CXIV. *On the Inorganic Constituents of Plants.**By* Drs. H. WILL and R. FRESENIUS.

SINCE the true value and importance of inorganic constituents for the existence of plants has been pointed out and established by Professor Liebig, it has become an object of high interest in vegetable physiology and agriculture, to possess an extended series of trustworthy analyses of the ashes of different plants, and of different parts of plants, conducted with reference to the points to which the Professor has directed attention in his work, "Organic Chemistry in its applications to Agriculture and Physiology." We say trustworthy, and thus specially directed analyses, since in those already at command the requisite conditions are but partially supplied.

To the exemplary labours of De Saussure concerning vegetation, is due the undisputed merit of having first incited to a knowledge of the importance of the inorganic constituents of plants; he established the fact by means of numerous analyses of vegetable ashes. The methods of chemical analysis, and especially of the quantitative estimation of the more important constituents of vegetable ashes (phosphoric acid for example), were not however at that time such as to render the results of De Saussure available for the determination of the functions fulfilled in plants by inorganic acids and bases.

Berthier* has also made a considerable number of analyses of the ashes of various woods; his only object however was to ascertain, if possible, what effects the ashes of the wood used as fuel in metallurgy would have upon those processes.

Berthier found by a comparison of his carefully obtained analytical results, that the nature of the ash depended to some extent upon the properties of soil; he observed that the composition of the ashes of the same kind of wood grown on different

* *Ann. de Chimie et de Phys.* xxxii. p. 240.

soils, differed considerably; he showed also that the ashes of different kinds of plants grown upon the same soil were dissimilar, and that plants which are identical or allied in kind, when grown upon the same soil, yield ashes, the compositions of which are also either allied or identical. Finally, Wiegmann and Polstorff*, by ascertaining the quantity of ashes of plants which have vegetated in sand and in artificial mould, have clearly shown that the increase of plants, their growth, and full development are inseparably connected with the organic materials contained in the earth, and that plants will not perfect their seeds if the earth is deficient in phosphates, &c.

All recorded observations clearly show that plants take up indiscriminately the soluble mineral constituents presented to them by the soil; and the results of ash-analyses as distinctly prove, that for the purpose of assimilation by their different parts and organs, they make a selection from those constituents; that the organism of vegetables, like that of animals, takes up and retains those substances which it requires.

It follows from what has been said, that in the analysis of ashes, a number of substances will be found which have not entered into the composition of any organ of the plant, substances which have been dissolved by the juices of the plant; and, since we have no means of safely separating them for the purposes of analysis, they will remain after the ignition mixed with the assimilable and assimilated mineral constituents of the plant.

Nature has provided in the seeds of plants, as in the eggs and milk of animals, all the substances which are necessary for the development of the young individual, so long as it is itself incapable of seeking sustenance externally. In the ashes of seeds we shall find therefore treasured up, and almost pure, the indispensable mineral food of the plants.

The examinations hitherto made of the ashes of seeds indicate that those of the *Cereal*ia, the *Leguminosæ*, the *Crucifera*æ, and among arborescent plants, the *Coniferæ*, consist almost entirely of the alkaline and earthy phosphates. They do not effervesce with acids, they contain however variable quantities of silica and sulphates, but chlorides are either entirely wanting, or merely traces of them exist. The ashes of the seeds of the oak, of the chestnut and of the beech, and probably of many other trees, effervesce strongly with acids; besides phosphates they contain a considerable quantity of carbonates, which have resulted from the salts of vegetable acids contained in the seeds. The proportion of chlorides, sulphates

* *Ueber die unorgan. Bestandtheile der Pflanzen; gekrönte Preisschrift.* Braunschweig, 1842.

and silica to the other constituents, is also in these ashes but small.

We conclude from these facts, that the salts of phosphoric acid are indispensable mineral constituents of the Cerealia, &c., and that the oak and the chestnut, &c. require, besides these, alkalies not united with mineral acids.

It would be very difficult at present accurately to distinguish the so-called essential and non-essential constituents of ashes. A plant requires for its different parts, and at different periods of its growth, a supply of mineral constituents, varying both in quantity and in quality. There is no ash-constituent which we can as yet decide to be entirely unessential. We can however distinguish those which have been assimilated by the plant and have formed a part of it from those which are within the plant, without having been assimilated by it, but await, as it were, their approximation in its future development and maturation. Among the latter we may class the alkaline chlorides and the sulphates, which are always present in vegetable ashes; they exist in the form of soluble compounds in the juices of every plant, and are doubtless indispensable to it, as yielding some of its elements; we have however as yet no reason for supposing that they themselves become constituents of the organs of the plant. According to Guibourt (*Journ. de Pharm.* xxvi. p. 264), the ashes of juicy saline plants contain only 17 per cent. of chlorides to 69 per cent. of carbonates. It would seem highly probable that the bases of salts of vegetable acids are derived from chlorides; the chlorides in this case suffer a decomposition, in which the electro-negative element plays but a subordinate part. These chlorides, which seem so necessary for saline plants, may probably be replaced by other compounds of the same basyles, provided they be not injurious to the plants, and that they be equally soluble with the chlorides, and consequently existing as largely in the juices of the plant.

We have further reason for supposing these constituents to be unessential, from the fact that their quantities from the same kind of plants are variable, without there being evidence that they are replaced by any other body. The quantity of sulphates found in an ash will, however, to some extent, be dependent on the management of the preparation of the ash. If a strong heat, with free access of air, be permitted, part if not all of the sulphur contained in nitrogenized vegetable substances will be converted into sulphuric acid during the ignition. On the other hand, however, if the ash has not been heated sufficiently long with free access of air, the addition of an acid to a portion of it will cause the evolution of a not inconsider-

able quantity of sulphuretted hydrogen, the source of which has been the deoxidized sulphates. In such a case, if it be wished to make a quantitative analysis of the ash, it must be heated with free access of air until the sulphurets are fully oxidated.

