IX. *On Thallium.* *By* WILLIAM CROOKES, *Esq.*

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Occurrence, Distribution, and extraction from the Ore.

1. SINCE the date of the last paper on Thallium which I had the honour of communicating to the Royal Society*, I have been unremittingly engaged in attempting to find a source from which this metal could be extracted in quantity. Having first discovered thallium in the deposit from the chambers of a sulphuric-acid manufactory, I naturally turned my attention towards similar deposits from English oil-of-vitriol works where pyrites was burnt. Applications were accordingly made to several large manufacturers for specimens of the pyrites which they used, and also for some of the deposit from their leaden chambers. These requests, with scarcely an exception, were readily responded to, and in a short time I was in possession of specimens from nearly thirty different establishments. In many instances thallium was detected in the pyrites, but I was disappointed to find that the deposits of sulphate of lead from the chambers contained no thallium whatever. I then applied to manufacturers who I had ascertained were constantly burning thalliferous pyrites, and obtained from them specimens of the products in different stages of their manufacture, but in no instance did I find an accumulation of thallium in any part of the operations.

2. In the operation of burning the pyrites, the thallium oxidizes with the sulphur and volatilizes into the leaden chambers; it there meets with aqueous vapour, sulphurous and sulphuric acids, and becomes converted into sulphate of the protoxide of thallium. This being readily soluble both in water and dilute sulphuric acid, and not being reduced by contact with the leaden sides, remains in solution and accompanies the sulphuric acid in its subsequent stages of concentration, &c. It is not probable therefore that any thallium can accumulate in the insoluble deposit, but it will remain dissolved in the liquid, where indeed I have found it—not however in quantities sufficient to be worth extracting, as it is present in scarcely a larger proportion than in the original pyrites. That this view of the path followed by thallium is correct, I am satisfied both from careful analyses of products from various manufactories, and also by experiments tried on a small scale in my own laboratory. M. LAMY states that he extracts thallium from similar deposits to those which I have examined; but as I have experimented on residues from English manufactories in which they burn pyrites almost, if not quite, as rich in thallium as that used in M. KUHLMANN'S works, there

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* Proceedings of the Royal Society, June 19, 1862.

must be some cause or local arrangement in their manufactory, different from what is usually adopted in this country, to occasion so large an accumulation of thallium at one particular stage of the operations*.

3. Having failed in my endeavours to find a residue from a manufactory which would yield thallium, I turned my attention to the ores in which it was likely to occur.

The unique collection of minerals brought together at the International Exhibition of 1862 enabled me, through the kindness of the various commissioners and class-superintendents, to verify the opinion which I had formerly expressed as to thallium being a very widely distributed element. It most frequently, indeed almost invariably, occurs in iron pyrites containing more or less copper; but I have also detected it in native sulphur, in zinc, cadmium, bismuth, mercury, and antimony ores, as well as in the manufactured products from these minerals. Thallium is confined to no particular country, but is at the same time by no means uniformly distributed in mineral veins from the same locality, or even in adjacent rocks in the same mine. Hitherto I have detected no approach to law in its distribution. In every country mineralogically represented in the late Exhibition I have detected the presence of thallium, when the minerals examined were at all numerous and could be regarded as fair average samples of the different deposits. Doubtless much of this apparent abundance is to be attributed to the extreme delicacy of the test employed, as ores in which thallium is present, only in the proportion of 1 to 100,000, give evident traces of it in the spectroscope. Many pyrites, however, contain more than a mere trace of thallium: it is present, in sufficient quantity to be readily extracted by direct treatment, in pyrites from various parts of North and South America, France, Belgium, Spain, as well as Cornwall, Cumberland, and many parts of Ireland.

4. The optical process of detecting thallium in a mineral is very simple. A few grains only of the ore have to be crushed to a fine powder in an agate mortar, and a portion taken up on a moistened loop of platinum wire. Upon gradually introducing this into the outer edge of the flame of a Bunsen's gas-burner, the characteristic green line will appear as a continuous glow, lasting from a few seconds to half a minute or more, according to the richness of the specimen. By employing an opake screen in the eye-piece of the spectroscope to protect the eye from the glare of the sodium line, I have in half a grain of mineral detected thallium when it was only present in the proportion of 1 to 500,000. After a few experiments of this kind, and having a thalliferous pyrites of known richness for comparison, it is easy to give a rough estimate as to the quantity of thallium present.

5. One of the richest thalliferous minerals in the Exhibition was the prominent block

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* This anomaly has just been cleared up by a paper communicated to the French Academy, on the 26th ultimo, by M. Fréd. Kuhlmann, in which he explains that, in order to prevent the passage of arsenic from the pyrites into the sulphuric acid, he interposes, between the pyrites-kilns and the ordinary leaden chambers, a large supplementary chamber, in which the products of combustion are lowered in temperature and deposit the more easily condensible volatile matters. It is in this deposit that thallium is found.

of pyrites, weighing nearly two tons, which formed so conspicuous an object in the Belgian department; it was exhibited by the Société Anonyme de Rocheux et d'Oneux of Theux, near Spa (Belgium, Class I., No. 18 in the Catalogue). Accompanying the principal block were several smaller specimens from different parts of the same locality. Thallium was detected in all, but in very varying proportions. By the great kindness of Professor CHANDELON of Liège, one of the jurors of Class II., I was enabled to examine a series of examples from four separate chambers, and eight different rocks from the mine whence these specimens were brought, he having most courteously taken the trouble to visit the locality and select the specimens for me. In some, as in rocks C, D, and G, no appreciable quantity of thallium was present; in chamber No. 1 there was a trace only, whilst in chamber No. 2, and in rock H, it was present in comparative abundance. Professor CHANDELON, to whom I desire to offer my hearty thanks for his uniform courtesy and valuable assistance, informs me that those portions of the mineral vein which I have found most rich in thallium are close to a vein of blende and calamine, which is worked in the neighbourhood for zinc. I am promised some of this blende and calamine for analysis; and it will be of some interest to know the relative quantity of thallium they contain in comparison with that in the adjacent pyrites. I have already found considerable quantities of thallium in metallic zinc and cadmium manufactured from this ore.

Professor CHANDELON not only troubled himself to make several journeys from Liège to the mines on my account, but likewise induced M. RÉNARD (the manager) and the proprietors to present me with upwards of two tons of the mineral carefully selected from those parts of the mine which I had found to be richest. This arrived in September last.

