

VIII. *On a simple Electro-chemical Method of Ascertaining the Presence of different Metals ; applied to detect minute quantities of Metallic Poisons. By EDMUND DAVY, F.R.S. M.R.I.A. &c. Professor to the Royal Dublin Society.*

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1. *Introduction.*

IT is now nearly a quarter of a century since the late Sir HUMPHRY DAVY, by a train of masterly researches, developed the general principles of electro-chemical action, which subsequently led him to many fine discoveries and important practical applications. Some years since, I repeated most of the interesting experiments noticed in his excellent Bakerian Lecture "On the chemical agencies of Electricity\*." On the decomposition of metallic salts by the Voltaic battery, Sir HUMPHRY is very brief. He clearly ascertained, however, that "when metallic solutions were placed in the circuit, metallic crystals or depositions were formed on the negative surface †;" and that "the metals passed towards the negative surface, like the alkalies, and collected round it †." In the course of my experiments on this subject, phenomena occurred which led me to think that some novel results might be obtained by instituting a series of experiments on metallic salts, using as a Voltaic arrangement the feeble power produced by the contact of small slips of different metals, with solutions of the common metallic salts. Operating in this manner, I could readily detect very minute quantities of different metals, coat platina with gold, silver, copper, &c., or cover gold with a surface of these metals, and tin, copper, brass, iron, &c. Several of those facts I have been in the habit of bringing forward and illustrating in my annual courses of lectures delivered both in the Royal Cork Institution, and in the Royal Dublin Society. Circumstances which it is unnecessary to mention, have hitherto prevented me from

\* Philosophical Transactions of the Royal Society, 1807.

† Ibid.

giving greater publicity to those facts. In the course of the present summer my attention has been directed to apply similar means to the detection of metallic poisons, a subject of acknowledged and increasing importance ; and the results I have obtained, and now beg leave to submit to the Society, appear to me both novel and interesting, and afford, if I mistake not, means more simple, delicate, and effectual, than any at present known for detecting the common metallic poisons.

The fear of trespassing too much on the time of the Society, induces me to limit the present paper to one part only of the subject. At no distant period I promise myself the pleasure of communicating the remaining part, which will embrace the different electro-chemical experiments I have made on the other metals and their compounds, together with the application of the facts to the processes of gilding, silvering, tinning, &c.

In the following pages I shall notice the simple electro-chemical apparatus, (or electro-chemical method as I shall call it,) employed in my experiments ; offer proofs of its efficacy to detect different metals, particularly metallic poisons ; adduce instances of the extreme delicacy and facility of the method ; and lastly, show, by similar evidences, that its accuracy is not impaired by the presence of organic substances whether vegetable or animal, or mixtures of both ; and that the method is therefore applicable to the detection of metallic poisons in all cases. I shall be under the necessity of making some minute (and I fear tedious) details, which I trust will be excused, as they are closely connected with the elucidation of the subject.

It forms no part of my object to examine the numerous known methods of detecting metallic poisons. Experience, I may presume, has made me tolerably familiar with the details of them. The electro-chemical method here proposed appears to me to rival the very best of them in point of accuracy, whilst in facility, simplicity and delicacy, it seems superior to them all.

## 2. *Of the Electro-chemical Apparatus.*

The electro-chemical apparatus I used was of the simplest kind. It consisted of two different metals, generally zinc and platina, which, according to Sir H. DAVY, form the most efficient combination ; the zinc being positive, and the platina negative, with regard to all the other metals. The zinc was usually

in the state of foil, or of thin sheet. The platina was in some cases a small crucible, or a spatula having a spoon at the end of it, but more frequently platina foil was employed. The foil was about two inches long, and two thirds of an inch wide. The zinc foil varied from about one third to one eighth of the size of the platina foil. The size and thickness of either metal may vary indefinitely, without materially altering the results. This simple arrangement is most easily applied to the decomposition of a great number of metallic compounds. It is only necessary to mix a drop or two of acid with a little of such compounds, whether solid or fluid, and apply the zinc foil, when the platina will be soon coated with the reduced metal. Solutions of many metallic salts do not require the addition of acid. I may remark that the small slips of platina and zinc foil are very convenient for many experiments on metallic poisons; as where the object is to ascertain the presence of arsenic or mercury, in a fluid in which it may exist in considerable quantity; or to determine whether any powder contain either of those metals in combination. One slip of platina will answer for an indefinite number of such experiments; one slip of zinc, too, may be employed for many experiments. It is only necessary either to dip the end, after being used, into a little water, and wipe it, or to cut the mere point off at once. The platina spatula with a spoon at the end of it, is well adapted for concentrating, or boiling nearly to dryness, fluids which may contain metallic poisons, but in such minute quantity, as to render concentration indispensably necessary to the success of the electro-chemical method of detecting them. The small platina crucible is a necessary appendage to the apparatus, in cases, where from previous trials by the platina foil, or spoon, and zinc, the existence of a metallic poison has been proved in a fluid or solid, in order to collect it in sufficient quantity, and exhibit it in a separate state.

