ARSENICAL POISONING BY WALL-PAPERS.

I.

REPORT ON EVIDENCE REGARDING THE INJURIOUS EFFECTS ON HEALTH ARISING FROM ARSENICAL WALL-PAPERS AND OTHER ARTICLES CONTAINING ARSENIC.

By T. LAUDER BRUNTON, M.D., F.R.S.

THE evidence on this subject consists partly of articles published in various journals, and partly of answers to a circular on the subject sent out by the Medical Society of London (see BRITISH MEDICAL JOURNAL, February 21st, 1880). The nature of the evidence is, first, that certain symptoms have occurred in persons exposed to the influence of certain conditions; secondly, that, on attempting to analyse these conditions with the object of finding out the cause of injury, none could be discovered at all likely to produce the symptoms, except arsenic; thirdly, that the symptoms coincided in many respects with those produced by arsenic when administered internally; fourthly, that the symptoms disappeared when the arsenic was removed, although, as far as could be ascertained, the other conditions remained unaltered. The number of cases on which the report of the Committee of the Medical Society of London was based was a little over one hundred; and, besides these, numerous cases have been reported in medical journals. Considering the extensive use of arsenic in wall-papers and articles of clothing and furniture, the number of cases may appear very small, and quite insufficient to prove the necessity for any form of legislative interference. This objection, we believe, however, to be invalid. It is exactly the same in kind as that which may be brought against interference with systems of drainage which contaminate drinking-water with typhoid excreta, or against the free distribution of milk supplied from dairies where typhoid or scarlet fever exists. The comparative smallness of the number of cases of poisoning by arsenical wall-papers is, we believe, simply due to ignorance of the injurious action of arsenic in papers, dress, or furniture, and consequent failure to perceive the connection between the illness and its cause. One circumstance which renders this connection more easily overlooked, is the fact that all persons are not equally susceptible to the injurious action of arsenic. It is well known that, in Styria, many persons are accustomed to take quantities of arsenic which would be fatal to others unaccustomed to it. It seems possible that the same may occur with arsenical papers; for, in a house at Hampstead, where the former occupants had enjoyed good health, another family, shortly after their entrance, began to suffer from symptoms of arsenical poisoning. The wall-paper was examined, and found to be arsenical. On its removal, all the symptoms ceased. The immunity which the first of these families enjoyed, although exposed to the action of the arsenical paper, may have been due to their having become gradually inured to the presence of arsenic; but it may also have been due to a less degree of sensitiveness; and this is all the more probable, because the second family have suffered three several times in the same way. Should one member of a family be more sensitive than others, he or she may suffer while the rest escape. In such a case, suspicion will be averted from the arsenical paper, as all have been exposed to its influence. In one case reported to the Medical Society, two children of an eminent consulting surgeon died from enteritis, while the nurses escaped. The cause of the illness and death of the children was a mystery, until the nursery papers were examined and found to contain arsenic. Another cause of the failure to connect the symptoms due to arsenic with its presence in wall-papers is, that the symptoms are those of irritation of the intestinal or respiratory tracts, or of the conjunctiva; and these may frequently be attributed to other causes than the true one, especially if no suspicion of the presence of arsenic be entertained. Thus, in thirty-five cases reported to the Medical Society, nausea, diarrhœa, and digestive disturbance occurred; and these symptoms might be ascribed to errors in diet, to chills, to imperfect drainage, or to worry or overwork; or might be vaguely ascribed to constitutional disturbance by those who did not suspect, and therefore failed to discover, the true cause. The same may be said of the cough and asthma which occurred in nine cases, or of the conjunctivitis which occurred in nineteen. In support of this view, it may be mentioned that one-fourth of the cases of poisoning reported to the Medical Society had occurred in the persons of the medical men themselves who reported them, or in members of their families and that a large proportion of the cases reported had been observed by men qualified in an especial way, either by knowledge or by training, to discover the true cause of the symptoms which occurred.