6. Numerous experiments have led me to adopt the following process for extracting the new metal from its ore. The pyrites is first broken up into pieces about the size of a walnut, and placed in cast-iron retorts, capable of holding 20 lbs. each; five of these are arranged in a reverberatory furnace, so that the flame may lick round and heat them uniformly; iron condensers being luted on, the temperature is raised until the retorts become of a bright red heat, at which they are kept for about four hours. They are then allowed to cool, and the product removed from the condenser; 100 lbs. of pyrites usually give from 13 to 17 lbs. of sulphur. The sulphur is of various colours, according to the temperature attained, sometimes being orange, sometimes purple-brown, sometimes bright grass-green, and is always highly crystalline. Experiments tried at various times during the distillation, show that thallium is present in the first portions of sulphur which distil over, as well as in the last, although the proportion somewhat increases towards the end. When the heat has been sufficient, and the yield of sulphur above 15 per cent., scarcely a trace of thallium remains behind in the retorts; but with a low heat, the sulphur is almost pure yellow in colour, and contains very little thallium. Each operation lasts about five hours; the iron retorts frequently serve for two, and sometimes for as many as five or six heatings. They gradually,

however, become converted into sulphide, and then melt away. This sulphide of iron contains no thallium. Within the last three months I have distilled upwards of 16 cwt. of iron pyrites, yielding me $2\frac{1}{4}$ cwt. of thalliferous sulphur. The results are appended:—

				lbs.	ozs.	
November	8, 1862,	14 lbs.	of pyrites yielded	2	6	of sulphur.
„	14, „	24	„ „	3	8	„
„	29, „	120	„ „	12	7	„
December	11, „	70	„ „	8	12	„
„	13, „	100	„ „	12	5	„
„	15, „	100	„ „	12	8	„
„	16, „	100	„ „	14	5	„
January	3, 1863,	100	„ „	13	5	„
„	5,	100	„ „	12	9	„
„	7,	100	„ „	11	4	„
„	8,	100	„ „	15	4	„
„	9,	100	„ „	14	7	„
„	10,	100	„ „	14	13	„
„	12,	100	„ „	16	3	„
„	14,	100	„ „	15	2	„
„	24,	100	„ „	16	4	„
„	26,	100	„ „	13	13	„
„	27,	100	„ „	17	2	„
„	29,	100	„ „	14	5	„
„	30,	100	„ „	11	9	„
		1828		252	3	

It may be of some interest to state that, although the mineral is put in in its ordinary air-dry state, I invariably get from each 100 lbs. of pyrites about half a pint of liquid distilled over before the sulphur comes. Upon evaporating this down, water, having a peculiar empyreumatic odour, goes off, oxide of iron is precipitated, and sulphite of the protoxide of iron separates in large, nearly colourless crystals: no thallium is present.

7. I have met with great difficulty in extracting economically, and without loss, the whole of the thallium from this sulphur. On the small scale, nothing is easier than to boil it, finely powdered, in fuming nitric acid or *aqua regia*, until the residuary sulphur is of a pure yellow colour, and then to extract the thallium from the solution by processes to be hereafter described; but such operations are impracticable when working by the hundredweight.

An attempt was made to separate the thallium by converting the thalliferous sulphur into chloride. Half a pound was treated in this manner; but upon rectifying the product, thallium was found in the distillate as well as in the residue. An immense number of experiments were tried to extract the thallium from the chloride of sulphur, but with no success, unless indeed means were employed which would have been equally easy and economical upon the original sulphur. The simplest plan would doubtless be to dissolve out the sulphur with bisulphide of carbon, in which sulphide of thallium is insoluble; and this is a plan that I hope before long to have in full work; hitherto, however, I have found the following the readiest method:—In a large cast-iron caldron dissolve 12 lbs. of good caustic soda in 1½ gallon of water, heat it to the boiling-point, and then add 18 lbs. of the sulphur in large lumps, just as it comes from the receivers. A few pounds should be added at a time, as dissolved, and the mixture kept gently boiling, water being added from time to time to replace that lost by evaporation. When no more sulphur can be dissolved, dilute the mixture with four or five times its bulk of water, and allow it to cool. A voluminous black precipitate will separate, which must be collected on a calico filter. The greater portion of the thallium remains in this precipitate in the form of sulphide, together with iron, copper, &c.; but some passes through dissolved in the alkaline liquid. I have hitherto been unable to recover the thallium from this solution without an incommensurate expenditure of both acids and time. After a slight washing, the black precipitate is transferred to a large dish, and boiled in sulphuric acid until sulphuretted hydrogen ceases to be evolved; nitric acid is then added in small quantities, and the mixture is boiled until all solvent action has ceased; it is then diluted with water, and filtered. Evaporate down until all excess of nitric acid is removed, and then add hydrochloric acid and sulphite of soda to the liquid; this produces an immediate precipitation of the thallium in the state of protochloride as a white crystalline precipitate, only slightly soluble in water; as, however, a certain quantity of this chloride remains dissolved, it is advisable to add, after the sulphite of soda, iodide of potassium, which precipitates the whole of the thallium in the form of an insoluble yellow iodide. If the solution turns almost black upon adding the iodide of potassium, or the precipitate comes down of a dirty grey colour, it is a sign that an insufficient quantity of sulphite of soda has been added; a further addition will remedy this. A little copper, which is generally present in the sulphur, will likewise be precipitated in the form of subiodide. The iodides are to be filtered off, and washed until they are free from iron. They may now be decomposed by heating with oil of vitriol, which converts them into sulphates; but the temperature required for this being very high, and the decomposition difficult to effect perfectly without loss of thallium by volatilization, I prefer the following, though somewhat longer process:—Boil the iodides in excess of sulphide of ammonium until they are entirely converted into sulphides; filter, and wash with weak sulphuretted water until no iodine can be detected in the washings; then boil the precipitate with strong sulphuric acid, adding a little nitric acid from time to time; evaporate until the sulphuric acid begins to go off in white vapours, and then, after dilution with water, add an excess of ammonia. Now add cyanide of potassium until the blue ammoniacal solution of copper is decolorized, and then a slight excess of sulphide of ammonium, and gently warm. Filter and wash with dilute sulphuretted water until all the cyanide of potassium, &c. is removed, and boil the precipitated sulphides with strong sulphuric and nitric acids until the mass becomes perfectly white. Drive off the whole of the nitric acid and the greater portion of excess of sulphuric acid by heat, and then boil the residue for some time in water. Filter, and wash well. A white insoluble residue will generally be left, containing a little thallium; but the greater portion of this metal will be in the solution in the form of sulphate.