### 3. *Experimental proofs of the efficacy of the Electro-chemical method to detect different metals, and especially metallic poisons.*

Solutions of gold, silver, mercury, copper, tin, lead, &c. are not decomposed, as is well known, by platina; but if a drop of each of those metallic salts, containing excess of acid, be severally placed on a surface of platina, and a slip of zinc brought in contact with both, each salt will be decomposed, and the

respective metal deposited on the platina. These are a few instances of the apparent reduction of metallic salts on platina by the agency of Voltaic electricity. It would be extremely easy to extend the list to an indefinite number of other cases, did I not fear to anticipate details which more properly belong to the subsequent part of the subject.

The compounds of arsenic, mercury, lead and copper afford the principal metallic poisons; and a knowledge of their properties, and of the best means of detecting them, derives interest from many considerations, but is particularly valuable from the paramount importance justly attached to chemical evidence in cases of accidental or intentional poisoning. I shall proceed to offer proofs of the efficacy of the electro-chemical method to detect the compounds of those metals in the order in which they have been enumerated.

*Compounds of Arsenic.*— $\left\{ \begin{array}{l} \text{Greyish black arsenic, protoxide of BERZELIUS, or} \\ \text{fly-powder.} \\ \text{White oxide of arsenic, or arsenious acid.} \end{array} \right.$

When half a grain, or less, of either of those solid compounds is placed on a slip of platina foil, mixed with a drop or two of muriatic acid\*, and the zinc applied†, the arsenic will presently be reduced to the metallic state; one part will be deposited on the platina, and the other part mixed in thin filaments with the fluid. The surface of the platina will become iridescent or exhibit variegated colours (resembling heated steel), as blue with tints of red, yellow‡, &c. Much of the arsenic is thus strongly attached to the platina, and cannot be removed by wiping or rubbing it with the finger or a cloth, nor by cold strong muriatic or sulphuric acid, nor by hot solutions of caustic alkalies; but it instantly disappears on being touched with the smallest drop of

\* By “muriatic acid” in this paper, the common strong acid of commerce is meant. I have used it in preference to the pure acid, from the facility with which it can be procured.

† By the words “zinc applied,” used here and in other places, is meant bringing the zinc in contact both with the platina and the substances to be acted on; or moving the zinc about on the platina, which seems the readiest way of effecting the reduction of many metallic compounds.

‡ Diluted muriatic acid occasions analogous effects, but they are more slowly produced, probably because the undiluted acid is a better solvent of the arsenical compounds, and a better conductor of electricity. Like effects occur with strong sulphuric acid, if the zinc be moved about on the platina, but they are not produced with strong nitric acid or aquafortis, and only very gradually by these acids when diluted.

strong nitric acid, or of the aquafortis of commerce. The arsenic is also readily removed by exposing the foil to the moderate heat of a spirit lamp, when it rises in the form of arsenious acid; but previous to this effect, the alliaceous, or garlick-like odour, so characteristic of this metal, is strongly produced\*, and the surface of the platina remains unaltered.

The following arsenical compounds, when exposed to similar treatment, afford analogous results, viz.

Arsenious acid in solution.

Arsenites of potash, lime, &c.

Arsenic acid.

Arseniates of potash, lime, &c.

Chloride of arsenic.

Sulphurets of arsenic, obtained by passing sulphuretted hydrogen gas through solutions of arsenious and arsenic acids.

In cases where the quantity of any arsenical compound in solution is very minute, the fluid should be concentrated, or boiled nearly to dryness, previous to the addition of the muriatic acid, and subsequent trial on the platina foil by zinc.

