

FURTHER DEVELOPMENT OF THE FLASK METHOD  
IN QUANTITATIVE ORGANIC MICRO-ANALYSIS (\*)

W. SCHÖNIGER

MICROANALYTICAL DEPARTMENT, SANDOZ LTD., BASLE, SWITZERLAND



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In order to determine the elements present in an organic substance, the latter must be destroyed and converted into simple inorganic compounds which can readily be estimated. This conversion can be achieved in various ways. If oxidative methods are employed, the substance may be burnt in a stream of oxygen, or decomposed with the aid of an oxygen donor (e.g. « sodium peroxide or nitric acid »). However, many of the processes require more or less complicated apparatus, and unfortunately such apparatus has, if anything, become still more complex during the last ten years. The present article describes a very simple combustion technique which was developed more than half a century ago, but had until recently been completely overlooked.

Prompted by Berthelot's experiments on the determination of sulphur in organic substances by combustion in the calorimetric bomb, Hempel (1) (Fig. n. 1) in 1892 devised a simple method for estimating the sulphur content of coal. The sample for analysis was pressed into a tablet around a fine platinum wire, and the tablet was placed in a platinum basket. The fine platinum wire was attached to two leads which passed through a rubber stopper. The basket was suspended from the stopper in a 10-litre bottle filled with oxygen and containing an absorbent solution. The sample was ignited electrically, and after absorption the sulphur content was determined gravimetrically. At almost the same time, Meslans (2) published a similar method for the determination of fluorine in combustible gases. Instead of a 10-litre bottle, he employed a 500-ml. flask provided with

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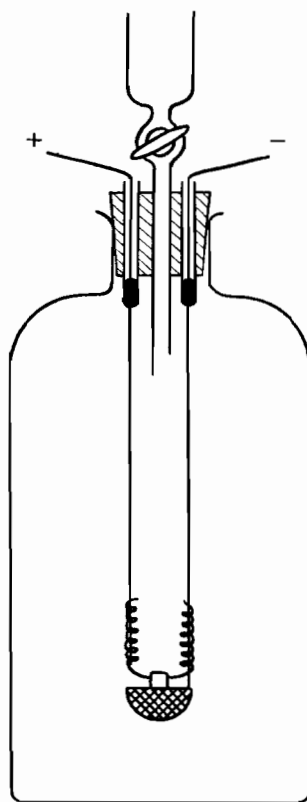


Fig. n. 1

a stopper with three holes. Through one of the holes was passed a tube with a platinum capillary sealed to its lower end. This served as the inlet tube for the combustible gas. The other two holes were for platinum wires which were connected inside the flask by a spiral of fine platinum wire. The spiral was electrically heated and passed in front of the capillary. The gas for analysis was led into the flask from a gas burette and was burnt in oxygen. The fluorine was determined either volumetrically by back-titration of excess alkaline absorbent solution, or gravimetrically as calcium fluoride.

In the years that followed, a few attempts were made to adapt Hempel's method of combustion in a closed chamber for the analysis of organic compounds and to win recognition for the method in organic elementary analysis. Thus, prior to the first World War, Graefe (3), Marcusson and Döschner (4) published papers which described sulphur determinations on organic substances by com-

bustion in a bottle. Both papers described a simplified method of mounting the sample and both indicated that it was also possible to determine chlorine by this technique. Early in the nineteen-twenties V o t o ě k (5) conducted a few studies on the use of this method for the determination of chlorine. He replaced the bottle which the other authors recommended for the combustion by a 5-litre separating funnel (Fig. n. 2), since this permitted easier quantitative recovery of the absorbent solution. For the subsequent determination of the chloride, he employed mercuric nitrate and sodium nitroprusside as indicator. Thereafter, this method was completely forgotten probably because it was overshadowed by the introduction of P r e g l ' s methods.

