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A Review of Techniques in the Lassaigne Sodium-Fusion

The sodium-fusion test forms an essential part of most qualitative organic analyses since it represents a rapid method for the detection of the presence of various elements in the substance tested. The elements usually tested for are nitrogen, sulfur, and the halogens—others being tested for usually only if their presence is suspected from other evidence.

Since its original use by Lassaigne in 1843 (1, 2) and subsequent modification by Jacobsen in 1879 (3), in which sodium replaced potassium as the active reagent, the test has altered very little, and basically is still in use today.

However, despite the fact that in essence this is a very simple test, and quantitative work has proved its sensitivity (4), poor results are often obtained by students at the bench. This fairly general lack of dexterity in using this test is also aggravated by the fact that most texts on practical organic chemistry present details of only two, or perhaps three, of the possible techniques of applying this test, it usually being true that under different circumstances different techniques yield the best results. Thus, the present article is intended to collect together the available methods with some indication of the most suitable circumstances in which each one may be best applied.

It should be noted that although alternative methods of detecting elements in organic compounds have been developed, such as Middleton's test (5–7) and a recent ignition method using oxygen developed by D. C. Ayres (8), these will not be dealt with in this article. A review article dealing with the history and some uses of the Lassaigne test entitled "A Lost Century, Lassaigne's Test for Nitrogen" was published by Tucker in 1943 (9).

Fusion of Sodium and Organic Compound

In all the techniques to be described for fusing metallic sodium with an organic compound, it is generally best to commence with very gentle heating, a point often not sufficiently stressed in the textbooks. After any reaction has begun, the ignition tube should be removed from the Bunsen flame until the reaction has almost ceased, when further heat may be applied. The extent of heating should be gradually increased until no further change appears to be taking place in the ignition tube. The tube should then be raised to red-heat for a few moments to complete reaction and to volatilize any unreacted organic material. The red-hot tube is then plunged into a boiling-tube, beaker, or evaporating basin containing water, care being taken to shield the mouth of the vessel with a wire gauze. Boiling of the water-extract is often advised in textbooks but appears unnecessary although the filtering of

hot solutions is generally faster than for cold solutions.

Methods of Fusion

1) The most common method is to place the organic sample and sodium at the bottom of an ignition tube and then to bring about reaction by gentle warming (5, 6, 10–12).

This technique has the advantage that it allows observation of whether the compound has "active-hydrogen" since, if easily replaceable hydrogen is present, direct reaction with sodium occurs in the cold.

The major disadvantage is that with very volatile materials, the organic substance may very easily be lost from the ignition tube before reaction with sodium can occur.

This still remains the most usual technique used.

2) A simple modification of (1) in which the sample and sodium are warmed in the ignition tube on a micro burner only to the extent of allowing the organic material to gently reflux within the tube.

When reaction begins the tube is removed from the burner and the reaction is allowed to subside.

This method is applicable to volatile materials or those which are rather inert. However, for volatile materials very great care is required and other more certain methods are available.

These methods will now be considered.

3) The organic sample and sodium are placed in the bottom of an ignition tube and covered by anhydrous sodium carbonate to approximately half-fill the tube. More sodium is placed on top of the sodium carbonate topped by a little more sodium carbonate. The contents of the tube is tamped down and this is heated over a macro-burner beginning at the *top* of the tube and working down. In this method, the sodium carbonate tends to hold the sample in contact with the sodium long enough for reaction to occur. The sodium half-way up the tube acts as a "scavenger" taking up any vapors of unreacted sample that may permeate up through the layer of sodium carbonate.

A variation of this method is to replace the sodium carbonate by glass-wool (10).

4) The organic sample is placed at the bottom of the tube and a piece of sodium placed about a quarter of the way from the top of the tube. The sodium is then heated over a micro-burner until it melts and the bead of molten sodium is allowed to roll down the inside wall of the ignition tube onto the sample at the bottom. The heat contained in the molten sodium is generally enough to cause reaction but if reaction does not occur, the method (2) above may be applied to the contents of the tube.

5) In another method, the sample and sodium are arranged in the ignition tube as in (4). The sodium is

then gently heated, with the tube held almost horizontally, and the vapors from the sample are allowed to pass over the piece of heated sodium (*13*).

6) A final method is to place the sodium only in the bottom of the ignition-tube and then to gently heat it until the sodium melts. Small quantities of organic material are then added and heating continued after cessation of any initial reaction (*6, 7, 14*).

The main advantage of this method is that a fairly large quantity of sample can be added (it is easy to estimate visually how much sodium remains) thus giving a fairly high concentration of nitrogen, etc., if present, with subsequent ease of detection.

The main disadvantage of the method is that with liquids cracking of the tube can occur.

Note. It appears that, particularly for highly substituted nitro-compounds with a low carbon content, better results are obtained by leaving a little liquid paraffin or solvent naphtha (in which sodium is stored) on the sodium and this supplies sufficient carbon to form a reasonable concentration of cyanide ions (*15*).

Notes on Testing for Nitrogen and Halogen

The test for sulfur with sodium nitroprusside is not dealt with since this is a very sensitive test and seldom leads to erroneous results—unless solutions become contaminated with sulfur in which case a positive result is obtained when sulfur is in fact absent!

Test for Nitrogen

This usually involves boiling an alkaline sample of the water-extract from the sodium fusion with ferrous sulfate and then cooling and acidifying with dilute sulfuric acid. The development of a blue coloration or a dark blue precipitate is confirmatory for nitrogen.

It seems that the development of a blue coloration and/or precipitate in a positive test depends on pH and on temperature. With pH only just below 7, the development of coloration is inhibited. It is, thus, necessary to ensure the presence of an excess of acid. Similarly, cooling of the solution is advisable because development of the blue coloration appears to be inhibited in hot solutions.

Test for Halogen

This is straightforward if sulfur and nitrogen are absent but even so should cause little difficulty when either or both are present in solutions. It must be remembered that the solution should always be acidified with nitric acid and if method (3) has been used, the solution must be boiled with excess nitric acid to ensure complete destruction of sodium carbonate.

The chief difficulty arises when cyanide or sulfide ions are present and these are removed by boiling in acid solution. The problem is that the use of too vigorous conditions also tends to remove any halide ions present. Thus, to avoid loss of halide ions, acidification should be with DILUTE nitric acid and the solution boiled to approximately half its original volume. The use of concentrated nitric acid should be avoided.

Note. If a good result is obtained for nitrogen, this indicates a thorough fusion and the presence of a high concentration of cyanide ions. Thus, if halide ions are also present it may be expected that a high concentration of halide ions will be present and with silver nitrate a dense precipitate of silver halide will be obtained. If only a faint halide test is obtained, removal of the interfering ions should be repeated, first under milder conditions (e.g., boiling for a shorter period of time or use of weaker acid) and then under stronger conditions (e.g., boiling the solution to a smaller volume or use of more concentrated acid). The results should indicate whether the faint precipitate with silver nitrate resulted from cyanide ions that had not been destroyed or from halide ions.

Conclusions

This article is based on difficulties experienced by the authors when using Lassaigne's test. The methods described above have been tried and are generally found to work under the circumstances indicated but any particular preference for certain methods is a matter for each operator to decide for himself.

Acknowledgment

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