Some arsenical compounds require a treatment somewhat different from those already enumerated, in order to exhibit the arsenic in a satisfactory manner. This is the case with the native sulphurets of arsenic, which being scarcely acted on by muriatic acid, require previous treatment with nitric acid. Thus, a little realgar or orpiment, in powder, was mixed with a drop of strong nitric acid in the platina spoon, heated, and the excess of acid expelled; a drop or two of muriatic acid being incorporated with the residual substance, the zinc was applied, and the arsenic readily reduced on the spoon, exhibiting its characteristic appearance. Arsenical pyrites, too, requires the previous addition of nitric acid. In operating on such arsenical compounds as require the use of nitric acid, as little as possible should be employed, and any excess ex-

\* Dr. Christison, in his valuable work "On Poisons," proposes to discard this test altogether, chiefly, it would seem, from its being obscured entirely by the presence of a very small portion of vegetable or animal matter; but as this objection does not apply to the electro-chemical mode of detecting arsenic, the alliaceous odour is regarded, especially in these experiments, as a striking character, exhibited by no other metal, as far as my experience extends.

pelled, as a minute quantity of this acid retards the reduction of the arsenic, or re-dissolves it.

The metallic arsenites and arseniates, where two metals are present, appear also in general to require a modified treatment, according to the object in view, and seem to offer proofs of the elegance of this mode of detecting metals. To give an instance or two, in the case of the arsenite or arseniate of copper. If a little of either of these compounds be dissolved in a few drops of muriatic acid, by heat, in the platina spoon, and a few tolerably quick contacts be made with zinc foil, the arsenic only will be reduced; part of it will be deposited on the spoon, and part will remain in the fluid as a dark grey or blackish substance.

If a little of either of the above compounds be dissolved in a few drops of diluted nitric acid, (consisting of one volume strong acid to three of water,) in the platina spoon; boiled nearly to dryness, and water added just enough to obtain a solution; if the point of a slip of zinc be now applied to the centre of the bulb of the spoon, the copper alone will presently be reduced on the platina, exhibiting an unusual metallic lustre, and forming a circle round the zinc. If the zinc be now removed, the copper will be re-dissolved by the slight excess of acid present. If the contact of the zinc be continued, in a short time the arsenic will form a circle on the platina, round the zinc, whilst beyond it the copper will make its appearance.

I found by repeated experiments, that the arsenic precipitated by zinc on platina foil from solid arsenious acid, or from arsenical solutions, and muriatic acid, could be readily obtained in the form of arsenious acid, by coiling the dried foil, and exposing it to the heat of a spirit lamp, in a tube closed at one end, or open at both, and stopped with a cork or corks, so as to allow the expanded air to escape.

With a view to gain some approximation as to the actual quantity of arsenic that could be detected by the electro-chemical method, and to ascertain if it could be procured from the platina in the metallic state, I placed on a new slip of platina weighing 22.14 grains, five drops of an aqueous solution of arsenious acid, and three drops of muriatic acid; a slip of zinc being applied, the arsenic was soon reduced, and much of it adhered to the platina, which, after being washed in pure water and dried, acquired an in-

crease of  $\frac{1}{300}$ th part of a grain\*. The platina was put into a small retort, which was then exhausted, twice filled with pure carbonic acid gas, and heated over a jar of the same gas, until all the arsenic rose and condensed in the upper part of the bulb of the retort as an extremely delicate whitish film, exhibiting no metallic lustre, even by the aid of a magnifying glass; nor could this be expected from the minute quantity of arsenic present, and the extent of surface over which it was spread by sublimation. The platina was found perfectly clean, and of precisely the same weight as at first. Some pure water was put into the retort, and occasionally agitated in contact with the sublimate, but after thirty hours a recent solution of sulphuretted hydrogen occasioned no change in the water. The actual quantity of arsenic attached to the platina in the foregoing experiment, was ascertained to be  $\frac{1}{300}$ th part of a grain. But this is very far from conveying a just idea of the degree to which this mode of detection may be carried: for a single drop of the aqueous arsenious acid would have afforded ample evidence of the arsenic as it respected colour, insolubility in muriatic and sulphuric acids, alliaceous odour, and volatility; which would give the  $\frac{1}{2300}$ th part of a grain. Even this very minute quantity gives us by no means the extreme limits to which this truly microscopic method of detecting metals may be carried. It is, however, quite unnecessary to pursue the subject further.

