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## ANALYTICAL PROCEDURES FOR THE FLASK COMBUSTION METHOD

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**Abstract**—The present day need for speedy analytical results without the sacrifice of accuracy has promoted the search for more rapid methods of analysis. In particular, this applies to the determination of halogens and sulphur in organic compounds, for the way in which these elements are determined by conventional methods is considered too long. Usually, the organic material is decomposed by a more or less complicated procedure leading up to a gravimetric or titrimetric finish according to the kind of decomposition method employed, and the variety of interfering elements present in the sample.

A simple method combined with a direct titration is considered ideal, and such advantage is procured by using a method developed from a macro-procedure. In this the sample is wrapped in a piece of ash-free filter paper and burned in a closed oxygen-filled flask containing the appropriate absorption solution. After a convenient period for complete absorption, the contents of the flask are titrated giving the halogen or sulphur contents.

Suitable methods of finish are described for the determination of chlorine, bromine, iodine, fluorine, sulphur, phosphorus and carbon-14 in organic compounds following release of the ions upon burning in the flask.

BEING in charge of a micro-analytical laboratory it is most important to give the chemists, who order the analyses, exact and reliable results in a very short time. Therefore, it is very essential for the sake of the analyst doing the work to use procedures which are rapid and more or less foolproof.

It has been concluded from experience in this laboratory that the way in which halogens and sulphur in organic compounds are usually determined is too lengthy. For the determination of these elements in organic compounds a host of methods are described in the literature. For example, there are two ways in which the combustion of the organic material can be carried out, namely (a) by oxidation and (b) by reduction procedures. In the first class of method oxidation may be accomplished by burning the compound in a stream of oxygen, either over platinum contacts or using a quartz baffle combustion tube in conjunction with a rapid flow of oxygen; by the Carius method, whereby the sample is heated in a sealed glass tube at temperatures above 250°C with nitric acid as the oxidation reagent; and by the Parr bomb combustion procedure where the organic compound is oxidized with sodium peroxide. In the reduction methods, release of the halide or sulphur element is accomplished by hydrogenation, catalytically, of the pyrolysis products of the organic material in a stream of hydrogen; or methods are used which are based on the principle of the Lassaigne test for sulphur, using potassium or magnesium to convert the organic-bound halogen or sulphur by heating in a sealed tube into easily determinable metal halide or sulphide. For the determination of the ionic halogen or sulphur produced by one of these procedures numerous methods have been described in the literature. Today titrimetric methods are normally used<sup>1-3</sup>.

All the methods described need a relatively long time for an estimation or have other disadvantages. The Parr bomb method for instance does not permit the potentiometric micro-determination of halogen.

A very simple and rapid method for the macro-determination of halogens described by Mikl and Pech<sup>4</sup>. The authors stated that the method is suitable for production control directly in the plant, but that possibly the principle could not be used for accurate analytical work<sup>5</sup>. Nevertheless an exact micro-analytical procedure was developed and has been tested now over more than 2 years not only in this laboratory but in others, and has been proved to be very reliable<sup>6, 7</sup>.

The principle of the method is as follows: The organic compound is burned after being wrapped in a piece of ash-free filter paper in an oxygen-filled flask. The combustion products are absorbed and the element which has to be determined is titrated in the liquid.