The carbonic acid, and the charcoal found in the ashes of most vegetable substances (with the exception of some seeds), are always to be viewed as accidental constituents, having their origin in the operation of combustion; their quantity also is dependent both upon the quantity and quality of the bases present, and upon the degree of heat which has been employed.

We now submit to view a list of the *inorganic* compounds or bodies which have hitherto been found in the normal ashes of vegetables. They are as follow:—

Bases.	Acids or bodies which replace them.
Potash.	Silicic acid.
Soda.	Phosphoric acid.
Lime.	Sulphuric acid.
Magnesia.	Carbonic acid.
Peroxide of iron.	Chlorine.
Oxide of manganese.	Iodine.
Alumina.?	Bromine.
	Fluorine*.

With the exception of iodine, bromine, fluorine and oxide of manganese, the acids and bases enumerated above are found in almost all vegetable ashes. Several chemists have stated that alumina also is found in the ashes of plants. Berthier, on the other hand, did not find a trace of it in the ashes which

* It has long been known that marine plants, and consequently their ashes also, contain iodine and bromine. In some the quantity of iodine is so considerable, that they are had recourse to in commerce for the production of that element, as in Scotland, for example. The existence of fluorine in some vegetable ashes, although extremely probable, has not been proved until recently. Careful experiments, conducted under my own superintendence, by Messrs. James, Müller and Blake severally, have shown that the ashes of French barley, grown in Switzerland, contain very distinct traces of it; both straw and grain were employed. The presence of silica in considerable quantity renders the detection of fluorine very difficult. The process followed was that of H. Rose, which consists in fusing the ash with carbonated alkali, dissolving in water, neutralizing with hydrochloric acid, in a platinum capsule, adding ammonia in excess, after expelling the carbonic acid by evaporation, and precipitating the filtered solution by means of chloride of calcium. In this experiment not less than 10 to 12 grammes of ash should be employed. Fluorine occurs in the teeth and bones of animals, having been derived by them from vegetable food; it will doubtless therefore exist still more abundantly in the ashes of plants: it almost constantly accompanies phosphoric acid, and must therefore be almost as generally diffused on the earth's surface as that acid itself, which is so indispensable both for the vegetable and animal kingdoms.—H. WILL.

he examined, and we have been unable to detect it in all carefully prepared ashes. De Saussure states that the ashes of the bilberry, the pine and the rose-laurel, contain respectively 17·5, 14·8 and 28·8 per cent. of alumina; it is evident however that he has mistaken the earthy phosphates for that substance, and when in subsequent analyses he determined the phosphates, he found no alumina, or merely a trace of it. The behaviour of alumina with solvents sufficiently proves that it cannot be taken up by plants. Pure alumina is equally insoluble in solutions of phosphoric and of carbonic acid; and though we find in almost all vegetable ashes phosphate of the peroxide of iron, which is so nearly allied to alumina in insolubility, it has probably been taken up by the plant as phosphate of the protoxide, which is soluble in a solution of carbonic acid. If the aluminous compounds, which are so abundant in the soil, were soluble, we should find them in all vegetable ashes; and even were the presence of alumina demonstrated in particular cases, we have sufficient reason for supposing that it, as well as the sand, which is frequently met with in the analyses of ashes, has been derived from dust, which has not been removed from the plant with sufficient care previously to the preparation of the ash.

Oxide of copper has also been found occasionally in vegetable ashes; Meissner and Saczeau observed it in those of the Cerealia. In some parts of Germany the seeds of the Cerealia are steeped in a solution of sulphate of copper before being sown, with a view of preventing the destruction of the crop by blight: and when oxide of copper is found in vegetable ashes, it may be attributed either to such treatment, or to the presence of cupreous minerals in the soil; it is always however to be looked upon as unessential or accidental, and not as a necessary constituent of the ashes of the plant.

The relative proportions of the constituents of vegetable ashes vary so much, according to the nature of the plant, or the part of the plant (and also according to the properties of the soil), that it has been attempted to classify plants by reference to the predominant constituent of their ashes. Such a classification will only be attainable when we can, with respect to a large number of analyses, ensure the necessary accuracy: for our immediate purpose, however, that of arranging a method of quantitative ash-analysis, the ashes of vegetables can be generally classed according to the prevalence of some of their constituents.

All vegetable ashes can be arranged according to their composition in the three following groups:—

(a.) *Ashes rich in Alkaline and earthy Carbonates.*—To this

group belong the ashes of woods, herbaceous plants and lichens, inasmuch as these abound in salts of organic acids.

(b.) *Ashes rich in Alkaline and earthy Phosphates*.—Almost all seeds yield ashes belonging to this division.

(c.) *Acids rich in Silica*.—The stems of the Grasses, the Equisetaceæ, &c., yield ashes of this kind.

It will be seen that this classification cannot be strict, and that besides the instances already known, many others will occur of members of the different classes assimilating. The ashes of the mistletoe (*Viscum album*), for example, form a link between the first and second groups, inasmuch as they contain considerable quantities both of carbonates and of phosphates; the same may be said of those of the seeds of the oak (*Quercus robur*) and of the chestnut (*Fagus castanea*). Again, the ashes of some seeds, as millet (*Millium sativum*), oats (*Avena sativa*), barley (*Hordeum vulgare*), contain so much silica that they might with equal propriety be placed in the third as in the second group.