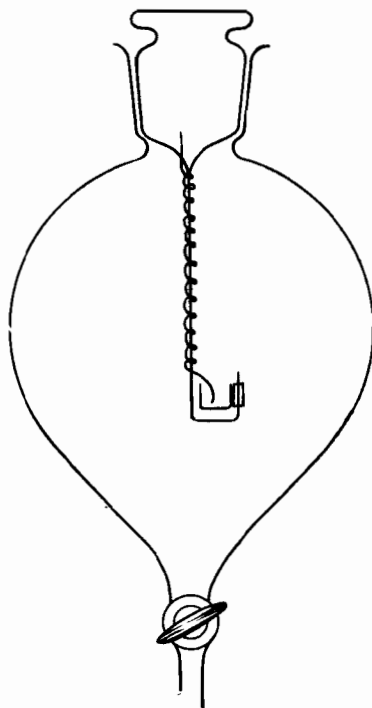


Fig. n. 2

At the First International Micro-chemical Congress held in Graz in 1950, R o t h (6) reported a method for the estimation of traces of sulphur. This can also be regarded as a flask method of combustion. The sample was weighed out in a porcelain crucible, mixed with Eschka-mixture and ignited with a strip of filter paper, impregnated

with potassium nitrate in a 2-litre bottle filled with oxygen. The subsequent colorimetric determination of the sulphur after combustion was effected outside the bottle.

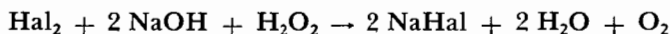
Shortly afterwards Mikl and Pech (7, 8) described a simple method for estimation of chlorine and sulphur in organic compounds which was likewise based on the combustion of a sample in a closed vessel: approx. 0.1 g substance was wrapped in a filter paper, the packet was moistened and attached to a glass rod which had a hole in its lower end for the purpose. The glass rod was inserted into a rubber bung which fitted the neck of a 1-litre bottle. The absorbent solution was introduced into the bottle. The bottle was filled with oxygen, the filter paper was lighted and the bung was inserted so that the substance burnt in the flask. Although Pech (9) reported that the technique was suitable for routine factory analysis only but not for research work, the published papers by Mikl and Pech prompted the development of a micromethod for the determination of halogen and sulphur compounds (10, 11). It was apparent from these preliminary investigations that the combustion principle might lend itself to the determination of other elements, and since then large numbers of papers have appeared which have fully confirmed that this is the case.

The combustion « apparatus » is incredibly simple. Moreover, combustion in a flask has additional advantages: the solution which is used for the final determination is practically free from foreign ions, and the method is thus particularly valuable for the determination of elements in trace amounts; in many cases the final determination can be carried out in the flask. Furthermore, the analyst is not restricted in his choice of method for the final determination; he can choose a procedure to which he is accustomed. Another important feature of the method is that it is ideal for serial analysis and thus a great asset for laboratories which are concerned with routine analysis.

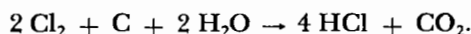
The next pages will give a more detailed review, element by element, of publications that have appeared in recent years.

#### HALOGEN DETERMINATION

All papers that have so far appeared, recommend the use of an absorbent solution containing alkali hydroxide and hydrogen peroxide for determination of halogen as halide. The halogen which is released in elementary form during combustion must be reduced before the final determination:

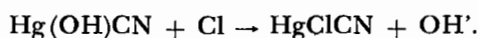


CORNER (12) who estimated chloride absorbed in water by electrometric titration with silver nitrate solution, adds carbon black to the absorbent solution, since according to GIBBS (13), chlorine reacts with water at room temperature in the presence of carbon to give hydrochloric acid:



A) For the *determination of chlorine or bromine*, the following titration methods have been proposed:

1) Mercuric oxycyanide method: the absorbent solution is neutralized, neutral mercuric oxycyanide is added and the equivalent amount of OH' is titrated (14):



2) Argentometric determination in neutral 80% isopropanol solution containing dichlorofluorescein (15) or in aqueous acetone with dithizon as indicator (16).