Another reason why arsenic as a cause of disease is overlooked, is that, when given as a medicine, it produces no injurious action in quantities which are probably larger than those which enter the bodies of persons exposed to the action of arsenical papers. The reason of this may be twofold: either it may be that the arsenic given off from the paper is absorbed by the lungs instead of the stomach, or it may be that the arsenic is given off from the paper in a specially poisonous form. The difference between the effect of poisons taken by the mouth and introduced into the body in other ways, is shown by the fact that the venom of vipers, although very poisonous when applied to a wound, is quite innocuous when swallowed. That arsenic, in different combinations, has different poisonous powers, is shown by the fact that, in the form of cacodyl, although exceedingly offensive to the sense of smell, it is not poisonous; while, on the other hand, arsenic, in the form of arsenes, appears to be more poisonous than arsenious acid.

At all events, however, a considerable amount of positive evidence has already been obtained of the injurious action of arsenical papers and fabrics; and, whatever may be the reason why it is not greater, it is sufficient to justify vigorous action in the matter.

II.

NATIONAL HEALTH SOCIETY: COMMITTEE ON ARSENIC IN DOMESTIC FABRICS.

Chemical Report on the Test to be employed for the Detection of Arsenic.—It was found that, on the Continent, Acts or decrees exist, forbidding the sale of wall-papers, curtains, carpets, and textile fabrics generally, if they contain arsenic. We had before us the decrees in force in Germany and Sweden. In the former, the prohibition of the sale of goods containing arsenic is absolute; in Sweden, a concession is made to manufacturers to this extent, that a paper or textile fabric shall be considered practically free from arsenic if an opaque black or brown arsenical mirror cannot be obtained from 68 square inches of paper, or 34 inches of a textile fabric, in a tube of 2 mm. (.078 inch) internal diameter. In the printed certificates issued by the Government, to be filled up by the chemist making the analysis, it is stated that the method known as the Von Babo and Fresenius test should be employed. The process is then minutely described, so as to insure uniformity of results. We ascertained from the Government analyst, in Stockholm, that the fact of the mirror being opaque is determined by observing whether or not a black line on a white ground could be seen through it. The fact that the presence of arsenic in domestic fabrics is injurious to health having been already ascertained by the Committee, the question for our consideration is simply that of the mode of testing. The first point for consideration is whether the prohibition of arsenic must be absolute, extending to the most minute trace, or whether such minute quantities may be allowed as arise from accidental and unavoidable contamination. A very large proportion of fabrics of all kinds are found absolutely free from arsenic, no known test discovering the slightest trace; but, again, with regard to many fabrics, some traces are unavoidable in consequence of the very wide diffusion of small quantities of arsenic in natural products. The consideration consequently arises: first, as to what amount of arsenic it is requisite to allow as unavoidable and accidental contamination, in order that trade may not be hampered or interfered with to any undue extent; and next, whether that allowance may be permitted with due consideration to health. There are manufacturers of wall-papers (the principal articles in question) who have, on principle, abjured the use of all arsenical colours; the result of their work affords, therefore, an excellent guide for what may be demanded without unreasonable interference with the freedom of trade. An examination of a very large number of papers, supplied by these manufacturers, leads to the conclusion that an allowance of half a grain of arsenic per "piece of paper"—a piece being 12 yards in length and 21 inches wide—would be ample for accidental and unavoidable contamination; and this quantity, it is considered, would not be injurious to health. It is found that a suitable size for a sample to be tested is 16 square inches, to be cut from one part; or, if thought well, from several parts of the pattern, so as to include

