A Course of Lectures ON URINE, URINARY DEPOSITS, AND CALCULI.

DELIVERED AT THE PATHOLOGICAL LABORATORY,
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BY

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LECTURE III.

Healthy Urine. III. INORGANIC CONSTITUENTS. *On the Salts generally; Changes effected in the Composition of the Salts by Incineration: Proportion of the Saline Matter in Urine: Phosphates; Common Phosphate of Soda; Alkaline Phosphate of Soda; Acid Phosphate of Soda; Phosphate of Soda and Ammonia; Phosphate of Magnesia; Phosphate of Ammonia and Magnesia; Phosphate of Lime; Estimation of the Alkaline and Earthy Phosphates; Quantity: Sulphates; Quantity: Estimation: Carbonates: Chloride of Sodium; Quantity; Detection; Circumstances affecting the Excretion of Chloride of Sodium: Bases in Urine: Soda and Potash: Lime: Magnesia: Iron: Silica: Alumina: Systematic Quantitative and Qualitative Examination of the Saline Matter of Healthy Urine.*

III.—INORGANIC CONSTITUENTS OF HEALTHY URINE.

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Earthy Phosphates.

The earthy phosphates met with in the urine are—1. The *ammonio-magnesian phosphate*, also termed *triple phosphate*, or *phosphate of ammonia and magnesia*; 2. *Basic phosphate of ammonia and magnesia*; 3. *Phosphate of Magnesia*.

These earthy phosphates occur in very small quantity in urine. The secretion in health contains not more than from 1 to 1.5 parts in 1000, and the solid matter contains from 1.5 to 2 per cent. The quantity present in different cases undergoes but slight variation, and seems to be determined, to a great extent, independently of the chemical changes going on in the body. Most of the solids and fluids of the organism contain small quantities of the earthy phosphates. The amount depends in great measure upon the quantity of alkaline earths present.

In healthy urine, these earthy phosphates are held in solution, in all probability, by the free acid of the urine, and in some measure by the acid phosphate of soda. The chloride of ammonium present may also contribute to maintain the earthy phosphates in solution in the urine (Dr. G. O. Rees). Very slight changes are sufficient to cause the precipitation of the *ammonio-magnesian phosphate*; and beautiful crystals of this salt are sometimes formed in urine which has a decidedly acid reaction.

We must carefully distinguish between *excess* of phosphates in the urine and a *deposit* of earthy phosphate; for we may suppose a large quantity of earthy phosphate in urine to pass unnoticed by the practitioner, because it is in a state of *solution*; while a smaller quantity in an *insoluble* state is likely to receive from him a larger share of attention than its slight importance demands.

Precipitation of Earthy Phosphates by Heat. It is very important to bear in mind that the earthy phosphates are precipitated from some specimens of urine by heat. This precipitate closely resembles that which is produced, in many specimens of albuminous urine, upon the application of heat. It is, however, at once distinguished from albumen by the addition of a few drops of nitric acid, which instantly dissolves the phosphate, while albumen is unaffected by it. Such a mistake has many times been made; and I need hardly say how important it is to avoid the possibility of such an error, as it may lead the practitioner to form an unfavourable prognosis in a case in which there is really no cause whatever for anxiety. The cause of this occasional precipitation of earthy phosphate is obscure. By Dr. Rees it is attributed to an excess of the phosphates being held in solution by chloride of ammonium. Dr. Brett considers that in these cases it is dissolved by carbonic acid; while Dr. Bence Jones attributes this precipitation

to the excess of free acid of the urine being neutralised by an alkali, or by common phosphate of soda.

Phosphate of Lime— $3 \text{ CaO}, \text{PO}^5$ —exists in healthy urine dissolved in acids, in certain salts, or in organic matters. Phosphate of lime is soluble in a solution of carbonic acid, in bicarbonates, and in chloride of ammonium. Albumen and fibrine always retain a certain quantity, and casein holds a large amount in solution. It is found in almost all the tissues, and, when separated, usually occurs in an amorphous state. The ash of urine contains between 2 and 3 per cent. of this phosphate, and that of excrements upwards of 12 per cent. It may be obtained in quantity from bones.