One group of workers (17) recommends the use of variamine blue B, which gives a blue coloration with the Ag ion as indicator.

LEHNER (56) employs a potentiometric method for determining traces of chlorine and makes use of a special combustion flask which has the advantage that only 2 ml of absorbent solution need be used.

3) Mercurimetric determination: standard mercuric nitrate or mercuric perchlorate solution can be used for the determination (18, 18a, 19). The mercuric reagent diphenylcarbazone is utilized as indicator and the pH must be accurately adjusted to within 2.5-3.5. The addition of water-miscible organic solvents, such as methanol, ethanol or isopropanol intensifies the coloration with the indicator and suppresses the dissociation of the mercuric halide which is in any case very slight.

4) Lastly, mention should be made of a colorimetric method for determining chloride, which has recently been described (20). The sample is burnt and after absorption, mercuric chloranilate (dissolved in 50% methylcellosolve) is added. In the reaction that ensues, the chloride ion liberates an equivalent amount of free chloranilic acid which can be colorimetrically determined by measurement at 2 wavelengths (530 or 305 m $\mu$ ).

5) For the *determination of bromine*, KOLTHOFF'S method (11) gives good results. The bromide is oxidized to bromate with hypochlorite and the bromate is then titrated with iodometrically.

B) *Iodine determination* (20 a). All but one group of workers recommend Leipert's method whereby the iodine is oxidized to iodate with bromine, excess bromine is removed, iodide is added and the iodine liberated is titrated with thiosulphate.

Erdey and co-workers (17) prefer an argentimetric method, using variamine blue R, as indicator (see above). However, the absorbent solution must be acidified with acetic acid, and the hypiodite and iodate that form must be reduced to iodide by addition of magnesium before titration.

C) *Determination of fluorine*: the latest investigations have shown that it is essential to add approx. 20 mg of sodium peroxide to the substance prior to combustion (21, 22). Belcher and co-workers (23) recommend the addition of approx. 1 mg of potassium chlorate instead of sodium peroxide. These additives are especially necessary for analysis of perfluorinated compounds, since without them  $\text{CF}_4$  can still be detected in the gaseous atmosphere of the flask after combustion (24).

The first method adopted for determination of fluoride ion was the titration method recommended by Brunisholz and Michod (25), using as indicator a solution of trivalent cerium with murexide. The suitability of this method was confirmed by Wallenfels and Draber (26), by Goldstein (27) and others.

Steyermark and co-workers (22) recommend a volumetric method using thorium nitrate with sodium alizarinsulphonate as indicator, the end point being determined photometrically. If mercury, phosphorus or arsenic is present in the compound, perchloric acid must be added and the solution distilled prior to titration (Ma and Gwirtzman (28)).

Senkowsky and co-workers (21) have proposed a colorimetric method of determination with the aid of zirkonyl eriochrome cyanin R complex, while Rogers and Yasuda (29) employ ferric salicylate as reagent. Both methods are based on the bleaching of a coloration by the fluoride ion. Hence, other anions which react similarly will interfere.

A short time ago, Belcher and co-workers (23) discovered a positive colour reaction for fluoride and are employing it for the colorimetric determination. According to these authors, the red chelate formed by trivalent cerium with alizarin complexon gives a blue complex in the presence of fluoride ion. The blue coloration, within certain limits of concentration, is proportional to the fluoride concen-

tration. They recommend these methods for ultramicro determinations.

(For further details, the reader is reverted to a review of methods for the determination of fluorine (30)).

#### DETERMINATION OF SULPHUR

The products of combustion are absorbed either in water to which perhydrol has been added or in a solution of alkali.

The most elegant method for the subsequent determination of sulphate and the one that is most frequently employed is that of Fritz and Yamamura (31) and Wagner (32). The sulphate is titrated with a standard solution of barium perchlorate in 80% isopropanol with « thorine » (disodium salt of 2-(2-hydroxy-3,6-disulpho-1-naphthylazo)-phenylarsonic acid) as indicator. The use of a special combustion flask permits the determination of traces of sulphur by this method (56).