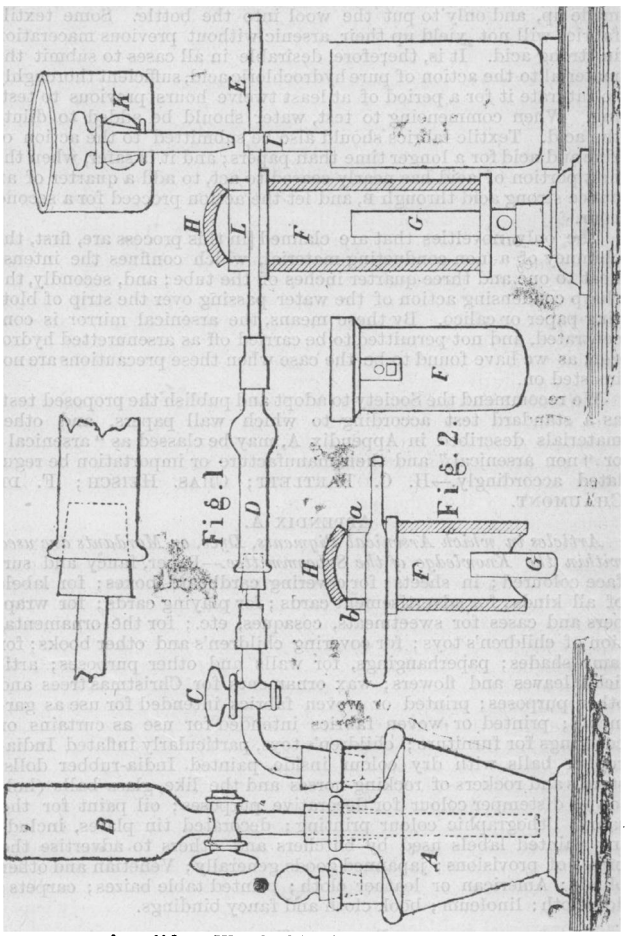
all the colours. The proposed limit of half a grain per piece gives .001 grain per sample of 16 square inches. For ordinary uniform materials, a square of 4 inches by 4 inches may, therefore, be taken as the portion to be tested. We may remark, that the quantity of arsenic which we allow to pass by these tests, is more than four times as much as would be permitted by the Swedish decree. We were at first of opinion that Reinsch's process, carefully conducted so as to ensure uniformity of results, might be employed; but several wall-papers and many textile fabrics having been found which gave no arsenical reaction with Reinsch's test, however carefully conducted, but which, nevertheless, were subsequently proved to contain notable quantities of arsenic, this method was proved not to be an absolutely reliable test. A modification of Marsh's test is recommended as the most reliable, and as most suitable for a standard test to be inserted in an Act of Parliament. Detailed instructions are subjoined for both tests, in order that those who still desire to use Reinsch's method may get results comparable with the prescribed test by the modification of Marsh's process where arsenic is found.

Standard Test.

No paper should be passed as "non-arsenical," unless, when treated as hereafter described, it fails to yield a mirror in a tube $\frac{1}{8}$ inch internal diameter, sufficient to cut off at any point a black line on a white ground, technically known as thick rule (eight to pica).

Specimen Zinc.