Acid Phosphate of Lime— $2 \text{ CaO}, \text{HO}, \text{PO}^5 + 3 \text{ HO}$. The existence of this phosphate in urine constantly, is questionable; but, as before remarked, the composition of the phosphates is constantly altering; and an acid phosphate of lime is readily formed by the action of an organic acid on the neutral phosphate of lime.

Phosphate of Ammonia and Magnesia, Triple, or Ammonio-magnesian, Phosphate— $\text{NH}^4 \text{O}, 2 \text{ MgO}, \text{PO}^5 + 12 \text{ HO}$. The presence of this salt, which is so frequently met with in the animal fluids, usually depends upon decomposition having commenced, in which case the ammonia set free combines with the phosphate of magnesia to form the triple phosphate. At the same time, there can be no doubt that crystals of triple phosphate are sometimes found in acid urine—not merely forming a pellicle which alone is alkaline, while the fluid beneath retains its acidity (*Thudichum*)—but as a distinct deposit, leaving a clear supernatant fluid. Lehmann and other observers doubt the correctness of this observation; but the fact has been observed in this country several times, and I have noticed it myself more than once or twice. It is quite possible that the acid reaction may depend upon chloride of ammonium, or some other neutral salt which reddens litmus, and not upon the existence of a free acid.

Crystals of triple phosphate are slightly soluble in pure water, but are rendered quite insoluble by a trace of ammonia and ammoniacal salts. They give beautiful colours when examined with a ray of polarised light.

Phosphate of Magnesia— $3 \text{ MgO}, \text{PO}^5 + 7 \text{ Aq}$. This phosphate is found in considerable quantity in the urine of certain herbivorous animals, and it appears to be a constituent of certain urinary calculi. It is doubtful if it is often present in human urine; but Robin and Verdel have discovered it in several organs, and also in morbid products. In animal fluids generally, the phosphate of magnesia combines with ammonia, forming the salt which has just been described. When discussing the deposits of phosphates, I shall have to revert to this subject.

Microscopical Characters of the Earthy Phosphates. The phosphate of lime is usually deposited from urine in an amorphous form. Under the microscope, even when the highest powers are employed, the deposit is found to consist of minute granules. (*Illustrations*, Plate XXI, fig. 4.) Occasionally it occurs as round or oval particles of a high refractive power. Sometimes two of these small particles are connected together, and produce a crystal of the dumb-bell form. They vary much in size, but are usually very small.

The phosphates of magnesia crystallise in several different forms, which seem to be determined by slight changes in circumstances. The first is the stellate form, which occurs when ammonia is added to healthy human urine. The crystal consists of from four to five feathery rays, with a minute oval mass situated at the origin of each ray from the centre. These crystals gradually assume the more common form of the triple phosphate: secondly, that of a beautiful triangular prism, with obliquely truncated extremities. Great variation, however, is observed in the form of these crystals; sometimes they appear almost square; and frequently they might be mistaken for octohedra, in consequence of approximation of the obliquely truncated ends, and the shortening of the intermediate portion of the crystal. The feathery crystals of triple phosphate are represented in the *Illustrations*, Plate IX, fig. 2. After standing for some time, the rays alter in shape, and gradually little triangular crystals begin to make their appearance, as represented at *a*. After the lapse of some days, they are entirely converted into the ordinary triangular crystals. (Pl. IX, fig. 1; Pl. XXI, figs. 1, 3; Pl. XXIII, fig. 1.) An unusual form of magnesian phosphate crystals is represented in fig. 237, p. 324, of *The Microscope in its Application to Practical Medicine*.