8. From this solution the metal is readily obtained in the metallic state by voltaic precipitation. Two or three cells of a Grove's battery, with platinum terminals dipping into the aqueous solution of the sulphate (either acid or rendered alkaline with ammonia), produce an immediate reduction, oxygen being evolved at one pole, and the metal coming down at the other. The appearance presented when a tolerably strong solution of thallium is undergoing reduction is very beautiful. If the energy of the current bears a proper proportion to the strength and acidity of the liquid, no hydrogen is evolved at the negative electrode, but the metal grows from it in large crystalline fern-like branches spreading out into brilliant metallic plates, and darting long needle-shaped crystals, sometimes upwards of an inch in length, towards the positive pole, the appearance strikingly resembling that known as the tin tree. Some of the tabular crystals, as seen in the liquid, are beautifully sharp and well defined, their angles being temptingly measurable; considerable difficulty is, however, met with in disengaging them from the electrode, and removing them in a perfect state from the liquid. So long as thallium is present in the solution, no hydrogen is evolved with a moderate current; as soon as bubbles of gas begin to form, the reduction may be considered complete. The crystalline metallic sponge may now be squeezed into a compact mass round the platinum terminal, and, being disconnected from the battery, quickly removed from the acid liquid, rinsed with a jet from a wash bottle, and transferred to a basin of pure water. The metal is then carefully removed from the platinum, and kneaded with the fingers into as solid a lump as possible. It will be found to retain its metallic lustre perfectly under water, and coheres together readily by pressure. The lump may now, after having been dried with blotting-paper, be put into a steel-crushing mortar and strongly hammered until it assumes the form of a solid ingot. To obtain this in a fused mass, the best plan is to break it up into small pieces, and drop them one at a time into a crucible containing fused cyanide of potassium, at a low red heat; they melt at once and run together at the bottom of the crucible into a brilliant metallic button: allow the crucible to cool, and dissolve out the flux with water, when the thallium will be left in the form of an irregular lump, owing to its remaining liquid and contracting after the cyanide has solidified. As long as the surface is wet, either with the solution of cyanide or with pure water, the metal presents a highly crystalline appearance, resembling tin when washed with acids; this disappears upon exposure to the air, owing to the formation of a pellicle of oxide.

Physical Characteristics of Thallium.

9. Thallium has a distinct colour of its own, not being absolutely identical with any

other metal. The true colour can be seen by scraping a piece of the metal under water, or fusing it in hydrogen and allowing the melted globule to flow away from the dross. In appearance it most resembles tin and cadmium, not being so brilliantly white as silver, but without the blue tinge belonging to lead. It is susceptible of taking a very high polish: by rubbing it under water with a fine polishing stone, the surface can be made smooth and bright, reflecting as perfectly as a mirror.

It oxidizes in the air with almost the rapidity of an alkali-metal. When freshly cut with a knife, if the eye follows the blade, the proper colour of the metal will be seen to assume, in a few seconds, a yellowish cast, caused by a thin coating of the protoxide, which continues to increase until the metallic lustre is obscured by a grey film, scarcely distinguishable from the superficial tarnish of metallic cadmium. At this stage the oxidation appears to be almost arrested, and the metal may be freely handled and exposed to the air, with scarcely any further change. After having remained in the air for some weeks, the surface becomes covered with a white powder, which easily rubs off, and has a strong biting taste.

When rubbed between the fingers, a faint peculiar smell may be observed, unlike that produced by any other metal under the same circumstances. If a perfectly bright surface of thallium is applied to the tongue, no taste whatever is observed; but a tarnished surface tastes strongly alkaline, and somewhat sweet like oxide of lead; whilst if the surface is more oxidized than usual, from the metal having been long exposed to the air, or previously raised to a high temperature, the taste is very caustic and biting, remaining on the tongue for some hours, and resembling that observed when the tongue is applied to the terminals of a voltaic pile.

10. Thallium is the softest known metal admitting of free exposure to the atmosphere: it can be cut, pressed out, and moulded with the finger-nail with the utmost ease; and whilst it is incapable of abrading the surface of a piece of lead, this latter metal scratches thallium with great facility. Thallium marks paper as easily as lead: the streak is blue at first, but almost instantly turns yellowish, and in the course of a few hours nearly fades out, from oxidation. The writing can, however, be restored at any time to more than its original blackness by exposure to sulphuretted hydrogen or sulphide of ammonium. Thallium is too soft to file well or be cut with a saw, as it clogs up the teeth directly, and it does not become brittle when exposed to a low temperature. It has very little tenacity, being inferior to lead in this respect. It is very malleable, and may be hammered out into leaves as thin as paper; it may also be moulded and pressed in a die, taking a very sharp impression. When repeatedly hammered, it does not appear to get sensibly harder or require annealing. I have succeeded in drawing it into wire; but, owing to its want of tenacity, this is a matter of some difficulty; the wire may, however, be obtained in a very easy way by pressure. Dr. MATTHIESSEN has been good enough to prepare for me several specimens of wire by pressing the metal with a powerful vice through a fine hole in a steel box, receiving the wire as it issued forth in tubes filled with dry carbonic acid, and various liquids: I have also prepared it since in similar

apparatus of my own. It is squeezed into wire more readily than lead, and when received into dry carbonic acid or petroleum, without contact with air, and instantly sealed up, its true metallic lustre and colour are very apparent; if, however, a very minute trace of air obtains access, it assumes a deep blue appearance. This is remarkable, as the first superficial coat of oxide which forms on a freshly cut surface, freely exposed to the air, is distinctly yellow.

