Micro Detection of Some Elements in Organic Compounds by a Modified Emich's Method

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Bennett, Gould, Swift, and Niemann [1] have presented a system for the rapid detection of nitrogen, chlorine, bromine, iodine, arsenic, sulfur and phosphorus in a single 1 mg sample of an organic compound. The method is a development of Johns [2] modification of Emich's [3] test. In the analysis the sample is combusted in a small Pyrex tube with a mixture of calcium oxide and zinc, whereby nitrogen compounds evolve ammonia. The other elements are bound to the calcium oxide-zinc mixture. Water dissolves only the halides; hydrogen sulfide and arsine are then removed by addition of perchloric acid, and phosphate is detected in the residual perchloric acid solution.

During work on a modified Lassaigne method [4] certain substances were also tested by Emich's method [1]. Analysis by the two methods could be performed simultaneously which is found to be more advantageous than performing a double test by one method. A complete test for all the elements given in the scheme can, with use of a minimum of equipment, be performed in an hour and, due to some time consuming operations in both methods (centrifugation *etc.*), the time is not significantly increased when a Lassaigne's test is carried out simultaneously.

Analysis by the method of Bennett *et al.* is superior to earlier methods. The author has, however, noted some objections which suggest some changes in the analytical scheme. The four main points are:

1. In the combustion of some nitrogen compounds cyanide as well as ammonia is formed. The disturbing cyanide is dissolved by water but can be boiled off with sulfuric acid before the precipitation of the silver halides.

2. It is possible to detect simultaneously the presence of chlorine, bromine and iodine using an ammonia-lead(IV) oxide method [4].

3. The small sulfur content of the combustion material (of best qualities) often gives a false sulfur reaction especially when water-containing compounds are analysed.

4. The hydrogen sulfide and arsine are more distinctly separated when the evolved gases are taken up in a double layer gel tube impregnated with lead acetate and silver nitrate [4].
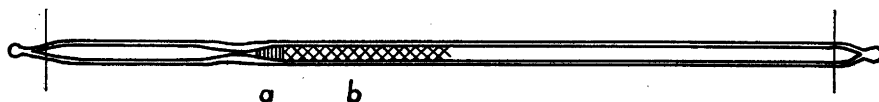
Fig. 1. (Scale 1 : 1). Sealed combustion tube (Corning pyrex) a) asbestos plug, b) calcium oxide — zinc mixture.

EXPERIMENTAL PART

Combustion and detection of nitrogen

A large number of sealed combustion tubes [1] (Fig. 1) can conveniently be prepared at one time and stored for future work. No change in activity has been noted after more than a year.

For the analysis both ends (only the tip of the short arm) are cut off. The sample (1 — 5 mg) is added. Liquids are drawn up by the packed $CaO-Zn$ column from a long capillary and solids are just shaken down through the tube. The long arm is sealed and the combustion can with some experience be carried out in an ordinary micro burner. The evolved gas is taken up upon a wet activated litmus * paper [1], which must be observed during the heating to detect the ammonia from difficultly combusted nitrogen compounds, as these colorations are of short duration.

Detection of halogen

After the combustion the long arm is opened, water [1] is added to obtain a 3 cm high column upon the combustion mixture. The tube is centrifuged — without sealing the short arm — in a test tube (75 × 10 mm). The short arm is washed with a few drops of water and adhering water is transferred to the test tube to give a total volume of about 1/4 ml. Three drops of sulfuric acid (1 : 3) are added and the liquid is boiled for 5 minutes to remove hydrogen cyanide. One drop of 0.5 M $AgNO_3$ precipitates the halides ** which can be separated by an ammonia-lead(IV) oxide method [4].

