

NEW APPARATUS

A MODIFIED APPARATUS FOR REINSCH'S TEST

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A modified method for the rapid identification of antimony, arsenic and mercury is described.

STANDARD procedures for the determination of arsenic (Analytical Methods Committee, 1960; Methods of Analysis A.O.A.C., 1960a) and mercury (Methods of Analysis, A.O.A.C., 1960b), although excellent in themselves, are time consuming and require considerable experience to obtain reproducible results. There is, therefore, still a need for some simple qualitative test of reasonable delicacy and of such simplicity that it may be made rapidly by any trained chemist with adequate laboratory facilities. Although it must be emphasised that irreplaceable materials should always be left for the expert attention of the forensic laboratory, there are many occasions when a rapid qualitative identification may be of the greatest value.

It is the purpose of this communication to describe a modification of Reinsch's test (1841), a reaction which has already been much investigated and variously modified (Gettler, 1937; Gettler and Kaye, 1950; Stolman, 1961; Umberger, 1960).

EXPERIMENTAL METHOD

The first stage of the test is made in the conventional way. 20 g. of the suspected material is placed in a 250 ml. conical flask fitted with a long air condenser and 2N HCl (50 ml.) added together with a piece of thin copper foil (1 cm. \times 0.5 cm.) which has been cleaned by rubbing with fine emery paper, immersing in 4N HNO₃ and washing in distilled water. The mixture is boiled gently for 30 min. the copper is then removed, washed thoroughly with water, dried between sheets of filter paper, washed in ethanol and ether, and examined. Discoloration may be due to antimony, arsenic, bismuth, mercury, selenium, silver, sulphur or tellurium. Even if no change is visible to the naked eye, the second stage of the test should be made. It is to this second stage, which consists of the sublimation of the deposit and microscopical examination of the sublimate, that the present modification applies.

The copper, which must be thoroughly dry, is folded and placed in the bottom of a Pyrex ignition tube (Fig. 1), into the neck of which is inserted a piece of thick walled capillary tubing 3 cm. long (A). This is surrounded by a brass collar (B) held in place by a piece of curved watch

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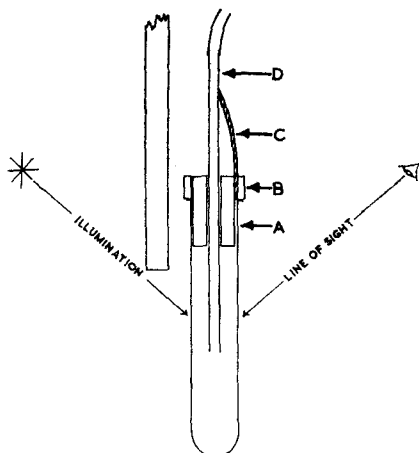


FIG. 1

spring (C), notched at its upper end to retain the melting-point tube, 10 cm. \times 0.1 cm. internal diameter (D). The top of the melting-point tube is connected by a piece of polythene tubing to an aspirator which enables a slow current of air (20–30 ml./min.) to be drawn up the tube. A metal strip, with a suitable hole drilled in it, forms a convenient support for the apparatus.

The bottom of the ignition tube is now heated in a small micro-bunsen flame. The deposit on the copper volatilises and is drawn into the melting-point tube where it is redeposited. The presence of this deposit is best seen by indirect illumination as shown in the Figure. It should be noted that considerably more heat is required for the volatilisation of antimony, selenium and tellurium than for either arsenic or mercury. Silver, which gives a whitish deposit on the copper, and bismuth, which gives a mechanically unstable black deposit, do not sublime.

As soon as the deposit begins to move up the tube the air flow is stopped and the flame removed. After being allowed to cool, the melting-point tube is removed and the deposit examined under low magnification ($\times 60$ – $\times 100$). Arsenic forms a crystalline deposit of As_2O_3 , antimony an amorphous deposit of Sb_2O_3 , while mercury gives globules of the metal. Selenium gives a sublimate easily seen by indirect light, but which is very difficult to see under the microscope. When seen, it has the appearance of a liquid. Tellurium has sometimes a crystalline form (rods or needles), but is often too finely divided to be distinguished from antimony.

In most instances the appearance of the sublimate will be distinctive enough for identification. It is as well, however, to carry out confirmatory tests as follows: (i) for arsenic, seal the lower end of the melting-point tube and replace the tube in the apparatus. Heat the outer tube strongly until the sublimate disappears. The thermal capacity of the thick-walled capillary tubing prevents the loss of the sublimate. Allow the apparatus to cool slowly until the outer tube is cool to the touch. Remove the melting-point tube and again examine under the microscope. A few

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large crystals of As_2O_3 , tetrahedral or octahedral, will be found. (ii) For antimony proceed in the same way; the sublimate will remain amorphous though it may become invisible. Cut off the sealed end of the tube, draw a small drop ($10\ \mu\text{l.}$) of concentrated HCl into and along the tube and expel it on to a white tile. Add a microdrop ($0.1\ \mu\text{l.}$) of a 10 per cent solution of sodium nitrite, and then a microdrop of an 0.1 per cent aqueous solution of rhodamine B. A mauve colour shows the presence of antimony. It is important that HCl be in excess. This test is not given by any other element under consideration.

Selenium may be identified by drawing a small drop of a 1 per cent solution of morphine in $2N$ acetic acid into and along the melting-point tube, expelling it on to a white tile, evaporating to dryness and moistening the residue with concentrated H_2SO_4 when a green colour is obtained. Under similar conditions tellurium gives a light brown which is not very distinctive.

(iii) For mercury, remove the copper from the ignition tube, add a few small crystals of iodine and warm carefully with the air flow turned on so that the iodine vapour is carried up the melting-point tube. As it passes the mercury an orange colour, due to the formation of mercuric iodide, will be seen. Examination under the microscope will show a mixture of both red tetrahedra and yellow rhomboids, the latter showing brilliantly under polarised light. Should the appearance not be distinctive the tube is sealed at one end, reheated, and allowed to cool slowly as for arsenic. The resublimation and slow cooling will give larger crystals. It is essential that the apparatus and iodine be completely dry as traces of water vapour may prevent the formation of typical crystals.

The sensitivities, given conservatively, are $10\text{--}20\ \mu\text{g.}$ for arsenic and antimony and $100\text{--}200\ \mu\text{g.}$ for mercury. $100\ \mu\text{g.}$ of bismuth, silver, selenium and tellurium may discolour the copper, but the two latter will not sublime unless present in milligram quantities.

It must be noted that certain organic compounds of mercury used for seed dressings, such as ethyl mercuric chloride, are not found by Reinsch's test. This is due to the stability of the carbon-mercury bond (Calfruny, 1961).

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