609. *Determination of Aldehydes in Combustion Products.*

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The standard methods of separately determining aldehydes in mixtures such as those obtained from combustion of hydrocarbons have proved unsatisfactory. A method is described in which the aldehydes are oxidised by silver oxide to the silver salts of fatty acids. The silver is determined volumetrically by potassium thiocyanate. Separation and determination of individual aldehydes is achieved by chromatography of the acids which can be liberated from the silver salts. The method has been successfully applied to the identification and determination of the aldehydes formed during the oxidation of higher hydrocarbons.

During research into the products of hydrocarbon combustion several difficulties were encountered in the determination of aldehydes owing to interference from some of the other products of the reaction. The standard method using hydroxylamine hydrochloride, although giving accurate results with pure samples, is not specific for aldehydes but determines ketones also.

Peroxides cause serious interference and, in agreement with Smith and Mitchell (*Analyt. Chem.*, 1950, **22**, 750), we have found that the discrepancy amounts to between two and four times the amount of peroxide present, depending upon the temperature and time of standing. In addition weak acids, if present in quantity comparable with that of the aldehydes, lead to uncertain results owing to their buffering action.

A modification of Ripper's bisulphite method described by Siggia and Maxcy (*Ind. Eng. Chem., Anal.*, 1947, **19**, 1023) has also been tried. Although hydrogen peroxide does not interfere when in small concentration, tertiary butyl hydroperoxide liberates approximately one molecule of alkali for every two of peroxide present and so leads to high results.

When analysing combustion products we have found that a method based on the oxidising action of silver oxide on aldehydes is more satisfactory. Aldehydes are thus oxidised to fatty acids which then dissolve more oxide to form salts, the silver in which may readily be determined by titration with potassium thiocyanate. Smith and Mitchell (*Analyt. Chem.*, 1950, **22**, 746) have recently described a method similar to ours in which the aldehydes are heated to 60° with silver oxide in a stoppered flask; standard sodium hydroxide is added to precipitate the silver and the excess is back-titrated with hydrochloric acid. This method, however, suffers from the disadvantage that acetaldehyde and formaldehyde are only partially estimated. The method described below has been tested with these aldehydes amongst others and gives results which are accurate to within 2% for straight-chain saturated aliphatic aldehydes up to hexanoic. Not only is the silver oxide method of use for aldehydes where other methods may fail owing to interference, but it can also be made a basis for the quantitative separation and determination of individual aldehydes in mixtures. The fatty acids can be prepared from the silver salts and then separated by chromatography whereas there is no simple method of analysing a mixture of aldehydes as such.

Experimental.

Determinations.—The product to be analysed is made up to a standard volume either with water or, if insoluble in water, with 50% aqueous *iso*propyl alcohol. Between 1 and 5 ml. of this solution, containing about 0·2 millimoles of aldehyde, is allowed to pass down a tube of 8-mm. bore, packed with silver oxide to a depth of 10 cm. The sample is washed through with water to make a total volume of 25 ml. and the emergent solution containing the silver salts of the fatty acids is titrated with N/50-potassium thiocyanate, with ferric alum in nitric acid as indicator. A small correction (0·15 ml. for every 10 ml. of solution) must be made for the oxide dissolved by the wash-water.

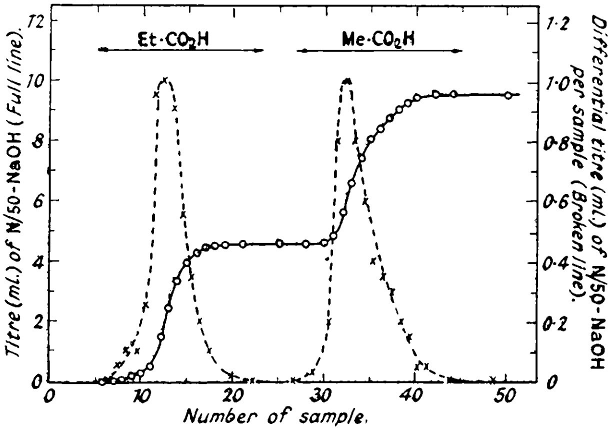
When not in use the column is kept immersed in distilled water to prevent the oxide from drying out. The column described is easily overloaded and if amounts of aldehyde in excess of 0·2 millimoles are used a low result may be obtained. Care must also be taken, especially when dealing with higher aldehydes, to ensure that the silver salts are completely washed out, as their solubility decreases markedly with ascent of the homologous series. This may in some cases necessitate the use of more than 25 ml. of wash-water.

The method has been tested for formaldehyde, acetaldehyde, propaldehyde, *n*-butaldehyde, and hexanal. Solutions of each were standardised by hydroxylamine hydrochloride. The results by the two methods, for polymer-free aldehydes, agreed to within 2%.

Aldehyde determinations have also been carried out in the presence of hydrogen peroxide, *tert.*-butyl hydroperoxide, acetone, dimethyl formal, ethyl acetate, and alcohols. None of these substances caused interference. Methyl and ethyl formate, however, are about 30% hydrolysed on a 10-cm. column and the formic acid liberated leads to a high result. Acids present in the original mixture dissolve silver oxide and must be allowed for.

Separation of Aldehydes.—The silver salt solution obtained from the oxide column is collected in a 30-ml. long-necked flask, treated with excess of sodium chloride to precipitate all the silver, and evaporated to dryness on a water-bath. The addition of sodium chloride is necessary since the silver salts readily decompose when heated. The free acids can then be obtained by Elsden's method (*Biochem. J.*, 1946, **40**, 252). The residue is treated with 0·2 ml. of water followed by enough powdered anhydrous potassium hydrogen sulphate to form a paste. This liberates the acids which are extracted with six 0·5-ml. portions of chloroform containing 1% of butanol. The acids in this solution are separated by partition chromatography on a suitably buffered silica column by the method of Moyle, Baldwin, and Scarisbrick (*ibid.*, 1948, **43**, 308) whereby the acids are titrated with alkali as they emerge from the column. Formaldehyde cannot be determined chromatographically by this method as it is very strongly adsorbed by the silica. It does not, however, interfere with the separation of the other acids.

The Figure shows the result of a separation which was carried out on a mixture of formaldehyde, acetaldehyde, and propaldehyde. Three separate solutions, each containing one of the aldehydes, were standardized by hydroxylamine hydrochloride. Equal amounts were then mixed and 3 ml. of the mixture were used for the experiment. The sample was treated as outlined above, a column buffered to pH 6·0 being used for chromatography. The following figures show that 97% yields of acetaldehyde and propaldehyde were obtained. The titres are in ml. of N/50-solution.



	C_2H_5·CHO	CH_3·CHO	CH_2O
Amount as detd. by hydroxylamine HCl (ml.)	4·80	5·15	11·28
Amount as detd. by oxidn. and chromatography (ml.)	4·65	5·00	—
Yield, %	97	97	—

Propionic acid which travels fastest was eluted with chloroform containing 1% of butanol, and acetic acid with a 10% solution. Formic acid is retained by the column and has no effect on determination of the other two. It must be determined by difference or by an independent method.

A similar separation has been carried out on a mixture of butaldehyde and hexanal. The overall yields were : hexanal 95%, butaldehyde 96%. In this case a column buffered to pH 8·2 was used, and the two acids eluted with 1% and 30% solutions of butanol in chloroform respectively.

The above technique has been used successfully to identify and determine the amounts of different aldehydes in the combustion products of higher hydrocarbons. An account of this work will be published later.

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