The division of plants into potash, lime and silica plants is quite inadmissible, since it would be inconsistent with the beautiful law of substitution established by Professor Liebig. According to this law, the predominance of the one or the other of the above-named bases in the ashes of a plant depends upon the quantities of each existing in the soil. Tobacco would generally be considered as belonging to the lime group; the result of recent analyses, of great interest in reference to the law mentioned above, prove however that tobacco would equally belong to the potash group if grown upon a soil in which that base abounded.

We now proceed to describe a method of quantitative ash-analysis which, as yet, we have found to be the simplest, and therefore most to be depended upon. The details of the process comprise but little that is new to science, whilst a method, more or less similar, might easily have been arranged by any experienced chemist. We are nevertheless of opinion that circumstances justify its ample consideration. The subject is as yet but partially investigated, and there are doubtless chemists appreciating its importance, and desirous of entering upon the inquiry, to whom it will be a desideratum to be possessed of a method, into the correctness of which they need not themselves laboriously examine.

Method of Quantitative Ash-analysis.

I. *Preparation of the Ash*.—It is evident that the removal of all foreign matter from the vegetable substances selected is of the greatest importance: whether seeds, herbs or roots,

they should be carefully examined and freed from adherent dirt before being burned. They must not be washed, however, since in that case some of the soluble salts would be extracted; for the same reason, plants which have been exposed in a withered or dead state, to rain or moist weather, should not be employed. Plants in a healthy and natural condition should always be selected, unless the object in view be the study of disease and its causes.

The information sought by means of ash-analysis, may have reference to the quantity and quality of the inorganic matter contained in a particular kind of plant, or part of a plant; or it may be desired by its aid to judge of the properties of the soil, as regards the presence in it of alkalies, alkaline earths and phosphates. If the latter be the object, a quantitative examination of the ashes of all the plants grown upon the soil will frequently suffice. A knowledge being once attained of the composition of the ashes, both of the cultivated plants and of the weeds, we shall be enabled to decide respecting the composition of the soil, and its suitableness for the production of each particular plant.

Woods, herbs and roots, after being thoroughly dried, should be burned upon a clean iron plate; but for leaves, fruits and seeds, it is more convenient to employ a hessian crucible, heated by means of burning charcoal, in which it is placed somewhat obliquely. The ash is occasionally very easily burned white, but some seeds require a more elevated temperature, to get rid of the charcoal which is intimately mixed with the phosphates; care should always be taken, however, to avoid heating so strongly as would cause the fusion or softening of the alkaline salts, should they abound, or it will be quite impossible to burn the charcoal, which in that case becomes inclosed in the mass. It has properly been observed by De Saussure, that the ashes are whitest when the access of air has not been impeded by stirring or shaking them together.

The ash thus prepared should, if necessary, be further heated to low redness in an open platinum capsule, over a spirit-lamp, with constant stirring; afterwards, and whilst still warm, it should be rubbed to a very fine powder, intimately mixed, and put into a well-closed bottle.

It is now determined, by means of a qualitative analysis, to which of the three groups the ash belongs. Its solubility in concentrated hydrochloric acid is first ascertained: this is in most cases complete, unless the ash be obtained from the stems of the grasses, which abound in silicic acid.

After the separation of the silica, the acid solution is treated

with acetate of ammonia, or it may be neutralized by means of caustic ammonia, free acetic acid being then added ; in most cases a yellowish-white gelatinous precipitate is formed, which consists of phosphate of the peroxide of iron. This precipitate is collected upon a filter, and ammonia is added in excess to the clear solution, by which a fresh precipitation will generally be occasioned. If a red precipitate be formed, it is peroxide of iron ; if, after standing some time excluded from the air, no precipitation takes place, we conclude that the ash contains no phosphate besides the one previously separated ; but if a white precipitate be formed (phosphate of lime and phosphate of magnesia), it is known that there is more phosphoric acid present than is required to combine with the peroxide of iron. Nothing further is necessary for the completion of the *qualitative* analysis, but to test for fluorine and oxide of manganese, and, in the case of marine plants, for iodine and bromine ; unless, indeed, it happen that the experimenter have reason to suspect the presence of other substances in the ash.

For the determination of the chlorine (iodine and bromine) and of the carbonic acid, separate portions of ash are always employed, as also for that of the alkalies, in ashes belonging to the third group. All the other constituents are determined in one quantity of ash, so that the silica has only to be separated once.

A. Analysis of Ashes rich in Carbonates and Phosphates.

1. *Determination of the Silica of the Charcoal and of the Sand.*—About 4 grammes of the ash, which has been found to be soluble in hydrochloric acid, is treated with the concentrated acid in a matrass, held obliquely, so as to avoid the loss of fluid during the evolution of carbonic acid ; gentle heat is then applied, until it is evident that everything is dissolved, excepting the carbonaceous and sandy particles. The whole is now carefully removed into a porcelain basin, evaporated to dryness over a water-bath, and then heated somewhat more strongly, as is usual in separating silica. The mass when cold is moistened with strong hydrochloric acid, is digested for half an hour with a sufficient quantity of water, and is boiled, after which the acid liquid is poured upon a stout filter which has been previously dried at 100° C. and weighed.

The silica will remain upon the filter, and if the ash was not perfectly white and pure, some sand and charcoal also. The filter is washed and dried, and the substance carefully removed from it into a platinum crucible without injury to the paper. This is easily effected if the matters be perfectly dry, the paper in most cases only retaining so much as to be

slightly coloured by the charcoal. The powder is now boiled for half an hour with pure potash ley (free from silica), by which the whole of the silica will be gradually dissolved, leaving the sand and the charcoal unacted upon. The insoluble matter is again collected on the same filter, washed, and dried at 100°C . until it no longer loses weight. The increase upon the weight of the dried filter is estimated as charcoal and sand.

