CHROM. 3574

DETERMINATION OF VERY SMALL AMOUNTS OF NITROGEN IN ORGANIC SUBSTANCES BY MEANS OF GAS CHROMATOGRAPHY REACTION TECHNIQUES

JAROSLAV FRANC, BOHUMIL TRTÍK AND KAREL PLAČEK

Research Institute of Organic Syntheses, Pardubice-Rybitví (Czechoslovakia)

(Received March 8th, 1968)

SUMMARY

A method was worked out for the determination of small amounts of nitrogen in organic substances (0.1 to 0.005%), operating to a precision of $S = \pm 7.3\%$, using a Kjeldahl digestion combined with reaction gas chromatography. Ammonium sulphate formed from the original nitrogen is decomposed in boiling sulphuric acid on platinum black to elementary nitrogen, which is determined by gas chromatography.

INTRODUCTION

The determination of nitrogen in organic substances is one of the most important assays in organic analysis. A great deal has been written in the literature about the classical methods, *e.g.* the Dumas or Kjeldahl methods, and it can be stated that these methods have been studied in great detail and that their application is generally subject to no difficulties. The difficulties only start when the nitrogen content in the sample decreases to values in the vicinity of 0.1%. With the Dumas method the determination is inaccurate, since the blank experiment value is generally greater than the volume of nitrogen liberated from the organic substance. This also applies to the Kjeldahl method. In the latter case, the use of large amounts of sodium hydroxide for neutralisation of the digestion mixture introduces large quantities of nitrogen, which are present as an impurity in the hydroxide, into the reaction mixture; thus the blank experiment value is again greater than the amount of nitrogen present in the sample being analysed. Similar difficulties pertain to all colorimetric methods, *e.g.* the Nessler or the indophenol methods. In both cases, neutralisation with hydroxide is essential; this is a cause of foreign nitrogen being introduced into the mixture.

The only possibility of obtaining reliable results is to work in a way which avoids these drawbacks. We have succeeded in applying the ZINNEKE method[1] in combination with gas chromatography. This method is based on the fact, that ammonium sulphate evolves elementary nitrogen in boiling sulphuric acid in the presence of platinum black. Therefore, we have combined in our method Kjeldahl's technique of digesting organic substances with the decomposition of the ammonium sulphate formed, as described by ZINNEKE, the evolved nitrogen being determined by gas chromatographic

techniques. In this way, a nitrogen content varying in the range of 0.1 to 0.005% may be determined very easily.

The determination of nitrogen in organic substances has been discussed in three papers[2-4]; in all three cases, however, the nitrogen concentrations in the sample are greater than with our method.

EXPERIMENTAL

Kjeldahl digestion

Four grammes of the sample, are weighed into a 250 ml Kjeldahl flask, and 2 g anhydrous cupric sulphate, 10 g potassium sulphate, 10 ml water and 30 ml conc. sulphuric acid are added. The mixture is heated gently at first for about 10 min, then more strongly for 2–4 h until the solution is clear. At the end of the digestion process, 20–30 ml conc. sulphuric acid are added as required. The mixture is then allowed to cool, and 5 ml water and 5 ml hydrogen peroxide are added. The mixture is heated again until white fumes start to appear. At this point the digestion process is complete, and the mixture may be transferred quantitatively into a 25 ml volumetric flask.

Calibration with ammonium sulphate

A standard amount of ammonium sulphate is digested in the same way and for the same time as above, in order to obtain a correction value for any possible losses in the digestion process. For the calibration, either 0.00705 g ammonium sulphate are weighed into 25 ml conc. sulphuric acid, or more generally a four-fold amount, in order to be able to use the standard for several analyses performed at the same time.

Reagent blank

The blank experiment is carried out in the same way (without the sample or ammonium sulphate).

Preparation of platinum black

Platinum black is precipitated on a platinum grid of suitable size (small enough to be placed in the reactor described below). Precipitation is carried out by electrolysis of a 2% hexachloroplatinic (IV) acid solution, which has been allowed to stand for some time and then filtered. The negative pole of a 4 V battery is connected to the platinum grid. The precipitation process takes roughly 10 minutes. The platinum grid is then thoroughly washed with distilled water. The precipitated Pt-black must actually be black, not grey as otherwise the reaction does not proceed readily. A platinum grid prepared in this way lasts for roughly twenty experiments.