In cases when the small platina crucible was used, the results were equally delicate, and much more simple and satisfactory. I put a single drop of aqueous arsenious acid, with about an equal bulk of muriatic acid, into the crucible; the zinc being applied for an instant, the arsenic was reduced on the platina. The crucible was then rinsed with pure water, dried, covered with a piece of plate glass, and heated with a spirit lamp; arsenious acid rose and condensed on the glass, whilst the surface of the crucible remained unchanged. The results were precisely similar, when a single drop of arsenic acid, of arsenite and of arseniate of potash, were exposed to similar treatment.

I put  $\frac{1}{100}$ th part of a grain of solid arsenious acid into a very small platina crucible, which I coated with gold on the inside, and mixed with it about half

\* In my experiments I used a very delicate balance of ROBINSON'S construction, which turns with the  $\frac{1}{1000}$ th part of a grain, when loaded with one hundred grains.

a drop of muriatic acid. A small slip of zinc being applied, the spot became of a dark steel-grey colour with a tint of green at its edge. Some pure water being put into the crucible, some extremely minute films of metallic arsenic appeared on the surface of it. The crucible, after being washed and dried, was heated, when the arsenic rose, leaving the gold surface unaltered.

Into the crucible used in the preceding experiment, I put  $\frac{1}{10}$ th of a grain of solid arsenious acid, and dissolved it in about five drops of muriatic acid. I then applied a slip of zinc for about half a minute; as soon as the contact of the zinc was made, the variegated colours from the arsenic were beautifully produced at the bottom of the crucible, an effect which was succeeded by a violent action, and all the arsenic was reduced. The crucible was now filled with pure water, and numerous steel-grey coloured filaments of metallic arsenic floated on the surface; some being collected on a slip of platina and heated, the alliaceous odour was strongly produced, and they were dissipated in a white vapour. The crucible being washed, and a few drops of diluted muriatic acid put into it, it was rinsed in pure water and dried, when its gold surface was so completely coated with arsenic of a dark steel-grey colour, that no vestige of the gold at the bottom of the crucible could be seen, even with the aid of a magnifying glass, though the surface was full of little inequalities. The arsenic on the crucible did not sensibly tarnish by exposure to the air for some days; a portion of it was then expelled by a heat of nearly  $400^{\circ}$  FAHR., when the gold became partially visible; the remainder of the arsenic continued of a steel-grey colour.

Though it seems unnecessary to bring forward more experiments in proof of the efficacy of the electro-chemical method to detect arsenic, it may be proper to recur to the evidence that arsenical compounds are by this method reduced to the metallic state. The experiments with the platina gilt crucible afford the most unequivocal proofs of metallic arsenic; whilst those with the platina foil and spoon, though seemingly more ambiguous, will, on examination, I presume, be found scarcely less satisfactory. Thus the partial oxidation of the surface exhibited in variegated colours; the strong cohesion of the arsenic to the platina, are characteristics of the metal. The alliaceous odour (in cases where no deoxygenating substance can be presumed to exist) is admitted to belong only to the metal; insolubility in strong muriatic acid, is a property of no



known oxide of arsenic, but of the metal. To which may be added the facts, that I have repeatedly coated the arsenic, deposited on platina, with copper, and also with mercury; and removed both, without affecting the arsenic. All these circumstances seem to prove the accuracy of the statements made on the subject.

Though zinc and platina were the metals used in the electro-chemical experiments on arsenic already noticed, I have also employed several other metals which generally afforded analogous results. Other metals might of course be substituted for zinc and platina, but as far as my experiments have extended I give these a decided preference. Iron and tin are much slower in their operation than zinc. Brass and copper are readily coated with metallic arsenic; but the objections to the use of the common metals as substitutes for platina, arise from the facility with which they are acted on by heat, air, acids, &c. and the difficulty with which arsenic is separated from them without injuring their surfaces. The advantage of colour which gold has over platina, when a grey metal, as arsenic, is to be reduced in contact with it, is cheaply purchased by simply gilding part of the inside of the platina crucible.

*Compounds of mercury.*—The compounds of mercury in general are readily reduced by being placed on a slip of platina foil, mixed with a drop of diluted \* aquafortis or muriatic acid, and the zinc applied, when the mercury is soon either partly attached loosely, or amalgamated with the platina, and partly combined with the zinc. This is the case with the black and red oxides, white precipitate, the acetate, subsulphate, cyanuret, fulminate, &c. The cyanuret, however, appears to be reduced more readily, and with greater lustre, when muriatic acid, undiluted, is employed, and the acetate and subsulphate best, when diluted aquafortis is used. The compounds of mercury soluble in water, in general require not the addition of acid.

From the importance of the compounds of mercury with chlorine, our details respecting them may be more minute.