The filtered solution, after the addition of hydrochloric acid in excess, evaporation to dryness, and treatment in the usual way, gives the quantity of silica.

The acid solution, originally filtered from the silica, sand and charcoal, after being well mixed, is divided into three, or more conveniently into four equal portions, one being reserved in case of misfortune with either of the other quantities. The division is best accomplished by means of an accurately graduated tube: the whole of the fluid is collected into the tube, the entire measure then representing the weight of ash experimented upon. The solution is now divided into three or four equal or known portions, the volume of each is noted, and they are distinguished by the letters *a*, *b*, *c* and *d*.

In (*a*) the peroxide of iron, oxide of manganese, and the alkaline earths are estimated.

In (*b*) the alkalies.

In (*c*) the phosphoric and sulphuric acids.

2. *Estimation of the Peroxide of Iron and of the Alkaline Earths.*—To the solution (*a*) ammonia is added until the precipitate which is thereby produced no longer entirely redissolves; acetate of ammonia is next added, and sufficient acetic acid to render the solution strongly acid. From the form and appearance of the precipitate it can easily be judged whether it still contains phosphate of lime; if this be the case, more acetic acid must be added. The yellowish-white precipitate which remains consists of phosphate of the peroxide of iron, $2\text{Fe}_2\text{O}_3 + 3\text{PO}_3$. Its separation from the fluid is assisted by gently heating it, it is then well washed upon a filter with hot water, ignited and weighed*.

* We have submitted to careful analysis the white, or rather greenish-yellow precipitate, formed by mixing solutions of the common phosphate of soda and a persalt of iron. The formula of this compound, when dried without heat over sulphuric acid, is $2\text{Fe}_2\text{O}_3 + 3\text{PO}_3 + 13\text{Aq}$. Of these 13 equivalents of water 6 go off at 100°C ., 4 more at from 300° to 400° , but the remaining 3 are only expelled by strong ignition. The rational formula is therefore $3\text{PO}_3, 2\text{Fe}_2\text{O}_3, 3\text{HO} + 4\text{HO} + 6\text{Aq}$. The numbers obtained by analysis were as follow:—

I. 1.8087 grm. of the substance dried over sulphuric acid lost at 100°C . 0.199 water = 1.100 per cent., and 0.131 more = 7.24 per cent. at 300° to 400° .

II. 1.4787 of the salt dried at 300° to 400°C . lost by ignition in one ex-

To the filtered solution neutral oxalate of ammonia is added as long as a precipitate is formed, and the quantity of lime is determined in the usual manner. When it has been shown by quantitative analysis, that besides phosphate of iron, the ash contains peroxide of iron or oxide of manganese (in which cases the presence of earthy phosphates is very rarely detected), the solution, previously to the separation of the lime, should be supersaturated with ammonia and precipitated by means of sulphuret of ammonium; the two oxides being afterwards separated according to the known methods.

If the ash under examination contained earthy phosphates, the solution filtered from the oxalate of lime will contain free acetic acid; if otherwise, ammonia will be free; it is next somewhat concentrated, rendered ammoniacal, treated with a solution of phosphate of soda, and separated from the precipitate, which is estimated as phosphate of magnesia.

3. *Estimation of the Alkalies.*—The solution (*b*) is treated with baryta water until it gives an alkaline reaction, it is then gently heated and filtered. By this means we get rid of all the sulphuric acid, phosphoric acid and peroxide of iron, as well as the magnesia and most of the lime. The precipitate is washed upon a filter as long as the liquid renders turbid a solution of nitrate of silver; the solution is next warmed, treated with caustic ammonia and carbonate of ammonia, and allowed to stand until the precipitate becomes heavy and granular. The whole is now filtered, and the solid matter is washed, after which the solution is evaporated to dryness, and the residue heated to redness in a platinum capsule to expel the ammoniacal salts. What remains consists of the chloride of potassium or sodium, or more generally of a mixture of the two. The weight being noted, a little water is added, which mostly leaves undissolved a trace of magnesia; this is collected on a filter, its quantity is subtracted from that

periment 7.13 per cent., and in second 6.62 per cent. water; the mean is 6.87 per cent. = 5.61 per cent. of the salt not dried at an elevated temperature.

III. 0.409 of the salt dried at 300° (= 0.5015 dried over sulphuric acid) yielded 0.158 peroxide of iron = 31.5 per cent.

The composition of the salt is therefore—

In 100 parts.		
	Calculated.	Found.
2Fe ₂ O ₃	32.09	31.50
3PO ₅	43.92	
3H ₂ O	5.54	5.61
4HO	7.38	7.24
6Aq. . . .	11.07	11.00
	100.00	

of the supposed alkaline chlorides and added to that of the magnesia as previously ascertained. The quantity of potash is determined by means of chloride of platinum in the usual way; and that of the soda is calculated from that of the chloride of sodium, indicated by deducting the weight of the chloride of potassium from that of the mixed alkaline chlorides.