11. I have carefully determined the specific gravity of thallium. It varies according to the treatment the metal has previously undergone. A lump melted and allowed to cool slowly under cyanide of potassium, was found to have a specific gravity of 11·81. The same lump, after being strongly hammered in a steel mortar, had its density increased to 11·88. Another portion, experimented on in the form of thick wire, had a density of 11·91 immediately it had been squeezed through the die. I believe that thallium is capable of undergoing still greater condensation. If in the process of squeezing it into wire the vice is screwed up until the thallium is just making its appearance through the fine aperture, and the pressure is then kept stationary, the issue of metal proceeds for a few seconds and then stops. Upon now applying the flame of a spirit-lamp to the die, a piece of wire from an eighth to half an inch long quickly shoots out. This cannot be due to ordinary expansion by heat, as it commences and terminates abruptly at an apparently definite temperature. Were it expansion by heat, the formation of wire would proceed nearly uniformly as the temperature increased. The most probable explanation is, that the application of heat gives the metal power suddenly to release itself from an abnormal state of condensation into which the enormous pressure had forced it.

Thallium wire is almost devoid of elasticity; it retains any form into which it is bent with scarcely a tendency to spring towards its former position.

When freshly prepared, thallium wire is perfectly amorphous, and remains so if kept at the ordinary temperature in petroleum or carbonic acid; in water, however, it gradually assumes a superficial crystalline appearance, resembling the *moire métallique* of tin plate: this effect is immediately produced when thallium in wire, ingot, or plate, tarnished or clean, is boiled in water.

12. In fusibility thallium stands between bismuth and lead, its melting-point being 550° Fahr.: it does not appear to become soft and pasty before undergoing complete fusion. Two pieces of the metal, when perfectly clean, are capable of welding together in the cold by strong pressure. I have repeatedly filled the steel die with small scraps and cuttings of thallium, and squeezed them out into one continuous length. Wire so made is apparently as tenacious as that obtained from one lump.

Thallium volatilizes easily: when heated out of contact with air, it evolves vapours at a red heat, and boils below a white heat. In a current of hydrogen gas it may be easily distilled at a red heat; it does not, however, condense very perfectly; for if the hydrogen be ignited, even after traversing four or five feet of cold glass tube, it burns with a bright green flame.

13. Thallium is a pretty good conductor of heat and electricity. My friend Dr. MATTHIESSEN is at present engaged in the quantitative determination of these constants of the metal, upon specimens with which I have supplied him. Its electro-chemical position is very near cadmium, being precipitated from the sulphate by zinc and iron, but not by cadmium or copper. Professor WHEATSTONE is examining in this respect specimens of the metal specially purified for the purpose.

Thallium is strongly diamagnetic. A small permanent horseshoe magnet was suspended vertically, poles downwards, to one arm of a very delicate balance, capable of turning to 0·0005 of a grain. After being accurately counterpoised, a lump of metallic thallium, weighing about 200 grains, was placed beneath the magnet, very close, but not touching. Upon now observing the weight of the magnet, it was seen to be decidedly repelled by the metal, losing in weight 0·003 of a grain.

By the kindness of Professor FARADAY, who himself tried most of the experiments, the above observation was verified with the large electro-magnet belonging to the Royal Institution. Upon suspending a long cylindrical helix of thallium wire horizontally in the magnetic field, and making contact with the battery, it was strongly driven to an equatorial position. A lump of the metal, suspended almost in contact with one of the magnetic poles, was repelled from it, being permanently deflected nearly a tenth of an inch from the perpendicular. From a comparison with bismuth under somewhat similar circumstances, I am inclined to believe that thallium is one of the most diamagnetic bodies known.

14. Thallium readily alloys with other metals. With 95 per cent. of copper it forms a hard button, flattening somewhat under the hammer, but soon cracking at the edges; the further addition of thallium produces a very hard and brittle gold-coloured alloy; and when the proportion of thallium is further increased, the colour of the copper is entirely lost. A very minute quantity of thallium, less than half a per cent., melted with copper, greatly diminishes its malleability and ductility, acting in this respect like arsenic. I believe that the variation in the physical properties of different specimens of commercial copper (a variation which has never yet received satisfactory explanation) is to be attributed to the presence of more or less minute traces of thallium, as I have found it present in many samples of *bad* copper, as well as in some specimens of crystallized sulphate (29). This subject is still under investigation.

Five per cent. of thallium alloy readily with tin, when they are melted together under cyanide of potassium; the resulting compound is perfectly malleable.

With mercury, thallium forms a solid crystalline amalgam.

Thallium melts readily with platinum: if a portion of the metal is placed on the end of a platinum wire and heated to redness, a fusible alloy is obtained, which is crystalline, very hard, and almost as brittle as glass under the hammer. If this alloy is heated before the blowpipe, the characteristic green colour is vividly communicated to the outer flame; before the oxyhydrogen blowpipe the green light is of extraordinary splendour. A similar alloy is left when the platinochloride of thallium is heated to redness in a crucible, chlorine going off together with a little thallium.

15. The remarkable simplicity of the spectrum of thallium has given rise to repeated experiments with a view to ascertain whether, and under what circumstances, it could be obtained compound. I have already stated[*] that "a flame of sufficient temperature to bring the orange line of lithium into view produces no addition to the one thallium-line; and an application of telescopic power strong enough to separate the two sodium lines a considerable distance apart still shows the thallium-line single." The former observation has lately been verified and extended by Dr. W. ALLEN MILLER[†], who has also noticed that at the high temperature of the electric spark several new lines, especially two green and a blue line, make their appearance. The latter observation, as to the unresolubility of the green line, was recently put to a crucial experiment. My friend Mr. BROWNING, the well-known philosophical-instrument maker, kindly allowed me to examine the thallium-spectrum in a spectroscope which he is making for Mr. GASSIOT. This instrument is furnished with nine flint-glass prisms of large size; and although as yet unfitted with the elaborate adjustments with which it will be ultimately furnished, it is even now capable of producing, with a moderate magnifying power, an apparent separation of the eighth of an inch in the two sodium-lines, at the standard microscopic distance of ten inches. Under this enormous amplifying power the thallium-line was still seen single, being as fine and sharply defined upon the black ground as either of the constituents of the double sodium-line. I have stated that in a spectroscope of the ordinary size the line appears to be identical in refrangibility with the line δ in the barium-spectrum; a comparison of the two spectra in this large instrument showed me that these lines do not coincide in position.

The delicacy of this optical test for thallium is very great. I prepared a standard solution of sulphate of thallium, and diluted it until it was in the proportion of one grain dissolved in fifteen gallons (or about 1,000,000 grains) of water. Upon dipping a platinum wire loop into this solution, and holding the moistened end in the flame of the spectroscope, the green line was distinctly visible. The quantity of liquid taken up by the platinum wire was about the fifth of a grain, containing, therefore, no more than $\frac{1}{5,000,000}$th of a grain of sulphate of thallium.

