primarily from the vegetable matter from which the coal originated. The widespread occurrence of arsenic in vegetation (2a, 46, 52, 54, 59, 86, 146), especially marine growths (18, 43, 85, 146), lends support to this conclusion. Small quantities of arsenic are commonly present in animal tissues (12, 13, 18, 45, 46, 52, 54, 59), and marine crustaceans and mollusks are exceptionally high in this element. In a study of the slimes of certain lagoons and their tributaries on the Baltic coast of Germany, Goy and Rudolph (50) found the arsenic content parallels the content of organic matter; they believe that bacteria are active in removing arsenic from the water and concentrating it in the slime.

In view of the foregoing, some relationship may be expected to exist between the arsenic content of phosphate rock and the quantities of iron, sulfide sulfur, organic carbon, or nitrogen present. The available data (table 9), however, do not point to a regular connection between the arsenic content and any of these constituents. Also, other data (not shown in table 9) indicate no relation between the arsenic and either the aluminum or the total  $R_2O_3$ . On the other hand, results for arsenic in the mechanical separates of a Wyoming pyritiferous, highly carbonaceous phosphate rock (table 10), as well as those for arsenic in the separates of an Idaho pyrite-free, highly carbonaceous rock, follow, in general, the results for total iron and organic carbon but not pyrite; arsenic, like the iron and organic carbon, shows marked accumulation in the "clay" fraction. Although the results indicate a better correlation of arsenic with total iron than with organic carbon, they do not permit one to decide whether the arsenic is associated with the iron or organic matter or both. The results on the Florida land-pegble (No. 947) and Tennessee brown-rock (No. 908) phosphates, both of which are low in organic carbon (0.29 and 0.11 percent, respectively) and are free from or very low in pyrite, show no correlation between arsenic and total iron in the mechanical fractions. In all the samples, the results indicate considerable loss of arsenic occasioned by suspension of the material in water incident to mechanical separation into fractions.

TABLE 9.—Comparative results for arsenic, organic carbon, nitrogen, pyritic sulfur, and iron in phosphate rock

Sample No.	Type or source of phosphate	Organic carbon <sup>1</sup>	As	N	FeS <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> <sup>2</sup>
		Percent	P. p. m.	P. p. m.	Percent	Percent
1290	Montana, Maxville <sup>3</sup>	3.84	12.8	( <sup>4</sup> )	2.87	( <sup>5</sup> )
1009	Montana, Garrison <sup>4</sup>	.14	165.0	80	.015	2.11
1010	do <sup>4</sup>	.09	18.2	80	.015	.88
1282	do <sup>4</sup>	.08	43.0	( <sup>4</sup> )	.0	3.10
948	Wyoming, Cokeville <sup>5</sup>	3.47	11.7	( <sup>4</sup> )	.97	.87
1283	Idaho, Conda	2.88	15.1	( <sup>4</sup> )	.0	1.64
973	do <sup>4</sup>	2.33	17.7	( <sup>4</sup> )	.0	.87
454	do <sup>4</sup>	2.20	18.4	( <sup>4</sup> )	.910	.80
1413	Idaho, Slight Canyon <sup>4</sup>	.88	9.3	( <sup>4</sup> )	.0	( <sup>4</sup> )
550	Idaho, Paris Canyon <sup>4</sup>	.02	21.6	( <sup>4</sup> )	.0	.87
1049	Tennessee, Kidney phosphate	1.48	8.9	2,800	1.51	1.70
552	Tunisia, Gafsa	.86	27.6	470	.0	.63

See footnotes at end of table.

TABLE 9.—Comparative results and type

Sample No.	Type or source of phosphate
771	Florida hard rock
932	do
1138	South Carolina land rock
1139	do
915	Florida waste pond
726	do
912	Florida land pebble
910	do
619	do
947	do
439	do
617	do
290	do
772	Tennessee blue rock
930	do
448	do
449	do
762	Tennessee brown rock
56	do
908	do
906	do
904	Grand Connetable Island
1031	Tennessee white rock
1048	do
1162	Morocco
985	Curacao Island
728	Florida soft
916	Tennessee phosphate base
917	do

- <sup>1</sup> Including also elemental carbon
- <sup>2</sup> Total iron.
- <sup>3</sup> Dark-colored pyritiferous rock.
- <sup>4</sup> Not determined.
- <sup>5</sup> Light-colored rock.
- <sup>6</sup> Dark-colored pyrite-free rock.
- <sup>7</sup> Standard sample number of the National Bureau of Standards.
- <sup>8</sup> Aluminum phosphate.

TABLE 10.—Distribution of arsenic

Mechanical fraction <sup>1</sup>	
Designation	Particle size
"Sand"	Microscopic
"Silt"	147 to 100 microns
"Clay"	50 to 10 microns
Solution and mechanical losses	< 5 microns
Original material	
"Sand"	147 to 100 microns
"Silt"	50 to 10 microns
"Clay"	< 5 microns
Solution and mechanical losses	
Original material	

- <sup>1</sup> The mechanical fractions were 100-mesh (147 $\mu$ ) sieve.
- <sup>2</sup> Including also elemental carbon
- <sup>3</sup> Total iron.
- <sup>4</sup> Calculated; based on the original material.



urned in these  
l. l. p. p. m. of  
eparated from  
e other hand,  
ic in coal was  
hich the coal  
in vegetation  
as (18, 43, 85,  
ties of arsenic  
5, 46, 52, 54,  
onally high in  
ons and their  
Rudolph (50)  
ganic matter;  
enic from the

e expected to  
the quantities  
present. The  
lar connection  
tments. Also,  
n between the  
he other hand,  
ning pyritifer-  
well as those  
carbonaceous  
rganic carbon  
shows marked  
alts indicate a  
ganic carbon,  
associated with  
Florida land-  
) phosphates,  
1 percent, re-  
w no correla-  
fractions. In  
arsenic occa-  
to mechanical

TABLE 9.—Comparative results for arsenic, organic carbon, nitrogen, pyritic sulfur, and iron in phosphate rock—Continued

Sample No.	Type or source of phosphate	Organic carbon †	As	N	FeS <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
		Percent	P. p. m.	P. p. m.	Percent	Percent
771	Florida hard rock	0.52	3.0	180	( <sup>1</sup> )	1.83
932	do	.18	9.1	50	0.0	.69
1138	South Carolina land rock	.51	12.9	510	.34	1.19
1139	do	( <sup>1</sup> )	27.5	( <sup>1</sup> )	.36	1.56
915	Florida waste pond	.47	5.3	440	( <sup>1</sup> )	4.23
726	do	.22	19.4	240	( <sup>1</sup> )	3.91
912	Florida land pebble	.38	10.6	130	( <sup>1</sup> )	.70
910	do	.33	21.2	60	( <sup>1</sup> )	2.59
619	do	.33	11.6	180	( <sup>1</sup> )	1.63
947	do	.29	17.3	80	( <sup>1</sup> )	1.60
439	do	.25	9.8	( <sup>1</sup> )	( <sup>1</sup> )	1.90
617	do	( <sup>1</sup> )	19.7	( <sup>1</sup> )	0.15	2.14
791	do	( <sup>1</sup> )	12.3	( <sup>1</sup> )	0	1.62
772	Tennessee blue rock	.36	17.4	340	2.03	3.54
630	do	.20	37.7	240	3.90	3.42
446	do	( <sup>1</sup> )	21.4	( <sup>1</sup> )	1.63	3.30
439	do	( <sup>1</sup> )	8.4	( <sup>1</sup> )	2.39	2.35
762	Tennessee brown rock	.29	7.9	150	0	2.25
756	do	.25	28.9	220	.89	3.39
908	do	.11	13.0	40	0	2.52
906	do	.09	24.2	60	0	3.42
1904	Grand Comestable Island	.28	30.5	490	0	4.43
1031	Tennessee white rock	.26	4.8	350	( <sup>1</sup> )	.92
1043	do	.09	5.2	160	( <sup>1</sup> )	1.75
1162	Morocco	.17	25.2	180	0	.12
983	Curacao Island	.17	11.8	130	0	.61
722	Florida soft	.16	5.9	180	( <sup>1</sup> )	1.54
916	Tennessee phosphatic limestone	( <sup>1</sup> )	6.9	( <sup>1</sup> )	.73	1.27
917	do	( <sup>1</sup> )	17.3	( <sup>1</sup> )	1.69	1.95

- <sup>1</sup> Including also elemental carbon.
- <sup>2</sup> Total iron.
- <sup>3</sup> Dark-colored pyritiferous rock.
- <sup>4</sup> Not determined.
- <sup>5</sup> Light-colored rock.
- <sup>6</sup> Dark-colored pyrite-free rock.
- <sup>7</sup> Standard sample number of the National Bureau of Standards.
- <sup>8</sup> Aluminum phosphate.

TABLE 10.—Distribution of arsenic among mechanical separates of ground phosphate rocks

Designation	Particle size	Wyoming phosphate No. 918						Idaho phosphate No. 973						
		Fraction of original material		P <sub>2</sub> O <sub>5</sub>	As	Organic carbon <sup>1</sup>	FeS <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> <sup>2</sup>	Fraction of original material		P <sub>2</sub> O <sub>5</sub>	As	Organic carbon <sup>1</sup>	Fe <sub>2</sub> O <sub>3</sub> <sup>2</sup>
		Percent	Percent						Percent	Percent				
"Sand"	147 to 50	49.8	33.41	P. p. m.	6.5	2.96	0.62	0.46	26.6	35.69	P. p. m.	6.6	2.22	0.16
"Silt"	50 to 5	43.6	23.73	7.5	4.25	1.17	1.11	45.5	32.96	8.2	2.03	.40		
"Clay"	<5	6.6	23.67	19.8	8.20	.42	2.22	27.9	23.66	32.8	3.03	2.04		
Solution and mechanical losses		0		3.9				.6		3.1				
Original material		100.0	30.19	11.7	3.47	.97	.87	100.0	32.53	17.7	2.34	.67		
Florida land-pebble phosphate No. 947														
		Percent	Percent	P. p. m.	Percent	Percent	Percent	Percent	Percent	Percent	P. p. m.	Percent	Percent	
"Sand"	147 to 50	48.2	30.97	16.2				1.57	37.6	34.49	10.7			2.16
"Silt"	50 to 5	42.0	31.93	14.1				1.68	46.9	34.85	7.7			2.36
"Clay"	<5	9.6	31.93	14.6				2.34	13.9	32.35	11.4			3.67
Solution and mechanical losses		2		2.2				1.7		3.8				
Original material		100.0	31.23	17.3				1.69	100.0	34.44	13.0			2.52

- <sup>1</sup> The mechanical fractions were prepared by Alexander and Jacob (5) from material ground to pass a 100-mesh (147 $\mu$ ) sieve.
- <sup>2</sup> Including also elemental carbon.
- <sup>3</sup> Total iron.
- <sup>4</sup> Calculated; based on the original material.

u, pyritic sulfur,

FeS <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> <sup>3</sup>
Percent	Percent
2.87	( <sup>1</sup> )
.015	2.11
.015	.56
0	3.10
.97	.87
( <sup>1</sup> )	1.64
0	.87
0	.80
( <sup>1</sup> )	( <sup>1</sup> )
0	.97
1.51	1.79
0	.65

PRIMARY AND SECONDARY DEPOSITS

Following Blackwelder's division (14) of the world's phosphate deposits into six genetic varieties, comprised in two broad groups (primary and secondary deposits), Mansfield (96, p. 362) has partially classified a number of the deposits. Accordingly, as far as possible the results for arsenic in phosphate are summarized under the two general groups in table 11. Although this grouping of the phosphates reveals no definite relationship between arsenic content and the type of the deposit, there is evidence that phosphates from primary deposits tend, in general, to contain somewhat more arsenic than do those from secondary deposits.

TABLE 11.—Arsenic content of phosphate rocks from primary and secondary deposits

Type of deposits and location	Samples analyzed	Arsenic	
		Range	Average †
<b>Primary:</b>	<i>Number</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
Arkansas.....	8	14.6-185.2	61.0
Tennessee blue rock.....	7	8.4-37.7	20.4
Algeria, Tunisia, and Egypt.....	9	7.0-30.7	18.0
Idaho, Montana, Utah, Wyoming, and British Columbia.....	43	4.5-100.0	16.4
Fluorapatite from Canada, Virginia, and U. S. S. R.....	5	4.3-26.2	13.8
<b>Average.....</b>			<b>26.0</b>
<b>Secondary:</b>			
South Carolina river rock.....	4	50.8-86.1	68.4
South Australia.....	2	20.3-24.3	22.3
Islands ‡.....	21	5.1-76.2	19.0
South Carolina land rock.....	4	9.2-27.5	17.1
Tennessee and Kentucky (brown rock and white rock §).....	32	4.8-50.1	11.6
Florida.....	54	4-21.2	11.0
<b>Average.....</b>			<b>25.0</b>

† Average of mean results for individual types or sources of phosphate.  
 ‡ Including aluminum phosphate for Grand Connetable Island and aluminum iron phosphate from Daito Islands.  
 § Including phosphate rock from Johnson County, Tenn.

GEOLOGIC AGE AND ARSENIC CONTENT

In table 12 the results for arsenic in mineral phosphates are grouped, as far as possible, according to the geologic age of the deposits (77, 139, 145). The average figures range from 7.3 p. p. m. in phosphates of Oligocene age (Florida hard rock, soft, and waste pond) to 47.8 p. p. m. in those of Miocene age (South Carolina land rock and river rock), whereas the averages for phosphates of all other periods and epochs are within the limits 11.9 and 24.8 p. p. m.

TABLE 12.—Geologic age

Period or epoch	Location
Post-Tertiary.....	Ishard, Mo., Florida, west white trails
Tertiary.....	Florida
Pliocene.....	Florida
Miocene.....	South Carolina
Oligocene.....	Florida
Eocene.....	Murree
Cretaceous (or Jurassic)	France
Carboniferous.....	Egypt, British and
Permian.....	British and
Mississippian.....	Tennessee
Devonian.....	Tennessee
Ordovician.....	Tennessee
Pre-Cambrian.....	Florida

† Average of mean results for 46 samples.  
 ‡ Including aluminum phosphate from Daito Islands.  
 § Including phosphate rock from Egoriev, Saratov, and Vysokaya.  
 ¶ Logan and Weber Canyons.

PHOSPHATES COMPARISON

Results for arsenic in mineral phosphates of the world are given in table 13. On the whole the arsenic content of phosphate rocks (western United States) is greater than that of halide minerals but less than that of sand, glauconite, and

TABLE 13.—Arsenic content

Material and source	Arsenic content (p. p. m.)
Phosphate rocks: world average	11.9
Fluorapatite: Virginia, U. S. S. R.	13.8
Igneous rocks:	
Earth's crust	11.9
America.....	11.9
Meteorites:	
Silicate phase.....	11.9
Iron phase.....	11.9
Trollite phase.....	11.9
Silicate rocks and minerals:	
Marls: Colorado and Kansas.....	11.9

See footnotes at end of table.

SODIUM 11

TABLE 12.—Geologic age as correlated with arsenic content of natural phosphates

Period or epoch	Type or source of phosphate	Samples analyzed	Arsenic	
			Range	Average <sup>1</sup>
Post-Tertiary	Island phosphates and Florida river pebbles <sup>1</sup>	22	P. p. m. 5.1-76.2	P. p. m. 19.7
Tertiary	Florida land pebble, hard rock, soft and waste pond; South Carolina, Tennessee white rock; <sup>2</sup> Morocco, and South Australia.	71	4-88.1	18.5
Pliocene	Florida land pebble	31	3.6-21.2	11.9
Miocene	South Carolina land rock and river rock	8	9.2-88.1	47.8
Oligocene	Florida hard rock, soft, and waste pond	22	4-18.6	7.3
Eocene	Morocco	4	7.7-24.2	14.7
Cretaceous (or Jurassic)	France, U. S. S. R., <sup>3</sup> Algeria, Tunisia, and Egypt	13	7.0-43.2	23.0
Carboniferous	British Columbia, Idaho, Montana, Utah, and Wyoming; and Tennessee kidney phosphate	44	4.5-106.0	16.2
Permian	British Columbia, Idaho, Montana, Utah, and Wyoming	41	4.5-106.0	16.3
Mississippian	Tennessee kidney phosphate and Utah <sup>4</sup>	3	8.9-19.2	15.4
Devonian	Tennessee blue rock	7	8.4-37.7	20.4
Ordovician	Tennessee and Kentucky brown rock, Tennessee phosphate limestone, Arkansas, and Estonia	42	5.1-188.2	24.8
Pre-Cambrian	Fluorapatite from Virginia and Canada	3	4.3-28.3	16.9

<sup>1</sup> Average of mean results for individual types or sources of phosphate.  
<sup>2</sup> Including aluminum phosphate from Grand Comnetable Island and aluminum iron phosphate from Daito Islands.  
<sup>3</sup> Including phosphate rock from Johnson County.  
<sup>4</sup> Egoriev, Sarafov, and Vyatka.  
<sup>5</sup> Lagan and Weber Canyons.