4. *Estimation of the Sulphuric and Phosphoric Acids.*—From the acidulous solution (c), the sulphuric acid is first separated by means of chloride of barium. The filtered liquid is nearly neutralized with ammonia, acetate of ammonia is added, and then a solution of perchloride of iron, until the liquid begins to turn red, owing to the formation of acetate of iron. Care must here be taken, that sufficient acetate of ammonia be added to convert the whole of the chlorine of the perchloride into sal-ammoniac. The solution is now boiled until it is colourless, all the iron being then precipitated. The precipitate, after being washed with hot water, consists of phosphates of iron and a quantity of basic acetate of iron. It is dried, ignited in a platinum crucible, treated with a few drops of nitric acid, re-ignited and weighed. It is next digested with concentrated hydrochloric acid, which speedily dissolves it. The solution is diluted with hot water mixed with tartaric acid, and ammonia is added until the yellowish-white precipitate which is at first formed disappears. A clear solution, but of a dingy green colour, is thus obtained, from which the iron is precipitated by means of sulphuret of ammonia. The precipitate and supernatant fluid are digested together in a warm place until the latter loses its green tinge and is of a clear yellow colour, resembling that of the sulphuret of ammonia. It is now rapidly filtered, access of air being excluded, and the precipitate is washed with hot water containing a little sulphuret of ammonia, until a drop of the filtered liquid, dried upon a platinum spatula and ignited, no longer indicates an acid reaction. The sulphuret of iron is dissolved from the filter by means of hot and dilute hydrochloric acid, the solution is boiled, treated with a few drops of nitric acid to peroxidize the iron, and ammonia is then added in excess. The precipitate is pure peroxide of iron, whose weight, deducted from that of the basic phosphate, gives the quantity of phosphoric acid. It is essential that the perchloride of iron used in this experiment be quite free from sulphuric acid.

5. *Estimation of the Chlorine.*—A fresh portion of ash (about 1 gramme) is weighed out, exhausted by means of hot water slightly acidulated with nitric acid, and the solution is precipitated with nitrate of silver. If the ash contain appreciable quantities of iodine or bromine, these bodies will be found in

the precipitated silver-salt; for their quantitative estimation, however, a larger portion of ash must be employed.

6. *Estimation of the Carbonic Acid*.—The quantity of carbonic acid is represented by the loss sustained on treatment of a known weight of ash with an acid; and we have elsewhere described the most convenient method and apparatus for the experiment.

B. *Analysis of Ashes abounding in Silica.*

Ashes of this kind, as we have already observed, are generally only partially soluble in acids; their alkalies must therefore be determined in a separate portion of ash. The chlorine and carbonic acid are determined in the same manner as when the ash is entirely soluble in acids. The quantity of chlorine found in ashes of this class is however probably always somewhat less than it should be, since the alkaline chlorides, when ignited with silica and carbon, undergo a partial decomposition.

1. *Estimation of the Silica, &c.*—Pure potash or soda ley is poured upon about 4 grammes of the ash and evaporated to dryness in a platinum or silver dish. The silicic acid compounds are by this treatment dissolved, leaving the sand unaffected. The heat should not be so great as to fuse the mass, or some of the charcoal will be oxidated at the expense of the water of the hydrated alkali. Dilute hydrochloric acid is poured upon the mass, the whole evaporated, and the silica, charcoal, &c. determined in the manner already described. The acidulous solution filtered from the insoluble matter is divided into two parts; one is employed for the determination of the sulphuric and phosphoric acids, and the other for that of the peroxide of iron and the alkaline earths, by the methods detailed above.

2. *Estimation of the Alkalies*.—A second portion of ash (say 3 grammes) is ignited in a crucible of platinum or silver with four times its weight of hydrated barytes, the acid solution which remains after separating the silica, &c. is precipitated successively with barytes water, and carbonate of ammonia, the alkalies being then obtained in the state of chlorides.

C. *Determination of the Quantity of Ash.*

It is often important, even indispensable, to ascertain the entire quantity of inorganic constituents contained in a plant or part of a plant. A certain quantity of fixed matter is annually removed from cultivated land in the crop, and it is a desideratum to have a scale for the reparation of this loss by means of manures. The chemist who is engaged with ash-analysis should therefore acquire information as to the quantity which will be

taken from a given surface by the crop. Rational agriculturists and woodreeves are always in possession of details of this kind, which are generally of sufficient accuracy for the ends to be answered by them.

The vegetable substance under examination should be dried over a water-bath at 100° C. until it no longer loses weight; if however any of its constituents be volatile, the drying is best conducted over sulphuric acid, without the application of heat. The quantity of substance to be burned to ash will depend upon the quantity of fixed matter it contains. Of herbs and seeds, which are rich in inorganic constituents, 2 to 3 grammes will be sufficient; of woods, however, which frequently contain only 0·2 per cent. of fixed matter, ten or more times that quantity must be taken. The combustion succeeds best in a thin platinum crucible; it is at first covered and heated only gently, but afterwards the lid is removed and a stronger heat employed until the whole of the charcoal is consumed. The ashes of seeds which do not effervesce with acids may be moistened with nitric acid and re-ignited, when they will very speedily be turned white.

We now submit a number of ash-analyses which were conducted according to the methods we have described. The first are those of ten kinds of tobacco, which were sent to Professor Liebig for the purpose by the director of the Imperial Austrian tobacco manufactory in Vienna. All these plants were cultivated in Hungary, upon land which had never been manured, and upon which the same plant had been grown for a considerable length of time.

The specimens 1, 2 and 3 were from the Debreczyner, No. 4 from the Banat, and Nos. 5 to 10 inclusive from the Fünfkirchner district. With the exception of Nos. 7, 8, 9 and 10, the leaves reached us in a sound and perfectly healthy state, still partially retaining their green colour. Differences were however clearly indicated by the varying size and greater or less luxuriance of the specimens.