Other methods that have been recommended are: acidimetric titration (11) (only applicable in the absence of interfering elements) and gravimetric determination with barium sulphate (33), amperometric determination with barium chloride (34) or lead nitrate (35), complexometric determination according to Schwarzenbach and co-workers (36), precipitation with barium sulphonate and subsequent photometric determination with EDTA (37), and colorimetric determination after a colour reaction with barium chloranilate (38).

#### SIMULTANEOUS DETERMINATION OF HALOGEN AND SULPHUR

Boëtius and co-workers (39) have devised a method for determining the sulphur and halogen content from a single sample. The sample is burnt and the sulphate in the absorption solution is titrated with a standard solution of barium nitrate using sodium alizarinsulphonate as indicator. Chloride or bromide is then determined by Volhard's method. If sulphur and iodine are present, the latter can be determined by Leipert's method, after determination of the sulphur as described above; under the given conditions no precipitation of barium iodate occurs.

The argentimetric method for determination of halide with the aid of variamine blue R as indicator (17) can be employed after the sulphate ion concentration has been determined according to Fritz and Yamamura (31) and Wagner (32), the only stipulation being that the solution must be boiled after titration to remove the isopropanol.



## DETERMINATION OF PHOSPHORUS

Numerous authors (40-42) have proposed colorimetric methods for determination of the phosphate produced, using the well-known molybdenum blue reaction. Dilute nitric acid, or better sulphuric acid, is employed as the absorption solution. At the ignition temperature pyro- and metaphosphate are formed along with orthophosphate and must be converted to the ortho form by acid hydrolysis.

Merz (42) claims that chlorine or bromine and phosphorus can be determined at the same time in aliquots of the absorption solution. If the phosphomolybdic acid is extracted with amyl alcohol/ether before reduction, Gubser (43) claims that as little as 0.0004 per cent phosphorus can be estimated in 50 mg of substance.

Belcher and Macdonald (44) have suggested a method whereby the combustion products are absorbed in sodium hypobromite. The phosphate is precipitated from hot solution with quinoline molybdate, the precipitate is filtered off and dissolved in excess alkaline solution and the phosphorus is estimated by back-titration with hydrochloric acid. Interference by  $\text{SiO}_2$  dissolved from the glass can be avoided by adding a little citric acid to the absorption solution before the precipitation. If the substance contains fluorine as well as phosphorus, boric acid must also be added to the solution.

Fleischer and co-workers (40) recommend the precipitation of the phosphate with magnesia mixture for semimicro work. The precipitate is filtered off, dissolved in hydrochloric acid and mixed with the excess standard EDTA-solution, the excess being back-titrated with magnesium chloride.

According to Bennewitz and Tänzer (45), there is no need to precipitate and dissolve the phosphate if the following procedure is adopted: absorption and hydrolysis are performed in the usual way, the solution is adjusted to pH 10, eriochrome black T is added and the solution is then titrated with standard magnesium chloride solution to the appearance of a red colour. An excess of magnesium chloride is added, the solution is mixed with an equal volume of ethanol and the magnesium chloride is back-titrated with EDTA.

A very simple and rapid method has been described by Püschel and Wittmann (45 a). In their method, water is used as absorption solution and the contents of the flask are boiled gently for 10 minutes. Hexamethylene-tetra-amine is added and the solution is titrated with a standard solution of trivalent cerium at boiling point with eriochrome black T as indicator.

## OTHER ELEMENTS

Götte and co-workers (46) determine  $^{14}\text{C}$  in the usual way after precipitation as barium carbonate.

Southworth et al. (47) have published a procedure for the amperometric titration of mercury with EDTA following combustion in the flask.