PHOSPHATES COMPARED WITH OTHER ROCKS, MINERALS, COALS, SOILS, SEDIMENTS, AND WATERS

Results for arsenic in rocks, minerals, coals, soils, sediments, and waters of the world, collected from various sources, are summarized in table 13. On the basis of these data, it can be concluded that the arsenic content of phosphate rocks is about the same as that of marls, shales (western United States), carbonate minerals, coals, and silicate rocks and minerals. Usually the quantity of arsenic in phosphate rock is greater than that in soils, sediments, and nitrate and halide minerals but is much smaller than that in oxide minerals, green-sand, glauconite, and especially sulfide minerals.

TABLE 13.—Arsenic in rocks, minerals, coals, soils, sediments, and waters

Material and location	Literature reference	Samples analyzed	Arsenic	
			Range	Average
Phosphate rocks; world deposits	(1)	205	P. p. m. 0.4-188.2	P. p. m. 20.9
Fluorapatite; Virginia, Canada, and U. S. S. R.	(2)	5	4.3-28.2	13.8
Igneous rocks:				
Earth's crust	(3, pp. 80-91)			1-9
America	(2)	329		4.8
Meteorites:				
Silicate phase	(108)	42		20
Iron phase	(108)	18		390
Troilite phase	(108)	5		1,020
Silicate rocks and minerals; 62 species	(104)	295	0-150	30
Marls; Colorado and Kansas	(59)	4	2.5-10.0	5.1

See footnotes at end of table.

306600°-41-3

world's phosphate to broad groups (62) has partially as far as possible under the two of the phosphates and the type of primary de-arsenic than do

ary and secondary

Arsenic	
Range	Average <sup>1</sup>
P. p. m.	P. p. m.
14.6-188.2	61.0
8.4-37.7	20.4
7.0-36.7	18.4
4.5-106.0	16.4
4.3-28.2	13.8
	26.0
56.8-88.1	68.1
20.3-24.3	22.3
5.1-76.2	19.6
9.2-27.5	17.1
4.8-58.1	11.5
4-21.2	11.0
	25.0

iron phosphate from

ates are grouped, deposits (77, 139, in phosphates of 1) to 47.8 p. p. m. and river rock), tions and epochs

TABLE 13.—Arsenic in rocks, minerals, coals, soils, sediments, and waters—Con.

Material and location	Literature reference	Samples analyzed	Arsenic	
			Range	Average
			P. p. m.	P. p. m.
Greensand, glauconite, and glauconite-rich sea sediments.	(49)	Number	65-325	
Shales:				
Colorado, Kansas, and Montana.	(146)	6	2-42	12
Bohemia and Middle Silesia.	(72)	11	65-4, 824	693
Bauxite.	(49)	7	0-325	
Oxidized iron ores.	(49)	19	65-650	
Oxides: 13 species.	(104)	47	5-400	96
Carbonates: 9 species.	(104)	13	0-80	17
Nitrates and halides: 7 species.	(104)	15	0-10	3
Sodium chloride; various grades of sea salt and rock salt.	(44)	9	0.025-1.75	.32
Salts of acids of Ti, P, V, Sb, Ta, S, Cr, Mo, and W: 19 species.	(104)	82	0-300	71
Sulfides, selenides, and tellurides: 19 species <sup>10</sup> .	(104)	144	10-600	146
Galena; Europe.	(71)	19	70-15, 80	2, 202
Sphalerite; Saxony and Silesia.	(71)	11	205-34, 630	6, 129
Chalcopyrite; Silesia.	(71)	3	255-3, 825	1, 933
Pyrite; Europe, Algeria, and United States.	(80, 88, 41, 71, 127, 148, pp. 76-96)	98	0-20, 00	5, 660
Native sulfur; Europe, Japan, and United States.	(80, 27, 47, 108)	11	0-200	43
Native metals: 7 species <sup>10</sup> .	(104)	46	0-300	64
Coals; Europe, New South Wales, New Zealand, and United States.	(19, 83, 43, 68, 84, 91, 105)	61	0-200	45
Clays and loams.	(104)	52	0-30	6
Soils: <sup>11</sup>				
Argentina.	(116)	20	Trace-22.5	4.4
Costa Rica.	(116)	6	3-5, 0	2.3
Italy.	(155)	20	1.9-60, 0	21.3
Mexico.	(146)	18	2.0-40, 0	14.3
New Zealand, Waiotapu Valley <sup>12</sup> .	(52, 65)	65	8-19, 000	
Puerto Rico.	(146)	6	3-1, 0	1.5
United States.	(59, 86, 95, 146)	233	2-38, 0	7.1
Sediments and sea-bottom material:				
Ocean sediments.	(49, p. 12)	57		4
Red clays; oceanic depths.	(81)	51		6.5
Terrigenous clays; oceanic depths.	(27)	52		Trace
Muds; lagoons and their tributaries, Baltic coast, Germany.	(60)	15	1.6-22.7	6.7
Silt; delta of Mississippi River.	(81)	235		2.6
Waters:				
Atlantic Ocean and Baltic Sea.	(44, 50, 112)	181	.0008-.08	.015
Vicinity of San Juan Islands, Washington State.	(135, p. 112)		.03-.03	
Thames and Medway estuaries.	(18)	16	106-757	.25
Lagoons and their tributaries, Baltic coast, Germany.	(60)	12	Trace-.008	.0024
Salt and mineral springs, France.	(44)	6	.01-.31	.18
Hot springs, Yellowstone National Park.	(4)	17	0-2.88	1.20
Streams, surface depressions, and hot and cold springs in Waiotapu Valley, New Zealand.	(52, 65)	39	Trace-33.71	3.14
Underground sources in Argentina.	(7, 3, 114)	22	0-1.40	.18
English rivers.	(18)	2		Trace

<sup>1</sup> Results from tables 3 to 7, exclusive of fluorapatite.

<sup>2</sup> Results from tables 5 and 7. I. Noddack and W. Noddack reported more than 1,000 p. p. m. of arsenic in fluorapatite from Zinnwald and 300 p. p. m. in fluorapatite from St. Gotthard, as determined by a spectrochemical method (104). By means of a similar method, Haberlandt found up to 2,200 p. p. m. of arsenic in apatite from Jumilla, Spain (56). Gileva and Melentiev reported 0.6 to 2.3 p. p. m. of arsenic (average 1.6 p. p. m.) in 11 samples of fluorapatite from various localities in the Kola Peninsula, U. S. S. R., as determined by a chemical method (48).

<sup>3</sup> The average arsenic content is estimated to be within these limits.

<sup>4</sup> A composite sample was analyzed.

<sup>5</sup> Analyzed by spectrochemical method.

<sup>6</sup> No arsenic was found in several specimens of micaceous iron shales and a hematite with jasper.

<sup>7</sup> A specimen of cerussite contained more than 1,000 p. p. m. of arsenic.

<sup>8</sup> The sample that contained 1.75 p. p. m. of arsenic was from a fissure in Vesuvius Volcano.

<sup>9</sup> Specimens of desclozite, monazite, pyromorphite, and vanadinite and a fluorapatite from Zinnwald contained more than 1,000 p. p. m. of arsenic.

<sup>10</sup> Including only those species of which the commonly accepted formulas do not show arsenic.

<sup>11</sup> Specimens of argyrodite, galena, tetrahedrite, franciscoite, stibnite, copper selenide, sulvanite, zinc blende, and stannite contained more than 1,000 p. p. m. of arsenic.

<sup>12</sup> Including the sample referred to in table 16, footnote 3.

<sup>13</sup> Phipps reported 11.16 percent arsenic in sulfur from the solfatara of Naples (107).

<sup>14</sup> Specimens of lead and bismuth contained more than 1,000 p. p. m. of arsenic.

<sup>15</sup> So far as known, these soils had never been artificially contaminated with arsenical compounds.

<sup>16</sup> Including samples of muds.

## ARSENIC IN CALCIUM DEFICIENT

For a number of producers to heat a temperatures (about 81 necessary merely to Thus, more or less elimination of carb part of the fluorine of the rock is raised phate,<sup>10</sup> more suitable acid-decomposition of phosphoric acid the Conda, Idaho, organic matter, with apparatus (90). Also used in this calcium

In 1918, Wagner that mine-run place Later experiments in fuel-fired furnace Florida land-puddle furnace production Tennessee brown-phosphate sand, is now phosphorus and used as fuels in the the sintered materials range from 2

Removal of fluxes the rock at 1,400<sup>11</sup> and water vapor of defluorinated phosph ammonium citrate for the growth of

As coal usually the presence of the investigators (6, 19 29 samples of coke to 243 p. p. m. as results of Goldschmidt arsenic in the ash. Determinations of considerably more usually remains in conditions (19, 22)

<sup>10</sup> The term "calcined" heating phosphate rock. For the purpose of this primarily for the purification processes.

<sup>11</sup> The term "sintered" The term "defluorinated" compared by defluorination as well as the material of rock (26).

ARSENIC IN CALCINED, SINTERED, NODULIZED, AND DEFLUORINATED PHOSPHATE ROCKS

For a number of years it has been the practice of several domestic producers to heat a portion of their output of phosphate rock at temperatures (about 815° to 1,370° C.) considerably higher than are necessary merely to remove the bulk of the moisture (11, 90, 101). Thus, more or less complete destruction of the organic matter and elimination of carbon dioxide and combined water are effected, and part of the fluorine may be volatilized, with the result that the grade of the rock is raised, and a product, commonly called calcined phosphate,<sup>10</sup> more suitable for the manufacture of phosphate chemicals by acid-decomposition processes is obtained. For use in the manufacture of phosphoric acid by the sulfuric acid process, phosphate rock from the Conda, Idaho, deposit must be heated to eliminate most of the organic matter, which otherwise would seriously foul the acid and apparatus (90). Although coal is used to some extent, oil is commonly used in this calcining process.

In 1918, Waggaman and Wagner (142) showed experimentally that mine-run phosphate rock can be smelted in the electric furnace. Later experiments (141) showed that such material can also be smelted in fuel-fired furnaces, and several years ago the suitability of sintered Florida land-pebble phosphate matrix<sup>11</sup> as a raw material for the blast-furnace production of phosphorus was demonstrated (117). Sintered Tennessee brown-rock matrix, as well as nodulized matrix and phosphate sand, is now being used in the electric-furnace production of phosphorus and phosphoric acid (26, 87, 139). Coal and oil are used as fuels in the preparation of the nodulized products, whereas the sintered material is prepared with coke. The maximal temperatures range from about 900° to 1,450° C.

Removal of fluorine from phosphate rock can be effected by heating the rock at 1,400° C. or higher temperatures in the presence of silica and water vapor (25, 83, 99, 119). When it is properly prepared this defluorinated phosphate<sup>12</sup> is almost completely soluble in neutral ammonium citrate solution, and it is an excellent source of phosphorus for the growth of plants on neutral and acid soils (79, 121).

As coal usually contains notable quantities of arsenic (table 13), the presence of this element in coke is to be expected. Thus, several investigators (6, 19, 91, 105, 125, 128, 137) have reported arsenic in 29 samples of coke (principally English), ranging in quantity from 2 to 243 p. p. m. and averaging 59 p. p. m. Also, the spectrochemical results of Goldschmidt and Peters (49) showed 65 to 650 p. p. m. of arsenic in the ash of numerous samples of brown coal and anthracite. Determinations of the so-called volatile and fixed arsenic indicate that considerably more than 50 percent of the arsenic in coal and coke usually remains in the ash when these fuels are burned under ordinary conditions (19, 62, 91, 105, 128, 137). It appears, therefore, that the

<sup>10</sup> The term "calcined phosphate" has also been applied to the citrate-soluble products obtained either by heating phosphate rock with alkali salts (65) or by heating it in the presence of silica and water vapor (119). For the purpose of this bulletin, however, the term will be restricted to phosphate rock that has been heated primarily for the purpose of increasing its grade and its suitability for treatment by acid-decomposition processes.

<sup>11</sup> The term "matrix," as used in this bulletin, refers to the natural mixture of phosphate rock and gangue.  
<sup>12</sup> The term "defluorinated phosphate" comprises the material known as calcined phosphate that is prepared by defluorinating phosphate rock at temperatures below the melting point (83, 99, 119, footnote 10), as well as the material known as fused phosphate rock which is prepared by defluorinating the molten rock (85).

Waters—Con.

Arsenic	
Age	Average
C. m.	P. p. m.
-325	
-42	12
+4, 824	693
+325	
+350	96
+400	17
+60	3
+10	
+1.75	.32
+300	71
+600	146
+15, 80	2, 202
+34, 830	6, 120
+3, 825	1, 933
+20, 60	5, 650
+300	43
+300	54
+207	45
+30	6
+22.5	4.4
+5.0	2.3
+40.6	21.3
+40.0	14.3
+10, 000	
+1.0	1.5
+38.0	7.1
	4
	6.5
+22.7	Trace
	6.7
	2.6
F. 08	.015
F. 03	
F. 757	.25
F. 608	.0024
F. 31	.18
F. 33	1.29
F. 33.71	3.14
F. 1.40	.18
	Trace

800 p. p. m. of arsenic determined by a spectro-  
 20 p. p. m. of arsenic in  
 of arsenic (average 1.0  
 U. S. R., as determined

with Jasper.  
 Lead,  
 native from Zinnwald  
 arsenic,  
 silvanite, zincblende,

phosphates.

direct heating of phosphate rock with coal or coke may lead to contamination of the product with arsenic from the fuel. Although data on the arsenic content of fuel oil are not available, Shirey (124) reports that a careful spectrochemical examination revealed no arsenic in a sample of ash specially prepared from the still-coke of Kansas crude petroleum.

The arsenic in 16 samples of calcined, nodulized, sintered, and defluorinated phosphates ranged from <1 to 150 percent of that in the parent rocks and was with few exceptions notably lower in the products than in the parent materials (table 14). In general, the arsenic content of the products does not appear to be related either to the arsenic content of the parent materials, the type of fuel used, or to the time or temperature of heating. The data (see tables 4 and 14) indicate, however, that only a small part of the arsenic in the parent rocks is retained in defluorinated phosphates.

TABLE 14.—Arsenic in calcined, sintered, nodulized, and defluorinated phosphate rocks

Unheated phosphate rock				Heated phosphate rock						Ratio: Arsenic in heated rock to As in unheated rock <sup>1</sup>
Sample No.	Type or source	P <sub>2</sub> O <sub>5</sub>		Sample No.	Type of product	Maximal heat temperature °C.	Time of heating at maximal temperature, minutes	P <sub>2</sub> O <sub>5</sub>		
		Percent	P. m.					Percent	P. m.	
1851	Florida land pebble	34.38	8.4	1850	Calcined rock <sup>1</sup>	845	20	35.75	6.6	0.75
1853	do	30.37	10.5	1852	do <sup>2</sup>	370	20	35.20	5.2	.43
1855	do	34.41	7.6	1854	do <sup>3</sup>	900	5	35.29	11.7	1.5
1857	do	32.35	15.4	1856	do <sup>3</sup>	1,095	5	34.51	12.2	.74
1859	do	35.38	3.6	1858	do <sup>3</sup>	1,230	5	35.25	5.1	1.4
1918	Tennessee brown rock	22.95	7.4	1917	Nodulized matrix <sup>4</sup>	900	15	25.15	1.4	.17
1861	do	31.40	6.6	1890	Calcined rock <sup>5</sup>	950	(*)	35.28	6.3	.93
1863	do	34.52	11.9	1862	do <sup>6</sup>	1,150	(*)	34.98	6.7	.56
1924	do	32.94	7.2	1923	Nodulized sand <sup>7</sup>	1,455	(*)	33.45	3.7	.51
1922	do	22.85	56.1	1921	Nodulized matrix <sup>8</sup>	(*)	15	23.38	16.0	.28
1922	do	22.85	56.1	1919	Sintered matrix <sup>9</sup>	(*)	(*)	23.79	8.2	.14
1865	Idaho, Conda	32.54	9.8	1864	Calcined rock <sup>1</sup>	910	45	34.41	9.5	.92
1447	Florida land pebble	34.37	11.4	1492	Defluorinated rock <sup>10</sup>	1,400	40	37.24	<1	<.01
(14)	Tennessee brown rock			1478	do <sup>11</sup>	1,400	(*)	37.25	1.4	---
(14)	do			1470	do <sup>12</sup>	1,600	(*)	28.95	<1	---
1292	Montana, Garrison	38.92	41.0	1490	do <sup>11</sup>	1,400	40	33.85	5.4	.13

<sup>1</sup> Approximate.

<sup>2</sup> Calculated from the arsenic-phosphorus ratios of the heated rock and the unheated rock, respectively.

<sup>3</sup> Heated with fuel oil.

<sup>4</sup> Matrix.

<sup>5</sup> Heated with coal.

<sup>6</sup> Not known.

<sup>7</sup> The fuel consisted of a mixture of approximately 50 percent of carbon monoxide from a phosphorus-condenser operation and 50 percent of gas oil.

<sup>8</sup> Mixture of matrix and washed phosphate sand.

<sup>9</sup> Heated with coke.

<sup>10</sup> 40- to 80-mesh particles screened from crushed rock.

<sup>11</sup> Prepared in the laboratory by heating the phosphate rock in an electric furnace in the presence of water vapor (29).

<sup>12</sup> A sample of the phosphate rock was not available.

<sup>13</sup> Prepared on a semiworks scale by heating phosphate rock in an oil-fired rotary kiln in the presence of water vapor.

<sup>14</sup> Prepared by subjecting molten phosphate rock to the action of water vapor (25).