In addition to the above we analysed the ashes of the grain of red and of white wheat (*Triticum vulgare*), of the seed and of the straw of rye (*Secale Cereale*), of peas (*Pisum sativum*), of the wood of the apple-tree (*Pyrus malus*), of the mistletoe (*Viscum album*) from the same tree, and of lichens (*Parmelia prunastri*, *fraxinea*, *parietina*, *furfuracea*): all were grown in the neighbourhood of Giessen.

TABULATED RESULTS OF THE ANALYSES OF THE ASHES OF TOBACCO.

(A.) *Actual results of the analyses of 100 parts of Ash.*

	Debreczyner.			Banat.	Fünfkirchner.					
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
					1840.	1841.	Dried at the temperature of a room.	Powder of leaves. 1841.	Powder of stalk.	Powder of leaves. 1839.
Potash	23.33	22.90	22.63	14.48	5.77	13.62	6.28	6.01	7.35	6.55
Soda	1.81					0.19				
Lime	22.19	18.51	25.29	22.16	30.08	30.99	31.98	31.74	27.09	27.44
Magnesia	5.79	5.79	5.93	12.51	9.80	7.71	9.46	10.01	10.31	7.46
Chloride of sodium	0.73	4.44	7.59	9.07	2.27	2.46	2.99	2.06	4.38	1.51
Chloride of potassium }			3.98	3.12	6.00		2.88	2.10	2.05	1.74
Phosphate of peroxide of iron }	7.04	4.50	5.19	5.41	4.27	3.02	3.37	4.32	5.19	3.69
Phosphate of lime }						4.16				
Sulphate of lime .	5.16	4.50	5.22	8.04	5.60	3.92	4.34	3.94	6.46	3.00
Silica	14.16	13.73	5.35	4.75	6.54	3.58	3.59	4.03	5.72	7.04
Carbonic acid.....	10.45	9.11	14.78	15.90	15.09	21.95	22.69	17.08	17.30	17.49
Charcoal and sand	10.31	13.50	4.73	6.46	13.72	8.04	11.62	19.36	13.80	23.75
	100.97	97.28	100.69	101.90	99.14	99.64	99.20	100.65	99.74	99.70

(B.) *Product of 100 parts of Ash, after deducting the carbonic acid, the charcoal and the sand.*

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Potash	29.08	30.67	27.88	18.20	8.20	19.55	9.68	9.36	10.37	11.21
Soda	2.26					0.27				
Lime	27.67	24.79	31.16	27.86	42.77	44.49	49.28	49.44	39.53	47.03
Magnesia	7.22	8.57	7.31	15.73	13.93	11.07	14.58	15.59	15.04	12.77
Chloride of sodium	0.91	5.95	9.34	11.41	3.22	3.54	4.61	3.20	6.39	2.58
Chloride of potassium }			4.90	3.92	8.53		4.44	3.27	2.99	2.97
Phosphate of peroxide of iron }	8.78	6.03	6.39	6.80	6.07	4.34	5.19	6.72	7.56	6.30
Phosphate of lime }						5.97				
Sulphate of lime...	6.43	5.60	6.43	10.11	7.96	5.63	6.68	6.14	9.42	5.11
Silica	17.65	18.39	6.59	5.97	9.32	5.14	5.54	6.28	8.34	12.03
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Oxygen in the bases united to organic acids .	16.06	15.47	16.31	16.99	18.78	20.15	21.09	21.50	18.75	20.05
Per-centage of ashes obtained from the dry leaves	18.9	22.2	24.5	19.8	23.0	21.08	23.28	23.28	22.83	27.36

Inorganic Constituents of Plants.

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(A.) Actual Results of the analyses of 100 parts of the ashes of

	Wheat.		Rye.		Peas.	Apple-tree.		
	Red. Grains.	White. Grains.	Grain.	Straw.		Wood.	Mistle- toe.	Lichen.
Potash	20·80	30·17	31·89	17·03	39·25	13·67	35·32	} 10·07
Soda	15·01		4·33		3·96	0·32		
Lime	1·83	2·76	2·84	8·98	5·87	45·19	19·40	10·33
Magnesia	9·12	12·08	9·86	2·39	6·41	5·30	9·59	5·33
Peroxide of iron...	1·29	0·28	0·80	1·35	1·04			
Phosphate of per- oxide of iron }						1·71	1·83	14·56
Phosphoric acid...	46·91	43·89	46·03	3·80	34·23	2·95	16·56	
Chloride of sodium			trace.	0·56	3·69	0·32	1·02	
Chloride of po- tassium }				0·25				
Sulphuric acid ...			1·42	0·81	4·89	0·66	1·41	
Silica	0·15		0·17	63·89		0·93	1·62	
Carbonic acid.....						24·18	13·09	4·64
Charcoal and sand	4·89	9·03	2·66	0·94	1·38	2·03	0·54	49·73
	100·00	98·21	100·00	100·00	100·72	97·26	100·38	94·66*

* The remaining constituents were not estimated.

(B.) Per-centage composition after deducting the carbonic acid, the charcoal and the sand.