Belcher and his associates (48) determine various metals, such as Zn, Mg and Cd, in the absorption solution by titration with EDTA and they confirm that organic substances containing boron can be completely combusted in the flask. The boron is then determined in the usual way by the mannitol titration. (See also 12,49).

According to Merz (50), arsenic can be determined colorimetrically in organic compounds by conversion to arsenic molybdenum blue. The products of combustion are absorbed in dilute iodine solution which oxidizes trivalent arsenic to pentavalent arsenic. The arsenic is then reacted with molybdenic acid and the arsenic molybdenic acid formed is reduced to arsenic molybdenum blue with hydrazine sulphate.

Gubser (43) determines as little as 0.002 per cent selenium in 50 mg substance using a colorimetric method.

Experiments on the estimation of carbon have been reported by Juvet and Chiu (50a). The substance is weighed out on glass fibre « paper » and electrically combusted. The  $\text{CO}_2$  formed is absorbed in alkaline solution and determined volumetrically. According to these authors, substances containing nitrogen, sulphur, boron and alkali can also be successfully analysed by this method.

## SPECIAL DETERMINATIONS

Barney II and co-workers (51) determine the phosphorus content of lubricating oils by flask combustion and state that the method is as accurate as the official ASTM procedure. Langecker (52) uses flask combustion to determine the iodine content of biological fluids containing contrast media, e.g. urine and bile. The use of flask combustion for official pharmacopoeal methods for the determination of substances containing iodine has been studied by Johnson and Vickers (53) who conclude that the technique is suitable for this purpose. Lisk (54) has described the use of the flask combustion technique for estimating residual chlorine-containing insecticides on animal feeding stuffs.

## GENERAL

After this short review of all the papers describing applications of

the flask combustion method, a few general suggestions for improving the technique are offered below.

Nowadays, instead of the bottle which H e m p e l (1) employed for macroanalysis, a 250-300 ml conical flask is almost always employed for micro-determinations (Fig. n. 3). If larger amounts of substances are to be combusted (approx. 50 mg), it is advisable to employ a 500 ml

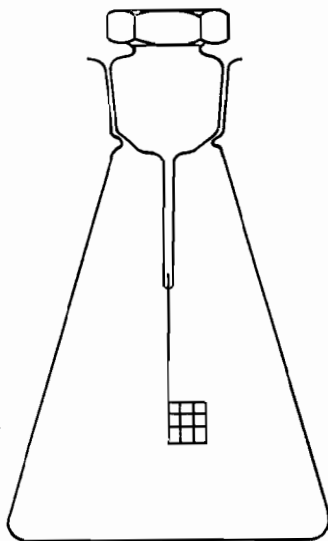


Fig. n. 3

flask. It is as well to ensure that the ground-glass stopper is not too tight, otherwise it may be difficult to open the flask due to the vacuum which arises when the combustion products are absorbed. A number of authors (19, 55) have proposed the use of a flask with a side-arm and stopcock for equalization of the pressure; in one paper a balloon attached to the side-arm (54) provides for equalization of pressure during combustion. L e h n e r (56) has proposed a variant of the method for the determination of trace elements which gives excellent results (Fig. n. 4).

For some procedures, it is doubtless an advantage to employ a quartz instead of a platinum holder, or indeed a quartz flask (50). It is unlikely that platinum exerts a catalytic action. Most probably it is the high combustion temperature and the characteristic manner in which combustion proceeds that ensure the disintegration of the organic