Glass reactor

The sample digest is decomposed in a glass reactor (Fig. 1). The volume of the reactor is slightly more than 1 ml, such that a volume of 1 ml makes the liquid level reach just below the side tube on which the syringe is fitted. The reactor is connected by means of a ground joint with a valve connected with the needle of a syringe; this is used for sample transfer into the chromatographic column. The reactor is heated by

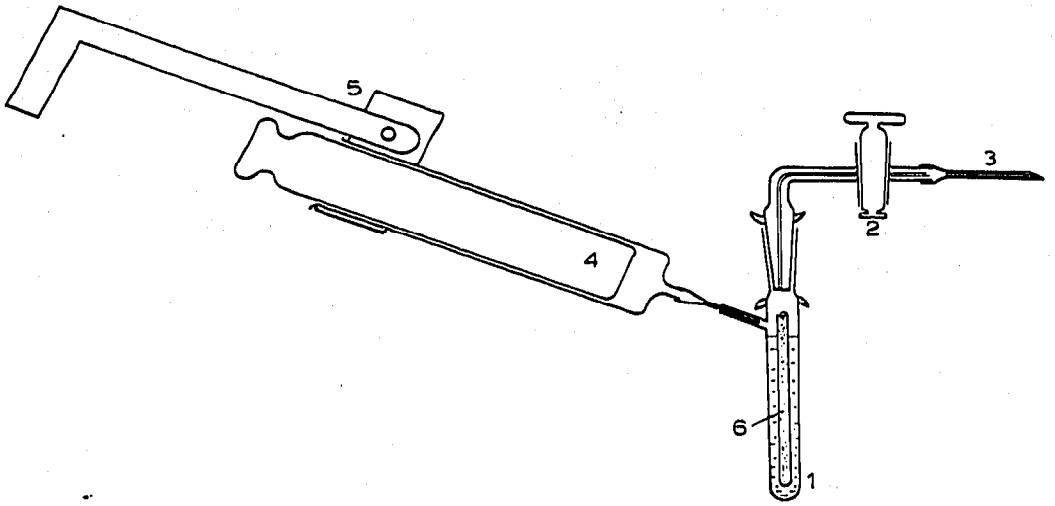

Fig. 1. Glass reactor. 1 = Glass reactor; 2 = glass valve; 3 = syringe needle; 4 = syringe, 20 ml volume; 5 = stop of the syringe piston; 6 = platinum grid with precipitated platinum black.

means of a brass block which can be heated up to 350° and which is placed on a movable support, permitting the reactor to be freely moved in and out of the heating block.

The reactor is attached to a 20 ml all-glass syringe which is fitted with a device which ensures that the syringe piston is not pushed out by overpressure of the carrier gas.

Gas chromatograph

The gas chromatograph is very simple and is shown diagrammatically in Fig. 2.

The pressure bottle (1) serves as a source of carrier gas (hydrogen), the flow-rate of which is controlled by the valve (2) being kept constant by the manostat (3), formed by four capillaries of 0.5 mm I.D. and 4 m total length. The carrier gas is first led to the comparison cell of the heat-conductivity detector (4) then through the glass valve (5) into the chromatographic column (12), which is 140 cm in length, 4 mm I.D. and is filled with molecular sieve 5 A. A tube (11) of the same diameter and 5 cm long, filled with sodium asbestos is fitted in front of the chromatographic column. The carrier gas goes from the column outlet through the measuring cell of the heat-conductivity detector 4 and the flow-rate meter (13). The top of the chromatographic column is fitted with a penicillin bottle-stopper through which a syringe needle passes; this is used to introduce the decomposition products from the reactor (7). The reactor is

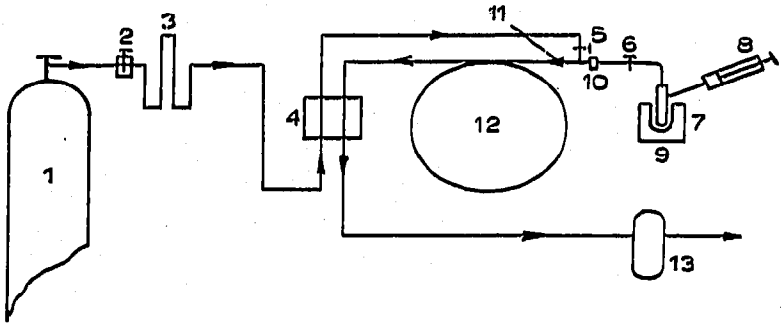

Fig. 2. Diagramatic drawing of the gas chromatograph connected to the decomposition unit. For explanations, see text.

separated from the column by the glass valve (6). On one side of the reactor, an all-glass syringe lubricated with silicone oil (8) is fitted. The entire reactor is heated by the brass block (9) which in turn is heated by electric current.

A recorder with a sensitivity of 0 to 0.1 mV (Laboratorní přístroje Model EZ-2) is connected to the detector.

The chromatographic column operates at room temperature; the same applies to the detector, so that no special thermostat is required. The hydrogen flow-rate is set at 3 l/h, the detector current is 150 mA.

Nitrogen determination

One ml of the Kjeldahl digest is taken from the 25 ml flask and introduced into the glass reactor. Since the digest is usually viscous, a 1 ml volume is first marked on the reactor. It is sometimes necessary to heat the sample slightly in order to decrease its viscosity. The platinum-black covered platinum grid is then placed in the reactor and air bubbles adhering to the grid are removed by gently tapping the grid. The reactor is then closed and connected to the chromatographic column. With valves (5) and (6) open, the reactor which still contains air is flushed with hydrogen by allowing the hydrogen pressure to move the syringe piston into the extreme position and then the entire contents of the syringe are evacuated into the column by pressing down the piston. After several seconds, the process is repeated. After some 15 repetitions the degree to which the reactor is free of nitrogen can be measured on the recorder.