A flame strongly coloured with thallium can be obtained by passing hydrogen over chloride of thallium at a high temperature and then igniting it. The absolute monochromatic character of the light renders everything illuminated by it either green or jet black: coloured sealing-wax, ribbons, a bouquet of flowers, as well as coloured precipitates, are entirely altered in appearance, whilst the human face assumes a horrible, corpse-like green hue.

The green thallium-line can be reversed in the spectrum; but this is an experiment of some difficulty. The effect can, however, be well seen by adopting the plan which I have used to show the same phenomenon in the case of sodium—by holding a small thallium-flame in front of a larger one coloured with the same metal, the mantle of the front flame being projected as a black line on the hinder flame. If a trace of lithia is

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[*] Proceedings of the Royal Society, June 19, 1862.

[†] Ibid. January 15, 1863.

added to the larger flame, insufficient to destroy the green colour, the effect of contrast is very striking; the border of the front flame being opake to thallium, whilst it is transparent to lithium, the flame appears of a beautiful green colour with a crimson edge.

16. The atomic weight of thallium has been a subject to which my attention has been directed for some months, in fact ever since I commenced to obtain the metal in sufficient quantities to enable me to purify it to the requisite degree without too much diminishing my stock. The investigation is far from concluded as yet, and the numbers which I have obtained must be regarded as only approximate. M. LAMY* gives the equivalent as 204. As, however, he gives no statement respecting the processes adopted to arrive at this figure, and we are not even informed of the number of experiments of which this is the mean result, of the quantities of material operated upon, or the divergence of each result from the mean 204, it is impossible to know what value is to be attached to it. Below I give the results of five separate determinations by different methods: I admit they do not agree so closely as one would like in experiments of this sort; indeed the discrepancies are beyond the probable error of analysis, and seem to point to some other disturbing cause not yet ascertained. I give, however, all the necessary figures, and the results may be taken for what they are worth.

About 200 grains of thallium, prepared as already described, were specially tested for, and purified from, metals with which it was likely to be contaminated, by processes appended in the *analytical notes*, and were obtained in the form of sulphate. This was recrystallized twice, and the metal precipitated from its aqueous solution by two Grove's batteries, platinum electrodes being employed. The metal was then fused under cyanide of potassium, and, after being cleaned in dilute acid, preserved for use in a dry bottle filled with coal-gas. Some of this purified metal was then dissolved in dilute sulphuric acid, the solution was evaporated down, and the residue heated until sulphuric acid ceased to come off; it was then redissolved in water, and the sulphate of thallium allowed to crystallize. The salt was then considered to be sufficiently pure for analysis.

I. Some of the crystals were heated to incipient fusion and weighed, they were then dissolved in water, and iodide of potassium was added until no further precipitation of iodide of thallium took place. The precipitate was then warmed and allowed to settle, collected on a tared filter, washed with water, dried in a water-bath and weighed.

II. Another portion of sulphate of thallium was heated and weighed as above described, and the aqueous solution precipitated with nitrate of baryta. The precipitated sulphate of baryta was then collected as usual, well washed, and weighed.

III. A third portion of sulphate of thallium was weighed as before, dissolved in a small quantity of warm water, and mixed with a slight excess of pure hydrochloric acid; alcohol was then added, and the precipitated chloride of thallium collected on a tared filter, washed with alcohol, and weighed.

IV. A piece of metallic thallium was weighed and converted into sulphate. The

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* Comptes Rendus, December 8, 1862.

excess of sulphuric acid being driven off by heat, the remaining sulphate of thallium was heated to its fusing-point and then weighed.

V. The sulphate of thallium obtained in experiment IV. was dissolved in water and mixed with an excess of bichloride of platinum. The precipitated platinochloride of thallium, which is more insoluble than the potassium salt, was then collected on a tared filter, washed, and weighed.

The following Table shows the experimental results obtained:—

Experiment I.

7·342 grains of sulphate of thallium yielded 9·655 grains of iodide of thallium. Calling x the equivalent of thallium, we have the following proportion,

$$7·342 : x+48 :: 9·655 : x+127, \therefore x=202·73.$$

Experiment II.

9·883 grains of sulphate of thallium gave 4·577 grains of sulphate of baryta.

$$9·883 : x+48 :: 4·577 : x+116·5, \therefore x=203·55.$$

Experiment III.

8·555 grains of sulphate of thallium yielded 8·127 grains of chloride of thallium.

$$8·555 : x+48 :: 8·127 : x+35·5, \therefore x=201·85.$$

Experiment IV.

10·113 grains of thallium yielded 12·503 grains of sulphate of thallium.

$$10·113 : x :: 12·503 : x+48, \therefore x=203·1.$$

Experiment V.

12·503 grains of sulphate of thallium yielded 20·312 grains of platinochloride of thallium.

$$12·503 : x+48 :: 20·312 : x+205·2, \therefore x=203·56.$$

I have therefore adopted the mean result 202·96 or 203 as the equivalent of thallium, writing the protoxide TlO and the sulphate $TlO.SO_3$, unless, indeed, as appears probable from theoretical considerations, these compounds have to be expressed Tl_2O and $Tl_2O.SO_3$, in which case the atomic weight would be half this number.

Chemical Properties of Thallium.

17. Thallium does not decompose pure water, either at the common temperature or when boiling. If, however, steam be passed over the metal at a red heat, it is decomposed, with formation of oxide of thallium and separation of hydrogen, the gas evolved burning with a decided green flame. The oxide which forms superficially when thallium