## ARSENIC IN SUPERPHOSPHATE

Aside from its presence in superphosphate, sulfuric acid used to produce it is used in some of the fertilizers (5, 28, 58, 130), principally, if not entirely, as sulfuric acid manufactured by the smelting of other ores in the industry; such acid contains considerable arsenic.

Native sulfur is also used in domestic fertilizer and contains little or no arsenic. If made from pyrite, it may contain a trace of arsenic in some cases. Abel (2a), who worked in 1920, when he reported that a sample from Phipson (108) report "exempt" from arsenic in volcanic sulfur of two samples of Japanese arsenic, respectively. French sulfur did not usually low arsenic content.

Arsonic is rarely found in sulfuric acid which has been made from pyrite where acid free from arsenic.

The phosphoric acid produced in the smelting of phosphate is made in blast furnaces (11). The acid produced by the smelting is made therefrom by the action of crude phosphoric acid produced as a by-product and Montana are used extensively in the manufacture of double phosphates are made with

<sup>15</sup> The term "double superphosphate" is used to designate the terms "triple superphosphate".

ARSENIC IN SUPERPHOSPHATES AND PHOSPHORIC ACID

Aside from its presence in the phosphate rock, arsenic may be introduced into superphosphate and phosphoric acid as an impurity in the sulfuric acid used to decompose the rock or in other reagents or fuels used in some of the manufacturing processes. The earlier investigators (5, 28, 58, 130, 131) attributed the arsenic in superphosphate principally, if not entirely, to its presence in the sulfuric acid. Sulfuric acid manufactured from pyrite or produced as a byproduct of the smelting of other sulfide ores is used extensively in the fertilizer industry; such acid, especially that made from pyrite, often contains considerable arsenic (1, 16, 28, 58, 88, 127, 130, 149, pp. 337-338).

Native sulfur is also an important source of sulfuric acid for the domestic fertilizer industry, but, unlike pyrite, it usually contains little or no arsenic. In 1859, Davy (28) remarked that sulfuric acid made from pyrite contains considerable arsenic, whereas native sulfur contains little or no arsenic and the sulfuric acid made therefrom is not so likely to contain this element. Davis and Davis (27) found no trace of arsenic in sulfur from the Texas deposits that were being worked in 1920, whereas a later sample of Texas sulfur, analyzed by Abel (2a), contained 7.0 p. p. m. of arsenic; the authors' analysis of a recent sample from Louisiana showed only 2.1 p. p. m. of arsenic. Phipson (108) reported that a sample of Sicilian sulfur was "quite exempt" from arsenic, and that only a trace of arsenic was present in volcanic sulfur of Hecla. According to Gibbs and James (47), two samples of Japanese sulfur contained 143 and 200 p. p. m. of arsenic, respectively, whereas the arsenic content of four samples of French sulfur did not exceed 33.3 p. p. m. In harmony with the usually low arsenic content of native sulfur, Wyld (149, p. 337) states:

Arsenic is rarely found, and never in more than insignificant traces, in acid which has been made from brimstone; most of the latter material, indeed, is used where acid free from arsenic is wanted.

The phosphoric acid required for the manufacture of double superphosphate<sup>13</sup> is made either by the sulfuric acid process (90, 144) or by smelting mixtures of phosphate rock, silica, and coke in electric or blast furnaces (17, 23, 37). The presence of arsenic in phosphoric acid produced by the sulfuric acid process, and in phosphate chemicals made therefrom has long been recognized (15, 39, 40, 88, 109, 120). Results, reported by Hill, Marshall, and Jacob (67), for arsenic in crude phosphoric acid manufactured commercially with sulfuric acid produced as a byproduct of copper-smelting operations in Tennessee and Montana are given in table 15. The Montana sulfuric acid is used extensively in the production of phosphoric acid for the manufacture of double superphosphate, and large tonnages of superphosphates are made with the Tennessee sulfuric acid.

<sup>13</sup> The term "double superphosphate" refers to the fertilizer material, usually containing about 45 to 50 percent of P<sub>2</sub>O<sub>5</sub>, made by treating phosphate rock with phosphoric acid. The term is synonymous with the terms "triple superphosphate" and "treble superphosphate."

y lead to con-  
Although data  
Shirey (124)  
revealed no  
e still-coke of

sintered, and  
t of that in the  
n the products  
l, the arsenic  
either to the  
used, or to the  
and 14) indi-  
in the parent

inated phosphate

Temperature, °C.	P <sub>2</sub> O <sub>5</sub>		Ratio of As in heated rock to As in unheated rock <sup>1</sup>
	Per- cent	P. p. m.	
20	35.75	6.5	0.75
20	35.29	5.2	.43
3	35.29	11.7	1.5
5	34.51	12.2	.74
5	36.25	5.1	1.4
15	25.15	1.4	.17
15	33.28	6.3	.93
15	34.98	6.7	.56
15	33.45	3.7	.51
15	23.38	16.0	.28
15	23.79	8.2	.14
45	34.41	9.5	.92
40	37.24	<1	<.01
37	37.25	<1	<.01
28	38.03	<1	<.01
40	38.83	5.4	.13

1 rock, respectively.  
from a phosphorus-  
the presence of water  
kilo in the presence

TABLE 15.—Arsenic in crude phosphoric acid manufactured by the sulfuric acid process

Type or source of phosphate rock	Source of sulfuric acid	Arsenic content of phosphoric acid <sup>1</sup>	
		Dilute <sup>2</sup>	Concentrated <sup>3</sup>
Florida land pebble.....	Copper-smelting operation in Tennessee <sup>4</sup>	P. p. m. 35.9	P. p. m. 19.3
Tennessee brown rock.....	do <sup>4</sup>	50.7	30.8
Idaho.....	Copper-smelting operation in Montana <sup>5</sup>	840.0	1,181.0

<sup>1</sup> Data reported by Hill, Marshall, and Jacob (67); results calculated to basis of acid containing 50 percent of  $H_3PO_4$ .

<sup>2</sup> The dilute acids made from the Florida, Tennessee, and Idaho phosphate rocks contained 27.42, 22.12, and 27.98 percent of  $H_3PO_4$ , respectively.

<sup>3</sup> The concentrated acids made from the Florida, Tennessee, and Idaho phosphate rocks contained 60.93, 67.11, and 52.19 percent of  $H_3PO_4$ , respectively.

<sup>4</sup> A sample of acid (60° B.) from this smelting operation contained 11.4 p. p. m. of As.

<sup>5</sup> A sample of acid (50° B.) from this smelting operation contained 841 p. p. m. of As.

Isakov (78) expressed the opinion, unsupported by experimental data, that the arsenic in thermal phosphoric acid comes from the phosphate ore and coke used in the process. As pointed out in a preceding paragraph, arsenic is a common constituent of coal and coke. In view of the volatility of arsenic compounds at high temperatures, phosphoric acid produced by furnace methods would be expected to be contaminated with arsenic from the coke used in the process. Swann (132) and Carothers (17) state that precipitator acid (85 to 95 percent  $H_3PO_4$ ) made by direct combustion of the electric-furnace gases contains about 100 to 150 p. p. m. of arsenic. According to information supplied to the authors by several domestic manufacturers, crude elemental phosphorus made from Florida land-pebble and Tennessee brown-rock phosphates by the electric-furnace process contains approximately 60 to 75 p. p. m. of arsenic, whereas the crude acid (about 75 to 80 percent  $H_3PO_4$ ) made from this phosphorus contains approximately 19 to 45 p. p. m. Crude elemental phosphorus made by the blast-furnace process contains approximately 120 to 150 p. p. m. of arsenic, or about twice the arsenic content of phosphorus made by the electric-furnace process.

The foregoing figures are very much smaller than those (0.53 to 1.92 percent) reported by Hampe (57), Husemann (76), and Winkler (147) for arsenic in elemental phosphorus produced in Europe during the last quarter of the nineteenth century. At that time, however, elemental phosphorus was commonly manufactured by distilling a mixture of coke and sirupy phosphoric acid (113); the acid was made by treating bone ash or phosphate rock with sulfuric acid and concentrating the dilute product. Thus the arsenic in the elemental phosphorus may have been derived from three sources, namely, the phosphatic raw material, the sulfuric acid (made principally, if not entirely, from pyrite), and the coke, of which the sulfuric acid probably contributed by far the greater portion.

Angell and Angell (5), Haselhoff (58), Stoklasa (130), and Stutzer (131) reported 40 to 2,600 p. p. m. of arsenic in samples of European ordinary superphosphates<sup>14</sup> manufactured about 40 years ago, princi-

<sup>14</sup> The term "ordinary superphosphate" refers to the fertilizer material, usually containing about 16 to 20 percent of  $P_2O_5$  and consisting of a mixture of approximately equal parts by weight of monocalcium phosphate and calcium sulfate, made by treating phosphate rock with sulfuric acid.

pally, if not entirely, on the other hand, Headden's sample of American crude phosphoric acid (such material that had results (table 16) for sulfuric acid produced 494.1 to 1,199.1 p. p. m. (35.7 p. p. m.) for sulfur recovered from the native sulfur phosphates made with the weight ratio of arsenic to arsenic in the crude acid (table 16, column 9) is usual phosphate rock is the principal source.

Analyses reported show 1,000 p. p. m. of arsenic in samples of double superphosphate from this State (table 16). The results from Florida land-pebble phosphates with phosphoric acid from elemental sulfur operations in Tennessee from 10.6 to 64.9 p. p. m. of arsenic, ordinary superphosphate sources, indicate that arsenic in these samples

Sample No.	Type or source	Phosphate content	
		Dilute	Concentrated
1875	Florida land pebble		
1803	do		
1879	do		
1867	do		
1830	Tennessee brown rock		
1899	do		
1884	Florida land pebble		
1882	do		
1801	do		
1893	do		
1873	do		

See footnotes at end of table.

<sup>14</sup> An advertisement of...



by the sulfuric acid

Arsenic content of phosphoric acid <sup>1</sup>	
Dilute <sup>2</sup>	Concentrated <sup>3</sup>
P. p. m.	P. p. m.
35.9	19.3
59.7	39.5
840.0	1,161.0

of acid containing 50 per-  
 cents contained 27.42, 22.12,  
 phosphate rocks contained 60.03,  
 of As.  
 of As.

by experimental  
 comes from the  
 pointed out in a  
 ent of coal and  
 at high temper-  
 eds would be ex-  
 oke used in the  
 precipitator acid  
 n of the electric-  
 nic. According  
 mestic manufac-  
 ida land-pebble  
 -furnace process  
 hereas the crude  
 phosphorus con-  
 tainental phosphorus  
 ately 120 to 150  
 at of phosphorus

n those (.053 to  
 06), and Winkler  
 a Europe during  
 time, however,  
 by distilling a  
 e acid was made  
 e and con-  
 the elemental  
 es, namely, the  
 incipally, if not  
 ic acid probably

30), and Stutzer  
 es of European  
 ears ago, princi-

e containing about 16 to  
 ht of monocalcium phos-

pally, if not entirely, with sulfuric acid produced from pyrite. On the other hand, Headden (59) found only about 1 p. p. m. of arsenic in a sample of American ordinary superphosphate, the only analysis of such material that has come to the authors' attention. The authors' results (table 16) for arsenic in ordinary superphosphate made with sulfuric acid produced entirely or partially from pyrite range from 194.1 to 1,199.1 p. p. m. and are very much higher than those (2.2 to 35.7 p. p. m.) for superphosphate made with acid produced entirely from native sulfur or as a byproduct of smelting operations or recovered from the raffination of petroleum. Aside from the superphosphates made with acid produced entirely or partially from pyrite, the weight ratio of arsenic in a given quantity of the superphosphate to arsenic in the corresponding quantity of the phosphate rock (table 16, column 9) is usually less than 2, thereby indicating that the phosphate rock is the principal source of arsenic in most of the samples.

Analyses reported by Young (151) and by the manufacturer<sup>16</sup> show 1,000 p. p. m. and 908.8 p. p. m. of arsenic, respectively, in samples of double superphosphate made from Idaho phosphate rock with phosphoric acid produced with sulfuric acid manufactured from Montana sulfide ores; the authors' result on a sample of double superphosphate from this source is 404.6 p. p. m. of arsenic (No. 1372, table 16). The results on samples of double superphosphate made from Florida land-pebble, Tennessee brown-rock, and Montana phosphates with phosphoric acid produced with sulfuric acid manufactured from elemental sulfur or as a byproduct of copper- and zinc-smelting operations in Tennessee and British Columbia, respectively, range from 10.6 to 64.9 p. p. m.; the data (see tables 8 and 16), like those for ordinary superphosphates made with sulfuric acid from the same sources, indicate that the phosphate rock was the principal source of arsenic in these samples.

TABLE 16.—Arsenic in superphosphates  
 ORDINARY SUPERPHOSPHATES

Sample No.	Phosphate rock <sup>1</sup>	Type or source	Phosphate rock <sup>1</sup>		Source of sulfuric acid	Superphosphate <sup>1</sup>			
			P <sub>2</sub> O <sub>5</sub>	As		Sample No.	P <sub>2</sub> O <sub>5</sub>	As	Ratio of As in superphosphate to As in phosphate rock <sup>3</sup>
			Per- cent	P. p. m.			Per- cent	P. p. m.	
1875	Florida land pebble.....	33.30	9.8	Louisiana sulfur <sup>4</sup> .....	1874	20.48	5.2	0.85	
1835	do.....	32.56	8.7	Texas sulfur.....	1802	20.48	10.1	1.8	
1870	do.....	32.10	16.2	do.....	1877	21.00	7.2	.88	
1867	do.....	35.21	4.3	Domestic sulfur.....	1866	21.85	4.1	1.5	
1889	do.....	33.24	6.4	do.....	1838	19.83	4.5	1.2	
1889	Tennessee brown rock.....	34.64	6.5	Texas sulfur.....	1898	21.55	14.3	3.5	
1899	do.....	33.86	15.2	Louisiana sulfur and Spanish pyrite. <sup>4</sup>	1883	20.93	1,096.0	110.7	
1884	Florida land pebble.....	33.16	8.2	Domestic sulfur and Spanish pyrite. <sup>5</sup>	1891	21.00	1,199.1	230.9	
1882	do.....	33.53	8.4	Spanish pyrite. <sup>6</sup>	1890	20.88	494.1	94.7	
1891	do.....	32.78	12.4	Copper-smelting operation in Tennessee. <sup>7</sup>	1894	20.43	8.3	1.1	
1896	do.....	33.76	12.0	do <sup>1</sup> .....	1872	20.78	6.0	.81	

See footnotes at end of table.

<sup>16</sup> An advertisement of the Anaconda Copper Mining Company in American Fertilizer 76 (2): 33, 1922.

TABLE 16.—Arsenic in superphosphates—Continued  
ORDINARY SUPERPHOSPHATES—Continued

Sample No.	Phosphate rock <sup>1</sup>			Source of sulfuric acid	Superphosphate <sup>1</sup>			
	Type or source	P <sub>2</sub> O <sub>5</sub>	As		Sample No.	P <sub>2</sub> O <sub>5</sub>	As	Ratio of As in superphosphate to As in phosphate rock <sup>2</sup>
1871	Tennessee brown rock.....	34.37	5.0	Copper-smelting operation in Tennessee. <sup>7</sup>	1870	20.30	6.2	3.1
1897	do.....	34.73	7.7	do. <sup>7</sup>	1896	21.43	11.3	2.4
1869	do.....	34.80	13.0	Zinc-smelting operation in Illinois. <sup>8</sup>	1868	21.20	2.2	.28
1930	Montana, Garrison.....	31.51	58.4	Zinc-smelting operation in British Columbia. <sup>9</sup>	1928	20.00	35.7	.96
(10)	Florida land pebble.....			(11)	1403	20.86	9.8	
(10)	do.....			(11)	1402	20.80	30.6	
(10)	Idaho, Conda.....			Not known	1933	20.33	9.8	
(10)	do.....			do.	1887	21.45	14.6	

## DOUBLE SUPERPHOSPHATES

1879	Florida land pebble.....	32.10	18.2	Texas sulfur.....	1878	48.84	11.6	.47
(10)	do.....			Domestic sulfur.....	1890	49.53	10.6	
(10)	Tennessee brown rock.....			Copper-smelting operation in Tennessee. <sup>7</sup>	1481	44.08	34.3	
(10)	do.....			do. <sup>7</sup>	1908	47.01	20.5	
1930	Montana, Garrison.....	31.51	58.4	Zinc-smelting operation in British Columbia. <sup>9</sup>	1929	45.65	64.9	.77
(10)	Idaho, Conda.....			Iron sulfide concentrate (11)	1372	47.33	401.6	
(10)	Tennessee brown rock.....			(11)	1362	18.37	118.5	
(10)	do.....			(11)	1950	50.31	109.1	
(10)	do.....			(11)	1896	47.18	22.0	
1926	do.....	31.81	13.3	(11)	1925	50.69	11.1	.52
(10)	Florida land pebble.....			(11)	1945	50.68	14.3	

- <sup>1</sup> The analyses are not converted to the moisture-free basis.  
<sup>2</sup> Calculated from the arsenic-phosphorus ratios of the superphosphate and the phosphate rock, respectively.  
<sup>3</sup> A sample of the sulfur contained 2.1 p. p. m. of As.  
<sup>4</sup> Approximately one-third of the acid was made from sulfur and two-thirds from pyrite.  
<sup>5</sup> One-fourth of the acid was made from sulfur and three-fourths from pyrite.  
<sup>6</sup> According to the manufacturer, the acid (35° B.) contained 910 p. p. m. of As.  
<sup>7</sup> A sample of acid (93° B.) from this smelting operation contained 11.4 p. p. m. of As (67).  
<sup>8</sup> According to the manufacturer, the acid from this smelting operation usually contains less than 5 p. p. m. of As.  
<sup>9</sup> According to the manufacturer, the acid (98 percent H<sub>2</sub>SO<sub>4</sub>) from this smelting operation contains less than 0.1 p. p. m. of As.  
<sup>10</sup> A sample of the phosphate rock was not available.  
<sup>11</sup> The acid was processed sludge acid from the raffination of asphalt-base petroleum.  
<sup>12</sup> The acid was untreated sludge acid from the raffination of asphalt-base petroleum.  
<sup>13</sup> Ammoniated double superphosphate, made with synthetic ammonia.  
<sup>14</sup> Obtained by floating the tailings from a copper-ore concentrator in Montana.  
<sup>15</sup> The phosphoric acid was made by the blast-furnace process.  
<sup>16</sup> The phosphoric acid was made by the electric-furnace process with direct oxidation of the furnace gas.  
<sup>17</sup> The phosphoric acid was made by the electric-furnace process; about one-third of the acid was made by direct oxidation of the phosphorus.  
<sup>18</sup> The phosphoric acid was made by the electric-furnace process with condensation and subsequent oxidation of the phosphorus.

