XXV.—*The Detection of Traces of Mercury Salts for Toxicological Purposes.*

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THE author has repeatedly had occasion, during the past twelve years, to detect very small quantities of mercury salts in organic fluids (for example, urine, stomach washings, etc.). It frequently happens, in cases of mercury poisoning in the East, that the only evidence available is the symptoms and a specimen of urine or stomach washings obtained possibly several days after the poison in question has been taken.

It is also of importance to follow the excretion of mercury when Spittel's* solution has been injected to cure syphilis, parangi, etc.

In these circumstances, it is often the case that the amount of mercury present is too small for certain identification by the usual methods. Hence a method by which such minimal quantities can be identified is a desideratum. The method now described is easy to work, and is a development of the Dupré method of detecting mercury in explosives.

The following investigations were carried out to discover the most delicate method of detecting mercury in solution.

Very dilute solutions of mercury salts were used, and these were

* Dr. Spittel's solution consists of :

Mercuric iodide	...	...	...	...	...	...	3.9 grams.
Arsenious iodide	...	...	...	...	...	...	2.6 „
Potassium iodide	...	...	...	...	...	...	27 „
Phenolphthalein solution (0.5 per cent.)	...	...	...	...	...	...	1 c.c.
Sodium hydroxide solution (25 per cent.)	added to alkaline reaction.						
Distilled water	up to 1136 c.c.						

15–17 c.c. of the above are injected intravenously every 5–7 days.

progressively diluted until one or the other of the previously described methods for identifying mercury failed.

Preliminary experiments on these lines showed that an electrolytic method was most hopeful, the mercury being identified by its spectrum in a Dupré tube.

The mercury spectrum is strongly shown when no method of micro-sublimation is satisfactory. In this preliminary work very dilute solutions containing mercury were electrolysed and the cathode examined spectroscopically in a Dupré tube.

The best way is to place the cathode into one limb of a Dupré tube. Subliming the mercury from the cathode into a glass tube and introducing this glass tube into the Dupré tube always resulted in some loss of mercury.

A number of points required investigation, namely:

- (1) Material and size of electrode, etc.
- (2) Current density and time of electrolysis.
- (3) Temperature and composition of solution used.
- (4) Temperature of Dupré tube, etc.

Material, etc., of Electrode.

Electrodes of aluminium, copper, gold foil, platinum wire, platinum foil, platinum gauze, gold-plated platinum gauze, silver foil, and silver gauze were tried.

A large number of experiments were made by progressively diluting a mercury solution until mercury could no longer be detected, using the above electrodes.

Gold foil was decidedly the most sensitive, and next to this silver gauze was best.

In every case, of course, the electrodes before use were heated to about 900° in a small electric muffle and then spectroscopically examined for mercury.

It was noted that, before heating, "pure" specimens of Kahlbaum's gold foil and silver gauze gave a strong mercury spectrum, the former most markedly.

With regard to the size of the cathode, a piece of gold foil 1.5 cm. long and 0.65 cm. broad was found satisfactory, the gold foil being welded autogenously to a platinum wire. Larger cathodes were used, but nothing was gained thereby even when several hundred c.c. of liquid were electrolysed.

Current Density and Time of Electrolysis.

Many determinations were made on dilute solutions (of the order of one part of mercuric chloride in one hundred million parts of water).

For example, 10 c.c. of such a solution (the solution being acidified with nitric acid) were electrolysed with 0.2 ampere for varying times. Ten minutes was found ample. No improvement was discovered by passing smaller currents (1—8 milliamperes) for twenty-four hours or longer.

With the same volume (10 c.c.) of solution a very slight improvement was found by increasing the current to 0.8 ampere, but a further increase to 2 amperes is a disadvantage, as the heating caused by the current volatilises some of the mercury.

With larger volumes of solution (for example, 200 c.c. and more) it was possible to use up to 2 amperes with advantage, the liquid being rapidly stirred by a powerful motor-driven stirrer.

