

A Rapid Method for the Detection of H, Cl, Br, I, S and N in Organic Compounds

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Recently a method for the detection of oxygen in organic compounds utilizing a cracking technique has been described by one of the present authors¹. The substance is pyrolyzed in an atmosphere of helium and the carbon oxide formed identified. In this paper the application of pyrolysis to the qualitative determination of several other elements will be described. It was found that, when organic substances were pyrolyzed over a glowing platinum wire in an atmosphere of hydrogen, there were formed hydrogen halides from halogen-containing compounds, hydrogen sulphide from sulphur-containing compounds and hydrogen cyanide from nitrogen-containing compounds. To analyze for hydrogen the substance was pyrolyzed in the presence of sulphur in an atmosphere of nitrogen — when the substance contained hydrogen, hydrogen sulphide resulted (*cf.* Ref.²). The inorganic compounds formed were identified by wet chemical methods.

The time of pyrolysis had to be adjusted to the aggregation state of the substance as well as to the element that was to be determined. Thus, a longer pyrolysis time was necessary for solid compounds than for liquids and, to get an adequate amount of hydrocyanic acid from a nitrogen compound, a longer pyrolysis time was necessary than for transferring the halogen and sulphur bound in organic compounds into their corresponding hydrogen compounds (*cf.* below). The present method has been applied to a substantial number of organic compounds of various types including aliphatic and aromatic halogen compounds, nitro compounds, amides, nitriles, amines, nitrogen-containing heterocyclic compounds, nitrogen-containing plastics, mercaptans, thioketones, sulphonic acids, and sulphur-containing heterocyclic compounds. Since the test was positive in every case, it seems that the method possesses a fairly general application for the determination of the elements specified in the heading. We believe that the method

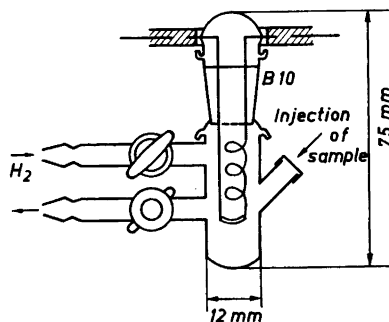


Fig. 1. Pyrolysis apparatus used for the elementary analysis.

has some advantages over the sodium fusion method of Lassaigne because of its immediate availability and the rapidity with which an analysis can be performed.

The apparatus used for the analysis is shown in Fig. 1. It represents a development of the apparatus previously used in this laboratory for the determination of oxygen¹. This apparatus was redesigned partly to allow an easier cleaning of the equipment and partly to make the connection of the contact wires to the apparatus more durable. The apparatus consisted of a pyrex glass tube with inlet and outlet tubes for the gas and a tube covered by a serum cap for the injection of liquid samples. The pyrex tube had a ground glass joint (B 10) at its upper end. A platinum glowing wire (0.5 mm diam.) was fastened in a stopcock, fitting the ground glass joint. The glowing wire was melted into tin in the inner parts of the side tubes connected to the stopcock and the outer copper contact wires were also fastened in the same way. This construction was more durable than the earlier one and it was also easier to replace a broken contact wire. At the lower end of the platinum spiral a small platinum bowl was welded to the platinum wire. Solid samples were placed in this bowl or liquid samples were injected into it through the side tube.

An analysis for C, Cl, Br, I, S, or N was performed in the following way. If the sample was a solid or a not too fugitive liquid, 3–5 mg of it was placed in the platinum bowl and the apparatus assembled. The inlet tube was connected to a hydrogen container and a stream of hydrogen passed through for some minutes. The

stopcock on the outlet tube was closed and thereafter the stopcock on the inlet tube. In this way, a slight hydrogen over-pressure was built up in the reactor tube. In the case of low-boiling liquids, 4–6 μ l were injected at this stage through the serum cap into the platinum bowl. A voltage of 5 V was then applied to the platinum wire, causing it to glow.

As mentioned above, the time of pyrolysis had to be adjusted to the aggregation state of the sample as well as to the element which was to be determined. For the determination of halogen and sulphur in liquid organic compounds, a pyrolysis time of 10–15 sec was enough while for solid substances 20–30 sec were necessary. To determine nitrogen in liquids, a pyrolysis time of 50–60 sec was required and in solids 100–110 sec. This means that, whenever a full analysis is wanted, the long pyrolysis times have to be applied. After the completion of the pyrolysis, a test tube with 0.5 ml 10% sodium hydroxide was connected to the outlet tube of the reactor and the pyrolysis products swept through the alkaline solution by a stream of hydrogen. The solution was analyzed for sodium halides, sodium sulphide and sodium cyanide using mainly the procedure described by Widmark³.

When analyzing for H, 10–15 mg of sulphur was placed in the platinum bowl and, in the case of solid samples or not too fugitive liquids, mixed with about 5 mg of the substance. Low-boiling liquids (about 5 μ l) were injected into the bowl after flushing the reactor with nitrogen. A pyrolysis time of 20–30 sec was found to be adequate and the pyrolysis products were absorbed, as before, in a 10% solution of sodium hydroxide and the solution analyzed for sodium sulphide.

1. Smith, B. and Ohlson, R. *Acta Chem. Scand.* **14** (1960) 2245.
2. Feigl, F. and Jungreis, E. *Microchim. Acta* **1958** 812.
3. Widmark, G. *Acta Chem. Scand.* **7** (1953) 1395.

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Ozonolysis of Naphthoquinones

III. 1,2-Naphthoquinone

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In our previous papers in this series^{1,2} we have confined ourselves to the discussion of the ozonolysis of some 1,4-naphthoquinones. We wish now to report on certain aspects of the behaviour of 1,2-naphthoquinone under ozonolytic cleavage.

The quinone, in chloroform, absorbed ozone readily though not quantitatively and the ozonisation was terminated when 3 moles of the gas had been applied. At this point the dark colour of the solution had changed to a light yellowish green. If the initial quinone solution was saturated or if carbon tetrachloride was added, a faintly yellow substance separated during ozonisation. It contained active oxygen but decomposed explosively in a few seconds if isolated and dried. This product may be a true ozonide, but a closer examination of it was difficult due to its labile character. Immediately after the ozonisation the solution contained about 1.2 g atoms of active oxygen per mole of starting material.

Table 1 gives the identified reaction products together with the results from the quantitative determinations.

Table 1.

Product	% recovered carbon	moles/mole reacted quinone
Carbon monoxide	0.80	0.08
Carbon dioxide	11.50	1.14
Formaldehyde	0.75	0.075
Formic acid	7.30	0.73
Phthalaldehydic acid	61.50	0.77
Phthalic anhydride	15.50	0.19

The carbon oxides were evolved during ozonolysis as well as during hydrolysis of the reaction mixture, the phthalic anhydride was then usually recovered as phthalic acid. It will be noticed that more than 97%