The high contents of arsenic (118.5 and 100.1 p. p. m.) in the two samples of double superphosphate (Nos. 1362 and 1950, table 16) made with phosphoric acid produced by the blast-furnace process indicate contamination with arsenic present as an impurity in the coke used in the process. On the other hand, the arsenic (11.1 to 22.9 p. p. m.) in the samples of double superphosphate (Nos. 1886, 1925, and 1945) made with electric-furnace phosphoric acid seems to have come principally, if not entirely, from the phosphate rock.

Rader and Hill (11) because of the presence of glass and cannot be stored contaminated with the superphosphates and in the same way. For a superphosphate that had about a year showed 12 with the walls of the bottle contained only of cured double superphosphate showed the same arsenic in wooden or fiberboard. In order to avoid the analyses reported in had never been stored.

## ARSENIC IN A MISCELLAN

The results for arsenic phosphate made from elemental sulfur from elemental sulfur of this type of phosphate of the ammonium phosphate rock with byproduct on phosphate rock was phosphate rock was. These figures are very by Young (151) on a Idaho rock with sulfur. Although other results come to the author, Smith (94) found 1879 imported from Germany.

The authors' results slags (table 17) are Kryukov (89) for a Republics. Likewise dicalcium phosphate p. p. m.) reported by in Europe about 50 years.

Arsenic, ranging in five samples of guano contained 21 reported a trace of arsenic of arsenic in a guano of the samples of that of the samples of content of some samples.

<sup>10</sup> Nitrophoska is the trade name (see, p. 432). All the mixtures are ammonium phosphate.

Rader and Hill (111) have pointed out that superphosphates, because of the presence of active fluorine compounds, readily attack glass and cannot be stored in glass bottles without danger of becoming contaminated with boron from the container. Contamination of superphosphates and phosphoric acid with arsenic may also occur in the same way. For example, analyses of a sample of fresh ordinary superphosphate that had remained undisturbed in a glass bottle for about a year showed 12.9 p. p. m. of arsenic in the material in contact with the walls of the bottle whereas, the material from the center of the bottle contained only 3.7 p. p. m. On the other hand, two samples of cured double superphosphate (Nos. 1362 and 1372, table 16) showed the same arsenic contents in portions stored for several years in wooden or fiberboard containers and in glass bottles, respectively. In order to avoid this possible source of contamination, all the analyses reported in table 16 were made on superphosphates that had never been stored in glass.

ARSENIC IN AMMONIUM PHOSPHATE, BONE, AND MISCELLANEOUS PHOSPHATE FERTILIZERS

The results for arsenic in three samples of fertilizer-grade ammonium phosphate made from Florida land pebble with sulfuric acid produced from elemental sulfur (table 17) fall within the range for arsenic in this type of phosphate rock (table 3). Likewise, the arsenic content of the ammonium phosphate (No. 1885) made from Garrison, Mont., rock with byproduct sulfuric acid is within the range of results (table 6) on phosphate rock from this locality. It appears, therefore, that the phosphate rock was the principal source of arsenic in the products. These figures are very much lower than that (1,200 p. p. m.) obtained by Young (151) on a sample of ammonium phosphate made from Idaho rock with sulfuric acid produced from Montana sulfide ores. Although other results for arsenic in ammonium phosphates have not come to the authors' attention, it is interesting to note that Longfield-Smith (94) found 189 to 1,136 p. p. m. in five samples of Nitrophoska<sup>16</sup> imported from Germany.

The authors' results for arsenic in imported and domestic basic slags (table 17) are far lower than that (12,118 p. p. m.) reported by Kryukov (89) for a sample produced in the Union of Soviet Socialist Republics. Likewise, the figure for arsenic in the sample of crude dicalcium phosphate is only a small fraction of those (280 to 1,700 p. p. m.) reported by Fresenius (40) for precipitated phosphate made in Europe about 50 years ago.

Arsenic, ranging in quantity from 0.2 to 2.2 p. p. m., was present in five samples of bonemeal and bone ash, and a sample of Peruvian guano contained 24.9 p. p. m. (table 17). Longfield-Smith (94) reported a trace of arsenic in a sample of raw bonemeal and 189 p. p. m. of arsenic in a guano from an unstated source. The arsenic content of the samples of fossil teeth and bone (table 17) is more than double that of the samples of modern bone but is no greater than the arsenic content of some samples of Florida phosphate rock (table 3).

<sup>16</sup> Nitrophoska is the trade name of a series of high-analysis fertilizer mixtures of German manufacture (112, p. 122). All members of the series contain diammonium phosphate. The other components of the mixtures are ammonium nitrate or urea and potassium chloride or potassium sulfate.

phate	As	Ratio of As in superphosphate to As in phosphate rock
P. p. m.	9.2	3.1
11.3	2.2	2.4
35.7	0.96	0.28
9.8	.....	.....
30.0	.....	.....
9.8	.....	.....
14.6	.....	.....

4	11.6	47
3	10.0	.....
3	34.3	.....
1	20.8	.....
5	64.0	77
3	404.6	.....
1	118.5	.....
1	100.1	.....
3	22.9	.....
3	11.1	52
3	14.3	.....

e rock, respec-

than 5 p. p. m.

u contains less

ve furnace gas.

l was made by

nd subsequent

r the two

table 16)

a process

y in the

(11.1 to

os. 1886,

seems to

ok.

Small quantities of arsenic were present in samples of calcium metaphosphate, Non-Acid phosphate, and flue dust from a phosphoric acid blast-furnace (table 17).

TABLE 17.—Arsenic in ammonium phosphate, bone, and miscellaneous phosphate fertilizers

Sample No.	Material	P <sub>2</sub> O <sub>5</sub> <sup>1</sup>	As <sup>1</sup>
		Percent	P. p. m.
1885	Ammonium phosphate <sup>2</sup>	48.99	74.2
1849	do <sup>2</sup>	49.37	15.1
1901	do	50.49	17.1
1902	do <sup>2</sup>	22.80	5.5
974	Basic slag, domestic	8.66	11.2
1164	Basic slag, imported	18.45	6.2
1108	do	18.07	2.1
971	Bone ash	49.38	8.8
780	Bonemeal	21.62	2.2
778	do	31.63	.2
777	do	33.11	1.1
1165	do	34.58	.6
1755	Fossil bone <sup>3</sup>	36.90	5.9
1754	Fossil teeth <sup>3</sup>	37.67	4.5
1475	Calcium metaphosphate <sup>4</sup>	63.87	2.6
1021	Dicalcium phosphate <sup>4</sup>	40.20	7.4
1588	Flue dust from phosphoric acid blast-furnace <sup>5</sup>	52.31	3.2
1106	Guano, Peruvian	14.40	24.9
1172	Non-acid phosphate <sup>6</sup>	26.58	3.1

<sup>1</sup> The analyses are not converted to the moisture-free basis.

<sup>2</sup> Monoammonium phosphate, fertilizer-grade, made from phosphoric acid produced from Garrison, Mont., phosphate rock by the sulfuric acid process. The sulfuric acid, manufactured in British Columbia from zinc-smelter gases, is said to contain less than 0.1 p. p. m. of As on the basis of 98 percent H<sub>2</sub>SO<sub>4</sub>.

<sup>3</sup> Monoammonium phosphate, fertilizer grade, made from phosphoric acid produced from Florida land-pebble phosphate by the sulfuric acid process. The sulfuric acid was made from domestic sulfur.

<sup>4</sup> Mixture of monoammonium phosphate and ammonium sulphate, fertilizer-grade. The phosphoric acid was made from Florida land-pebble phosphate by the sulfuric acid process. The sulfuric acid was made from domestic sulfur.

<sup>5</sup> Analysis reported by Jacob, Hill, Marshall, and Reynolds (81, p. 39).

<sup>6</sup> From Florida land-pebble phosphate deposit.

<sup>7</sup> Made by reacting phosphorus pentoxide with Tennessee brown-rock phosphate (24).

<sup>8</sup> Crude material made from phosphoric acid produced from Florida land-pebble phosphate by hydrochloric acid treatment. The hydrochloric acid was obtained as a byproduct of the manufacture of salt cake.

<sup>9</sup> Tennessee brown-rock phosphate was smelted in this furnace. The flue dust also contains considerable potassium (136).

<sup>10</sup> Manufactured in 1925 by heating Florida land-pebble phosphate with a potassium salt (2).

Although no determinations of arsenic in nitrogenous and potassic fertilizers were made by the authors, results obtained by other workers are of interest. Thus, Longfield-Smith (94) found traces of arsenic in samples of tankage, castor pomace, cottonseed meal, kainite, potassium nitrate, potassium sulfate, and Chilean sodium nitrate; a sample of synthetic sodium nitrate contained 235 p. p. m. of arsenic, and 24 samples of ammonium sulfate contained 0 to 1,666 p. p. m. (average 682 p. p. m.). Abel (2a) reported 3.1 to 1,098.1 p. p. m. of arsenic in five samples of ammonium sulfate and 3.4 p. p. m. in a sample of iron sulfate. By use of a spectrochemical method, Gaddum and Rogers (42) found arsenic, ranging in quantity between 1,000 and 5,000 p. p. m., in a sample of ammonium sulfate, but they were unable to detect arsenic in other samples of a wide variety of fertilizer and lining materials, elemental sulfur, and sulfates of barium, cadmium, cobalt, copper, iron, magnesium, manganese, nickel, and zinc. The spectrochemical analyses of Noddack and Noddack (104) showed no arsenic in Stassfurt carnallite, 1 p. p. m. in Stassfurt kainite, and 0.2 p. p. m. in Chilean sodium nitrate.

## EFFECT OF ARSENIC

In view of the general paucity of the effects of this element naturally arises. Although field, numerous investigating summaries of some of the probable effects of the fertilizers.

In 1859, Davy (28) reported no pronounced injurious effects of a diluted solution of arsenious acid on potatoes in plots of ground the presence of 25 p. p. m. 6 weeks after the appearance wheat seemed to be stimulated 75 p. p. m., and radishes. In each case, higher concentration proportion to the quantity. Vandecaveye, Horner, and p. p. m. of arsenic as arsenic been subjected to arsenic of arsenic poisoning in the larger quantities of arsenic survive the shooting star sprayed with lead arsenate when the content of water very poor when it was

Young (151) reported that fertilized Merrihue corn toxic in concentration of arsenic (2 p. p. m.) and an organism died at concentrations (20 p. p. m.)

Morris and Swinburn (10) compounds on a wide variety. Transpiration of tomato as arsenious oxide, and the concentration of arsenic and potassium arsenite to arsenic, but the results. Confirming the earlier work were decidedly more compounds differed in becoming inert in a sample. Abel (2a), injury to areas where the plants contained 1008.1 p. p. m. been caused by the arsenic.

Experiments by the important soil types

## EFFECT OF ARSENIC ON PLANTS AND SOIL ORGANISMS

In view of the general presence of arsenic in phosphates, the question of the effects of this element on plants and on the soil population naturally arises. Although the authors have done no work in this field, numerous investigations have been made by others. The following summaries of some of the results afford a basis for the evaluation of the probable effects of the quantities of arsenic present in phosphate fertilizers.

In 1859, Davy (28) reported that transplanted pea plants suffered no pronounced injurious effects when they were watered with a saturated solution of arsenious oxide at 2- to 3-day intervals for more than a week. Stewart and Smith (129) stated that growth of beans and potatoes in plots of gravelly bench loam seemed to be stimulated by the presence of 25 p. p. m. of arsenic added as disodium arsenate 3 to 6 weeks after the appearance of the plants above the soil; peas and wheat seemed to be stimulated by arsenic in concentrations as high as 75 p. p. m., and radishes by concentrations as high as 250 p. p. m. In each case, higher concentrations of arsenic were toxic, roughly in proportion to the quantity applied. In pot experiments with barley, Vandecaveye, Horner, and Keaton (140) found that addition of 39 p. p. m. of arsenic as arsenious oxide to a fertile soil that had never been subjected to arsenical sprays caused only very slight symptoms of arsenic poisoning in the seedlings. The toxic effect increased with larger quantities of arsenic, and with 136 p. p. m. the plants failed to survive the shooting stage. With soils from orchards that had been sprayed with lead arsenate, the crops of alfalfa and barley were good when the content of water-soluble arsenic was 1.5 p. p. m. or less, and very poor when it was 3 to 12 p. p. m.

Young (151) reported a stimulating effect on growth of timothy from arsenic (0.1 to 10 p. p. m.) added to tumblers of adequately fertilized Merrimac coarse sandy loam, whereas arsenic was highly toxic in concentrations of 100 p. p. m. or more. A low concentration of arsenic (2 p. p. m.) stimulated the growth of green algae (*Crucigina* and an organism designated as No. 4) in culture media, but higher concentrations (20 p. p. m. or more) were toxic.

Morris and Swingle (102) studied the effect of numerous arsenic compounds on a wide variety of plants under greenhouse conditions. Transpiration of tomato plants was decreased by 7.5 p. p. m. of arsenic as arsenious oxide, and the injury increased in direct proportion to the concentration of arsenic; similar results were obtained with sodium and potassium arsenites. Beans and cucumbers were very susceptible to arsenic, but the cereals and grasses were much more resistant. Confirming the earlier observations of Stoklasa (130), the arsenites were decidedly more toxic than the arsenates. Furthermore, the compounds differed considerably in their reaction in the soil, some becoming inert in a much shorter time than others. According to Abel (2a), injury to pineapple plants has been reported in Hawaiian areas where the plants were fertilized with an ammonium sulfate that contained 1098.1 p. p. m. of arsenic. This injury is believed to have been caused by the arsenic in the fertilizer.

Experiments by Dorman, Tucker, and Coleman (34), with several important soil types of the Cotton Belt, showed no germination- or

in meta-  
phosphoric

phosphate

	As 1
P. p. m.	
99	74.2
27	15.1
49	17.1
80	5.5
66	11.2
45	5.2
07	2.1
36	2.8
82	2.2
83	2.2
11	1.1
56	6.6
90	5.0
67	4.5
97	2.6
30	7.4
31	3.2
40	24.9
50	3.1

Dr. Garrison,  
British Columbia,  
arsenic H<sub>2</sub>SO<sub>4</sub>.  
Florida land-  
farm.  
phosphoric acid  
acid was made

by hydro-  
lysis of salt

considerable

(9).

potassic  
workers  
arsenic in  
e, potas-  
a sample  
, and 24  
(average  
arsenic in  
ample of  
lum and  
,000 and  
re unable  
fizer and  
admium,  
ac. The  
owed no  
, and 0.2

seedling-injury to oats, Austrian Winter peas, and hairy vetch from the application of 400 pounds of calcium arsenate per acre, equivalent to approximately 75 p. p. m. of arsenic, immediately before planting. Although larger applications were injurious and the effect was more serious on the lighter soils, much of the toxicity of the arsenate was lost in the first year.

Stoklasa (130) observed that growth of oats in sand culture was stimulated by addition of 15 p. p. m. of arsenic (as arsenic pentoxide) to the phosphorus-free nutrient solution, whereas the arsenic had no stimulating effect in the presence of an adequate supply of phosphorus. Hurd-Karrer (75) obtained indications that phosphate applications reduce or prevent arsenic injury to plants where the type of soil is such as to permit the phosphate to remain available.

The effect of arsenic on the ammonifying, nitrifying, and nitrogen-fixing organisms of the soil has been studied by Greaves (51). With lead arsenate, an application of 60 p. p. m. of arsenic markedly stimulated nitrification, and 350 p. p. m. was not harmful. Ammonification was reduced about 50 percent by 1,250 p. p. m. of arsenic, whereas fixation of atmospheric nitrogen was doubled by 250 p. p. m. Paris green was much more toxic to the organisms than was lead arsenate.