*Corrosive sublimate.*—If a drop of an aqueous solution of corrosive sublimate be put on a bright surface of copper, it will soon, as is well known, render the copper of a greyish black colour. If a similar experiment be made and

\* By “diluted” as applied to aquafortis and muriatic acid in this paper, is meant, the strong acids of commerce, to which an equal bulk of water has been added.

the zinc applied, the mercury will presently be reduced to the metallic state, and the copper will be whitened. The results will be analogous, if similar experiments are made with solutions of corrosive sublimate in alcohol and ether, provided a little water be employed when the zinc is applied, or if *platina* be substituted for the copper.

The following is a beautiful and extremely delicate mode of reducing corrosive sublimate, and of obtaining the mercury in a sensible form ; and it may of course be applied to other compounds of mercury. Put a drop or two of an aqueous solution of corrosive sublimate into a small platina crucible, add about an equal bulk of muriatic acid, and apply the zinc for a short time, when the mercury will be reduced ; part of it on the platina, which will appear of a brighter white colour, and part of it will amalgamate with the zinc, whitening it and making it brittle at the point of contact. Wash the crucible with pure water, dry, and cover it with a piece of plate glass, and heat it with a spirit lamp : the mercury will rise and be condensed as an extremely fine white powder without metallic lustre, and it may be easily collected from the glass by the finger, so as to be exhibited in minute globules, visible by a high magnifying power, even when a single drop only of the solution has been operated on.

I repeated the preceding experiment in the platina gilt crucible. The instant the zinc was applied the surface of the gold was whitened. Afterwards the mercury was collected by sublimation on glass.

The solution of corrosive sublimate may of course be readily reduced on platina when the zinc is applied without the addition of any acid, as in the ingenious mode proposed some time since by Mr. Sylvester, and afterwards simplified by Dr. Paris. I am disposed to prefer the use of platina to that of gold, not only on account of the great difference in their commercial value, but because I found the surface of gold tarnished after the mercury had been sublimed from it, which was not the case with the platina. I did not, indeed, ascertain if the gold I employed contained any alloy ;—it was supposed to be pure.

A very simple mode of detecting corrosive sublimate, whether solid or dissolved in water, alcohol or ether, which I have not seen any where noticed, is, to put on a bright surface of copper, a bit of the solid compound, or a drop of

its solution, and to add a drop of muriatic acid to it, when the mercury will be immediately reduced, and the copper whitened. Similar effects also take place when a number of other compounds of mercury are similarly treated, as the oxides, cyanuret, the yellow precipitate from corrosive sublimate by the fixed alkalies, the white precipitate by ammonia, &c. Acetate of mercury does not yield to such treatment, unless heat be applied, when the copper is readily whitened; but with diluted aquafortis, the acetate is easily reduced on copper.

*Calomel* is slowly decomposed in a platina crucible, when mixed with diluted muriatic acid, and the zinc applied; the reduced mercury is deposited on the platina and combined with the zinc, or in case gold is present, it is whitened.

The following is a much readier and better mode of treating calomel. Mix a little of this compound, with a few drops of diluted aquafortis, and boil for an instant or two in a small platina crucible, add a little water, and apply the zinc; the mercury will be readily reduced. Break the contact of the zinc with the platina, and the bright mercurial surface of the latter will at once become tarnished. Restore the contact, and the lustre of the surface will reappear; and these changes will occur as often as the contact is broken and renewed. Add some pure water whilst the zinc is in contact, and the surface will remain bright. The mercury may be collected by sublimation, as in the case of corrosive sublimate. Operating in this manner, the mercury from a very small quantity of calomel may be obtained. Calomel may also be readily detected, by placing it on a clean surface of copper, mixing a little muriatic or diluted muriatic acid with it, and applying a gentle heat; when the mercury will be instantly reduced, and the copper whitened.

*Compounds of lead.*—The soluble compounds of lead, in general, like those of mercury, are readily reduced to the metallic state when placed on a surface of platina, and the zinc applied; as the nitrate, acetate, &c. The insoluble compounds, as the oxides, patent yellow, the carbonate, sulphate, tartrate, &c. require previous mixture with diluted aquafortis or muriatic acid. The lead thus reduced is usually of a dark grey colour, and exhibits little lustre, unless pressed, as by the blade of a knife, when its metallic lustre becomes quite apparent. It feels quite soft as the zinc is drawn over it. Its cohesion to the platina is generally so feeble that most of it may be easily removed by a cloth

or the finger. It is also presently dissolved by the aquafortis and muriatic acid of commerce, and by strong nitric acid.