is exposed to the air is the protoxide, a powerful base, soluble in water, forming a liquid which is strongly alkaline to test-paper. If a lump of thallium, weighing 50 or 100 grains, is placed, after exposure to the air for a few days, in an ounce of water and boiled for a few seconds, the solution will be found to possess alkaline characters. It turns litmus paper strongly blue, browns turmeric paper, has a metallic alkaline taste, and perfectly neutralizes acids. It also precipitates alumina from a solution of alum, evolves ammonia from chloride of ammonium, and reacts with hydrochloric acid, iodide of potassium, sulphide of ammonium, &c., in the characteristic manner of a thallium-salt. As might be imagined, thallium is readily acted on by air and water jointly; and by shaking up pure thallium wire in a bottle with an insufficient quantity of water to cover it, allowing fresh air to have access from time to time, a strong solution of oxide of thallium can be obtained. When thallium is melted in the air, it behaves very similarly to lead, rapidly oxidizing and becoming coated with a fusible oxide resembling litharge. Upon continuing the heat, this increases, whilst the bright globule in its centre diminishes in size. The fused oxide is absorbed by bone-ash, and I have ascertained that a silver-thallium alloy can be cupelled like silver-lead. When the metal is strongly heated on charcoal before the blowpipe, it volatilizes in brownish fumes, which are without odour. Upon removing the heat, the red-hot globule of metal continues to burn and give off vapours for some time afterwards, like pure antimony under similar circumstances. On cooling, the adjacent parts of the charcoal are coated with globules of sublimed metal. The oxide resembling litharge is the same as that formed by the superficial action of air on the metal, or steam at a high temperature; it may also be prepared in strong solution by decomposing sulphate of thallium with baryta water and filtering. The oxide may be obtained in the crystalline and anhydrous state by evaporating this solution to dryness *in vacuo*. Its physical characters having been fully described by M. Lamy, I have not further experimented with it.

Alcohol exerts a curious action upon thallium. A coil of pure thallium wire was placed in a tube with some absolute alcohol, just sufficient to cover it. At first no action was apparent, except a slight opalescence of the spirit. In the course of a few hours this had disappeared, and upon close examination needle-shaped crystals, together with a few drops of a colourless heavy liquid, were observed adhering to the sides of the tube and sinking in the alcohol. In three days the wire was nearly eaten away, whilst the oily drops had considerably increased in bulk. The alcoholic liquid was carefully decanted from the heavy oil and tested: dilution with water produced no change in it; it was strongly alkaline to test-paper, and reacted in other respects like a strong solution of protoxide of thallium. Upon the addition of a drop of hydrochloric acid, a thick curdy precipitate of protochloride of thallium was produced.

The oily liquid was decomposed upon the addition of water, solidifying to a yellow crystalline mass of protoxide of thallium, which dissolved on further addition of water and heating.

Upon evaporating the alcoholic liquid over a water-bath, a further formation of the heavy oil took place. The production of this oily liquid, by dissolving oxide of thallium in alcohol and evaporating, has been previously observed by M. Lamy, who calls it Thallic Alcohol.

18. Thallium dissolves in sulphuric acid with ease, evolving hydrogen. The gas given off burns with a flame in which thallium can frequently be detected with the spectroscope, although I have hitherto failed in proving the existence of a gaseous compound of hydrogen and thallium. Upon evaporating the solution, sulphate of thallium crystallizes out. I have little to add to M. Lamy's description of this salt. It forms large, well-defined colourless crystals; when heated to a little above the boiling-point of sulphuric acid, they fuse to a clear liquid, which on cooling appears glassy and slightly crystalline. The salt is soluble in twenty or thirty times its weight of cold water, and in much less when boiling, crystallizing out with facility upon cooling.

Thallium dissolves with the utmost rapidity in nitric acid. A piece of the metal thrown into this acid mixed with half its bulk of water, runs about on the surface like sodium on water, rapidly dissolving, and evolving nitric oxide mixed with nitrous oxide. I have not found any ammonia produced in this reaction. When the liquid cools, it becomes almost solid, from the crystallization of nitrate of thallium, which is nearly insoluble in nitric acid, although it is very soluble in water.

Hydrochloric acid attacks thallium but slowly, the action soon ceasing, owing to the formation of a layer of difficultly soluble chloride of thallium. When hydrochloric acid or a soluble chloride is added to a solution of the protoxide of thallium or one of its soluble salts, a white curdy precipitate of protochloride of thallium, $Tl\,Cl$, is thrown down, scarcely differing at first sight from chloride of silver. It has, however, a crystalline appearance, is slightly soluble in cold water, moderately so in boiling water, from which it crystallizes out on cooling like chloride of lead, and is insoluble in alcohol. When boiled in nitric acid or *aqua regia* it is converted into a higher chloride, crystallizing out in large spangles of a yellow colour. The same chloride is formed by the action of nitrohydrochloric acid upon the metal or its sulphide. It is more soluble in water and acids than the protochloride, and is precipitated in the latter form upon the addition of sulphite of soda to its solution.

I have already described [*] the properties of the sulphide of thallium and some other of its insoluble salts. Having since worked upon purer as well as larger quantities of the metal, I have an addition or two to make to my previous descriptions. Thus the protiodide of thallium is of a bright yellow colour, the red tinge which I formerly noticed in it being due to the presence of a persalt of thallium. It is insoluble in excess of dilute solution of iodide of potassium, being soluble only when the latter is concentrated. The protocarbonate is soluble in water.

Concentrated acetic acid dissolves thallium slowly when heated, forming a soluble

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[*] Proceedings of the Royal Society, June 19, 1862.

acetate; very dilute cold acid has no action upon thallium. Owing to the solubility of the oxide of thallium, no precipitate is produced in the protosalts of this metal by potash, soda, or ammonia.

Neutral or slightly acid protosalts of thallium are incompletely precipitated by sulphuretted hydrogen, and not at all when a large excess of acid is present. Sulphide of ammonium, as I have already stated, precipitates them perfectly, reducing the metal to the state of protosulphide when in a higher state of oxidation.

19. The compounds of thallium are not only volatile when heated in the dry state, but many of its salts volatilize when their aqueous solutions are boiled. The chlorides are especially volatile, insomuch that loss is experienced in evaporating them down. Ten grains of pure metallic thallium were dissolved in a considerable excess of nitrohydrochloric acid, and the solution was gently boiled down in a retort. Upon testing the acid distillate by supersaturation with ammonia and addition of sulphide of ammonium, a considerable precipitate of sulphide of thallium was formed. Nitrohydrochloric acid was then added to the residue of sesquichloride of thallium remaining in the retort, and the distillation was repeated over a water-bath, care being taken that the evaporation in this case was conducted below the boiling-point of the liquid. Upon now testing the distillate, traces of thallium were still found in it: the metal in this case could not have been carried over mechanically, as the liquid in the retort had not once entered into ebullition.