	Wheat.		Rye.		Peas.	Apple-tree.		
	Red. Grains.	White. Grains.	Grain.	Straw.		Wood.	Mistle- toe.	Lichen.
Potash	21·87	33·84	32·76	17·19	39·51	19·24	40·71	
Soda	15·75		4·45		3·98	0·45		
Lime	1·93	3·09	2·92	9·06	5·91	63·60	22·37	
Magnesia	9·60	13·54	10·13	2·41	6·43	7·46	11·06	
Peroxide of iron...	1·36	0·31	0·82	1·36	1·05			
Phosphate of per- oxide of iron }						2·41	2·11	
Phosphoric acid...	49·32	49·21	47·29	3·82	34·50	4·15	19·09	
Chloride of sodium				0·57	3·71	0·45	1·17	
Chloride of po- tassium }				0·26				
Sulphuric acid ...	0·17		1·46	0·83	4·91	0·93	1·62	
Silica			0·17	64·50		1·31	1·87	
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	
Quantity of oxy- gen in the bases of the phosphates ... }	12·35	11·92	11·97		11·18			

On comparing these analyses of tobacco-ash, it is at once seen that plants of the same kind, grown upon the same soil, yield ashes, the composition of which differs but little. This is very evident with respect to those of the Debreczyner leaves (1, 2 and 3). The proportion of bases combined with organic acids is, so far as their oxygen is concerned, very nearly the same in each case. The quantity of lime in the ashes of the Banat leaves is almost the same as in those of the Debreczyner leaves, whilst the quantity of potash in the former is scarcely two-thirds as great as in the latter; the quantity of magnesia, however, the equivalent of which is so small, is nearly doubled. The ashes of the Fünfkirchner leaves exhibit a still wider difference; in four instances the quantity of potash is scarcely one-third of that in the Debreczyner leaves; in place of this potash, however, we find an increase in the quantity of lime, amounting to nearly 50 per cent. Again, the quantity of magnesia is the same as in the ashes of the Banat leaves, whilst the lime in the latter only amounted to 27 per cent.

It is evident that these differences depend entirely upon the variable quantities of the several bases contained in the soils. In these differences we recognise moreover a beautiful confirmation of the law of mutual replacement of bases laid down by Professor Liebig. Supposing this law to be subject to no modification, and considering the accuracy of the analyses, we should have expected that in equal weights of the various ashes (the abnormal matters being deducted), the quantities of oxygen united to these bases would have been more nearly identical. In the case of plants containing much sap, this difference in the quantities of oxygen contained in the bases united to organic acids, is easily accounted for; partly by the reactions which we have already stated take place during the ignition of the ash, and partly by the influence which, as in the case of tobacco, the presence of nitrates, according to their quantity, will exert upon the amount of carbonates found in the ash.

The ashes of seeds, so far as their composition is known, consist, like those of the blood of man and other animals, principally of the phosphates of the alkalies and alkaline earths. The curious fact, moreover, has lately been observed, that the phosphoric acid is not in all seeds combined with the same number of equivalents of fixed base. Analyses conducted by ourselves and under our superintendence, show that peas, beans, horse beans, &c., that is, the Leguminosæ, and the seeds of the Coniferæ (the pines), &c., contain tribasic phosphates ($\text{PO}_5 + 3\text{MO}$). The seeds of the Cerealia (rye, wheat, millet,

buck-wheat, and also hemp and linseed) contain, on the other hand, bibasic phosphates ($\text{PO}_5 + 2\text{MO}$). This relation is maintained also when the seeds are grown in different localities. The solution of ashes containing tribasic phosphates gives a yellow precipitate with nitrate of silver, even if made immediately after ignition, whilst that of those containing bibasic phosphates gives a pure white precipitate. The quantities of oxygen contained in the bases of these seeds (deducting the sulphates and chlorides) are so nearly alike, that it is evident that the law of replacement of bases applies also to the phosphates. The following analyses demonstrate this fact.

I. Analyses of Seed-Ashes containing tribasic phosphates, sometimes also mixed with bibasic phosphates.

The analyses marked thus * were conducted under the superintendence of Dr. Will.

	Peas.			
	Fresenius and Will (Giessert).	Bichon (Holland).	Thon (Kurlhessen).	Boussingault (Bechelbronn).
Potash	39.51	34.19	35.20	36.31
Soda	3.98	12.86	10.32	2.56
Lime	5.91	2.46	2.70	10.39
Magnesia	6.43	8.60	6.91	12.24
Peroxide of iron.....	1.05	0.96	1.94	
Phosphoric acid.....	34.50	34.57	34.01	31.00
Sulphuric acid	4.91	3.56	4.28	4.83
Chlorine (or chlor. sodium)	3.71	0.31	2.56	1.13
Silica		0.25	0.29	1.54
Oxygen in the bases	11.18	12.23	11.44	13.51

	Horse-Beans (Vicia faba).			Beans (Phaseolus vulgaris).	
	Bichon (Holland).	Boussing. (Alsace).	Buchner (Giessen).*	Thon (Kurlh.).	Boussing. (Alsace).
Potash	20.82	47.14	32.71	21.71	51.36
Soda	19.06		12.75	21.07	
Lime	7.26	5.33	4.72	5.38	6.07
Magnesia	8.87	8.98	6.13	7.35	12.03
Peroxide of iron.....	1.03		0.66	0.34	
Phosphoric acid.....	37.94	35.67	39.11	35.33	28.53
Sulphuric acid	1.34	1.66		2.28	1.36
Chlorine	1.48	0.71		3.32†	0.10
Silica	2.46	0.51	0.47	1.48	1.05
Oxygen in the bases	13.56	12.42	12.69	13.04	14.73

† Chloride of sodium.