Estimation of the Earthy and Alkaline Phosphates. The earthy phosphates (*phosphate of lime and phosphate of magnesia*) are easily detected by ammonia. If I add a few drops

of solution of ammonia to this specimen of healthy urine, a turbidity is soon observed, owing to the precipitation of phosphate of lime in an amorphous form, and triple or ammoniacomagnesian phosphate in flocculent snow-like crystals, which increase in size for some time after their first precipitation. Stirring favours the separation of the phosphates; but the form of the crystals must, of course, be studied in a mixture which has been allowed to remain quiet. If it is required to estimate the proportion of these earthy phosphates, it is only necessary to separate them by filtration, ignite in a platinum capsule, and weigh the ash.

Alkaline Phosphates. The phosphoric acid combined with the alkalies may be precipitated from the fluid filtered from the earthy phosphates by the addition of a salt of lime or magnesia, when an insoluble deposit, composed of phosphate of lime or phosphate of ammonia and magnesia, is produced. If we wish to ascertain the quantity of alkaline phosphates present, it is only necessary to filter the precipitate, dry, ignite, and weigh it. From the phosphate of lime or phosphate of magnesia it is easy to calculate the proportion of phosphoric acid present; but, for ordinary purposes, it is enough to consider the weight as corresponding to the quantity of alkaline phosphates present in the urine, there being but slight difference in the equivalent numbers of the salts. The volumetric method of estimation, in which the phosphate is precipitated by a persalt of iron, will be described in a future lecture. Nitrate of silver produces in urine a yellow precipitate of tribasic phosphate of silver, which is soluble both in excess of ammonia and also in nitric acid. Upon adding a few drops of the former to the yellow deposit in this test-tube, it instantly dissolves. Now, when I add just nitric acid enough to neutralise the ammonia present, the yellow precipitate reappears; but, when I allow one drop more to fall in, it is immediately redissolved. I might repeat this many times. The precipitate of chloride of silver is quite insoluble in nitric acid, although soluble in ammonia; so that, in testing for chloride of sodium in urine, it is always important to add a few drops of nitric acid, to prevent the precipitation of the phosphate of silver.

Sulphates. Unlike the phosphates, the sulphates are present in very small quantities in the fluids of the body generally. The urine, however, contains a large quantity. This class of salts is not present in the milk, bile, or gastric juice. The blood contains only .20 per 1000; while, in healthy urine, sulphates exist in the proportion of from 3 to 7 parts per 1000.

The proportion of sulphates undergoes a considerable increase after violent exercise, and under the influence of a purely animal diet—conditions under which the urea suffers a considerable augmentation. In fact, in all those conditions which are associated with an increased formation of urea, a large proportion of sulphates will also be observed. It would appear that the oxygen, hydrogen, carbon, and nitrogen of the albuminous substances, are eliminated in the form of urea; while the sulphur is removed in the state of sulphuric acid.

Dr. Bence Jones's experiments have shown that both vegetable and animal food increase the proportion of sulphates in the urine. When sulphuric acid, sulphur, or sulphates, are taken internally, the amount of these salts is augmented. These facts prove that the sulphates found in the urine are in great part formed during the disintegration of tissues. They must be regarded as excrementitious, and are probably not concerned in the nutrition of tissues.

The sulphuric acid eliminated in the urine occurs in the form of sulphate of potash and soda.

The urine contains about 3.5 grains per 1000 of sulphate of potash, and about 3.0 grains of sulphate of soda. About thirty grains of sulphuric acid, corresponding to about fifty-seven grains of the mixed sulphates, are excreted by a healthy man in twenty-four hours.

Sulphate of Lime has not been detected in human urine, but it has been found in that of animals, and is a constituent of some urinary calculi. I have seen crystals of sulphate of lime in the uriniferous tubes; and it is probable that it may be present in the urine, in some cases, in appreciable quantity. Traces of sulphate of lime are found in the blood. It is found in the pancreatic juice which has been kept for a few hours in a warm place, so that decomposition of some of the organic materials may take place.