Having for upwards of a year had considerable quantities of liquids containing thallium evaporated in open dishes in my laboratory, it was natural to anticipate, after the above experiment, that some quantities of the metal had been thus volatilized along with the aqueous vapour, and would be found adhering to the walls and deposited with the dust on the upper shelves of the room; a small portion of dust was accordingly removed from a shelf at a height of above 10 feet from the ground, and tested for thallium. A brilliant green line in the spectroscope showed me that this metal was present in more than minute traces.

20. Thallium may be determined quantitatively by precipitation, either as protochloride, iodide, or double chloride of platinum and thallium. The chloride must be washed with alcohol, as it is slightly soluble in water. The iodide and platinochloride are practically insoluble.

Position of Thallium amongst elementary bodies.

21. When I discovered thallium two years ago, owing to the excessively minute portion of substance which I had under examination, misled by its constant occurrence with sulphur and selenium, and basing my conjectures upon some of the properties first noticed—namely, its complete volatility below a red heat, its precipitation in the elementary form by zinc, its non-precipitation from an acid solution by alkalies, and its solubility in water when fused with nitre and carbonate of soda—reasoning upon these observations, I ventured to suggest that it was *probably* a metalloid belonging to

the sulphur group, although, I added, "I hesitate to assert this very positively"*. In speaking of a metalloid of the sulphur group, I should explain that I had in view, not a decidedly non-metallic body like sulphur, but one of the connecting links between metals and non-metals—a metalloid in the strict meaning of the word, like tellurium or arsenic. If I had formed any particular view upon the matter, knowing so little of the properties of the new body, it was that it might possibly prove to be a higher link in the sulphur, selenium, and tellurium chain. It was not long before further research showed me that the body under examination had, in addition to the characters already mentioned, others which gave it strictly metallic characters; and although no formal publication of this isolated fact was immediately made, the element was commonly spoken of in scientific circles as a new metal, and was so described by me at the Exhibition on the 1st of May last. I enter thus into details on so trifling a subject because French chemists are inclined to attach undue importance to the term, and misinterpret the meaning of metalloid.

Even with our present knowledge of the chemical and physical characteristics of thallium, it is not easy to assign its true position in the scale of elements. I cannot admit, with the French chemists, that it is an alkali-metal. Almost the only property which thallium possesses in common with the alkali-metals is the solubility of its oxide, and perhaps its forming an insoluble platinum-salt. But oxides of lead, silver, and mercury are also soluble in water, reacting in many respects like alkaline solutions; and oxide of thallium is far more analogous to these than to potash and soda, inasmuch as it has scarcely any affinity for water, becoming anhydrous, in a vacuum, even in the cold. In opposition to these reasons for classing it with the alkalies, we have numerous facts to prove that its true position is by the side of mercury, lead, or silver. The ready dehydration of its basic oxide—the insolubility of its sulphide, iodide, chloride, bromide, chromate, phosphate, sulphocyanide, and ferrocyanide—its great atomic weight—its ready reduction by zinc to the metallic state—and, according to Dr. MILLER, the complexity of its photographic spectrum—all prove that thallium cannot consistently be classed anywhere but amongst the heavy metals, mercury, silver, lead, &c.

22. Those who remember how readily figures can be moulded to suit any theory, will attach slight importance to the argument adduced by M. DUMAS in favour of thallium being related to potassium and sodium because its equivalent is rather near a figure obtained by adding twice the atomic weight of one metal to four times the atomic weight of the other. By similar processes of addition, multiplication, or subtraction it would not be difficult to prove a relationship between thallium and any desired group. Thus twice the equivalent of tellurium added to that of arsenic would make one equivalent of thallium, an argument in favour of its being a metalloid; one equivalent of mercury and one equivalent of lead added together make one equivalent of thallium, as also do one equivalent of silver and two equivalents of molybdenum—each proving it to be a heavy metal of the silver and lead group. Were it worth while

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* Chemical News, March 30, 1861, p. 193, and Phil. Mag., April 1861.

to pursue these relationships further, it would not be difficult to find many coincidences less strained than the one brought forward by M. DUMAS.

Analytical Notes on Thallium.

23. The chemical identification of thallium when associated with other metals is not difficult. I have already discovered very exact methods of detecting the presence of thallium in, and separating it from, most of its associated metals, and further experiment will doubtless still more increase the accuracy of its analytical detection and estimation.

In starting with the analysis of a thalliferous mineral by the ordinary analytical tables, in which Group I. is precipitated by hydrochloric acid, Group II. by hydrosulphuric acid, Group III. by ammonia, and Group IV. by sulphide of ammonium, a slight analytical difficulty will be at first met with, as, unless special precautions are taken, thallium will appear in all four groups. Thus if the thallium be in the state of a sesquisalt, no precipitate will be produced in a moderately dilute solution upon addition of hydrochloric acid; if, on the contrary, it be as a protosalt, the great bulk will come down in this group. In either case it will be advisable to reduce the remainder of the metal to the state of a protosalt, by passing sulphurous acid through the filtrate and heating. If, upon allowing the solution to cool after this treatment, a white crystalline precipitate of protochloride of thallium is produced, it will show that the metal originally existed in the state of a sesquisalt. This precipitate may be filtered off and examined separately. In the filtrate from this, even were there sufficient acid present to prevent the sulphide of thallium by itself from being precipitated by sulphuretted hydrogen, it will be partially carried down by other metals of this group which may be present. What escapes this precipitant will in a similar manner be partially carried down with the oxides of the third group, whilst the remaining thallium escaping the first three group-tests will be precipitated by sulphide of ammonium.

Thallium may be very accurately separated from most metals. Some of the analytical methods which I have employed for many months are very delicate; others, on the contrary, still require elucidation.

24. *Thallium from Zinc.*—(I will assume that a piece of commercial zinc has to be tested for thallium.) Dissolve the metal in sulphuric acid, adding a little nitric acid towards the end to effect the perfect solution of the black residue. Evaporate to drive off nitric acid; dissolve in a small quantity of water; filter from sulphate of lead, if any be present, and heat the moderately acid solution with excess of sulphite of soda. Allow the liquid to cool, and add a few drops of solution of iodide of potassium. A yellow precipitate of iodide of thallium will be thrown down. Many specimens of commercial zinc, tested in this manner, will be found to contain thallium.

25. *Thallium from Iron* (thalliferous iron pyrites).—Dissolve 30 or 40 grains of the finely powdered mineral in nitrohydrochloric acid; evaporate with excess of hydrochloric acid to drive off the nitric acid; redissolve in water; add sulphite of soda in

excess, and heat until all the iron is reduced to the proto-state; and then add iodide of potassium. Iodide of thallium will be precipitated. This test is sufficiently delicate to show thallium in a pyrites which does not contain more than 1 in 10,000.