Detection of sulfur and arsenic

The wet calcium oxide-zinc mixture is pushed into the bottom of a test tube (75 × 10 mm) with a stainless wire. The tube is held horizontally and 3 drops of concentrated perchloric acid are placed in the middle of the tube. The acid must not touch the combustion mixture or the opening of the tube. The tube is closed with a rubber plug containing a two-layer gel tube [4]. The under layer is impregnated with lead acetate and the upper with silver nitrate. The tube is raised to mix the combustion mixture and the acid. After a minute the tube is heated for a few seconds in a flame. The gel tube is removed after a further two minutes. Hydrogen sulfide gives a black zone in the lead acetate layer. (Sensitivity: over all 10 μg S; gel tube 1 μg.) Arsine (and phosphine, only from trivalent or elementary phosphorus) gives a black zone with a yellow top in the silver nitrate layer. (Sensitivity: over all 5 μg As; gel tube 1 μg.)

Detection of phosphorus

The residue in the test tube is treated with a few drops of water. One drop of the solution is drawn up from a corner of a molybdate paper [1]. After drying, the paper is treated with benzidine and sodium acetate solutions. A blue spot with a stronger coloured edge indicates the presence of phosphate.

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* Ordinary red litmus is sufficient when the evolved ammonia is >10 μg N, taken as H_4NCl.

** Silver sulfate sometimes precipitates, but is dissolved by a few drops of water.

DISCUSSION AND RESULTS

Detection of nitrogen

In the analysis of the compounds tabulated in the earlier work [4] it was found that some nitrogen compounds gave litmus colours difficult to distinguish from stronger blanks (5 μl water or xylene). Examples of such compounds are: diphenylamine, p-diazobenzenesulfonic acid, phenylbenzoyldiazomethane, triazobenzene, 2,4-dimethyl-3,5-dicarbetoxypyrrole, 2-phenylindole, and kynurenic acid.

The amount of ammonia evolved in these cases was smaller than that from azobenzene, which according to Bennett et al.[1] is equal to 5—10 μg N as NH_4Cl. However, in no case, did the test fail completely, when activated papers were observed during the combustion. Test samples of over 5 mg should not be used as fumes of uncombusted material make it difficult to observe the litmus papers.

Brown and Hoffpaniere [5] report that triphenyl phosphate gives a false litmus reaction with Emich's test. In the present investigation triphenyl phosphate gave no litmus colour, and a negative Lassaigne test; the tricresyl phosphate used was contaminated with nitrogen compounds which were detected by both methods.

Detection of halogen

The aqueous extracts of the combustion mixture from the nitrogen compounds ($\sim$ 5 mg) given in Table 1 have been tested for cyanide. Each solution was boiled for 5 minutes with sulfuric acid in a test tube closed with an alkaline iron (II) sulfate paper [4]. The paper was then treated with dilute sulfuric acid to convert cyanide to Prussian blue which gave a blue spot on the paper. The

Table 1. Nitrogen compounds investigated for formation of cyanide. The Prussian blue reactions have been compared with reactions from sodium cyanide solutions of known strength.

n-Propylamine	20 μg CN	Phenylhydrazine	20 μg CN
Diethylamine	20	Azobenzene	1
Tetramethylammonium iodide	50	Methylorange	30
Aniline	5	Phenylbenzoyldiazomethane	0
vic-Xylidine	5	p-Diazobenzenesulfonic acid	10
Mesidine	5	Triazobenzene	40
Diphenylamine	0	Pyrrole	40
Triphenylamine	1	N-Phenylpyrrole	10
Bis-(2-aminothiazole)	50	2,4-Dimethyl-3,5-dicarb-	
Acetamide	40	ethoxypyrrole	0
Acetanilide	20	Indole	20
Chloropicrin	50	2-Phenylindole	0
Nitromethane	30	Imidazole	5
Nitrobenzene	0	Benzotriazole	0
Trinitrotoluene	40	2-Methylbenzothiazole	10
iso-Amylnitrite	10	Pyridine	0
Dimethylglyoxime	50	Nicotinic acid	30
Acetonitrile	50	a,a'-Dipyridyl	10
Benzonitrile	5	Quinoline	1
Phenyl-iso-thiocyanate	0	Acridine	0
Ethylthiocyanate	50	Uric acid	50
Dimethylketazine	30	Piperazine	10

spots of Prussian blue have been compared with spots obtained from sodium cyanide of known strength, giving a rough estimation of the amount of cyanide formed during the combustion. Amounts of cyanide less than 10 μg give no visible precipitate with AgNO$_3$ and are thus without practical importance. Different forms of combustion do not seem to influence the formation of cyanide.