I coated one side of a platina spatula with gold, mixed a drop of acetate of lead with one of diluted aquafortis, and applied the zinc; when the lead being reduced, the surface was washed, and by slight friction most of the lead was removed; but there remained sufficient to show the colour and lustre of the metal. It dissolved by diluted aqua regia, leaving the surface of gold apparently unaltered.

*Compounds of copper.*—The soluble salts of copper, as the perchloride, permuriate, sulphate, nitrate, &c. when dissolved in water, require only to be placed on platina, and the zinc applied, when the copper will be presently reduced and cover the platina. The compounds insoluble in water, as the protochloride, proto-muriate, the carbonate, oxides, &c. when previously mixed with a little muriatic acid, or diluted aquafortis, are also readily reduced. The last acid seems best adapted in the case of different pigments of copper, as Olympean and SCHEELÉ'S greens, common verdigris, refiner's verditer, &c.

The copper reduced on platina, by zinc, usually exhibits the colour and lustre of the metal. Its surface is in some cases blackish, and requires gentle rubbing to show the metallic appearance. It has, in general, greater lustre, in cases when diluted aquafortis is used, and the acid only in slight excess when the zinc is applied. It is soluble in muriatic acid, but more readily in strong or diluted aquafortis.

4. *Experimental evidences that the accuracy of the Electro-chemical method of detecting metals is not impaired by the presence of mixed vegetable and animal substances, when applied to the detection of metallic poisons; particularly to the common compounds of Arsenic, Mercury, Lead, and Copper, in such mixtures.*

I have ascertained that the electro-chemical method is competent to the detection of very minute quantities of the different metals, when their compounds are mixed with vegetable and animal substances. But the object of this section is to notice briefly a number of miscellaneous experiments on the principal well known poisonous compounds of arsenic, mercury, lead, and copper, when mingled with organic fluids and solids, &c.

*Arsenious acid.*—I mixed a small quantity of solid arsenious acid in powder, with the following substances, separately, viz. wheaten flour and its paste; bread; cake with currants and caraway seeds; starch in powder, and in solution; rice in powder, and boiled with water to a pulp; potatoes boiled, and roasted; sugar in powder, and in syrup; vinegar, and raspberry vinegar; port and sherry wines; gruel, thick and thin, with sugar and milk, also with sugar and wine; milk and cream; white and yolk of egg, both fluid and coagulated; gelatine (isinglass) in solution; bile discharged from the stomach, mixed with saliva, and watery fluid.

In a number of those instances, it was only necessary to put a little of the mixture into the platina spoon, incorporate a few drops of muriatic acid with it, and apply a slip of zinc, when the arsenic was readily precipitated on the platina. In cases when the arsenious acid existed only in very minute quantity, or when the water present was considerable, the fluid was concentrated by boiling, or evaporated nearly to dryness, previous to the application of the zinc, when the arsenic was in like manner deposited.

Arsenious acid was also mixed with butter, lard, and oils; some of the respective mixtures being boiled a short time in the platina spoon with muriatic acid, or in solution of fixed alkali, then muriatic acid added in excess, and the zinc applied, when the arsenic readily appeared.

A few drops of an aqueous solution of arsenious acid were mixed with some sheep's blood; muriatic acid was added; the whole formed a deep wine yellow solution. A drop or two being put on the platina foil, and the zinc applied, coagulation took place, and the arsenic precipitated. Ox-bile being treated in a similar manner afforded analogous results.

In one instance, I mixed five grains of solid arsenious acid in about half a pint of tea sweetened with sugar and milk. It was kept hot for some minutes, and occasionally stirred. A little of the tea being put into the platina spoon, and muriatic acid added, the application of the zinc produced no immediate effect. But on boiling the spoonful of tea nearly to dryness, then adding two or three drops of muriatic acid to the residual brown substance, and agitating, a yellow solution was formed. A slip of zinc being now applied, a white coagulum, which soon changed to brown, appeared, and the arsenic was copiously precipitated on the spoon.

In another experiment, a small quantity of arsenious acid, in powder, was mixed with hot tea. Some hours after it had cooled, it was filtered, and on being treated as in the preceding experiment, the arsenic appeared in a similar manner. Coffee, on being exposed to like treatment, afforded analogous results.