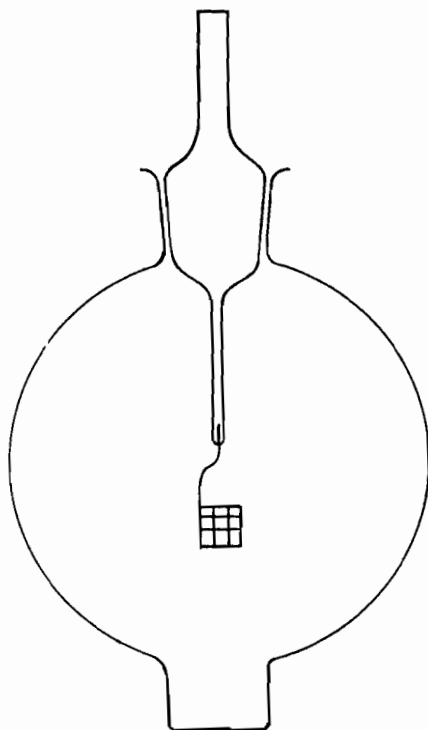


Fig. n. 4

substance. To gain an accurate insight into the combustion process, temperature measurements have been carried out with recording thermometers. These investigations have shown that temperatures of approx.  $1300^{\circ}\text{C}$  and often still higher are attained. Simultaneous recordings of the temperature in the packet of substance and outside the sample holder reveal a characteristic combustion pattern: in the vicinity of the substance, a very hot zone is generated through which the vaporized substance must flow. This explains how complete combustion occurs in spite of the very short reaction time (approx. 20 sec.).

As has already been mentioned, for combustion of fluorine-containing compounds it is advisable to add approx. 20 mg  $\text{Na}_2\text{O}_2$  to the sample so as to prevent the formation of  $\text{CF}_4$ . The latter can be detected in the gas phase unless this precaution is taken (21-24).

Liquids can be measured out as follows, using a method proposed by Kirsten (57). A piece of polyethylene tube approx. 15 mm long and 1 mm in inner diameter is sealed at one end and a little cotton

wool is inserted into it. The liquid to be analysed is introduced into the tube by means of an injection syringe. The tube is weighed and its other end is then sealed. It can then be wrapped in a piece of filter paper in the usual way. Good results are obtained with the methylcellulose capsules available on the market (58). Capsule combustion gives even higher temperatures than combustion in filter paper. Tests have been carried out to ascertain whether these capsules are advantageous for the combustion of solid substances. B e n n e w i t z (58a) applies liquids with a boiling point higher than 200° C directly to filter paper and weighs out more volatile liquids in a thin-walled glass bulb (see also (10)), which is not, however, broken before combustion.

Other authors recommend the use of home-made « vials » of cellulose adhesive tape with a filter insert (12), and some have recommended the use of a ball of cotton wool as a vehicle for liquids (46). Cones of filter paper with a coating of collodium (52) as well as cones of cellulose acetate foil (54) are also employed, and both are advantageous for the preliminary concentration of solutions and extracts.

For the combustion of substances which yield oxides adhering to the platinum grid (organometallic compounds), the following modifications have proved useful (59): a reduction adaptor is fitted in the neck of the flask and a longer glass rod, bearing a platinum grid, is sealed to the ground-glass stopper. When combustion and absorption have taken place, the reduction adaptor is removed, whereupon the platinum grid can be immersed in the absorption solution and any adherent deposit conveniently dissolved.

For the combustion of substances which are unstable on heating temperature an apparatus has been described in which the substance can be burnt in a stoppered flask by electrical ignition (60).

In conclusion, mention should be made of a new technique developed by the Du Pont Company, Wilmington, U.S.A.. In their laboratories, combustion in a polyethylene flask cooled on the outside with ice water has proved successful, and the method has been developed for determining traces of potassium and sodium in the flask (61).

This brief review will have served to show that the method of flask combustion has proved its worth in the day-to-day practice of the organic analyst. With the combustion flask a large number of the elements that can occur in organic compounds can be determined in a most simple manner. Such methods have the following principal advantages:

The combustion apparatus is extremely simple,

The analyst has complete freedom of choice as regards the method he employs for the estimation,

The process lends itself to rapid routine analysis of large numbers of samples,

Flask combustion offers a simple method of determining trace elements.

There can be no doubt that still further applications will be found for the combustion technique in the near future. Quite conceivably, the inorganic analyst will find it worthwhile to investigate whether this technique may not be of value to him also.

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