Stewart and Smith (129) found that absorption of arsenic by plants increased with the quantity applied to the soil and reached values as high as 2,150 p. p. m. in pea plants (dry basis) grown on soil to which 500 p. p. m. of arsenic had been added. Vandercavey and coworkers (140) reported 13.3 p. p. m. of arsenic in the tops of barley grown on arsenic-contaminated soil, whereas the roots contained 1,250 p. p. m. Arsenic was present in the leaf blades and petioles of rhubarb, in the young leaves of rye and buckwheat, and in the stems, leaves, and green pods of broadbeans grown by Angell and Angell (5) on soil fertilized with superphosphate in which the arsenic content had been increased to 3,800 p. p. m. by addition of arsenious oxide, but no trace of arsenic was found in the fruit or seed of any of the plants. Analyses by Williams and Whetstone (146) showed 0 to 10 p. p. m. of arsenic (average less than 0.77 p. p. m.) in the air-dry substance of 91 samples of numerous species of cultivated and wild plants from various sections of the United States, grown on soils containing 4 to 36 p. p. m. of arsenic (average 8 p. p. m.) on the air-dry basis. According to Grimmett and coworkers (52, 54) samples of oat straw and grain grown on natural arsenical soils in New Zealand contained only 3.0 and 2.3 p. p. m. of arsenic, respectively, and were not harmful to stock. Likewise, pasture grasses grown on these soils and containing 0.5 to 17.4 p. p. m. of arsenic were not toxic to animals grazed thereon.

#### ARSENIC SUPPLIED TO SOIL BY SUPERPHOSPHATE

The annual application of phosphate fertilizer to the soils of the United States seldom, if ever, exceeds the equivalent of 2,000 pounds of ordinary superphosphate per acre; in general farming, the application is seldom equivalent to more than 200 pounds of superphosphate per acre; usually it is much less. Now let it be supposed that a superphosphate containing approximately 1,200 p. p. m. of arsenic, the largest quantity found in any material analyzed in this investigation (No. 1881, table 16), is applied to the soil at the rate of 2,000 pounds per acre within 3 inches of the plant rows, which are 3 feet apart.

Then assuming the plowed layer (6% incrustation of the entire the concentration in row, if all the arsenic. With a 200-pound application arsenic concentration. Analyses of 30 samples of these materials an average of 126.2 p application of superphosphate, the respective increases would be 0.126 and 0.756 the increases would

When all the factors on soil organisms are under consideration, it seems that phosphate fertilizer applications, even in annual applications, are safe. Likewise, Haselhoff (131) found that pean superphosphate had an injurious effect on plants, unless it contains not more than 0.5 p. p. m. of arsenic. Stoklasa (130), unless it contains not more than 0.5 p. p. m. of arsenic, is not injurious to animals. He

There is no question that arsenic might be present in superphosphate, but the amount of arsenic in it (its rate of increase in the soil and in the compounds) is practically

Results are given for superphosphates from various sources, sintered, nodulized, and granulated. 30 samples of commercial superphosphate, manufactured from domestic phosphate, produced by the sulfate process, basic slag superphosphate, and basic slag superphosphate.

It is shown that arsenic is not entirely, in the acid-soluble compounds causes no injury to free glassware is used in the preparation of samples of superphosphate with nitric acid.

The results for arsenic in a Florida soft phosphate. With the different grades of phosphate rock (p. p. m. of arsenic) the results (p. p. m. of arsenic) are: rock 68.4, Arkansas

ry vetch from  
re, equivalent  
fore planting.  
fect was more  
arsenate was

of culture was  
nic pentoxide)  
rsenic had no  
of phosphorus.  
a applications  
type of soil is

and nitrogen-  
s (51). With  
ekedly stimu-  
monification  
enic, whereas  
p. m. Paris  
ead arsenate.  
nic by plants  
ed values as  
soil to which  
ad coworkers  
ley grown on  
250 p. p. m.  
abarb, in the  
leaves, and  
l (5) on soil  
ent had been  
side, but no  
f the plants.

0 p. p. m. of  
istance of 91  
from various  
e 36 p. p. m.  
According to  
w and grain  
ed only 3.0  
harmful to  
d containing  
aed thereon.

soils of the  
0 pounds of  
application  
osphate per  
at a super-  
arsenic, the  
vestigation  
900 pounds  
feet apart.

Then assuming the customary figure, 2,000,000 pounds of soil in the plowed layer (6 inches) of an acre, the increase in the arsenic concentration of the entire layer would be 1.2 p. p. m., and the increase in the concentration in the layer extending 3 inches on either side of the row, if all the arsenic were retained therein, would be 7.2 p. p. m. With a 200-pound application of this superphosphate the increases in arsenic concentration would be 0.12 and 0.72 p. p. m., respectively. Analyses of 30 samples of ordinary and double superphosphates, typical of these materials as used in all sections of the United States, gave an average of 126.2 p. p. m. of arsenic (table 16). With a 2,000-pound application of superphosphate containing this quantity of arsenic the respective increases in the concentrations of arsenic in the soil would be 0.126 and 0.756 p. p. m., whereas with a 200-pound application the increases would be only 0.0126 and 0.0756 p. p. m., respectively.

When all the factors affecting the action of arsenic on plants and on soil organisms under practical conditions of farming are taken into consideration, it seems highly improbable that the arsenic in domestic phosphate fertilizer exerts any toxic effects, even with very large annual applications of the fertilizer over extended periods of time. Likewise, Haselhoff (58) concluded that the arsenic content of European superphosphates (40 to 1,490 p. p. m.) was not sufficient to have an injurious effect on plants under practical conditions. According to Stoklasa (130), superphosphate is not dangerous to vegetation unless it contains more than 4,000 p. p. m. of arsenic, and Stutzer (131) expressed the opinion that the arsenic content of superphosphate (100 to 500 p. p. m.) is too low to render plants fertilized therewith poisonous to animals. Headden (59) states:

There is no question but that soils which may have originally been entirely free from arsenic might show its presence after years of fertilization with superphosphate, but the accumulation in this manner is extremely slow compared with its rate of increase in cases where spraying [of orchards or crops with arsenic compounds] is practiced.

### SUMMARY AND CONCLUSIONS

Results are given for acid-soluble arsenic in 210 samples of mineral phosphates from various deposits of the world; 16 samples of calcined, sintered, nodulized, and defluorinated phosphates of domestic origin; 30 samples of commercial ordinary and double superphosphates manufactured from domestic rock; 6 samples of crude phosphoric acid produced by the sulfuric acid process; and 19 samples of ammonium phosphate, basic slag, bone materials, and miscellaneous phosphate fertilizers.

It is shown that arsenic occurs in phosphate rock principally, if not entirely, in the acid-soluble condition, and that the presence of fluorine compounds causes serious error in its determination unless arsenic-free glassware is used for the acid digestion. The danger of contamination of samples of fluorine-bearing phosphoric acid and superphosphate with arsenic from glass containers is pointed out.

The results for arsenic in mineral phosphates range from 0.4 p. p. m. in a Florida soft phosphate to 188.2 p. p. m. in an Arkansas phosphate. With the different types and sources of domestic phosphate the average results (p. p. m.) are in the descending order, South Carolina river rock 68.4, Arkansas 61.0, Montana 47.6, Tennessee blue rock 20.4.

Utah 17.8, Oklahoma 17.6, South Carolina land rock 17.1, Tennessee brown rock and phosphatic limestone 14.6, Idaho 12.6, Wyoming 12.1, Florida land pebble 11.9, Tennessee white rock 10.6, Kentucky 9.9, Florida waste pond 9.0, Florida soft 7.5, Virginia fluorapatite 5.5, and Florida hard rock 5.4. The results for foreign phosphates range from 5.1 p. p. m. in a calcium phosphate from Nauru Islands to 76.2 p. p. m. in an aluminum iron phosphate from Daito Islands.

The occurrence of arsenic in mineral phosphates is discussed from the following points of view: (1) Arsenic-bearing constituents; (2) primary and secondary deposits; (3) geologic age of deposits; and (4) a comparison of phosphates with other rocks, minerals, coals, soils, sediments, and waters. Accordingly, the data indicate that there is, in general, no orderly relationship between the arsenic content and the geologic age of phosphate rock or between the arsenic content and the quantities of other constituents (phosphorus, iron, sulfide sulfur, organic carbon, or nitrogen), although the arsenic follows the inorganic sulfides and organic matter in the mechanical fractions of certain phosphates (Cokeville, Wyo., and Conda, Idaho). There is evidence that phosphates from primary deposits tend to contain somewhat more arsenic than do those from secondary deposits. The arsenic content of mineral phosphates is similar, in general, to that of marls, domestic shales, carbonate minerals, coals, and silicate rocks and minerals; usually it is higher than that of soils, clays, sediments, and nitrate and halide minerals, but is much lower than that of oxide minerals, greensand, glauconite, and especially sulfide minerals.

In proportion to their phosphorus contents, calcined, sintered, or nodulized phosphates usually contain notably less arsenic than do the parent phosphate rocks. Only a small portion of the arsenic in the parent phosphate rock is retained in defluorinated phosphate.

The results for arsenic in ordinary superphosphates made with sulfuric acid produced entirely or partially from pyrite range from 494.1 to 1,199.1 p. p. m. and are very much higher than those (2.2 to 35.7 p. p. m.) for superphosphate made with acid produced entirely from native sulfur or as a byproduct of certain smelting operations in Illinois and Tennessee. Except for material made with acid produced entirely or partially from pyrite, the phosphate rock is the principal source of arsenic in most superphosphates.

The results for arsenic in double superphosphates range from 10.6 p. p. m. in a material made with phosphoric acid produced with sulfuric acid manufactured from native sulfur to 404.6 p. p. m. in a material made with the aid of sulfuric acid produced from Montana sulfide ores. Owing to contamination of the product with arsenic from the fuel (coke), the arsenic content (100.1 to 118.5 p. p. m.) of double superphosphate made with blast-furnace phosphoric acid is much higher than that (11.1 to 22.9 p. p. m.) of double superphosphate made with electric-furnace acid.

Arsenic was found in ammonium phosphate (5.5 to 74.2 p. p. m.), basic slag (2.1 to 11.2 p. p. m.), and bone ash and bonemeal (0.2 to 2.2 p. p. m.). Calcium metaphosphate, fossil bone and teeth, dicalcium phosphate, fine dust from a phosphoric acid blast-furnace, Non-Acid phosphate, and Peruvian guano contained arsenic in quantities ranging from 2.6 in the first material to 24.9 p. p. m. in the last.

When all the factors soil organisms under consideration, it seems contributed to the soil toxic effects even with over extended periods

- (1) ANONYMOUS.  
1891. ARSENIC IN
- (2) ————  
1927. KREISS FOR  
PETHULIZ
- (2a) ABEL, F. A. E.  
1933. ARSENIC IN
- (3) ALEXANDER, LYLE T.  
1930. MECHANICAL  
U. S. DEPT.  
OF AGRICULTURE
- (4) ALLEN, E. T., DAY, J.  
1935. HOT SPRINGS  
INST. WASH.
- (5) ANGELL, ARTHUR, and  
1902. ARSENIC IN
- (6) ARCHBUTT, L., and J.  
1901. THE DELIVER  
SOC. CHEM.
- (7) BADO, AFIGLIO A.  
1917. LA PRESENZA  
RANCI  
AG. SCI. ITAL.
- (8) ———— and ZANELLO, G.  
1921. LA PRESENZA  
POZZO DI  
AG. SCI. ITAL.
- (9) BAIFON, CHARLES J.  
1910. NITRATES  
EDUC. DEPT.
- (10) BAXTER, GREGORY J.  
ROBIN, JOSEPH S.  
1930. RECOMMENDATIONS  
CALIF. DEPT.  
AGRICULTURE  
WATER  
SULFUR  
CHEM. DEPT.
- (11) BECKER, CHARLES A.  
1936. DRYING AND  
FIELD  
677, 1936
- (12) BERTRAND, GABRIEL  
1902. SUR L'ANALYSE  
Acad. Sci.
- (13) ————  
1902. SUR L'ANALYSE  
Acad. Sci.
- (14) BLACKWELDER, F. W.  
1915. ORIGIN OF  
Geol. Surv.
- (15) BONJEAN, ED.  
1904. PROSPERITE  
REV. I. C.
- (16) BUCHNER, GEORG  
1891. ARSENIC IN



When all the factors affecting the action of arsenic on plants and on soil organisms under practical conditions of farming are taken into consideration, it seems very unlikely that the quantities of arsenic contributed to the soil in phosphate fertilizers are sufficient to produce toxic effects even with very large annual applications of the fertilizer over extended periods of time.

## LITERATURE CITED

- (1) ANONYMOUS.  
1891. ARSENIK IN DEN ROHEN SÄUREN. *Chem. Ztg.* 15: 43.
- (2) ————  
1927. KREISS POTASSIUM PHOSPHATE CO. MAKES AN ALL-AMERICAN FERTILIZER. *Fert. Green Book* 8 (4): 21-24, illus.
- (2a) ABEL, F. A. E.  
1933. ARSENIC IN PINEAPPLES. *Pineapple Quart.* 3: 118-124.
- (3) ALEXANDER, LYLE T., and JACOB, K. D.  
1930. MECHANICAL ANALYSIS OF FINELY DIVIDED NATURAL PHOSPHATES. U. S. Dept. Agr. Tech. Bul. 212, 24 pp., illus.
- (4) ALLEN, E. T., DAY, ARTHUR L., and MERWIN, H. E.  
1935. HOT SPRINGS OF THE YELLOWSTONE NATIONAL PARK. Carnegie Inst. Wash., Pub. 466, 525 pp., illus.
- (5) ANGELL, ARTHUR, and ANGELL, A. F.  
1902. ARSENIC IN CROPS. *Chem. and Drug.* 60: 430.
- (6) ARCHBUTT, L., and JACKSON, P. G.  
1901. THE DETERMINATION OF MINUTE QUANTITIES OF ARSENIC IN COKE. *Soc. Chem. Indus. Jour.* 20: 448-450.
- (7) BADO, Atilio A.  
1917. LA PRESENCIA DEL VANADIO Y ARSÉNICO EN LAS AGUAS SUBTERRÁNEAS DE BELL-VILLE (CÓRDOBA). *Soc. Cient. Argentina An.* 84: [284]-295, illus.
- (8) ———— and ZANETTA, ALBERTO J.  
1921. LA PRESENCIA DE VANADIO Y ARSÉNICO EN ALGUNAS AGUAS DE POZO DE LA CIUDAD DE BUENOS AIRES. *Assoc. Quím. Argentina An.* 9: 24-25.
- (9) BARTON, CHARLES J., and YOE, JOHN H.  
1940. NULL-TYPE PHOTOELECTRIC SPECTROPHOTOMETER. *Indus. and Engin. Chem., Analyt. Ed.*, 12: 166-168, illus.
- (10) BAXTER, GREGORY P., COLLINS, W. D., FARR, H. V., FREEMAN, J. V., ROSIN, JOSEPH, SPENCER, G. C., and WICHERS, EDWARD.  
1930. RECOMMENDED SPECIFICATIONS FOR ANALYTICAL REAGENT CHEMICALS—CALCIUM CARBONATE, CALCIUM CARBONATE LOW IN ALKALIES, CALCIUM CHLORIDE (CaCl<sub>2</sub>·2H<sub>2</sub>O), CUPRIC OXIDE WIRE FORM, CUPROUS CHLORIDE, LEAD ACETATE, MAGNESIUM SULFATE, SODIUM METAL, ZINC SULFATE. *Indus. and Engin. Chem., Analyt. Ed.* 2: 351-354.
- (11) BECKER, CHARLES N.  
1936. DRYING AND PROCESSING OF PEBBLE PHOSPHATE IN THE FLORIDA FIELD. *Amer. Inst. Mining and Metall. Engin. Tech. Pub.* 677, 13 pp., illus.
- (12) BERTRAND, GABRIEL.  
1902. SUR L'EXISTENCE DE L'ARSENIC DANS L'ORGANISME. [Paris] *Acad. des Sci. Compt. Rend.* 134: 1434-1437.
- (13) ————  
1902. SUR L'EXISTENCE DE L'ARSENIC DANS LA SÉRIE ANIMALE. [Paris] *Acad. des Sci. Compt. Rend.* 135: 809-812.
- (14) BLACKWELDER, ELIOT.  
1915. ORIGIN OF THE ROCKY MOUNTAIN PHOSPHATE DEPOSITS. (Abstract) *Geol. Soc. Amer. Bul.* 26: 100-101.
- (15) BONJEAN, ED.  
1904. PHOSPHATE DE SOUDE RENFERMANT DE L'ARSÉNIATE DE SOUDE. *Rev. Internatl. des Falsif.* 17: 171-172.
- (16) BUCHNER, GEORG.  
1891. ARSENIK IN DEN ROHEN SÄUREN. *Chem. Ztg.* 15: 13.