In a three-necked bottle* of the form A, Fig. 1, of about 10 ounces capacity, place 200 grains of pure zinc.† To the centre neck, fit a tube funnel and stop-cock, B, and to one of the side necks a right-angled tube, and stop-cock, C. The third neck should be closed with a ground stopper. Connect with C a chloride of calcium tube, D, and with this a tube of hard glass, E, $\frac{1}{8}$-inch internal diameter, and about .04 inch thick in the glass, if the paper or other material to be tested does not contain sulphur; but if, on being treated with hydrochloric acid, it yields sulphuretted hydrogen, the modification of this tube E, hereafter mentioned, must be adopted. Let this tube traverse a clay chimney, F, $1\frac{1}{2}$-inch diameter, and 6 inches high, in the top edges of which two slots have been filed to admit E, to the depth of one inch, and let E be supported on a thin bridge of the same material as the chimney, $\frac{1}{4}$-inch wide and a $\frac{1}{8}$-inch thick slightly notched, to rest on the sides of the chimney. This chimney surrounds a Bunsen's burner, G, of $\frac{1}{2}$-inch diameter. Over the top of the chimney, place an arched cover, H. Round E, at $\frac{3}{8}$-inch from the chimney,‡ roll a strip of thick blotting-paper or calico, $\frac{1}{4}$-inch wide, secured by a thread, as at I. This should go at least twice round the tube, and hang down, as shown in Fig 1; on to this, water is dropped from a bottle, K, at the rate of about 120 drops per minute (in very hot weather even faster). When the apparatus is thus arranged, pour through B two ounces of dilute hydrochloric acid, one part acid to eight water. If any sample of zinc do not yield hydrogen with sufficient rapidity with this acid, slightly stronger must be employed. The hydrogen should be evolved with sufficient rapidity to keep alight at the end of the tube when fired. Close stop-cock on B, and let hydrogen escape through C, D, E, till all air is expelled. Now light G, and when E is quite red-hot, close C, and introduce through the stoppered neck the 16 square inches of paper, cut into strips of one inch by two inches, and rolled up, so as to pass readily through the neck. This must include within the 16 square inches of paper portions of every part of the pattern, so that all the colours may be tested. Replace the stopper, open stop-cock C, and let the action continue for one hour. Now, extinguish G, and observe if a brown or black mirror be formed in E, between I and the chimney. If no mirror be formed, the paper is absolutely free from arsenic; if a mirror be formed, which, if the operation be properly conducted, will occupy about $\frac{3}{16}$ inch in the tube, lay E along the black line before spoken of, in front of and pointing towards a window, and observe, with one eye exactly over the tube, whether at any point the mirror be thick enough to obscure the line. Should this not be the case, the paper may be passed as containing no more arsenic than may have got into it from unavoidable causes; should the line be at any point obscured, it only remains to make sure that the mirror is arsenical. If, when sublimed with access of air, the mirror yield octahedral crystals, it is arsenical. This operation is best performed as follows. The portion of the $\frac{1}{8}$-inch tube containing the mirror being cut out, take a thin hard glass tube, $\frac{1}{4}$-inch internal diameter and $1\frac{3}{8}$-inch long, sealed at one end, and lipped like a test-tube at the other. Suspend this by dropping it through a hole cut in a piece of stout sheet-brass or copper, not less than four by two inches, so that the lip just supports the tube, and place the brass or copper plate on the ring of a retort stand. Heat the tube nearly to redness, to expel the last trace of moisture; when cold, insert the portion of the $\frac{1}{8}$-inch tube containing the mirror, and place, over the mouth of the tube and resting on it, a microscopic slide, warmed in a spirit-lamp till all the moisture at first deposited has disappeared. Now heat the tube with the spirit-lamp, letting the flame play on the under side of the brass plate. In a few seconds, a sublimate will



appear on the slide. Watch this till it begins to shrink from the edges, and form a patch just the size of the bore of the tube. Remove the lamp, allow the slide to cool, and examine the sublimate with a magnifying power of not less than 220 diameters. If the sublimate is found to consist of octahedral crystals, it is arsenical. Such crystals are well shown on the photographs taken by Mr. J. H. Jennings, of 14, Beach Avenue, Nottingham.

If, on being treated with hydrochloric acid, a paper or other substance yield sulphuretted hydrogen, as before mentioned, or if, on being treated as above described, a yellow or whitish-yellow sublimate be found instead of a mirror, the following modification must be adopted.

Substitute for the tube E a tube of $\frac{1}{4}$-inch diameter, having the $\frac{1}{8}$ tube sealed on to its end (Fig. 2); at *a*, the junction of the two,

* This form is recommended, as, in case of frothing, which frequently occurs, the froth is not driven into the tubes.

† Zinc sufficiently pure for this purpose can only be prepared by dissolving the purest commercial zinc in pure acid, so as to expel any arsenic as arseniuretted hydrogen; precipitating the zinc with pure carbonate of soda, washing the precipitate, and, when dry, reducing it. Messrs. Johnson and Matthey, of Hatton Garden, prepare zinc exactly in this manner, and supply it in bars, guaranteed free from arsenic. This zinc gives off hydrogen so freely, that it is desirable to have the requisite quantity in one piece in the bottle, so as not to expose too great a surface to the action of the acid.