I mixed five grains of pulverized arsenious acid in a small basin of warm and rather thick pea-soup, having fragments of the fibrous part of beef diffused through it. The platina spoonful of it was boiled nearly to dryness, several drops of muriatic acid were added, and by agitation most of the solid matter was dissolved, forming a thickish fluid. The zinc being applied, a white coagulum changing to brown appeared, and the arsenic soon covered the surface of the spoon. Similar results were obtained when giblet soup was treated in like manner.

*Corrosive sublimate.*—A few drops of a solution of corrosive sublimate in water, were well mixed with a solution of gelatine (isinglass): a drop or two of the mixed fluids being placed on the platina spatula, and the zinc applied, the mercury presently precipitated; and this effect was more readily produced when a little diluted muriatic acid was previously added to the mixture. When a solution of nutgalls was added to the mixed gelatine and corrosive sublimate, also when corrosive sublimate was added to yolk of egg, the results, by similar treatment, were precisely analogous.

A small quantity of solution of corrosive sublimate was put into fluid albumen (white of egg). To some of the precipitate in a platina crucible, a little diluted muriatic acid was added, and the zinc applied; the albumen coagulated, and in about a minute some mercury was reduced in the crucible, and by continuing the experiment for a few minutes the quantity increased considerably. A similar experiment being repeated in a platina gilt crucible, in a short time the gold partially assumed a dark blueish grey colour. The mercury from both experiments was collected by sublimation on glass, as detailed before.

When solution of corrosive sublimate was mixed with flour into a soft paste, put into the platina crucible, and diluted muriatic acid added, in the course of a few minutes after the zinc was applied, similar results as in the foregoing instances, were obtained.

Corrosive sublimate in powder was mixed with butter, and diluted muriatic acid was incorporated with the mixture; a little of the same being placed on

the platina spatula, and the zinc applied to the fluid, the mercury was presently reduced. The experiment was successfully repeated with diluted aquafortis, instead of muriatic acid.

Solution of corrosive sublimate was respectively mixed with saliva, sheep's blood, and ox bile; the zinc being applied to each, on platina, the mercury was soon reduced.

A few drops of solution of corrosive sublimate were mixed with some human bile, and watery fluid discharged from the stomach, and rather more than half its bulk of muriatic acid was added; a small teaspoonful of the mixed fluids was put into the platina crucible, and the zinc applied for about two minutes, when the surface of the crucible had acquired a dark grey colour; on being heated, metallic mercury was obtained. The experiment was repeated, with similar results, in a platina gilt crucible.

A solution of corrosive sublimate, in small quantity, was mixed with milk; muriatic acid, equal to about one half the milk, was added. Some of the mixed fluids was put into the platina crucible, and the zinc being applied a short time, a grey surface of mercury appeared on the platina. A similar experiment was made in the platina gilt crucible, which soon exhibited a partially whitened surface. From both experiments mercury was sublimed.

A few drops of solution of corrosive sublimate were mixed in a cup of tea sweetened with sugar and cream. About a teaspoonful was put into the platina crucible, with nearly an equal bulk of muriatic acid. A slip of zinc being applied for about a minute, a greyish substance was found at the bottom of the crucible, which, when washed, dried, and heated, afforded metallic mercury. These experiments were repeated with success, both in the platina crucible and in the platina gilt crucible; and precisely similar results were obtained with coffee, under like treatment.

It is proper to remark, that the experiments noticed in this section, were, in general, carried on only for a few minutes, so that the decompositions were mostly partial, and probably in no instance complete. This statement is confirmed by facts, for I repeatedly found that after a given effect had taken place in the platina crucible in a few minutes, a still further effect was soon produced, by transferring the same materials to the platina gilt crucible.

When a solution of corrosive sublimate (in small quantity) was added to some sherry or port wine in a platina crucible, and the zinc applied, a beautiful effect gradually took place. In the course of about a quarter of an hour, calomel was formed, and deposited at the bottom of the crucible in successive circles, which extended beyond each other, and differed slightly in their shades of colour, being alternately lighter and darker. The zinc became brittle at its point of contact, from amalgamation. These experiments were repeated in the platina gilt crucible with similar results, part of the gold was whitened, and calomel and mercury were afterwards sublimed from both crucibles.

With raspberry vinegar and solution of corrosive sublimate, the results appeared to be similar to those produced with the wines.