- (17) CAROTHERS, J. N.  
1938. ELECTRIC FURNACE PHOSPHATES. *Electrochem. Soc. Trans.* 73: 42-46.
- (18) CHAPMAN, A. CHASTON.  
1926. ON THE PRESENCE OF COMPOUNDS OF ARSENIC IN MARINE CRUSTACEANS AND SHELL FISH. *Analyst* 51: 548-562.
- (19) CHAPMAN, ALFRED C.  
1901. ARSENIC IN COAL AND COKE. *Analyst* 26: [253]-256.
- (20) CLARK, JOHN.  
1887. NEW METHODS OF ESTIMATING ARSENIC IN PYRITES, ETC. *Soc. Chem. Indus. Jour.* 6: 352-354.
- (21) CLARKE, F[RANK] W[IGGLESWORTH], and STEIGER, GEORGE.  
1914. THE RELATIVE ABUNDANCE OF SEVERAL METALLIC ELEMENTS. *Wash. Acad. Sci. Jour.* 4: 58-62.
- (22) ——— and WASHINGTON, HENRY STEPHENS.  
1924. THE COMPOSITION OF THE EARTH'S CRUST. *U. S. Geol. Survey Prof. Paper* 127, 117 pp.
- (23) CURTIS, HARRY A.  
1935. T. V. A. MAKES  $H_3PO_4$  ELECTRICALLY AT WILSON DAM. *Chem. & Metall. Engin.* 42: 320-324, illus.
- (24) ——— COPSON, R. L., ABRAMS, A. J., and JUNKINS, J. N.  
1938. FULL-SCALE PRODUCTION OF METAPHOSPHATE ACHIEVED AT WILSON DAM. *Chem. & Metall. Engin.* 45: 318-322, illus.
- (25) ——— COPSON, RAYMOND L., BROWN, EARL H., and POLE, GORDON R.  
1937. FERTILIZER FROM PHOSPHATE ROCK: CONVERSION BY FUSION AND TREATMENT WITH WATER VAPOR. *Indus. and Engin. Chem., Indus. Ed.* 29: 766-770, illus.
- (26) ——— MILLER, A. M., and NEWTON, R. H.  
1938. T. V. A. REVIEWS ITS EXPERIENCE IN PHOSPHATE SMELTING. *Chem. & Metall. Engin.* 45: 116-120, illus.
- (27) DAVIS, HAROLD S., and DAVIS, MARY D.  
1920. THE DETECTION OF ARSENIC IN SULFUR. *Jour. Indus. and Engin. Chem.* 12: 479-480.
- (28) DAVY, EDMUND WILLIAM.  
1859. ON THE PRESENCE OF ARSENIC IN SOME ARTIFICIAL MANURES, AND ITS ABSORPTION BY PLANTS GROWN WITH SUCH MANURES. *London, Edinb. and Dublin Phil. Mag. and Jour. Sci.* (4) 18: 108-113.
- (29) DECKERT, W.  
1935. ZUR FRAGE DES PHYSIOLOGISCHEN ARSENS UND DER VERWENDUNG DES KJELDAHLKOLBENS ZU SEINEM NACHWEIS. *Ztschr. f. Analyt. Chem.* 101: 338-339.
- (30) DERMER, R. B., and SCHRIKKER, J. A.  
1933. DETERMINATION OF ARSENIC IN PLANT MATERIALS. *Assoc. Off. Agr. Chem. Jour.* 16: 226-232.
- (31) DENIGÈS, G.  
1920. RÉACTION DE COLORATION EXTRÊMEMENT SENSIBLE DES PHOSPHATES ET DES ARSÉNATES, SES APPLICATIONS. [Paris] *Acad. des Sci. Compt. Rend.* 171: 802-804.
- (32) ———  
1921. DÉTERMINATION QUANTITATIVE DES PLUS FAIBLES QUANTITÉS DE PHOSPHATES DANS LES PRODUITS BIOLOGIQUES PAR LA MÉTHODE CÉRULÉOMOLYBDIQUE. *Soc. de Biol. [Paris] Compt. Rend.* 84: 875-877.
- (33) DOHERTY, W. M.  
1896. ARSENIC IN COAL. *Chem. News* 73: 191-192.
- (34) DORMAN, CLARENCE, TUCKER, FREDERICK H., and COLEMAN, RUSSELL.  
1939. THE EFFECT OF CALCIUM ARSENATE UPON THE PRODUCTIVITY OF SEVERAL IMPORTANT SOILS OF THE COTTON BELT. *Amer. Soc. Agron. Jour.* 31: 1020-1028.
- (35) DRINKWATER.  
1885. ON A NEW VARIETY OF PYRITES FOR SULPHURIC ACID MANUFACTURE. *Analyst* 10: 109-111.
- (36) DUNN, J. T., and BLOXAM, H. C. L.  
1933. THE OCCURRENCE OF LEAD, COPPER, ZINC, AND ARSENIC COMPOUNDS IN ATMOSPHERIC DUSTS, AND THE SOURCES OF THESE IMPURITIES. *Soc. Chem. Indus. Jour., Trans. and Commun.* 52: [189T]-192T.

- (37) EASTERWOOD, HENRY  
1933. MAKING THE  
*Metall.* 12
- (38) FERNEY, FRANCIS N.  
1936. PHOSPHORIC  
& Metall.
- (39) FEUBEL, ALBERT.  
1912. ÜBER DEN  
NATRIUM
- (40) FRESSENIUS, H.  
1889. ÜBER DEN  
DESSEN U.
- (41) FULTON, H. B.  
1886. ARSENIC IN  
TREATME  
Chem. in
- (42) GADDUM, L. W., and  
1936. A STUDY OF  
Fla. Agr.
- (43) GAUTIER, ARMAND.  
1902. LOCALISATION  
DES ANIM  
des Sci. C
- (44) ———  
1903. ARSENIC DE  
DE CUIV  
QUELQUE  
Rend. 13
- (45) ———  
1903. L'ARSENIC  
ANIMALE  
301.
- (46) ——— and CLAYTON  
1904. ORIGINE  
[Philos. A]
- (47) GIBBS, H. D., and  
1905. ON THE  
Jour. 27
- (48) GILBY, Z. M., and  
1939. ARSENIC IN  
Sci. 1
- (49) GOLDSCHMIDT, V. M.  
1934. ZUR  
Mat. 1
- (50) GOY, [S.] and  
1927. ÜBER DEN  
Ztschr.
- (51) GREAVES, J. I.  
1917. THE  
BOT.
- (52) GRIMMETT, R. I.  
1939. ARSENIC IN  
ING OF  
illus.
- (53) ——— and MELBY  
1939. OCCURREN  
VALLEY  
Zool. 1
- (54) ——— McIN  
1939. OCCURREN  
VALLEY  
ANIM  
Sci.
- (55) GUERNEY, J.  
1924. THE  
Ill.

- (37) EASTERWOOD, HENRY W.  
1933. MAKING PHOSPHORIC ACID IN THE BLAST FURNACE. *Chem. & Metall. Engin.* 40: 283-287, illus.
- (38) FERNEY, FRANCIS X.  
1936. PHOSPHORIC ACID AND PHOSPHATES FROM NELSONITE ORE. *Chem. & Metall. Engin.* 43: 22-26, illus.
- (39) FEUBEL, ALBERT.  
1912. ÜBER DEN ARSENGEHALT UND SEINE WIRKUNG IN TECHNISCHEM Natriumphosphat. *Färber-Ztg.* 23: 235-236.
- (40) FRESSENIUS, H.  
1889. UEBER DEN ARSENGEHALT DER FUTTERKNOCHENMEHLE UND DESSEN BESTIMMUNG. *Ztschr. f. Analyt. Chem.* 28: 64-67.
- (41) FULTON, H. B.  
1886. ARSENIC IN SPANISH PYRITES, AND ITS ELIMINATION IN THE LOCAL TREATMENT FOR PRODUCTION OF COPPER PRECIPITATE. *Soc. Chem. Indus. Jour.* 5: 296-300.
- (42) GADDUM, L. W., and ROGERS, L. H.  
1936. A STUDY OF SOME TRACE ELEMENTS IN FERTILIZER MATERIALS. *Fla. Agr. Expt. Sta. Bul.* 290, 15 pp.
- (43) GAUTIER, ARMAND.  
1902. LOCALISATION DE L'ARSENIC NORMAL DANS QUELQUES ORGANES DES ANIMAUX ET DES PLANTES. SES ORIGINES. [Paris] *Acad. des Sci. Compt. Rend.* 135: 833-838.
- (44) ————  
1903. ARSENIC DANS LES EAUX DE MER, DANS LE SEL GEMME, LE SEL DE CUISINE, LES EAUX MINÉRALES, ETC. SON DOSAGE DANS QUELQUES RÉACTIFS USUELS. [Paris] *Acad. des Sci. Compt. Rend.* 137: 232-237, 374-375.
- (45) ————  
1903. L'ARSENIC EXISTE-T-IL DANS TOUS LES ORGANES DE L'ÉCONOMIE ANIMALE? [Paris] *Acad. des Sci. Compt. Rend.* 137: 295-301.
- (46) ———— and CLAUSMANN, P.  
1904. ORIGINES ALIMENTAIRES DE L'ARSENIC NORMAL CHEZ L'HOMME. [Paris] *Acad. des Sci. Compt. Rend.* 139: 101-108.
- (47) GIBBS, H. D., and JAMES, C. C.  
1905. ON THE OCCURRENCE OF ARSENIC IN WINES. *Amer. Chem. Soc. Jour.* 27: 1484-1496.
- (48) GILEVA, Z. M., and MELENTIEV, B. N.  
1939. ARSENIC IN THE APATITES OF THE Khibiny TUNDRAS. *Acad. des Sci. U. S. S. R. Compt. Rend. (Dok.)* 2: 118-119.
- (49) GOLDSCHMIDT, V. M., and PETERS, Cl.  
1934. ZUR GEOCHEMIE DES ARSENS. *Gesell. der Wiss. zu Göttingen, Math. Phys. Kl., Fachgruppe IV Nachr. (n. f.)* 1 (2): [11]-22.
- (50) GOY, [S.] and RUDOLPH, W.  
1927. ÜBER DEN GEHALT VON OSTPREUSSISCHEN GEWÄSSERN AN ARSEN. *Ztschr. f. Angew. Chem.* 40: 945-948.
- (51) GREAVES, J. E.  
1917. THE INFLUENCE OF ARSENIC ON THE BACTERIAL ACTIVITIES OF A SOIL. *Sci. Monthly* 5: 204-209.
- (52) GRIMMETT, R. E. R.  
1939. ARSENICAL SOILS OF THE WAIOTAPU VALLEY. EVIDENCE OF POISONING OF STOCK AT REPOROA. *New Zeal. Jour. Agr.* 58: 383-391, illus.
- (53) ———— and McINTOSH, I. G.  
1939. OCCURRENCE OF ARSENIC IN SOILS AND WATERS IN THE WAIOTAPU VALLEY, AND ITS RELATION TO STOCK HEALTH. PART I. *New Zeal. Jour. Sci. and Technol., Agr. Sect.* 21: [137A]-145A, illus.
- (54) ———— McINTOSH, I. G., WALL, E. M., and JONES, G. B.  
1939. OCCURRENCE OF ARSENIC IN SOILS AND WATERS IN THE WAIOTAPU VALLEY, AND ITS RELATION TO STOCK HEALTH. PART III. EXPERIMENTS, OBSERVATIONS, AND ANALYTICAL RESULTS ON FARM ANIMALS AT REPOROA. *New Zeal. Jour. Sci. and Technol., Agr. Sect.* 21: 150A-160A, illus.
- (55) GUERNSEY, E. W., and YEE, J. Y.  
1924. THE PREPARATION AND CHEMICAL NATURE OF CALCINED PHOSPHATE. *Indus. and Engin. Chem.* 16: 228-232, illus.

- (56) HABERLANDT, HERBERT.  
1938. SPECTRAL ANALYTICAL INVESTIGATIONS AND LUMINESCENCE OBSERVATIONS ON FLUORITE AND APATITE. *Mitt. Inst. Radiumforsch.* (No. 414), Akad. der Wiss. Wien, Math.-Nat. Kl. Sitzber. Abt. 2a 147: 137-150. [Abstract in Chem. Abs. 34: 2289-2290, 1940.]
- (57) HAMPE, W.  
1890. MITTHEILUNGEN AUS DEM CHEMISCHEN LABORATORIUM DER BERGAKADEMIE ZU CLAUSTHAL. *Chem. Ztg.* 14: [1777]-1780, illus.
- (58) HASELHOFF, E.  
1899. UEBER DEN ARSENGEHALT DER SUPERPHOSPHATE. *Landw. Wehnl. f. Schleswig-Holstein* 49: [637]-639.
- (59) HEADDEN, WM. P.  
1910. THE OCCURRENCE OF ARSENIC IN SOILS, PLANTS, FRUITS AND ANIMALS. *Colo. Sci. Soc. Proc.* 9: [345]-360.
- (60) HENDRICKS, S. B., HILL, W. L., JACOB, K. D., and JEFFERSON, M. E.  
1931. STRUCTURAL CHARACTERISTICS OF APATITE-LIKE SUBSTANCES AND COMPOSITION OF PHOSPHATE ROCK AND BONE AS DETERMINED FROM MICROSCOPICAL AND X-RAY DIFFRACTION EXAMINATIONS. *Indus. and Engin. Chem.* 23: 1413-1418, illus.
- (61) ——— JEFFERSON, M. E., and MOSLEY, V. M.  
1932. THE CRYSTAL STRUCTURES OF SOME NATURAL AND SYNTHETIC APATITE-LIKE SUBSTANCES. *Ztschr. f. Kristallographie, Kristallgeometrie, Kristall Phys., Kristall Chem.* 81: 352-369, illus.
- (62) HERTZOG, E. S.  
1935. DETERMINATION OF ARSENIC IN COAL. *Indus. and Engin. Chem., Analyt. Ed.* 7: 163-165, illus.
- (63) HILL, W. L., and HENDRICKS, S. B.  
1936. COMPOSITION AND PROPERTIES OF SUPERPHOSPHATE: CALCIUM PHOSPHATE AND CALCIUM SULFATE CONSTITUENTS AS SHOWN BY CHEMICAL AND X-RAY DIFFRACTION ANALYSIS. *Indus. and Engin. Chem., Indus. Ed.* 28: 440-447, illus.
- (64) ——— and JACOB, K. D.  
1933. DETERMINATION AND OCCURRENCE OF IODINE IN PHOSPHATE ROCK. *Assoc. Off. Agr. Chem. Jour.* 16: 128-137.
- (65) ——— JACOB, K. D., ALEXANDER, L. T., and MARSHALL, H. L.  
1930. CHEMICAL AND PHYSICAL COMPOSITION OF CERTAIN FINELY DIVIDED NATURAL PHOSPHATES FROM FLORIDA. *Indus. and Engin. Chem.* 22: 1392-1396, illus.
- (66) ——— MARSHALL, H. L., and JACOB, K. D.  
1931. COMPOSITION OF MECHANICAL SEPARATES FROM GROUND PHOSPHATE ROCK. *Indus. and Engin. Chem.* 23: 1120-1124, illus.
- (67) ——— MARSHALL, H. L., and JACOB, K. D.  
1932. COMPOSITION OF CRUDE PHOSPHORIC ACID PREPARED BY SULFURIC ACID PROCESS. *Indus. and Engin. Chem.* 24: 1064-1068, illus.
- (68) ——— MARSHALL, H. L., and JACOB, K. D.  
1932. MINOR METALLIC CONSTITUENTS OF PHOSPHATE ROCK. *Indus. and Engin. Chem.* 24: 1306-1312, illus.
- (69) ——— MARSHALL, H. L., and JACOB, K. D.  
1933. OCCURRENCE OF SULFUR, ORGANIC MATTER, NITROGEN, AND WATER IN PHOSPHATE ROCK. *Assoc. Off. Agr. Chem. Jour.* 16: 260-276.
- (70) HILLEBRAND, W. F., and LUNDELL, G. E. F.  
1929. APPLIED INORGANIC ANALYSIS; WITH SPECIAL REFERENCE TO THE ANALYSIS OF METALS, MINERALS AND ROCKS. 929 pp., illus. New York and London.
- (71) HOEHNE, KARL.  
1934. QUANTITATIV CHEMISCHE UND ERZMIKROSKOPISCHE BESTIMMUNG VON ARSEN, ANTIMON, ZINN UND WISMUT IN VORWIEGEND SCHLESISCHEN BLEIGLANZEN. *Chem. der Erde* 9: [219]-268, illus.
- (72) ——— and PETRASCHKE, W. E.  
1936. DER ARSENGEHALT EINIGER OBERKARBONISCHER UND ROTLEIGENDER SEDIMENTE IN MITTELSCHLESSEN UND BOHMEN. *Chem. der Erde* 10: [475]-478.
- (73) HOFFMAN, JAMES I., and LUNDELL, G. E. F.  
1938. ANALYSIS OF VOLATILIZATION PERCHLORIC ACID. *Jour. Res. Nat. Bur. Stand.* 42: 1-10.
- (74) ——— and LUNDELL, G. E. F.  
1939. VOLATILIZATION PERCHLORIC ACID. *Jour. Res. Nat. Bur. Stand.* 43: 1-10.
- (75) HURD-KARRER, ANNIE.  
1936. INHIBITION OF ARSENIC VOLATILIZATION BY PERCHLORIC ACID. *Acad. Sci. J. U. S. A.* 1: 1-10.
- (76) HUSEMANN, TH.  
1879. MITTHEILUNGEN AUS DEM CHEMISCHEN LABORATORIUM DER BERGAKADEMIE ZU CLAUSTHAL. *Arch. der Pharm.* 1: 1-10.
- (77) INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.  
1928. LES RESERVES DE PHOSPHORE PAR L'INITIATIVE INTERNATIONALE DES SERVICES CHIMIQUES. *Publ. Serv. Ch. Pays.* 2 v., illus.
- (78) [ISAKOV, E. N.]  
1939. [REASONS FOR THE OCCURRENCE OF ARSENIC IN COAL.] *Jour. Russian Chem. Soc.* 17: 1-10.
- (79) JACOB, K. D., BARTHOLOMEW, F. R., and HILL, W. L.  
1935. NUTRIENT VALUE OF SUPERPHOSPHATE DETERMINED BY FEEDING EXPERIMENTS. *Jour. Agr. Res.* 48: 1-10.
- (80) ——— HILL, W. L., and JACOB, K. D.  
1930. THE COMPOSITION OF SUPERPHOSPHATE. *Jour. Agr. Res.* 43: 1-10.
- (81) ——— HILL, W. L., and JACOB, K. D.  
1933. THE COMPOSITION OF SUPERPHOSPHATE. *Jour. Agr. Res.* 46: 1-10.
- (82) ——— and REYNOLDS, D. B.  
1928. THE COMPOSITION OF SUPERPHOSPHATE. *Jour. Agr. Res.* 41: 1-10.
- (83) ——— REYNOLDS, D. B.  
1936. PHOSPHORIC ACID AND SUPERPHOSPHATE. *Jour. Agr. Res.* 49: 1-10.
- (84) JOH, ROBERT, and JACOB, K. D.  
1902. ARSENIC IN COAL. *Jour. Agr. Res.* 15: 1-10.
- (85) JONES, A. J.  
1922. THE ARSENIC IN COAL. *Jour. Agr. Res.* 35: 1-10.
- (86) JONES, J. S., and HILL, W. L.  
1937. THE SIGNIFICANCE OF ARSENIC IN COAL. *Jour. Agr. Res.* 50: 1-10.
- (87) KIRKPATRICK, SIDNEY.  
1937. PHOSPHORIC ACID AND SUPERPHOSPHATE. *Jour. Agr. Res.* 50: 1-10.
- (88) KOHN-ARREST, F.  
1918. PRESENCE OF ARSENIC IN COAL. *Jour. Agr. Res.* 31: 1-10.
- (89) [KRYUKOV, V. A.]  
1931. [THE PRESENCE OF ARSENIC IN COAL.] *Jour. Russian Chem. Soc.* 9: 1-10.