The sulphates present in the urine are all soluble, like the alkaline phosphates; and, in order to prove their presence in a fluid, it is necessary to add some salt, the base of which forms an insoluble precipitate with sulphuric acid. Baryta salts are the most convenient for this purpose. Either the nitrate of baryta or the chloride of barium may be employed. In testing

for sulphates in urine, it is necessary to add a little free nitric or hydrochloric acid previous to the addition of the baryta salt, in order to prevent the precipitation of a phosphate as well as a sulphate of baryta. The former is very soluble in free acid; the latter quite insoluble. If the quantity of sulphate is to be estimated, it is necessary to boil the mixture, or to drop the baryta salt into the boiling solution; otherwise the precipitated sulphate of baryta will pass through the pores of the filter. The phosphoric acid may be estimated in the clear fluid which passes through the filter by the addition of ammonia, which throws down phosphate of baryta. The contact of the air must, in this case, be avoided.

Carbonates. Carbonate of soda is not usually reckoned as a constituent of healthy urine, as its presence is entirely dependent upon the kind of food which the person has taken. For instance, carbonate of soda will often be found in the urine after large quantities of fruit have been eaten, in consequence of the salts of the vegetable acids becoming converted into carbonates during their passage through the organism. In the urine of herbivorous animals, alkaline carbonates are found; and frequently the carbonate of lime is also present. In the urine of rodents, these salts, particularly the latter, are abundant. Moreover, carbonate of soda may actually have been present in the urine, although it cannot be detected in the ash; for, if common phosphate of soda be heated with carbonate of soda, the carbonic acid is expelled, and the tribasic phosphate of soda remains. Hence the absence of carbonate from the ash of urine is not always a positive proof that the fluid did not contain lactates before it was subjected to chemical operations. On the other hand, a carbonate may be detected in the ash, although none was present in the urine, in consequence of the decomposition of oxalates and lactates during incineration.

Testing for Carbonate. The presence of carbon is very easily recognised by the effervescence set up immediately a little dilute acid is added to the ash. The best plan to test for carbonate in the ash is the following. A small portion of the dry ash is placed on a glass slide, and covered lightly with an ordinary square of thin glass. A drop of acid is then allowed to fall on the glass, so that it will gradually pass between the glasses by capillary attraction, and come into contact with the salt. If any bubbles of gas escape in consequence of the action of the acid, they will be confined beneath the thin glass, and one cannot fail to see them. If they be very small, the specimens may be subjected to microscopical examination. In this manner, the slightest trace of carbonic acid can hardly escape notice.

If the quantity of carbonate is to be estimated, the ash must be placed in a little apparatus, from which it is conducted by a tube into another vessel containing lime or baryta water; or it may be caused to pass through the potash apparatus used in organic analysis. From the weight of the carbonate, that of the carbonic acid is easily calculated. In the last case, its weight is obtained directly.

Chloride of Sodium. Common salt is always present in healthy urine, although the proportion is liable to great variation, owing to the circumstance that the chloride of sodium is always derived from the food. The importance of this substance to the organism is sufficiently proved by the fact that all kinds of food contain a certain quantity, and almost every specimen of water holds some proportion in solution. Again, it is well known that the health of animals deprived of the proper amount of salt deteriorates. It is to be detected in nearly all the tissues of the animal body, and is found in large quantity wherever cell-development is actively going on. This is true both with regard to healthy tissues and morbid growths. Common salt crystallises in cubes; but, in the presence of urea and some other organic substances, it assumes the form of a regular octohedron. As is well known, it is readily soluble in water (31.84 parts in 100), diffuses itself rapidly through a large bulk of fluid, and, in a dilute state, permeates tissues with great facility.

Besides common salt, urine also contains a certain quantity of chloride of potassium.