*Sugar of lead, acetate of lead.*—A solution of sugar of lead, in small quantity, was separately mixed with flour into a thin paste, with saliva, port and sherry wines, raspberry vinegar, and yolk of egg. A little of each mixture was put on the platina spatula, and the zinc applied, when the lead was soon reduced on the platina.

A little of the solid compound of albumen (white of egg) and sugar of lead was placed on the spatula, and mixed with a drop or two of diluted aquafortis; the zinc being applied, the lead was reduced to a dark grey colour; by gently rubbing it with the finger the lustre of the metal became apparent. The results were analogous when sugar of lead was mixed with sheep's blood and ox bile, and exposed to similar treatment.

A mixture of gelatine (isinglass) and sugar of lead was put on the spatula, and the zinc applied; the lead was slowly reduced: the effect was more rapid when a drop of diluted aquafortis or muriatic acid was previously added. The results were precisely similar when a solution of nutgalls was added to the mixed solutions of gelatine and sugar of lead. The yellow soft solid readily yielded metallic lead on platina by means of zinc.

A small quantity of sugar of lead was put into some tea sweetened with sugar and cream; some of the yellow matter produced being put on the spatula, and the zinc applied, the lead was slowly deposited. The results were similar when sugar of lead was mixed with milk and with coffee. The addition of a little diluted aquafortis appears, in a number of cases, more readily to



reduce the lead, but as a slight excess of acid will redissolve the lead (partially or wholly), a longer contact of the zinc is necessary to neutralize the acid, and render the lead permanent.

*Sulphate of copper, blue vitriol.*—A small quantity of sulphate of copper in solution was added to the following substances, viz. flour forming a soft paste, milk, tea and coffee sweetened with sugar and cream, gelatine (isinglass) in solution, and with nutgalls, albumen (white of egg) and yolk of egg, saliva, sheep's blood, and ox-bile. On a little of each mixture being placed on the platina spatula, and the zinc applied, the copper was presently reduced on the platina. In some cases, the surface was of a blackish colour, but its proper colour and lustre became apparent on rubbing it. The addition of a little diluted aquafortis or muriatic acid to the mixtures, usually facilitated the reduction of the copper.

A little sulphate of copper in powder was mixed with butter and lard, placed on the spatula, and a drop of diluted aquafortis incorporated with them. On the zinc being applied, the copper was readily reduced.

##### 5. *Some general Remarks, and Conclusion.*

The experiments detailed in this paper seem to prove, that the common compounds of arsenic, mercury, lead, and copper, may be readily reduced to the metallic state, on platina, by the electro-chemical method described; and that this method is also competent to the detection of those metals, in cases when their compounds are mixed in very small quantity with vegetable and animal substances. It may, I think, be further deduced, that the method is applicable in cases when those compounds exist in the most complicated mixtures of organic substances. For, though I have had no opportunity of applying it to the contents and tissues of the stomach in instances of poisoning, yet its efficacy in such cases can scarcely be doubted, as no animal or vegetable substances can, I apprehend, resist the action of the mineral acids, which are almost indispensably necessary to the success of the method. In some instances, where the common tests will not act at all, and in others, where they only act fallaciously, the electro-chemical method will, in general, be found to act with certainty.

The general results appear to be strictly electro-chemical, or to arise from

the union of a chemical and an electrical action, and seem to be comprehended in the principle developed by Sir HUMPHRY DAVY relating to the changes and transitions by electricity, viz. that "the metals are attracted by negatively electrified metallic surfaces, and repelled by positively electrified metallic surfaces, and these attractive and repulsive forces are sufficiently energetic to destroy the usual operation of elective affinity\*."

If the decompositions which I have noticed were effected by the mere contact of the zinc with acid solutions of the metals, there would, indeed, be reductions, but no depositions on the platina. The electrical action arising from the contact of the two metals, in cases when small slips of zinc and platina were employed, was quite sufficient to destroy or suspend the usual operation of chemical affinity. Thus, in numerous instances of the decompositions of metallic compounds, the platina remained covered with the reduced metal during the contact of the zinc; but on removing the zinc, the coating was readily redissolved by the slight excess of acid present. The transition of the reduced metal to the surface of the platina, is the effect that gives to the method a beauty, simplicity, and delicacy, exceeding, in my opinion, all other modes of detecting the metals already referred to, together with a number of others which remain to be noticed.

As this paper has already exceeded the limits at first intended, I shall defer noticing a number of useful applications of the facts, until I shall have the honour of submitting to the Society the remaining part of the subject.

\* Phil. Trans. 1807.