When the nitrogen content has reached an acceptably low value, valve (6) is closed, heating block (9) is moved toward the reactor, which is then heated for some 20 min and its contents are boiled gently (*i.e.* a temperature of roughly 330°). After this time, valve (6) is opened and the syringe piston is allowed to rise to the 10 ml mark, valve (5) is closed, the piston is pressed down, valve (6) is closed and valve (5) is opened. The recorder records a chromatogram on which nitrogen is separated from all other gases which may be present. The area of the chromatographic peaks is then measured.

The values of the blank experiment and of the ammonium sulphate standard are determined in the same way.

Calculations

Nitrogen content values are determined from the formula

$$\% \, N = \frac{A \cdot 530.9 \cdot P_n}{B \cdot P_{st} \cdot C}$$

where A = weight of standard ammonium sulphate sample (g)
B = volume of ammonium sulphate standard solution (ml)
C = sample weight in 25 ml
P_n = area of chromatographic peak of the sample
P_{st} = area of chromatographic peak of the standard
(the blank experiment value must obviously be subtracted from the P_n and P_{st} areas).

RESULTS AND DISCUSSION

As already stated in the introduction, the method described may be used to determine nitrogen concentrations varying from 0.1 to 0.005 %. The determination of these low nitrogen amounts is possible for two reasons. Firstly, as stated in the introduction, no other reagents are used and therefore no foreign nitrogen is introduced in the form of nitrogen-containing impurities. The second reason consists in the relatively high sensitivity of the gas chromatography apparatus described. On the one hand, this involves the use of hydrogen as carrier gas together with heat-conductivity detection, and the other a highly sensitive recorder (0–0.1 mV). With this arrangement, a full recorder deflection is already obtained with 0.05 ml N_2, *i.e.* roughly 0.06 mg N_2.

Since a micromethod is involved, some degree of experience and careful work are needed. There are several important circumstances which ought to be mentioned.

First of all it is essential to decompose the ammonium sulphate at the prescribed temperature, *i.e.* in gently boiling sulphuric acid. At lower temperatures the decomposition process is not quantitative.

On introducing the platinum grid into the reactor, all air bubbles must be removed by careful tapping. Although oxygen is separated from nitrogen in a chromatographic column filled with molecular sieve, and since the ratio of the gases in air is known, the respective amount can be subtracted, it is preferable to have as little air as possible in the apparatus. The fact that oxygen is separated from nitrogen in the column is another advantage of the method, as it is not always known with sufficient accuracy, how much air has penetrated into the reaction space, *i.e.* the blank experiment value corresponding to each analysis is obtained automatically.

As mentioned in the experimental part, a tube containing sodium asbestos is placed between the reactor and the column. This serves to capture aerosol drops of sulphuric acid or small amounts of sulphur dioxide which would very rapidly decrease the resolution capacity of the column filling to a substantial degree.

During the Kjeldahl digestion, a large amount of sulphur dioxide is generally formed, some of which could remain dissolved in the acid and be liberated in the reactor. Therefore, this sulphur dioxide is oxidised to trioxide at the end of the digestion process with hydrogen peroxide. There is, however, another reason for removing sulphur dioxide. When sulphur dioxide is liberated in the reactor, it passes into the syringe and raises the piston to a different position each time. For an accurate determination it is essential that the piston is always in exactly the same position each time before the nitrogen liberated is released into the column, otherwise the results are non-reproducible because differing amounts of nitrogen remain in the free spaces.

With regard to the Kjeldahl digestion, it cannot be done with selenium as catalyst. ZINNEKE[1] states that the presence of selenium interferes with the catalytic decomposition of ammonium sulphate on platinum black. Obviously, the method can only be used to determine nitrogen in those compounds which can be converted to ammonium sulphate by a Kjeldahl digestion.

In conclusion, it must be mentioned, that the method described can also be used for the determination of larger amounts of nitrogen, although we believe that in such cases the simple Kjeldahl method is handier. The above method is useful, however, in those cases where only small sample amounts are available.

The main field of application of this method will be found in those cases where

an organic non-nitrogenous substance contains nitrogenous impurities and where highly accurate determinations are required. The method is very precise, the deviation statistically determined being $S = \pm 7.3\%$ for the 0.1 to 0.01% N range.

Naturally, the entire apparatus can be used with no modification whatever for trace analysis of the most variegated impurities, as long as these can be converted to gaseous products.

REFERENCES

1 F. ZINNEKE, *Angew. Chem.*, 64 (1952) 220.
2 B. A. STEWART, L. K. PORTER AND W. E. BEARD, *Anal. Chem.*, 35 (1963) 1331.
3 M. COULSON, *J. Gas Chromatog.*, 5 (1966) 285.
4 R. D. MARTIN, *Anal. Chem.*, 38 (1966) 1209.