Quantity. Healthy urine contains from three to eight grains of chloride of sodium in 1000; the solid matter, about 6 per cent.; and the fixed salts, about 25 per cent. or more. Under ordinary circumstances, from 100 to 300 grains of salt are removed from the body in twenty-four hours; but the proportion is influenced by a great variety of circumstances, and is especially affected by the quantity of fluids taken. The amount is very variable in different individuals, according to the proportion of salt taken with the food. The secretion of

chloride of sodium, as you would suppose, attains its maximum a few hours after a meal, and but little is eliminated during the night.

Detection. Chloride of sodium is very easily detected in urine. It is only necessary to acidulate the specimen with a few drops of nitric acid, and then add nitrate of silver. The white precipitate of chloride of silver is quite insoluble in nitric acid, but soluble in ammonia. In order to make a quantitative determination, the chloride of silver is to be dried; and it should be burnt and fused in a *porcelain* capsule before being weighed. The volumetric process, however, is the most accurate.

Circumstances affecting the Excretion of Salt. Chloride of sodium is not formed in the organism, but seems to exert some important and beneficial effects during its passage through the tissues; and whenever the nutritive changes are very active, there seems to be an unusual demand for chloride of sodium. But the precise part which the substance plays is at present unknown. The quantity of salt excreted in the urine undergoes great changes in certain diseases. We shall consider them in a future lecture. The proportion also varies considerably from day to day, under the influence of an ordinary diet in health; and the ingestion of large quantities of water causes the elimination of a greatly increased amount of common salt. Thus, in one experiment, continued for four days, the following results were obtained: During the first three days, about thirty-six ounces of urine were passed per diem; the specific gravity varied from 1015 to 1024. The total quantity of solid matter passed in twenty-four hours was about 750 grains, and the chloride of sodium amounted to 113 grains. On the fourth day a large quantity of water was taken; 258½ ounces of urine, of specific gravity 1003, were passed; containing a total of 1034·48 grains of solids, and 232·8 grains of chloride of sodium. The phosphoric acid was diminished, and the sulphuric acid was increased by upwards of one-third.*

Soda and Potash. In healthy urine but a very small quantity of potassium is present in the form of chloride; but of soda salts there is a large proportion. The potash salts, as was first pointed out by Liebig, are found in considerable quantities in the muscles, while the soda salts predominate in the blood. Although phosphate of potash be taken in the food, the corresponding soda salt, which is necessary to the blood, is still found in that fluid; and there can be no doubt that in the organism the chloride of sodium is decomposed by the phosphate of potash—a phosphate of soda, and a chloride of potassium being formed.

To separate the sodium from the potassium in urine, a somewhat tedious analysis, of which I will just give a rough outline, is necessary. After destroying the organic matter by ignition, the whole of the phosphoric and sulphuric acids are removed, and the potassium and sodium converted into chlorides. A solution of bichloride of platinum is then added, and a chloride of potassium and platinum, and a chloride of sodium and platinum are formed. The potassium salt is most insoluble, and separates in the form of small octohedra, which do not polarize light. These may be separated by filtration. The sodium salt remains in solution, and may be obtained in the form of crystalline needles by concentrating the solution. These crystals exhibit the most beautiful colours when a ray of polarized light is transmitted through them.

Lime may be detected in urine by dissolving the salts in acetic acid, and adding a little oxalate of ammonia to the filtered solution. Oxalate of lime is precipitated as a white, granular powder, which passes through the pores of a filter, unless the mixture be boiled previous to filtration. As already mentioned, lime occurs in urine as a phosphate, and occasionally as a carbonate. It forms a urinary calculus very rarely met with in man; but not uncommon in some herbivorous animals. The urine of the horse always contains a number of spherical masses, composed of carbonate of lime, which may be regarded as microscopic calculi.

Magnesia must be precipitated as ammoniaco-magnesian phosphate, from a concentrated solution of the salts after separation of the lime. The solution should be evaporated to a small bulk, and when quite cold a little of the solution of phosphate of soda should be added to the mixture, rendered alkaline by the previous addition of ammonia; unless there be already a sufficient quantity of ammoniacal salt in the mixture, some muriate of ammonia should be added, as the magnesian salt is slightly soluble in pure water, but insoluble in solutions of ammoniacal salts.