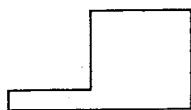


FIG. 1

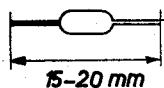


FIG. 2

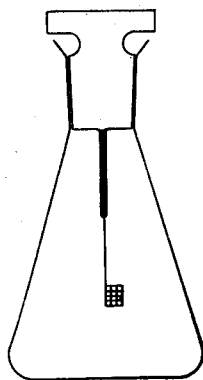


FIG. 3

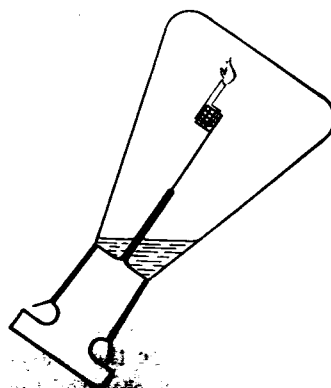


FIG. 4

The exact combustion procedure consists of weighing 3 to 10 mg of sample, which is weighed on a piece of ash-free filter paper (Fig. 1), or by using a weighing stick or a platinum boat. High boiling liquids can be weighed directly on the filter paper, or using a special capillary (Fig. 2), the tip of which is broken immediately before the sample is inserted in the flask. The filter paper is folded so that no substance can fall out, and is inserted in the platinum wire net which is attached to a ground-glass stopper (Fig. 3). The absorption liquid (the solution used depending on the type of determination) is introduced into a 300 ml Erlenmeyer flask (Fig. 3), oxygen from a cylinder is blown into the flask for several seconds, the tip of the paper strip is ignited and the ground-glass stopper quickly inserted into the joint of the flask. The combustion of the organic material takes place in about 20 sec. To ensure that absolutely no trace of combustion products escapes, it is recommended to tilt the flask in such a way that the stopper is sealed with the absorption liquid as shown in Fig. 4. The flask is allowed to cool and occasionally shaken. After 10-20 min the stopper is removed (there is usually a slight vacuum in the flask owing to the decrease in gas volume by the carbon dioxide absorption) and rinsed with distilled water. The element in question can now be determined in the most reliable way. We prefer to use the range of methods of finish described briefly below:

**Chlorine.** Titrimetric determination according to Vieböck<sup>8</sup> by argentometric titration using dichlorofluorescein indicator<sup>9</sup>, and by potentiometric determination.

**Bromine.** The same methods as described above are used, and in addition the iodometric method, which has been originally described by Kolthoff<sup>10</sup> and now used by us on a routine basis.

**Iodine.** We use the Leipert<sup>11</sup> method, i.e. oxidation of the iodine in the absorption liquid to iodate with bromine in acetic acid, and titration with sodium thiosulphate.

**Sulphur.** With compounds containing only carbon, hydrogen, oxygen or sulphur the sulphate can be determined acidimetrically<sup>12</sup> (see also Lysyj and Zaremba<sup>13</sup>); compounds containing also chlorine or bromine can be titrated by the method described in Milton and Waters<sup>14</sup>. At one time we were also using the complexometric method recommended by Flaschka<sup>15</sup> and co-workers, but we found that the method described by Fritz and Yamamura<sup>16</sup> and by Wagner<sup>17</sup> is more reliable. The sulphate is titrated in 80 per cent isopropanolic solution with 0.01 or 0.005 N barium perchlorate (also in 80 per cent alcohol) using thiorin as indicator (see also Alicino<sup>18</sup>, and Ottosson and Snellman<sup>19</sup> who titrate the sulphate conductimetrically).

**Fluorine.** Several test compounds could be determined according to the method of Brunisholz and Michod<sup>20</sup>, but larger amounts of sample had to be used for the combustion which is carried out in a 500 ml flask taking 15 to 25 mg of material. Care has to be taken when using this form of combustion for the fluorine determination because it has been reported that it is possible that the decomposition can be incomplete.

**Phosphorus.** Experiments in this laboratory proved that it is also possible to determine phosphorus as phosphate after the compound has been burned in the flask. The determination can be done colorimetrically in the well known fashion according to a procedure given recently by Fleischer and co-workers<sup>21</sup>. The same authors also describe a complexometric method for semi-micro-amounts (see also Belcher and Macdonald<sup>22</sup>).

**Carbon-14.** Götte and co-workers<sup>23</sup> report that they were using our combustion method for the determination of the carbon-14 content in labelled compounds. After the combustion (using from 0.1 to 100 mg of compound burned in a 500 ml flask) the barium carbonate is precipitated and the amount of carbon-14 is determined as usual.

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