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DETECTION OF NITROGEN AND SULPHUR IN SUBSTANCES SEPARATED BY PAPER AND THIN-LAYER CHROMATOGRAPHY

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SUMMARY

A procedure has been developed for the detection of sulphur and nitrogen in substances separated by paper and thin-layer chromatography, using a single apparatus for both elements. The substances are pyrolysed together with the chromatographic support, and the sulphur products are converted into hydrogen sulphide and the nitrogen products into ammonia on a platinum gauze in a stream of hydrogen. The hydrogenation products are then suitably detected.

INTRODUCTION

The Lassaigne test for sulphur, nitrogen and the halogens is used as one of identification methods for unknown compounds^{1,2}. In paper and thin-layer chromatography, it is often necessary to decide whether the substances separated contain nitrogen, sulphur or a halogen. As microgram amounts of substances are usually applied to the start of the chromatogram, the components separated sometimes occur in amounts of fractions of microgram and it is then not simple to detect sulphur, nitrogen and the halogens.

The only paper on this problem describes the detection of chlorine, bromine, sulphur and molybdenum in substances on chromatograms using X-ray fluorescence³. The instrumentation is expensive and unavailable in most laboratories. Moreover, nitrogen cannot be detected by this method. Hence a simple method is required that is capable of detecting sulphur, nitrogen and the halogens by a single procedure, with only small modifications (*i.e.*, using a single apparatus).

Attempts to solve this problem have been described. For the detection of nitrogen, methods based on the modified Lassaigne test have been proposed^{4,5}, usually using other detection reagents after alkaline fusion. Other methods convert the nitrogen present into nitrous acid, which is then detected⁶, or heat the nitrogen-containing substance in a capillary with a mixture of calcium and zinc oxides, detecting the ammonia formed by an acid-base indicator⁷. Nitrogen is also determined photometrically in a phenolic oxidizing medium⁸. An ultramicro method based on the Dumas method cannot be used for this purpose⁹⁻¹².

Sulphur can be detected in several ways. Sulphur is converted into sulphur dioxide, which is either titrated coulometrically¹³ or oxidized with potassium per-

manganate and determined according to the Pregl method¹⁴. On an ultramicro scale, sulphur is oxidized with a mixture of copper(II) and boric oxides and the sulphur trioxide formed is detected with *p*-rosaniline¹⁵.

In many methods, sulphur is reduced to hydrogen sulphide. For example, the test sample is heated with sodium carbonate and potassium hexacyanoferrate(III)¹⁶. In another procedure, the sample is heated with mercury, oxidized with perchloric acid and the sulphur dioxide formed is reduced with hypophosphorous acid, the hydrogen sulphide being detected with 4-(2-pyridyl)resorcinol¹⁷. Huber *et al.*¹⁸ converted hydrogen sulphide into methylene blue. Sulphur is often reduced by metals to hydrogen sulphide, *e.g.*, by magnesium¹⁹, potassium²⁰ and sodium²¹. Sulphur was also converted into barium sulphate, which was reduced to barium sulphide with hydrogen, liberating hydrogen sulphide on acidification²². Kristen²³ converted sulphur to sulphur dioxide and reduced the latter to hydrogen sulphide with a stream of hydrogen in a quartz tube. Feigh and Stark²⁴ developed a spot test, based on heating the sample with benzoin in a capillary. In a method developed by Widmark²⁵, the sample is decomposed with a mixture of calcium and zinc oxides and lead(II) acetate is used for the detection. Widmark²⁶ also modified the Lassaigne reaction. Sulphur was also converted into hydrogen sulphide on platinum foil²⁷. Further older papers can be found in a review by Kainz²⁸.

Most of the above work is not suitable for the detection of nitrogen and sulphur in microgram samples, because of either insufficient sensitivity or difficult manipulation on the microscale. Moreover, no method permits the detection of sulphur, nitrogen and the halogens in a single procedure.

In addition to the last requirement, the method must be relatively simple, rapid and sufficiently sensitive. These requirements are met by the present method, in which the test sample, together with the chromatographic support, is pyrolysed in a stream of hydrogen and the mixture of pyrolysis products is led over a platinum gauze heated at 950–1000°. Hydrogen sulphide, ammonia and the hydrogen halides are formed from sulphur, nitrogen and the halogens, respectively. Sulphur is detected from the coloration of a silica gel column soaked with lead(II) acetate and nitrogen from the coloration due to the reaction of ammonia with phenol and 2,6-dibromoquinonechloroimine. The detection of halogens will be published elsewhere.

EXPERIMENTAL

The apparatus is shown in Fig. 1. The test sample is placed in a platinum boat on a thermocouple (4) in the pyrolysis furnace (3). A stream of hydrogen flows from a cylinder (1), through a gas purifier (2) and a three-way stop-cock (8) over the sample and then into the hydrogenation furnace (5), which contains a quartz tube containing platinum gauze heated at 950–1000°, and then through other three-way stop-cock (7) into the detection device (6). Nitrogen is reduced to ammonia, the halogens to the hydrogen halides, sulphur to hydrogen sulphide and carbon to methane.