- (73) HOFFMAN, JAMES I., and LUNDELL, G. E. F.  
1938. ANALYSIS OF PHOSPHATE ROCK. [U. S.] Natl. Bur. Standards  
Jour. Res. 20: 607-626, illus.
- (74) ——— and LUNDELL, G. E. F.  
1939. VOLATILIZATION OF METALLIC COMPOUNDS FROM SOLUTIONS IN  
PERCHLORIC OR SULFURIC ACID. [U. S.] Natl. Bur. Standards  
Jour. Res. 22: 465-470, illus.
- (75) HURD-KARRER, ANNIE M.  
1936. INHIBITION OF ARSENIC INJURY TO PLANTS BY PHOSPHORUS. Wash.  
Acad. Sci. Jour. 26: 180-181.
- (76) HUSEMANN, TH.  
1879. MITTHEILUNGEN AUS DER SCANDINAVISCHEN PHARMACEUTISCHEN  
LITERATUR. I. VERGIFTUNG MIT SCHWEDISCHEN ZÜNDHÖLZERN.  
Arch. der Pharm. (3) 15: 518-521.
- (77) INTERNATIONAL CONGRESS OF GEOLOGISTS.  
1928. LES RÉSERVES MONDIALES EN PHOSPHATES. INFORMATION FAITE  
PAR L'INITIATIVE DU BUREAU DU XIV<sup>e</sup> CONGRÈS GÉOLOGIQUE  
INTERNATIONAL ESPAGNE, 1928 AVEC LA COLLABORATION DES  
SERVICES GÉOLOGIQUES ET DES SPÉCIALISTES DES DIFFÉRENTS  
PAYS. 2 v., illus. Madrid.
- (78) [ISAKOV, E. N.]  
1939. [REASONS FOR THE PRESENCE OF ARSENIC IN THERMAL PHOSPHORIC  
ACID.] Jour. Chem. Indus. [U. S. S. R.] 16 (1): 22-23. [In  
Russian.]
- (79) JACOB, K. D., BARTHOLOMEW, R. P., BROWN, B. E., PIERRE, W. H., REID,  
F. R., and TIDMORE, J. W.  
1935. NUTRIENT VALUE OF THE PHOSPHORUS IN CALCINED PHOSPHATE AS  
DETERMINED BY GROWTH OF PLANTS IN GREENHOUSE EXPERI-  
MENTS. Jour. Agr. Res. 50: 837-848.
- (80) ——— HILL, W. L., and HOLMES, R. S.  
1930. THE COLLOIDAL NATURE OF SOME FINELY DIVIDED NATURAL  
PHOSPHATES. Colloid Symposium Ann. 7: 195-204.
- (81) ——— HILL, W. L., MARSHALL, H. L., and REYNOLDS, D. S.  
1933. THE COMPOSITION AND DISTRIBUTION OF PHOSPHATE ROCK WITH  
SPECIAL REFERENCE TO THE UNITED STATES. U. S. Dept. Agr.  
Tech. Bul. 364, 90 pp.
- (82) ——— and REYNOLDS, D. S.  
1928. THE FLUORINE CONTENT OF PHOSPHATE ROCK. Assoc. Off. Agr.  
Chem. Jour. 11: 237-250.
- (83) ——— REYNOLDS, D. S., and MARSHALL, H. L.  
1936. PHOSPHATE FERTILIZERS BY CALCINATION PROCESS—VOLATILIZA-  
TION OF FLUORINE FROM PHOSPHATE ROCK AT HIGH TEMPERA-  
TURES. Aider. Inst. Mining and Metall. Engin. Tech. Pub.  
695, 14 pp., illus.
- (84) JOB, ROBERT, and YOUNG, J. B.  
1902. ARSENIC CONTENT OF CERTAIN PENNSYLVANIA ANTHRACITES. Soc.  
Chem. Indus. Jour. 21: 693.
- (85) JONES, A. J.  
1922. THE ARSENIC CONTENT OF SOME OF THE MARINE ALGAE. Pharm.  
Jour. [London] 109: 86-87.
- (86) JONES, J. S., and HATCH, M. B.  
1937. THE SIGNIFICANCE OF INORGANIC SPRAY RESIDUE ACCUMULATIONS  
IN ORCHARD SOILS. Soil Sci. 44: 37-63, illus.
- (87) KIRKPATRICK, SIDNEY D.  
1937. PHOSPHORUS FOR PROGRESS. Chem. & Metall. Engin. 44: 644-  
[650], illus.
- (88) KOHN-ARREST, E.  
1918. PRÉSENCE ACCIDENTELLE DE L'ARSENIC DANS LES PRODUITS CHI-  
MIQUES USUELS ET DANS QUELQUES ALIMENTS. NÉCESSITÉ D'UN  
CONTRÔLE DE LA PURETÉ DES PRODUITS. Rev. des Prod. Chim.  
21: 199-202, 214-216, illus.
- (89) [KRYUKOV, V. A.]  
1931. [THE PHYSIOLOGICAL INFLUENCE OF THOMAS SLAG AND ITS IMPURI-  
TIES VANADIUM AND ARSENIC ON PLANTS.] Udobrenie i Urozhaï  
1931 (3): 627-635. [Abstract in Chem. Abs. 26: 1373, 1932.]

- (90) LARISON, E. L.  
1929. MANUFACTURE OF HIGH-ANALYSIS PHOSPHATES. *Indus. and Engin. Chem.* 21: 1172-1175, illus.
- (91) LING, ARTHUR R., and NEWLANDS, B. E. R.  
1901. EXAMINATION OF FUELS EMPLOYED IN MALTING, WITH SPECIAL REFERENCE TO THE ARSENIC THEY CONTAIN. *Fed. Inst. Brewing Jour.* 7: 314-326.
- (92) LOCKEMANN, GEORG.  
1935. ZUR FRAGE DES PHYSIOLOGISCHEN ARSENS UND DER VERWENDUNG DES KJELDAHLKOLBENS ZU SEINEM NACHWEIS. *Ztschr. f. Analyt. Chem.* 100: 20-29.
- (93) ———  
1935. SCHLUSSWORT ZU DEN AUSFÜHRUNGEN VON DR. W. DECKERT: "ZUR FRAGE DES PHYSIOLOGISCHEN ARSENS UND DER VERWENDUNG DES KJELDAHLKOLBENS ZU SEINEM NACHWEIS." *Ztschr. f. Analyt. Chem.* 101: 340-341.
- (94) LONGFIELD-SMITH, L.  
1933. ENFORCEMENT OF ARSENICAL SPRAY LAW. REPORT OF CHEMIST. ANALYTICAL WORK. *Fla. Dept. Agr. Quart. Bul.* 42 (2): 27-33, illus.
- (95) MCHARGUE, J. S.  
1935. REPORT ON LESS COMMON ELEMENTS IN SOILS. *Assoc. Off. Agr. Chem. Jour.* 18: 207-210.
- (96) MANSFIELD, GEORGE ROGERS, and GIRTY, G. H.  
1927. GEOGRAPHY, GEOLOGY, AND MINERAL RESOURCES OF PART OF SOUTHEASTERN IDAHO WITH DESCRIPTIONS OF CARBONIFEROUS AND TRIASSIC FOSSILS. *U. S. Geol. Survey Prof. Paper* 152, 453 pp., illus.
- (97) MARSHALL, H. L.  
1934. THE OCCURRENCE OF FERROUS IRON IN PHOSPHATE ROCK. *Jour. Agr. Res.* 49: 71-76.
- (98) ——— JACOB, K. D., and REYNOLDS, D. S.  
1932. OCCURRENCE OF FLUORINE IN NATURAL PHOSPHATES: FURTHER STUDIES. *Indus. and Engin. Chem.* 24: 86-89.
- (99) ——— REYNOLDS, D. S., JACOB, K. D., and TREMEARNE, T. H.  
1937. PHOSPHATE FERTILIZERS BY CALCINATION PROCESS: REVERSION OF DEFLUORINATED PHOSPHATE AT TEMPERATURES BELOW 1,000° C. *Indus. and Engin. Chem., Indus. Ed.* 29: 1291-1298, illus.
- (100) MELLOR, J. W.  
1929. ARSENIC. In *his A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, v. 9, ch. 51, illus. London, New York [etc.].
- (101) MEMMINGER, C. G., WAGGAMAN, W. H., and WHITNEY, W. T.  
1930. THE CALCINATION OR ENRICHMENT OF PHOSPHATE ROCK. *Indus. and Engin. Chem.* 22: 443-446, illus.
- (102) MORRIS, H. E., and SWINGLE, D. B.  
1927. INJURY TO GROWING CROPS CAUSED BY THE APPLICATION OF ARSENICAL COMPOUNDS TO THE SOIL. *Jour. Agr. Res.* 34: 59-78, illus.
- (103) NODDACK, IDA, and NODDACK, WALTER.  
1930. DIE HÄUFIGKEIT DER CHEMISCHEN ELEMENTE. *Naturwissenschaften* 18: [757]-764, illus.
- (104) ——— and NODDACK, WALTER.  
1931. DIE GEOCHEMIE DES RHENIUMS. *Ztschr. f. Phys. Chem. Abt. A: Chem. Thermodynamik* 154: 207-244.
- (105) O'CONNOR, HENRY, and DRINKWATER.  
1908. REMOVAL OF ARSENIC FROM GAS COKE. *Jour. Gas Lighting* 102: 164-165.
- (106) PARDEE, J. T.  
1936. PHOSPHATE ROCK NEAR MAXVILLE, PHILIPSBURG, AND AVON, MONTANA. *U. S. Geol. Survey Bul.* 847: 175-188, illus.
- (107) PRIPSON, T. L.  
1862. SUR LE SOUFRE ARSÉNIFÈRE DES SOLFATARES DE NAPLES ET LA PRÉPARATION DU SÉLÉNIUM. [Paris] *Acad. des Sci. Compt. Rend.* 55: 108-109.
- (108) ———  
1901. ON THE PRESENCE OF ARSENIC IN VARIOUS COMMERCIAL PRODUCTS. *Chem. News* 83: 61.

- (109) PINCHBECK, G.  
1900. ARSENIC
- (110) RADER, LEWIS F.  
1936. OCCURRENCE OF ARSENIC IN PHOSPHATE ROCK. *Jour. Agr. Res.* 49: 71-76.
- (111) ——— and HILL, J. H.  
1938. DETERMINATION OF ARSENIC IN PHOSPHATE ROCK. *Jour. Agr. Res.* 51: 107-110.
- (112) RAKESTRAW, N. O.  
1933. ARSENIC
- (113) READMAN, J. B.  
1890. AN ACCIDENTAL POISONING BY ARSENIC. *Soc. Chem. Indus. Trans.* 1890: 107-108.
- (114) REICHERT, FEDERICO  
1921. IODOLOGIA DEL SODIO. *Ann. Chim. (N. S.)* 21: 107-110.
- (115) ——— and TRELAWNY, J. H.  
1921. SOBBUSI. *Ann. Chim. (N. S.)* 21: 107-110.
- (116) REYNOLDS, D. S.  
1935. FURTHER STUDIES ON THE OCCURRENCE OF FLUORINE IN NATURAL PHOSPHATES. *Indus. and Engin. Chem.* 27: 107-110.
- (117) ——— and JACOB, K. D.  
1933. VOLATILE FLUORIDES IN PHOSPHATE ROCK. *Jour. Agr. Res.* 49: 71-76.
- (118) ——— JACOB, K. D.  
1929. RATIO OF FLUORINE TO PHOSPHORUS IN PHOSPHATE ROCK. *Jour. Agr. Res.* 49: 71-76.
- (119) ——— JACOB, K. D.  
1934. PHOSPHATE ROCKS OF THE UNITED STATES. *Jour. Agr. Res.* 49: 71-76.
- (120) ROSS, WILLIAM H.  
1922. THE OCCURRENCE OF ARSENIC IN PHOSPHATE ROCK. *Jour. Agr. Res.* 49: 71-76.
- (121) ——— and JACOB, K. D.  
1937. REPORT ON THE OCCURRENCE OF ARSENIC IN PHOSPHATE ROCK. *Jour. Agr. Res.* 50: 107-110.
- (122) ——— and MERRILL, J. H.  
1932. SYNTHESIS OF ARSENIC TRIOXIDE. *Jour. Agr. Res.* 49: 71-76.
- (123) SCHRICKEK, JOSEF  
1939. IMPROVED PHOSPHATE ROCKS. *Jour. Agr. Res.* 52: 107-110.
- (124) SHIREY, WILLIAM  
1931. METALLURGY OF ARSENIC. *Jour. Agr. Res.* 49: 71-76.
- (125) SIMMERSDACH, O.  
1917. ARSENIC IN PHOSPHATE ROCK. *Jour. Agr. Res.* 49: 71-76.
- (126) SLATER, C. S., HULL, J. H.  
1937. TRACE ELEMENTS IN PHOSPHATE ROCK. *Jour. Agr. Res.* 50: 107-110.
- (127) SMITH, H. A.  
1871. ARSENIC IN PHOSPHATE ROCK. *Jour. Agr. Res.* 49: 71-76.
- (128) SMITH, R. F., WALKER, J. H.  
1901. ARSENIC IN PHOSPHATE ROCK. *Jour. Agr. Res.* 49: 71-76.