	Poleck.*			Muller.
	Scotch Fir.	Silver Fir.	Pinus Picea.	Brassica Napus.
Potash	22·37	18·57	21·75	21·34
Soda	1·26	5·78	6·76	5·26
Lime	1·86	1·54	1·54	14·63
Magnesia	12·57	16·79	16·79	11·96
Oxide of iron	2·51	1·31	1·31	2·84
Phosphoric acid	45·95	39·65	39·65	41·68
Chloride of sodium			0·57	
Silica		0·57	11·71	1·52
Sulphuric acid	10·44	11·71		0·77
Oxygen in the bases	12·94		14·60	14·17

II. Analyses of Seed-Ashes with bibasic phosphates.

	Wheat.				
	Fresenius and Will (Giessen).		Bichon (Holland).	Thon (Solz in K.).	Boussingault (Bechelbronn).
	Red.	White.			
Potash	21·87	33·84	6·43	24·17	30·12
Soda	15·75		27·79	10·34	
Lime	1·93	3·09	3·91	3·01	3·00
Magnesia	9·60	13·54	12·98	13·57	16·26
Peroxide of iron	1·36	0·31	0·50	0·52	
Phosphoric acid	49·32	49·21	46·14	45·53	48·30
Sulphuric acid	0·17		0·27		1·01
Chlorine (chlor. sodium)					
Silica ...			0·42	1·91	1·31
Quantity of oxygen in the bases }	12·35	11·92	14·20	12·98	11·84

	Rye.		Buckwheat.	Maize.
	Fresenius and Will (Giessen).	Bichon (Cleve).	Bichon (Cleve).	Letellier (Bechelbronn).
Potash	32·76	11·43	8·74	30·8 & loss.
Soda	4·45	18·89	20·10	
Lime	2·92	7·05	6·66	1·3 ...
Magnesia	10·13	10·57	10·38	17·0 ...
Peroxide of iron	0·82	1·90	1·05	
Phosphoric acid	47·29	51·81	50·07	50·1 ...
Sulphuric acid	1·46	0·51	2·16	
Silica	0·17	0·69	0·69	0·8 ...
Quantity of oxygen in the bases }	11·97	12·30	11·96	

	Bichon.	Poleck.*	Leuchtweiss.*		Boussing.
	Barley.	Millet.	Hemp-seed	Linseed.	Oats.
Potash	3.91	9.58	21.67	25.85	12.9
Soda	16.79	1.31	0.66	0.71	
Lime	3.36	0.61	26.63	25.27	3.7
Magnesia	10.05	7.66	1.00	0.22	7.7
Peroxide of iron...	1.93	0.63	0.77	3.67	1.3
Phosphoric acid...	40.63	18.19	34.72	40.11	14.9
Sulphate of lime...		0.60	0.18	1.70	
Chloride of sodium		1.43	0.09	1.55	0.5
Silica	21.99	59.63	14.04	0.92	53.3
Sulphuric acid ...	0.26				1.0
Carbon					4.7
Oxygen of the } bases	11.70		13.88	12.76	14.95

III. Additional Analyses of Seed-Ashes.

	Kleinschmidt. Acorn.*	Buch. Saintfoin.*
Potash	64.64	6.75
Soda		20.33
Lime	4.89	
Magnesia	5.57	8.57
Peroxide of iron....		
Phosphoric acid....	15.62	54.89†
Sulphate of lime ...	4.73	2.87
Chloride of sodium...	0.98	2.18
Silica	0.96	1.10
Phosphate of per- oxide of iron ... }	2.61	3.31

	Fruit of the Horse-chestnut. De Saussure.
Carbonate of potash	51
Phosphate of potash	28
Chloride of potassium and sulphate of potash	3
Earthy phosphates	12
Silica	0.5
Metallic oxides	0.25
Loss	5.25

It is of great importance that analyses should be made of the ashes of the most widely differing plants, and also of those of the same kind of plant grown on very different kinds of soil. This can only be accomplished, however, by the persevering cooperation of many chemists. The examples given above show how beautiful and fertile in their consequences are the results obtained by ash-analyses; and we hope that by means of the methods herein described, the work will be rendered somewhat more easy.

The difference in the solubility of the nitrogenous ingredients of the Leguminosæ, as regards their vegetable casein, and the nitrogenous ingredients of the Cereals, in respect of vegetable fibrin, arises evidently from the greater amount of alkaline bases contained in the seeds of the Leguminosæ, in comparison to the quantity of phosphoric acid, to which they have immediate reference. This larger quantity of base causes the

† Phosphate of lime.

solubility of the Leguminosæ in water, whilst the vegetable fibrin of the Cereals is insoluble therein. There is therefore ground for supposing that the phosphates are also bibasic in the Leguminosæ as well as in the Cereals; the third atom of the base would be consequently combined with the vegetable casein, and the tribasic phosphate be formed during the incineration.

The great quantity of sulphuric acid (from 3·5 to 4·9 per cent.) contained in the ashes of peas is remarkable in comparison to that of other seeds: in the ashes of beans it amounts to 2 per cent., in the ashes of wheat and rye to only 0·5 per cent., and is frequently altogether wanting. It is probable that the cause arises from the small quantity of phosphoric acid present, whilst the sulphur of the nitrogenous ingredients is more easily retained as sulphuric acid by the alkaline bases during the incineration. If fresh-prepared ashes from seed containing tribasic phosphates are exposed to the air, they take up carbonic acid. This is the reason why Boussingault* found in the ashes of horse-beans one per cent., and in that of the common beans 3·3 per cent. of carbonic acid.

Upon comparing the ashes of the wood of the apple-tree with that of the mistletoe growing from it, the difference in the quantity of potash and phosphoric acid contained in each is immediately evident: for whilst the ashes of the apple-tree wood contain only 19 per cent. of potash and 4 per cent. of phosphoric acid, we find that the ashes of the wood of the mistletoe contain double the quantity of potash and five times the quantity of phosphoric acid.

The mistletoe therefore appears to perform upon the tree the same functions (as far as regards the inorganic ingredients) as the fruit, in absorbing from the sap the phosphates. This is no doubt the cause of the injury produced on trees by parasitic plants. Further analytical investigations with this and other parasites will show whether this can be considered as a general law.

* *Economie Rurale*, t. ii. p. 327.