‡ The chimney is conveniently made by cutting the bottom off a Daniell's porous cell, and the cover by cutting a piece $1\frac{1}{2}$ inch long off a similar cell and splitting it into three. The bridge also is best made of the same material.

place a small plug of asbestos; fill the portion which traverses the chimney with a mixture of dry carbonate of soda and charcoal; and behind this, at *b*, place another plug of asbestos. The rest of the arrangement is the same as in Fig. 1. The red-hot carbonate of soda and charcoal retain any sulphur, etc., but permit the arsenic to pass. In this case, a little water is formed, and carried forward with the arsenic, which prevents the mirror having such well-defined limits as when it is perfectly dry; but a few experiments, made with known quantities of arsenic, will enable the operator to say with accuracy if a paper contain more than the permitted maximum of arsenic. It is remarkable how small a quantity of sulphur will completely mask a considerable amount of arsenic. Thus, sufficient ultramarine, mixed with a white pigment to give it a greyish tint, will quite prevent the formation of an arsenical mirror with four times the maximum quantity of arsenic permitted.

In the case of textile fabrics to be worn next the skin (as gloves, socks, or vests), experience has shown us that no trace of arsenic, however small, should be permitted. Curtains, carpets, etc., come under the same rule as wall-papers. In the case of carpets, it is better to remove the hempen backing on which they are frequently made up, and only to put the wool into the bottle. Some textile fabrics will not yield up their arsenic without previous maceration in strong acid. It is, therefore, desirable in all cases to submit the material to the action of pure hydrochloric acid, sufficient thoroughly to saturate it for a period of at least twelve hours previous to testing. When commencing to test, water should be added to dilute the acid. Textile fabrics should also be submitted to the action of zinc and acid for a longer time than papers; and it is safer, when the first portion of acid has nearly ceased to act, to add a quarter of an ounce strong acid through B, and let the action proceed for a second hour.

The only novelties that are claimed in this process are, first, the chimney of a non-conducting material, which confines the intense heat to one and three quarter inches of the tube; and, secondly, the sharp condensing action of the water passing over the strip of blotting paper or calico. By these means, the arsenical mirror is concentrated, and not permitted to be carried off as arsenuretted hydrogen, as we have found to be the case when these precautions are not insisted on.

We recommend the Society to adopt and publish the proposed test; as a standard test according to which wall papers, and other materials described in Appendix A, may be classed as "arsenical" or "non arsenical," and their manufacture or importation be regulated accordingly.—H. C. BARTLETT; CHAS. HEISCH; F. DE CHAUMONT.

APPENDIX A.

Articles in which Arsenical Pigments, Dyes, or Mordants are used within the Knowledge of the Subcommittee.—Paper, fancy and surface coloured; in sheets; for covering cardboard boxes; for labels of all kinds; for advertisement cards; for playing cards; for wrappers and cases for sweetmeats, cosaques, etc.; for the ornamentation of children's toys; for covering children's and other books; for lamp shades; paperhangings, for walls and other purposes; artificial leaves and flowers; wax ornaments for Christmas trees and other purposes; printed or woven fabrics intended for use as garments; printed or woven fabrics intended for use as curtains or coverings for furniture; children's toys, particularly inflated India-rubber balls with dry colour inside, painted India-rubber dolls, stands and rockers of rocking-horses and the like, glass balls (hollow); distemper colour for decorative purposes; oil paint for the same; lithographic colour printing; decorated tin plates, including painted labels used by butchers and others to advertise the prices of provisions; japanned goods generally; Venetian and other blinds; American or leather cloth; printed table baizes; carpets; floorcloth; linoleum; book cloth and fancy bindings.

POPULAR TEST.

Although the Committee are of opinion that Marsh's test alone gives results of sufficient delicacy and accuracy to justify the taking of legal proceedings thereon, and have therefore adopted it in a modified form as the standard test to be appended to the proposed Bill, they are fully aware of the insuperable difficulties that stand in the way of its general employment in ordinary business transactions. It can only be practised by experts, and the fee which they would very properly require would, in the great majority of cases, deter the public from availing themselves of their assistance, although when a prosecution was contemplated it would be otherwise. Reinsch's test though less delicate, and indeed not absolutely free from the possibility of error, has been proved in hundreds of comparative trials to be, when carried out as they direct, accurate enough for all ordinary practical purposes, *i.e.*, for indicating the presence of a dangerous amount of arsenic, and when no graver consequences are involved than the acceptance or rejection of a particular paper.