- (109) PINCHBECK, G.  
1900. ARSENIC IN SODIUM PHOSPHATE. *Pharm. Jour.* [London] 65: 216.
- (110) RADER, LEWIS F., JR., and HILL, W. L.  
1936. OCCURRENCE OF SELENIUM IN NATURAL PHOSPHATES, SUPERPHOSPHATES, AND PHOSPHORIC ACID. *Jour. Agr. Res.* 51: 1071-1083.
- (111) ——— and HILL, W. L.  
1938. DETERMINATION AND OCCURRENCE OF BORON IN NATURAL PHOSPHATES, SUPERPHOSPHATES, AND DEFLUORINATED PHOSPHATE ROCK. *Jour. Agr. Res.* 57: 901-916, illus.
- (112) RAKESTRAW, NORRIS W., and LUTZ, FRANK B.  
1933. ARSENIC IN SEA WATER. *Biol. Bul.* 65: 397-401.
- (113) READMAN, J. B.  
1890. AN ACCOUNT OF THE MANUFACTURE OF PHOSPHORUS.—PART I. *Soc. Chem. Indus. Jour.* 9: 163-165.
- (114) REICHELT, FEDERICO, and TRELLES, ROGELIO A.  
1921. IODO Y ARSÉNICO EN LAS AGUAS SUBTERRANEAS (DATOS PARA LA HIDROLOGÍA DE LA REPÚBLICA ARGENTINA). *Asoc. Quím. Argentina An.* 9: 80-85.
- (115) ——— and TRELLES, ROGELIO A.  
1921. SOBRE LA PRESENCIA DEL ARSÉNICO COMO ELEMENTO NORMAL EN LAS TIERRAS VEGETALES. *Asoc. Quím. Argentina An.* 9: 89-95.
- (116) REYNOLDS, D. S.  
1935. FURTHER STUDIES ON THE WILLARD AND WINTER METHOD FOR THE DETERMINATION OF FLUORINE. *Assoc. Off. Agr. Chem. Jour.* 18: 108-113.
- (117) ——— and JACOB, K. D.  
1933. VOLATILIZATION OF FLUORINE IN THE MANUFACTURE OF PHOSPHORUS AND PHOSPHORIC ACID BY FURNACE PROCESSES. *Indus. and Engin. Chem., Indus. Ed.* 25: 1321-1323.
- (118) ——— JACOB, K. D., and HILL, W. L.  
1929. RATIO OF FLUORINE TO PHOSPHORIC ACID IN PHOSPHATE ROCK. *Indus. and Engin. Chem.* 21: 1253-1256.
- (119) ——— JACOB, K. D., and RADER, L. F., JR.  
1934. PHOSPHATE FERTILIZERS BY CALCINATION PROCESS: ACTION OF SILICA AND WATER VAPOR ON PHOSPHATE ROCK. *Indus. and Engin. Chem., Indus. Ed.* 26: 406-412, illus.
- (120) ROSS, WILLIAM H., DURGIN, C. B., and JONES, R. M.  
1922. THE COMPOSITION OF COMMERCIAL PHOSPHORIC ACID. *Jour. Indus. and Engin. Chem.* 14: 533-535.
- (121) ——— and JACOB, K. D.  
1937. REPORT ON PHOSPHORIC ACID. AVAILABILITY OF CALCINED PHOSPHATE AND OTHER NEW PHOSPHATIC MATERIALS AS DETERMINED BY CHEMICAL AND VEGETATIVE TESTS. *Assoc. Off. Agr. Chem. Jour.* 20: 231-249.
- (122) ——— and MERZ, ALBERT R.  
1932. SYNTHETIC NITROGENOUS FERTILIZERS. In Curtis, H. A., ed., *Fixed Nitrogen*, pp. 409-466, illus. New York.
- (123) SCHBICKER, JOHN A., and DAWSON, PAUL R.  
1939. IMPROVED MOLYBDENUM BLUE REAGENTS FOR DETERMINATION OF PHOSPHORUS AND ARSENIC. *Assoc. Off. Agr. Chem. Jour.* 22: 167-179, illus.
- (124) SHIRRY, WILLIAM B.  
1931. METALLIC CONSTITUENTS OF CRUDE PETROLEUM. *Indus. and Engin. Chem.* 23: 1151-1153.
- (125) SIMMERSBACH, OSKAR.  
1917. ARSEN IN KOHLE UND KOKS. *Stahl u. Eisen* 37: 502.
- (126) SLATER, C. S., HOLMES, R. S., and BYERS, H. G.  
1937. TRACE ELEMENTS IN THE SOILS FROM THE EROSION EXPERIMENT STATIONS, WITH SUPPLEMENTARY DATA ON OTHER SOILS. U. S. Dept. Agr. Tech. Bul. 552, 24 pp.
- (127) SMITH, H. A.  
1871. ARSENIC IN PYRITES AND VARIOUS PRODUCTS. *Chem. News* 23: 221.
- (128) SMITH, R. F. WOOD, and JENKS, R. L.  
1901. ARSENIC IN COAL AND COKE. *Soc. Chem. Indus. Jour.* 20: 437.

ATURE

is. and Engin.

WITH SPECIAL  
Inst. Brewing

VERWENDUNG  
chr. f. Analyt.

CKERT: "ZUR  
VERWENDUNG  
Ztschr. f.

OF CHEMIST.  
2 (2): 27-33,

oc. Off. Agr.

OF PART OF  
RBONIFEROUS  
aper 152, 453

ROCK. Jour.

ES: FURTHER

H.

EVERSION OF  
LOW 1,000° C.  
98, illus.

rganic and  
at, New York

OCK. Indus.

PLICATION OF  
es. 34: 59-78,

Naturwissen-

hem, Abt. A:

ighting 102:

AND AVON,  
4, illus.

APLES ET LA  
Sci. Compt.

AL PRODUCTS.

- (129) STEWART, JOHN, and SMITH, EDWIN S.  
1922. SOME RELATIONS OF ARSENIC TO PLANT GROWTH: PART 2. *Soil Sci.* 14: 119-126, illus.
- (130) STOKLASA, JULIUS.  
1898. ÜBER DIE PHYSIOLOGISCHE BEDEUTUNG DES ARSENS IM PFLANZEN-ORGANISMUS. *Ztschr. f. das Landw. Versuchsw. Österr. 1:* [155]-193, illus.
- (131) STUTZER, A.  
1901. IST EIN GEHALT AN ARSENİK IM SUPERPHOSPHAT SCHÄDLICH? *Deut. Landw. Presse* 28: 61.
- (132) SWANN, THEODORE.  
1922. MANUFACTURE OF PHOSPHORIC ACID IN THE ELECTRIC FURNACE BY THE CONDENSATION AND ELECTRIC PRECIPITATION METHOD. *Jour. Indus. and Engin. Chem.* 14: 630-631.
- (133) TABER, W. C.  
1931. REPORT ON ARSENIC. *Assoc. Off. Agr. Chem. Jour.* 14: 436-447.
- (134) TAYLOR, W. C.  
1936. ARSENIC ELIMINATED FROM PYREX CHEMICAL GLASSWARE. *Indus. and Engin. Chem., News Ed.* 14: 23.
- (135) THOMPSON, THOMAS G., and ROBINSON, REX J.  
1932. CHEMISTRY OF THE SEA. *In Physics of the Earth—v. Oceanography, Natl. Res. Council Bul.* 85: 95-203, illus.
- (136) THORNTON, S. F., and KRAYBILL, H. R.  
1937. FURTHER STUDIES ON THE DETERMINATION OF AVAILABLE POTASH IN FERTILIZERS. *Assoc. Off. Agr. Chem. Jour.* 20: 287-292, illus.
- (137) THORPE, T. E.  
1903. THE ESTIMATION OF ARSENIC IN FUEL. [London] *Chem. Soc. Trans.* 83: 969-974, illus.
- (138) TRUOG, EMIL, and MEYER, A. H.  
1929. IMPROVEMENTS IN THE DENIGÈS COLORIMETRIC METHOD FOR PHOSPHORUS AND ARSENIC. *Indus. and Engin. Chem., Analyt. Ed.* 1: 136-139, illus.
- (139) TYLER, PAUL M., and MOSLEY, HERBERT R.  
1939. RECENT DEVELOPMENTS IN THE TENNESSEE PHOSPHATE INDUSTRY. *Amer. Inst. Mining and Metall. Engin. Tech. Pub.* 1053, 22 pp., illus.
- (140) VANDECAVEYE, S. C., HORNER, G. M., and KEATON, C. M.  
1936. UNPRODUCTIVENESS OF CERTAIN ORCHARD SOILS AS RELATED TO LEAD ARSENATE SPRAY ACCUMULATIONS. *Soil Sci.* 42: 203-215, illus.
- (141) WAGGAMAN, WILLIAM H., EASTERWOOD, HENRY W., and TURLEY, THOMAS B.  
1923. INVESTIGATIONS OF THE MANUFACTURE OF PHOSPHORIC ACID BY THE VOLATILIZATION PROCESS. *U. S. Dept. Agr. Bul.* 1179, 55 pp., illus.
- (142) ——— and WAGNER, C. R.  
1918. THE USE OF "MINE RUN" PHOSPHATES IN THE MANUFACTURE OF SOLUBLE PHOSPHORIC ACID. *Jour. Indus. and Engin. Chem.* 10: 353-355.
- (143) WALKER, PERCY H., and SMITHER, F. W.  
1917. COMPARATIVE TESTS OF CHEMICAL GLASSWARE. *Jour. Indus. and Engin. Chem.* 9: 1090-1092, illus.
- (144) WEBER, WILLIAM C.  
1932. MAKING STRONG PHOSPHORIC ACID AT TRAIL. *Chem. & Metall. Engin.* 39: 659-662, illus.
- (145) WILLIAMS, J. STEWART.  
1939. PHOSPHATE IN UTAH. *Utah Agr. Expt. Sta. Bul.* 290, 44 pp., illus.
- (146) WILLIAMS, KENNETH T., and WHETSTONE, RICHARD R.  
1940. ARSENIC DISTRIBUTION IN SOILS AND ITS PRESENCE IN CERTAIN PLANTS. *U. S. Dept. Agr. Tech. Bul.* 732, 20 pp., illus.
- (147) WINKLER, CLEMENS.  
1900. UEBER DIE VERMEINTLICHE UMWANDELUNG DES PHOSPHORS IN ARSEN. *Deut. Chem. Gesell. Ber.* 33: 1693-1697.

- (148) WYLD, WILFRID.  
1923. RAW MATERIALS IN THE MANUFACTURE OF GLASS. London and Edinburgh: Butterworths, 1923, 100 pp., illus.
- (149) ———  
1924. THE MANUFACTURE OF GLASS. London and Edinburgh: Butterworths, 1924, 100 pp., illus.
- (150) YOE, JOHN H.  
1924. THE ADSORPTION OF ARSENIC BY SOILS. *Amer. Chem. Soc. Div. Ind. Engin. Chem.* 46: 100-102, illus.
- (151) YOUNG, R. S.  
1935. CERTAIN RARE EARTH ELEMENTS AND THEIR RÔLE IN THE MANUFACTURE OF GLASS. *Mem.* 174, 1935, 100 pp., illus.
- (152) ZINZADZE, CH.  
1931. MICRO-DOSAGE DE L'ARSENIC DANS LES TERRES. *Ann. Agron.* 1931, 100 pp., illus.
- (153) ———  
1935. COLORIMETRIC METHOD FOR THE DETERMINATION OF ARSENIC IN GLASS. *Analyst.* 60: 100-102, illus.
- (154) ———  
1935. PHOTOELECTRIC METHOD FOR THE DETERMINATION OF ARSENIC IN GLASS. *Analyst.* 60: 100-102, illus.
- (155) ZUCCARI, GINO.  
1913. SULLA PRESENZA DI ARSENICO NELLE TERRE. *Ann. Agron.* 1913, 100 pp., illus.



- (148) WYLD, WILFRID.  
1923. RAW MATERIALS FOR THE MANUFACTURE OF SULPHURIC ACID, AND THE MANUFACTURE OF SULPHUR DIOXIDE. 558 pp., illus. London and Edinburgh.
- (149) ————  
1924. THE MANUFACTURE OF SULPHURIC ACID (CHAMBER-PROCESS). 424 pp., illus. London and Edinburgh.
- (150) YOE, JOHN H.  
1924. THE ADSORPTION OF ARSENIOSIC ACID BY HYDROUS ALUMINUM OXIDE. Amer. Chem. Soc. Jour. 46: 2390-2397, illus.
- (151) YOUNG, R. S.  
1935. CERTAIN RARER ELEMENTS IN SOILS AND FERTILIZERS, AND THEIR RÔLE IN PLANT GROWTH. N. Y. (Cornell) Agr. Expt. Sta. Mem. 174, 70 pp.
- (152) ZINZADZE, CH.  
1931. MICRO-DOSAGE DES ACIDES PHOSPHORIQUE ET ARSENIQUE PAR CÉRULÉO-MOLYBDIMÉTRIE: APPLICATION AUX EXTRAITS DE SOL. Ann. Agron. [Paris] (n. s.) 1: [321]-336, illus.
- (153) ————  
1935. COLORIMETRIC METHODS FOR DETERMINATION OF ARSENIC IN PHOSPHORUS-FREE SOLUTIONS. Indus. and Engin. Chem., Analyt. Ed. 7: 230.
- (154) ————  
1935. PHOTOELECTRIC PHOTOMETERS FOR USE IN COLORIMETRY. Indus. and Engin. Chem., Analyt. Ed. 7: 280-281, illus.
- (155) ZUCCÀRI, GINO.  
1913. SULLA PRESENZA DELL' ARSENICO COME ELEMENTO NORMALE NELLE TERRE. Gaz. Chim. Ital. 43 (2): 398-403.

ULTURE

PART 2. Soil

IM PFLANZEN-  
SW. ÖSTER. 1:

F SCHÄDLICH:

ERIC FURNACE  
TION METHOD,

14: 436-447.

CARE. Indus.

— v. Ocean-

TABLE POTASH  
20: 287-292,

Chem. Soc.

METHOD FOR  
seu., Analyt.

IE INDUSTRY.  
ub. 1053, 22

RELATED TO  
42: 203-215.

nd TURLEY,

RIC ACID BY  
tol. 1179, 55

FACTURE OF  
n. Chem. 10:

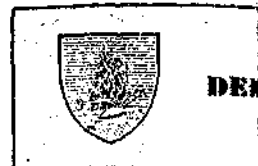
, Indus. and

. & Metall.

44 pp., illus.

IN CERTAIN  
illus.

OSPHORS IN



**ORGANIZATION OF THE UNITED STATES DEPARTMENT OF AGRICULTURE  
WHEN THIS PUBLICATION WAS EITHER FIRST PRINTED OR LAST REVISED**

<i>Secretary of Agriculture</i> .....	CLAUDE R. WICKARD.
<i>Under Secretary</i> .....	PAUL H. APPLEBY.
<i>Assistant Secretary</i> .....	GROVER B. HILL.
<i>Director of Information</i> .....	MORSE SALISBURY.
<i>Director of Extension Work</i> .....	M. L. WILSON.
<i>Director of Finance</i> .....	W. A. JUMP.
<i>Director of Personnel</i> .....	JAMES L. BUCKLEY.
<i>Director of Research</i> .....	JAMES T. JARDINE.
<i>Director of Marketing</i> .....	ROY F. HENDRICKSON.
<i>Solicitor</i> .....	MASTIN G. WHITE.
<i>Land Use Coordinator</i> .....	M. S. EISENHOWER.
<i>Office of Agricultural Defense Relations</i> .....	M. CLIFFORD TOWNSEND, <i>Director</i> .
<i>Office of Plant and Operations</i> .....	ARTHUR B. THATCHER, <i>Chief</i> .
<i>Office of C. C. Activities</i> .....	FRED W. MORRELL, <i>Chief</i> .
<i>Office of Experiment Stations</i> .....	JAMES T. JARDINE, <i>Chief</i> .
<i>Office of Foreign Agricultural Relations</i> .....	LESLIE A. WHEELER, <i>Director</i> .
<i>Agricultural Adjustment Administration</i> .....	R. M. EVANS, <i>Administrator</i> .
<i>Bureau of Agricultural Chemistry and Engineering</i> .....	HENRY G. KNIGHT, <i>Chief</i> .
<i>Bureau of Agricultural Economics</i> .....	H. R. TOLLEY, <i>Chief</i> .
<i>Agricultural Marketing Service</i> .....	C. W. KITCHEN, <i>Chief</i> .
<i>Bureau of Animal Industry</i> .....	JOHN R. MOHLER, <i>Chief</i> .
<i>Commodity Credit Corporation</i> .....	J. B. HUTSON, <i>President</i> .
<i>Commodity Exchange Administration</i> .....	JOSEPH M. MEHL, <i>Chief</i> .
<i>Bureau of Dairy Industry</i> .....	O. E. REED, <i>Chief</i> .
<i>Bureau of Entomology and Plant Quarantine</i> .....	P. N. ANNAND, <i>Chief</i> .
<i>Farm Credit Administration</i> .....	A. G. BLACK, <i>Governor</i> .
<i>Farm Security Administration</i> .....	C. B. BALDWIN, <i>Administrator</i> .
<i>Federal Crop Insurance Corporation</i> .....	LEROY K. SMITH, <i>Manager</i> .
<i>Forest Service</i> .....	EARLE H. CLAPP, <i>Acting Chief</i> .
<i>Bureau of Home Economics</i> .....	LOUISE STANLEY, <i>Chief</i> .
<i>Library</i> .....	RALPH R. SHAW, <i>Librarian</i> .
<i>Bureau of Plant Industry</i> .....	E. C. AUCHTER, <i>Chief</i> .
<i>Rural Electrification Administration</i> .....	HARRY SLATTERY, <i>Administrator</i> .
<i>Soil Conservation Service</i> .....	H. H. BENNETT, <i>Chief</i> .
<i>Surplus Marketing Administration</i> .....	ROY F. HENDRICKSON, <i>Administrator</i> .

This bulletin is a contribution from

*Bureau of Plant Industry*..... E. C. AUCHTER, *Chief*.  
*Division of Soil and Fertilizer Investigations*..... ROBERT M. SALTER, *Chief*.

**Field Studies  
Cabbage**

By W. J. REID, *Jr.*, *an associate entomologist, Truck Crop and Garden Quarantine*<sup>2</sup>

United States Department of Agriculture, Bureau of Plant Quarantine, in cooperation with the State Plant Quarantine Stations of Louisiana

*Introduction*  
Scope of the work  
Cultural practices  
Insects involved  
Materials compared  
Experimental methods  
Initial studies  
Spring of 1933  
Fall of 1933

In those parts of the field where the reduction of cabbage root-knot residues following the use of especially nematicides (Nemacur, this plant (fig. 1) (Riley)), the damage to the imported cabbage in sufficient numbers occasionally they are being harvested and for the natural root-knot series of experiments recommendations especially would eliminate the

<sup>1</sup> Received for publication July 1, 1933.  
<sup>2</sup> W. J. Reid, Jr., Bureau of Plant Quarantine, United States Department of Agriculture, Baton Rouge, Louisiana.  
to C. F. Stahl, who has been in Louisiana since 1934.