The detection device (6) is varied depending on the element being detected (Fig. 2). For the detection of sulphur, a glass tube (I.D. 1.5 mm) is used, packed with silica gel soaked with a 0.5% solution of lead(II) acetate. The presence of sulphur is shown by a black-brown coloration of the column.

Nitrogen is detected using a glass tube containing a strip of filter-paper

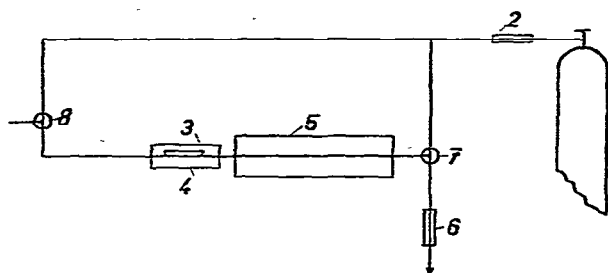


Fig. 1. Apparatus for the detection of nitrogen and sulphur. For description, see text.

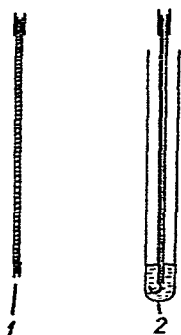


Fig. 2. Detection devices: 1, for sulphur; 2, for nitrogen.

(150 × 2.5 mm) soaked with a mixture of a 1% aqueous solution of phenol and a 1% solution of 2,6-dibromoquinonechloroimine in ethanol. These solutions are mixed immediately before the experiment, are placed in a small test-tube and the glass tube is placed so that the filter-paper is partly immersed in the solution. The presence of ammonia is shown by an intense blue coloration of the paper. If sulphur, nitrogen and a halogen are present simultaneously, the device for detection of nitrogen is preceded by a vent containing caustic asbestos, in which hydrogen sulphide and the halides are trapped. Samples obtained by scraping from a thin-layer chromatogram or cut from a paper chromatogram require no pre-treatment and are placed directly in the furnace (3). However, a blank determination must always be carried out, both with Silufol and without it, in order to check that the apparatus is clean.

The three-way stop-cock (7) is placed beyond the furnace (5) so that carrier gas can be flushed backwards during placement of the sample, as even small amounts of air polluted with nitrogen-containing substances seriously interfere in the detection of nitrogen.

RESULTS AND DISCUSSION

As with any sensitive micro-scale method, great care must be exercised not to pollute the sample with nitrogen or sulphur. Sulphur usually originates only from the chromatographic plate or paper, but nitrogen often comes from atmospheric pollution with ammonia or nitrogen oxides. A length of the platinum gauze of 20 cm was found to be optimal for the detection of both nitrogen and sulphur.

The time changes in the coloration of the silica gel column with lead(II) acetate and of the paper strip with a mixture of 2,6-dibromoquinonechloroimine and phenol must be monitored as the colour intensity increases faster in the presence of sulphur and nitrogen than in the blank determination. This is especially important with small amounts of these elements, *i.e.*; when the difference between the sample and the blank is small (see Fig. 3).

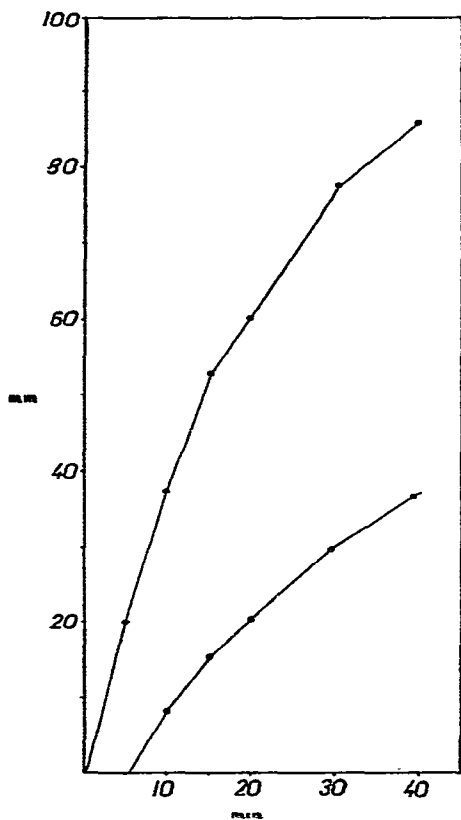


Fig. 3. Time dependence of the length of the coloured zone of the paper strip in the detection of nitrogen. Upper curve, 10- μ g semicarbazide sample on Silufol; lower curve, blank.

The sensitivity of the detection of nitrogen could be further increased, but this is not desirable because the blank values are rather high.

A pyrolysis temperature of 700° was selected, as was found to be sufficient for the substances studied. The flow-rate of hydrogen that serves as the hydrogenation medium and the carrier gas was adjusted to 0.35 l/h, which was found to be optimal for hydrogenation, for rinsing the reaction products from the tube and for detection. With volatile substances, the flow-rate must first be decreased and then adjusted to the above value.

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