Its advantages are that it could be undertaken by any professed chemist at a fee within the means of everyone, no small consideration when a large number of papers have to be examined; indeed, with the apparatus provided at the suggestion of the Society by Messrs. Griffin, of 22, Garrick Street, London, manufacturers, tradesmen, and intelligent householders might use it for themselves.

They thus hope that the end they have in view, the discouragement of the employment of arsenical colours, would be more speedily attained by the education of the public generally, than by a few isolated cases of prosecution.

They, therefore, give directions for the performance of Reinsch's test.

Testing by Reinsch's Process.—The following is the mode in which this test should be used.—Sixteen square inches of the paper, either in one piece or several, so as to include all parts of the pattern, to be cut up and put in a test-tube or flask, with 2 ounces of dilute hydrochloric acid (4 distilled water to 1 of acid), and brought to the boiling point, a vertical condenser being used, if convenient; it is however, not essential. A piece of copper foil, 1 inch by ½ inch, clean and bright, is now placed in the flask, suspended by a thin platinum wire, by means of which it can be withdrawn, from time to time, for examination. After boiling gently for half an hour, the copper must be rinsed repeatedly in water, and finally held under a tap, in a pair of forceps, to remove all traces of acid, etc. On no account is the copper to be touched with the fingers, as, even when wet, the grease of the finger interferes with the subsequent operations. No great stress can be laid on the amount of discoloration, as it varies very much, even with the same amount of arsenic, in the presence of other substances, such as sulphur, mercury, etc. The copper must then be treated as follows.—Dry it between two pieces of clean blotting-paper, and, holding it in the forceps, warm it very gently over a spirit-lamp; then, still holding it in the forceps, cut it into strips. Take a thin glass tube, ¼ inch internal diameter, and 1⅜-inch long, sealed at one end, and lipped like a test-tube at the other. Suspend this by dropping it through a hole cut in a piece of stout sheet-brass or copper, not less than 4 by 1 inches, so that the lip just supports the tube, and place the brass or copper plate on the ring of a retort-stand. Heat the tube nearly to redness, to expel the last trace of moisture; and, when cold, put the copper strips within, and place over it, resting on the mouth of the tube, a microscopic slide, warmed in a spirit-lamp till all the moisture at first deposited has disappeared. Now heat the tube with the spirit-lamp, letting the flame play on the under side of the brass plate. In a few seconds, a sublimate will appear on the slide. Watch this until it begins to shrink from the edges and form a patch just the size of the bore of the tube. Remove the lamp, allow the slide to cool, and examine the sublimate with a magnifying power of 220 diameters. If the sublimate consist of octahedral crystals, the discoloration of the copper is due to arsenic.

It is of course essential that the copper and hydrochloric acid used for this test be free from arsenic.

III.

ON THE BEHAVIOUR OF ARSENIC IN CONTACT WITH PUTREFYING ORGANIC SUBSTANCES.

BY THOMAS STEVENSON, M.D.,
Professor of Toxicology, Guy's Hospital.

IT has now for some time been a well established fact that nitrogenous organic substances, *e.g.*, flesh, give rise during putrefaction to the formation of alkaline or basic substances. Ammonia is the best known of these products. There are, however, other and less known bases, or alkaloids, as the organic bases are termed, also produced during decay, *i.e.*, substances formed, as the chemist terms it, on the same type as ammonia. Two chemical bodies are said to be of the same type when they contain the same number of atoms, or groups of atoms (compound radicals), arranged in the same manner. Thus bodies so diverse as water and alcohol are said to belong to the same type, because one of the two atoms of hydrogen contained in the molecule of water in alcohol is replaced by a group of atoms of carbon and hydrogen, known collectively as ethyl; and water and alcohol, regarded in some aspects, have similar chemical properties. Ammonia, abundantly produced during putrefactive decomposi-