Thallium from Manganese may be separated as thallium from iron.

26. *Thallium from Mercury.*—I have not yet ascertained a delicate and reliable method of separating thallium from salts of the suboxide of mercury. It is, however, very readily separated from persalts of mercury; and therefore the best plan is to peroxidize both metals by boiling with nitrohydrochloric acid; then reduce the thallium with sulphite of soda, and add iodide of potassium to the almost neutral solution. If much mercury be present, the precipitate will be almost pure scarlet; but on further addition of iodide of potassium, drop by drop, the iodide of mercury will dissolve, and will leave the iodide of thallium as an insoluble yellow powder. Upon warming the liquid the precipitate collects together and readily settles to the bottom. This is a very delicate test.

27. *Thallium from Lead.*—Evaporate the solutions to dryness with excess of sulphuric acid, and extract with hot water. Sulphate of lead will be left behind, whilst sulphate of thallium will be dissolved. This is a very ready process, but is not quite so accurate as the succeeding one.

28. *Thallium from Bismuth or Lead.*—Dilute the solution and add a *slight* excess of carbonate of soda; add solution of cyanide of potassium (free from sulphide), and allow the mixture to stand for an hour at the temperature of about 100° F.; then filter and wash: the residue will contain all the bismuth or lead. To the clear filtrate add sulphide of ammonium, and warm gently for some time; the deep-brown sulphide of thallium will gradually collect together in flakes at the bottom of the vessel. It must be washed with water containing a little sulphide of ammonium, as it readily oxidizes when moist, and might pass through the filter as sulphate of thallium.

This is an exceedingly delicate test for thallium in bismuth; and by its means it can be detected in most specimens of commercial bismuth and its salts, even when sold as pure. The presence of thallium in some samples of bismuth has been suspected by Dr. W. BIRD HERAPATH*. The analytical method which he gives is not calculated to detect it except perhaps when present in comparatively large quantities. By the above process it will be found to be a very frequent constituent of bismuth compounds, even when working upon no more than 50 grains of material.

29. *Thallium from Copper.*—To the acid solution add ammonia in excess, and then cyanide of potassium until the blue colour has entirely disappeared; then add sulphide of ammonium, and gently warm for some time. Sulphide of thallium will gradually collect together in the liquid. By this test I have detected the presence of thallium in many specimens of copper as met with in commerce, as well as in crystallized sulphate of copper. It is extremely delicate.

Through the kindness of Dr. MATTHIESSEN I have been enabled to examine for thal-

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* Pharmaceutical Journal, Jan. 1, 1863.

lium a specimen of copper prepared in Spain by a process called "cementation." This consists in allowing copper pyrites to oxidize slowly, washing out the resulting sulphate of copper, and precipitating the solution with metallic iron. The pulverulent copper is then heated until it coheres, and the metal sent into the market in the form of pigs, no further purification being attempted.

This metal was found by Dr. MATTHIESSEN to have a conducting-power for electricity of about 15, pure copper being 100. The exact metallic impurity which rendered it so preeminently bad had not been ascertained. It was tested for thallium in the manner above described, and found to contain a large quantity. It is evident, from the way the copper was extracted, that any thallium which might have been present in the pyrites would accompany the copper.

30. *Thallium from Cadmium.*—To the acid solution of these metals add bichromate of potash, then excess of ammonia, and boil; insoluble chromate of thallium will be precipitated. This is not so delicate a test as some of the above, although by its means I have frequently detected thallium in metallic cadmium and its salts. Commercial sulphide of cadmium, as sold for artists' use, varies considerably in tint. Dark-coloured samples frequently contain thallium. I may especially instance, as being highly thalliferous, a beautiful specimen of this sulphide from Nouvelle Montagne, near Liège, which formed a prominent object in the Belgian department of the late Exhibition.

31. *Thallium from Gold.*—The gold may be separated by the usual process of reduction to the metallic state with oxalic acid, all the free nitric acid having been previously removed by evaporation with hydrochloric acid.

32. *Thallium from Antimony, Tin, and Arsenic.*—A very good method of separating these metals is to add excess of sulphide of ammonium to the alkaline solution. Sulphide of thallium will be precipitated, whilst the other sulphides will remain dissolved.

Most of the above processes have been tried with weighed quantities of the different metals, seldom taking more than 1 of thallium to 1000 parts of the other metal. They can therefore be relied upon to that extent; whilst some of them are much more delicate, as, for instance, the separation of thallium from iron, copper, bismuth, and lead.

It is advisable, in testing for small quantities of thallium, to appeal to the spectroscope for confirmatory evidence of the presence of this element in any precipitate suspected to contain it.

33. *Thallium from Sulphuric and Hydrochloric Acids.*—I have frequently met with specimens of commercial hydrochloric and sulphuric acids which contained almost enough thallium to be worth extracting. I may especially mention a very crude yellow hydrochloric acid now to be met with at about 8 shillings the hundredweight. Two ounces of this was neutralized with soda, and a few drops of sulphide of ammonium were added. A black precipitate was obtained, which in the spectroscope showed evident presence of thallium. At my request, Messrs. HOPKIN and WILLIAMS, the well-known manufacturing chemists, treated 112 lbs. of this acid in the above manner, and forwarded me

the black precipitate obtained. It was worked up in the manner described in the first part of this paper (7.), and yielded a little over four grains of metallic thallium.

From sulphuric acid it may be separated in a similar way.

It is not difficult to understand how thallium gets into these acids. Messrs. CHANCE Brothers and Co., of Birmingham, makers of the thalliferous hydrochloric acid, have obligingly informed me that the process by which it is produced is the ordinary one of decomposing common salt in cast-iron pans and fire-brick furnaces. The acid is condensed in high stone towers or chambers filled with coke, and is afterwards collected in gutta-percha cisterns, and bottled or drawn off. The sulphuric acid used in the manufacture is obtained from iron pyrites burnt in kilns. Upon examining specimens of pyrites and lead-chamber-deposit forwarded by Messrs. CHANCE and Co., I find that the former contains thallium, but scarcely any appreciable traces are in the deposit, thus agreeing with the results of my previous investigations on this subject.