It is possible when using 2 amperes to electrolyse too long, thus heating the solution and losing mercury. For example, three portions of 200 c.c. each of mercuric chloride solution (one in a thousand million) were electrolysed with 2 amperes and rapid stirring with the following results:

		Time of electrolysis.	Result.
I.	...	10 minutes	Cathode gave a strong mercury spectrum.
II.	...	1 hour	Cathode gave faint mercury spectrum.
III.	...	2 hours	Cathode gave no mercury at all.

The solution became very hot towards the end of the electrolysis. Five amperes heats the liquid too much, with a consequent reduction in the amount of mercury which could be identified.

The temperature should never be allowed to reach even 50°, as a marked loss of mercury occurs when the electrolyte becomes warm. With regard to the composition of the electrolyte, it is satisfactory to acidify it with a few drops of nitric acid.

The addition of ammonium oxalate solution or excess of potassium cyanide does not increase the delicacy of the test.

Temperature of Dupré Tube, etc.

After the electrolysis is finished, the cathode is washed with water only (*not* with alcohol and ether) without interrupting the current and placed in one limb of a Dupré tube. This limb is immersed in oil heated by a small electric heater, the whole being jacketed by asbestos cloth. A bath temperature of 200—250° was found to be suitable.

Various gases were tried in the tube, hydrogen giving the best result.

The tube is exhausted by a Gaede rotary oil pump (a mercury pump, of course, cannot be used) and well washed out with hydrogen. It is then exhausted again (a matter of a few seconds) and

the tap closed. The spectrum is conveniently examined end-on to the capillary by a Hilger direct-vision spectroscope with scale, a cylindrical condensing lens being used to focus the light from the tube into the slit. A moderately powerful coil (15 cm. spark) is suitable. It was found that the mercury spectrum is shown by a gold cathode used when 200 c.c. of a solution of one part of mercuric chloride in a thousand million is electrolysed with 2 amperes for ten minutes, the solution being violently stirred.

When only small quantities of fluid are available (for example, 10 c.c. of urine) it is convenient to electrolyse, without stirring, in a small quartz dish for ten to fifteen minutes, using 0.2 ampere.

It is thus possible to detect one part of mercuric chloride in one hundred million parts of urine, using only 10 c.c. of urine.*

A number of attempts were made to see if this method of identification could be rendered quantitative, micro-sublimation not being satisfactory when dealing with such very small quantities of mercury.

It was hoped that a method based on the intensity of the lines in the spectrum, or the rate at which they disappeared when the Dupré tube was continuously exhausted might prove available, but up to the present all attempts to develop this have been unsatisfactory.

Among the various observations made on dilute solutions of mercury salts are the following:—

(1) Very weak solutions (1 in 100,000,000) do not “keep” well in soft glass, or even in ignited quartz glass bottles. The addition of a few drops of dilute nitric acid effects no improvement.

For example, an aqueous solution of one part of mercuric chloride in one hundred million, which gave a strong mercury spectrum when electrolysed just after being made up, gave no spectrum when kept in a closed quartz glass vessel at 30° for a week, and the same effect was noticed with urine containing mercury.

If the closed quartz vessel is opened, the contents poured out, and the vessel repeatedly extracted with small quantities of concentrated nitric acid, the mercury, which appears to be adsorbed by the walls of the vessel, is brought into solution and can be identified by electrolysis as described above.

Even a more concentrated solution (1 in 10,000,000) when kept in a closed quartz vessel and warmed for fifteen days, likewise deposited all the mercury salt on the sides of the tube. The mercury on the sides of the tube was removed by repeated washing with concentrated nitric acid and identified as above.

(2) When working with very dilute solutions there is a marked

* For example if 0.06 gram of mercuric iodide is injected intravenously, mercury can be detected up to three days in the urine. After three days there is less than one part of mercury in one hundred million parts of urine.

loss of mercury when the solution is evaporated even in a quartz dish alone or in the presence of nitric acid, hydrochloric acid and potassium chlorate, or potassium permanganate and sulphuric acid. Hence attempts to increase the delicacy of the reaction by concentrating extremely dilute solutions are not very successful. The most delicate method is to use a large volume of the liquid in question and stir well while electrolysing. This is much more sensitive than the Wolff-Schneider method (Witthaus, "Toxicology," p. 779).

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