* These analyses were performed by my friend and former assistant, Dr. Von Bose.

The solution should be stirred in all cases, and by this means a precipitate can often be produced, although before not the slightest turbidity was observable.

Iron. Traces of iron may be detected in healthy urine if a large quantity of the secretion be operated upon. Like many other mineral substances, iron passes off in small quantities in the urine, and is generally found in the urine of persons taking preparations of iron. Dr. Harley has shown that iron is a constituent of one of the colouring matters of the urine (*Urematine*).

Silica. Berzelius, many years ago, demonstrated the presence of *silicic acid*, or silica, in urine. Mere traces are met with in the ash after the removal of the salts insoluble in water, by the addition of strong nitric acid. The silica remains undissolved. This substance is derived principally from wheat, which, like other plants belonging to the *cerealia*, contains a considerable proportion of silica. Silica has been occasionally met with in urinary calculi, in appreciable quantity.

[To be continued.]

Transactions of Branches.

EAST YORK AND NORTH LINCOLN BRANCH.

PRESIDENT'S ADDRESS.

By THOMAS SANDWITH, M.D., Beverley.

[Delivered at the Annual Meeting, May 26th, 1859.]

GENTLEMEN,—If we are to believe many of our contemporaries, we have not only *new* diseases, but *new* remedies and *new* methods of treatment. A little medical antiquarianism, however, will, I think, show them the fallacy of some of these opinions, and satisfy them that there really are no new diseases, and that many of the remedies and practices supposed to be new were familiar to our forefathers. The same scepticism which, in times past, consigned to oblivion many valuable medicines, prevails at present, even in quarters where better things might have been expected; and, when a new *Pharmacopœia* makes its appearance, many formulæ we now regard as almost infallible will, no doubt, be sent to “the tomb of all the Capulets”, hereafter to appear as new inventions and discoveries.

1. The profession was under deep obligations to the late Mr. C. Haden for the revival of the use of *colchicum* in gout and rheumatism, in which diseases the remedy is so singularly efficacious as to be entitled to the appellation of a specific. But the virtues of colchicum were known to Schroder, who flourished more than two centuries ago, and who, in his *Pharmacopœia* (p. 654), says: “*Pituitam crassam, lentam, aliosque humores viscidos, peculiariter a juncturis efficaciter trahit; ob id articularum affectibus, chiragræ, podagræ, etc., conducit.*”

Whether the root called *hermodactyls* is colchicum, is uncertain. Some suppose it to be the *colchicum Illyricum* of Linnaeus. It appears, however, to have been a certain remedy for the gout, and for this purpose was employed by Alexander of Tralles. In an old London *Pharmacopœia* (1627) is a formula for an electuary called *Caryocostium*, the principal ingredients were hermodactyls and diagridium; and of its singular efficacy, Barys, the inventor, gives an instance in his own person. “When he was brought so low with the gout”, says Harris, “that he could move neither hand nor foot, nor any part of his whole body besides the tongue; yet, upon taking half an ounce of the said electuary, after it had given him but four or five stools, he found himself so mightily relieved, that he was able to go of himself to and from his place of ease, and could take a walk freely into his study, although, upon the first operation of it, he was fain to be carried or lifted upon the stool by no less than four men. Nay, the very next day he was perfectly freed from his distemper.” (Harris's *Pharmacopœia Anti-Empirica*, p. 296.) I need not add that, in the present *Pharmacopœia Londinensis*, there is no formula for the *Caryocostium*.

The faculty were startled, some years ago, by the recommendation of large doses of *emetic tartar* in pneumonia by Laennec; but the claim to priority is due to old Marryatt, who, in his *Art of Healing* (1775), recommended the same practice in ardent fevers, peripneumony, and pleurisy. He began the treatment with five grains of emetic tartar, with a drachm of nitre or sugar, divided into six papers, one of which was to be