Because of the disturbing formation of cyanide, the scheme of Bennett *et al.* for halogens has been changed. The proposed scheme is similar to the one used in the Lassaigne work. Nitric acid has also been used to acidify the solution prior to boiling off the hydrogen cyanide, but in this case iodine is also removed from the solution *.

The amount of precipitated silver halides from an Emich combustion with a given amount of halogen compound is smaller than from a Lassaigne test. The halides appear to be incompletely dissolved during the centrifugation and the combustion is incomplete. It sometimes happens that the silver precipitate is too small to be separated into its components.

Fluorine is not included in this system and attempts to extend the scheme to this element have been without success. Moreover, the chlorine in the inert, low-boiling fluorocompounds, *e. g.* freones, cannot always be detected.

Detection of sulfur

The detection of sulfur can be considered as the weakest point in this analytical method because of the occurrence of false sulfur reactions. The use of gel tubes [6] makes it possible to estimate the sulfur content roughly, thus reducing the number of false blanks. In a series of about 200 analyses there have been 26 false reactions. Of these 18 have been so weak ($< 10 \mu$g S) that it has been possible to distinguish them from real reactions. Of the remainder 4 were equivalent to 50 μg S.

It has not been possible to settle the cause of these reactions, but the small sulfur content of the glass seems to be the most likely source of sulfur. In blank tests there are more sulfur reactions when water is combusted than with xylene and there has been no distinct increase in sulfur reaction with increased amounts of zinc and calcium oxide. The calcium oxide is prepared by igniting oxalate, containing 0.001 % sulfate. Each tube therefore contains about 0.2 μg S which is below the sensitivity of the gel tube.

Detection of arsenic

The detection of arsine is simplified by the use of gel tubes. Even 1 μg As can be detected distinctly in the presence of hydrogen sulfide. With large amounts of sulfur ($> 200 \mu$g S) the whole PbAc$_2$ column is consumed and black Ag$_2$S is formed in the AgNO$_3$ layer. If the gel tube is removed before this occurs arsine can then be detected.

The 80-mesh zinc (Baker, lot 22 845) used in this investigation contains a little arsenic but no other disturbing elements, in contrast to "anal. pure"

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* The iodine can mostly be detected with the aid of a strip of starch paper inserted in the opening of the tube.

zinc dust which generally contains nitrogen and often chlorine. The blanks often form a small yellow zone ($<$ 1 μg As), and very occasionally a zone with a hardly visible black bottom (1 μg As). However, this causes no trouble as it is possible to estimate the amount of black arsine complex in the gel tube. The 40-mesh zinc, free from arsenic, is too coarse to be used.

On combustion of trivalent and elementary phosphorus, phosphides are formed which evolve phosphine on the addition of perchloric acid. Phosphine gives the same reaction as arsine, but is less sensitive. The blackened gel particles in the tube can then be analysed for arsenic by testing with sulfide [4].

Detection of phosphorus

The sensitivity of the phosphate test is very high ($<$ 1 μg) and in no case was phosphorus undetected. Even when elementary or tri-valent phosphorus is combusted there is still sufficient phosphate formed to be clearly indicated.

Of the arsenic compounds tested none has given a positive phosphate test and by use of properly prepared reagents the blanks are very weak in colour. Small amounts of silicate (from the glass) do not interfere as the blue spot from the silicate-molybdate-benzidine reaction is devoid of a sharp blue edge.

SUMMARY

The system presented by Bennett et al. for a rapid micro detection of As, Br, Cl, I, N, P, and S in organic compounds has been checked and some changes have been proposed. It is found that:

1) Disturbing cyanide is formed on combustion of some nitrogen compounds. The cyanide can be boiled off before the precipitation of the silver halides.

2) The simultaneous presence of Cl, Br, and I can be detected using an NH_3-PbO_2-method.

3) False sulfur reactions are often obtained.

4) H_2S and AsH_3 are more distinctly separated when taken up in a double layer gel tube impregnated with $PbAc_2$ and $AgNO_3$.

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