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Note

Detection of halogens in substances separated by paper and thin-layer chromatography

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Although many methods have been developed for the detection of various elements, most often nitrogen, sulphur and the halogens, in organic compounds, these methods are applicable only when a large amount of the test compound is available. However, when substances are separated by paper or thin-layer chromatography, only a few micrograms or even less of sample are often available.

One of the most common methods for the detection of chlorine, bromine and iodine is the Beilstein test, based on the green coloration of a flame containing the test substance and passing through a copper gauze¹. This method is very sensitive, but some substances that do not contain a halogen also yield a positive Beilstein test²⁻⁶, e.g., benzoic acid, urea N-derivatives, quinoline with substituents in the *o*-position and *dl*-tartaric acid. A spectral study⁷ has shown that the flame coloration caused by CuCl^+ is identical with that caused by CuOH^+ , so that any material capable of producing the latter compound can be confused with a substance containing a halogen.

Another procedure for the detection of chlorine, bromine and iodine involves mineralization of the sample with sodium and detection of the halide formed with silver nitrate solution or by combustion of the sample in an oxygen atmosphere. These methods require large amounts of sample.

We recently developed a method for the detection of nitrogen and sulphur in substances separated by paper and thin-layer chromatography, based on hydrogenation of the substance on platinum and suitable detection of the hydrogenation products⁸. This method was developed to detect halogens in the form of hydrogen halides on the same apparatus. The work described here is an extension to a simple, rapid and sensitive method for the simultaneous detection of nitrogen, sulphur and halogens in compounds separated by paper or thin-layer chromatography.

EXPERIMENTAL

The apparatus (Fig. 1) consists of a pressure cylinder from which the carrier gas (hydrogen) is led through a purifier into a pyrolyser containing the sample in which the elements are to be detected. An oven with a quartz tube packed with platinum gauze is connected to the pyrolyser, followed by a detector which is exchanged for each particular element.

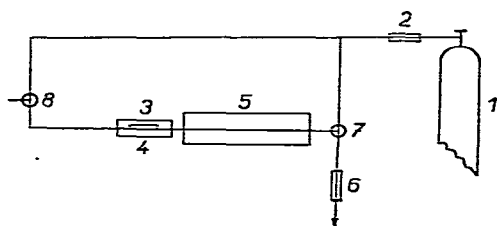


Fig. 1. Scheme of the apparatus for the detection of nitrogen, sulphur and halogens.

A pressure cylinder (1) is connected to a gas purifier (2), after which the gas stream is divided into two branches, one leading through a three-way stop-cock (7) and the other through another three-way stop-cock (8) into an oven (3) with a thermocouple (4) and then through a hydrogenation oven (6).

The apparatus is operated as follows. The test sample is placed in a platinum boat on the thermocouple (4) in the pyrolysis oven (3). The carrier gas (hydrogen at a flow-rate of 0.5 l/h) is led from a cylinder (1) through a purifier (2) and the three-way stop-cock (8) into the pyrolyser (3). The hydrogen stream is further led into the hydrogenation oven (5) with a quartz tube containing platinum gauze heated to 950–1000°, and then through the other three-way stop-cock (7) into the detector (6). A halogen is reduced to the hydrogen halide on the platinum gauze in the presence of hydrogen. The detector can be exchanged for different detections. For the detection of halogens, a strip of filter-paper soaked in a solution of 2,6-dichlorophenolindophenol is used. The presence of a hydrogen halide is indicated by a change in the coloration from blue to pink.

The sample for analysis is obtained either by scraping off the appropriate areas on a thin-layer chromatogram or by cutting out from a paper chromatogram. The untreated sample is placed directly in the oven (3). A blank determination with the same amount of carrier gas must always be carried out. The three-way stop-cock (7) is placed after the oven (5) in order to permit a back-flow of the carrier gas during insertion of the sample so as to prevent contamination of the instrumental volume by the surrounding atmosphere.

The detection reagent is prepared as a 0.1% solution of 2,6-dichlorophenolindophenol in deionized water, which is diluted to a concentration of 0.015% before the experiment, and detection paper strips (Whatman) are impregnated with it. A damp detection paper is placed in a glass tube (about 10 cm long and with an inner diameter of 1.5 mm), one end of which is connected to the outlet of the hydrogenation device and the other is placed in a small container with 0.2 ml of the detection agent, so that the paper is damp throughout the experiment. For the detection of halogens, larger amounts of sample (20–50 μg) must be used than in the detection of sulphur and nitrogen.

The time is measured from the instant of switching on the oven (3) and the length of the pink zone on the detection paper is measured at certain time intervals, preferably at 2, 4, 6, 8, 10, 12, 15, 20 and 25 min. The oven (3) is switched off after heating the sample for 10 min. The dependence of the coloration of the paper on time is plotted graphically.

DISCUSSION

For the detection of halogens, the same criteria for secondary contamination hold as in the detection of nitrogen and sulphur⁸. As already mentioned, the apparatus is the same for all detections, only the detector is varied.

During hydrogenation of pyrolytically decomposed organic compounds, carbon is converted into methane, nitrogen into ammonia, sulphur into hydrogen sulphide and halogens into hydrogen halides. Mutual interferences among these elements during their detection should be examined. Methane is inactive in all three detection procedures. A greater problem is the presence of sulphur and nitrogen during the detection of hydrogen halides. Sulphur yields hydrogen sulphide which is acidic and affects the coloration of the paper impregnated with 2,6-dichlorophenolindophenol. Nitrogen forms ammonia, which might obscure the effect of hydrogen halide if present in large amounts. However, no interference was observed in the detection of chlorine in *p*-chlorodiethylaniline, 3,6-dichloro-*p*-phenylenediamine, phenyltrimethylammonium iodide and 1,4-dichloro-2-nitrobenzene. The presence of halogens does not affect the detection of sulphur and nitrogen because of the character of the detection.

We tested various absorption devices for removal of hydrogen sulphide produced in the presence of sulphur, but were unsuccessful. Therefore the Beilstein test should be used in such instances, although it is ambiguous.

The advantages of the procedure described here are the possibility of effecting the detection of sulphur, nitrogen and halogens on the same apparatus, and the feasibility of detecting chlorine, bromine, iodine and fluorine, in contrast to other methods that require a separate test for fluorine. We feel that the method should be a valuable aid in the identification of unknown substances on chromatograms, in spite of certain drawbacks.

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