

marine eggs<sup>13</sup>) has a number of theoretical connotations in the chemistry of proteins and their biological manifestations.

(13) Tyler and Fox, *Biol. Bull.*, **79**, 153 (1940).

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### ELEMENTARY ISOTOPIC ANALYSIS. DETERMINATION OF OXYGEN

Sir:

At present oxygen in organic compounds is usually determined by difference, that is, after deducting the percentage of carbon, hydrogen and any other constituents from 100. The ter Meulen catalytic method,<sup>1</sup> proposed in recent years, is the only direct method, but it is complicated and requires careful manipulation.

In view of the availability of mass spectrographs and heavy oxygen, it occurred to us to develop an isotopic method. It is a very simple adaptation of the isotope dilution principle originally introduced by G. v. Hevesy and F. Paneth. A known weight ( $a$ ) of the substance to be analyzed ( $x\%$  O) is equilibrated with a known volume of oxygen gas ( $= b$  g.), containing a known amount of O<sup>18</sup> ( $= m\%$ ) in excess of the normal concentration. The excess of O<sup>18</sup> in the mixture after equilibration ( $= n$ ) is determined by mass spectrograph. Thus  $a$ ,  $b$ ,  $m$  and  $n$  being determinable, it follows simply from the mixture rule that

$$x = \frac{b(m - n)100}{an} \% \text{ Oxygen} \quad (1)$$

The equilibration takes place in a platinum test-tube of 80 ml. volume, at 600–800°, connected to a vacuum system. The time required is about one-half hour. The following oxygen determinations show results obtainable by this method:

Detn. no.	1	2	3	4	5
Substance analyzed	Formic acid HCOOH (excess of O <sub>2</sub> )	Formic acid HCOOH (deficiency of O <sub>2</sub> )	Acetic acid CH <sub>3</sub> COOH	1-Nitroethane CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	Ethyl ether (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
$a$ , i. e., mg. sample	38.2	60.4	26.0	20.9	52.70
$b$ , mg. oxygen-18 gas taken (using at. wt. of O = 16.00) (ml. at N. T. P.)	20.0	22.2	36.5	31.4	12.03
$m$ , mole % O <sup>18</sup> ·O <sup>16</sup> in $b$ above normal concn. (–0.40%)	(14.0)	(15.5)	(25.5)	(22.0)	(9.4)
	2.00	2.00	2.07	2.10	2.145
$n$ , mole % O <sup>18</sup> ·O <sup>16</sup> of equilibrated mixt. (–0.40%)	0.85	0.69	1.50	1.64	1.15
$x$ , % oxygen in substance, calcd. from formula (1)	70.8	69.8	53.4	40.3	19.8
% oxygen, theoretical.	69.5	69.5	53.3	42.6	21.6

These experiments, particularly 2 and 3, show even better agreement than is to be expected. With the comparatively small O<sup>18</sup> concentration available to us, the average probable error is  $\pm 3.0\%$  of the oxygen content.

Since ( $m - n$ ) and  $n$  enter into our equation,

(1) For a comprehensive and critical review of this and other less developed methods see: P. J. Elving and W. B. Liggett, *Chem. Rev.*, **34**, 129–156 (1944).

the accuracy is highest when the amount of isotopically labeled element added approximately equals the element content of the sample. The precision of oxygen determinations can be increased simply by production of O<sup>18</sup> in high concentration. With about 20 at. per cent. O<sup>18</sup> an average precision of  $\pm 0.1\%$  of the oxygen content of the sample analyzed should be attainable.

The two experiments with formic acid show that it is not necessary to completely combust the sample to CO<sub>2</sub> and H<sub>2</sub>O. As in Experiment 1, equilibrium is attained, with CO and CH<sub>4</sub> in the gas mixture.

The most reliable O<sup>18</sup> figures are obtained from the CO<sub>2</sub>-peaks. The same method may be used for solid organic compounds, and of course can be extended to inorganic compounds which would equilibrate with an O<sup>18</sup>-containing molecule.

Description of our equipment and our detailed results will be published elsewhere. The method is now being extended to the determination of carbon, hydrogen and nitrogen.

We are greatly indebted to Dr. Harry Thode of Toronto, Canada, for a generous supply of H<sub>2</sub>O<sup>18</sup>, without which this investigation would not have been possible.

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### BUBBLE FORMATION FROM CONTACT OF SURFACES

Sir:

If commercial bottled soda water is poured carefully into a specially cleaned wet glass container the liquid remains free of bubbles and supersaturated with carbon dioxide, in contrast with soda water in an ordinary tumbler, where gas phases (gas nuclei) are present to start bubble formation.

A clean wet quartz rod in the soda water will also form no bubbles. However, if the quartz rod is drawn over the surface of the glass so as to produce a scratch, bubbles arise at the contact of the two surfaces and a chain of bubbles may continue to form at points along the scratch for a considerable time period.

The above observations are widely known. We have, however, now been able to show that bubbles