

Quantitative Analysis by the Variation of the Specific Activity of an Added Radioactive Isotope

IN a mixture of ions, one of them can be estimated by adding to the solution its radioactive isotope. The specific activity is modified, and one can deduce from that modification the concentration of the inactive ion initially present.

Various researches have already been undertaken in this direction. Delépine¹ in 1925 indicated the possibility of estimating the quantities of optical isomers in a given sample. Later, Hevesy and Hobbie² estimated traces of lead in rocks using its natural isotope radium D as an indicator. In 1939 Schoenheimer, Ratner and Rittenberg³, and Ussing⁴, effected the estimation of organic compounds with the aid of heavy isotopes, and Rittenberg and Forster⁵ gave detailed examples of analysis of amino-acids.

The artificial radioactive isotopes which had not yet been employed in analysis naturally afforded great interest. In this first account, we review briefly the results obtained in the estimation of potassium effected in the presence of lithium and sodium.

To the solution containing these three elements a measured quantity of ions ($K^+ + K$), having a known activity, was added. From the new mixture the potassium is precipitated as an insoluble salt such as the perchlorate. One part of it is isolated and weighed, and from the new activity the quantity of inactive ions initially present in the solution is deduced. The advantage of this method is obvious: the precipitation does not need to be quantitative, it is sufficient to isolate one part of the salt in a pure state to find out its specific activity.

Our determination of quantities of K from 1-0.1 gm. (in potassium chloride) mixed with 13.6 gm. of salts (sodium and lithium nitrates) gave results accurate to within 1 per cent. One can also consider the estimation of complex organic compounds such as the alkyl halides, compounds of arsenic, sulphur, etc. The estimation of proteins containing phosphorus should be interesting, as the half-life of radio-phosphorus is long (14 days). The analysis of iodine compounds of the thyroid gland will doubtless be feasible by this method, using iodine of half-life (8 days).

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¹ Delépine, *C.R. Congr. Soc. Sav.* (1925).

² Hevesy and Hobbie, *Z. anal. Chem.*, **85**, 1 (1932).

³ Schoenheimer, Ratner and Rittenberg, *J. Biol. Chem.*, **130**, 703 (1939).

⁴ Ussing, *Nature*, **144**, 977 (1939).

⁵ Rittenberg and Forster, *J. Biol. Chem.*, **133**, 737 (1940).

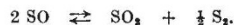
A New Flame Phenomenon

IN the course of an examination during 1938 of the effect of the quality of coal gas upon the completeness of combustion in domestic gas appliances, a speedy method of determining total air requirement was developed.

progressive reduction in the air/gas ratio the violet-blue flame gradually increases in length, while the intensity of the colour increases to a maximum and then decreases. Finally, the whole flame is suddenly extinguished at an air/gas ratio well below that required for complete combustion of the gas.

The name 'calyx'—owing to its resemblance to the calyx of a flower—has been given to the violet-blue flame. The violet-blue colour appears to be the more intense the higher the sulphur content of the gas. In collaboration with Dr. E. C. W. Smith, a spectrogram of the calyx flame obtained with town gas has been taken and this shows very clearly the characteristic S_2 lines between 3369 Å. and 4434 Å. No other lines are visible. Dr. G. Whittingham¹ has observed the S_2 lines in a spectrogram of a coal gas flame to which sulphur dioxide has been added.

Consideration of the equilibria existing in the flame produced by a coal gas/air mixture containing slightly less than the theoretical amount of air suggests that the sulphur may arise from the reaction:



At the temperature existing in the flame, this system is composed predominantly of SO , and a considerable fall in temperature is necessary for the formation of S_2 in sufficient concentration to give a visible flame. This may explain the dark space between the main flame and the calyx.

It is probable that the violet-blue zone that can be seen as a thin line beneath a kettle when an aerated coal gas flame impinges upon it is essentially the same phenomenon. The local conditions under which it is formed are similar to those necessary for the formation of a strongly developed calyx, namely, a deficiency of air and a relatively low temperature.

Experiments were made with hydrogen and air, in both of which the sulphur concentration was known to be less than 0.5 parts in two million parts by weight; and the violet-blue flame was detectable although it was more diffuse than the well-defined calyx flames obtained with coal gas and air. Another striking difference is that with hydrogen the violet-blue flame appears to be in a state of considerable turbulence not observed in the case of the other gases.

Measurements were made with various coal gases, for the detailed analyses of which we are indebted to the Gas Research Board. Gas and air-rates were measured by means of calibrated flow meters, both gas and air being saturated with water vapour at room temperature. Starting with the mixture on the air-rich side, the air-rate was gradually decreased, and at the point of appearance of the calyx a sample of the products of combustion was taken for analysis. The existence of the calyx is sensitive to changes of the proportion of air of less than 1 per cent of the total air requirement. The results of the tests are given in the table appended.

From the point of view of appliance design, the CO/CO_2 ratios are of direct significance. These are all within the range normally regarded in the gas industry as indicating satisfactory combustion, and the corresponding air/gas ratios therefore give the minimum proportion of air required to burn the gas completely. The air/gas ratios calculated from analytical data approximate to the observed values.

Kind of gas	Gross C.V. B.Th.U. per cu. ft.	A.T.B. No. (B scale)	Sulphur grains per 100 cu. ft.	Products			Air/Gas ratio		
				CO_2 %	O_2 %	CO/CO_2 ratio	Observed	Calculated	
Carburetted water gas	433	21.5	10	16.8	0.1	0.015	3.89	(a) 3.75	(b) 3.81
Vertical retort gas—C	451	33.0	24	11.8	0.5	0.0059	3.89	3.83	3.86
Vertical retort gas—D	449	31.3	20	12.3	0.3	0.0078	3.87	3.77	3.84
Town gas—D.	449	29.1	18	13.1	0.2	0.0070	3.82	3.78	3.84
Vertical retort gas—E (unstripped)	485	39.2	33	12.1	0.1	0.010	4.17	3.97	4.23

(a) Calculated from the gas analysis, assuming the unsaturated hydrocarbons to be C_3H_4 .

(b) Calculated by the formula, developed by Mr. J. W. Wood

$$C.V. \times \frac{1.055}{100} - 0.97 + (0.97 \times \% \text{ inerts}) - \frac{\% \text{ oxygen}}{21}$$

Previously this figure had normally been obtained by one of two methods: (a) calculation from the composition of the gas; (b) direct combustion by explosion or catalytic oxidation. In the method to be described, the air required per cubic foot of gas for complete combustion can be determined directly by measurement of rates of flow of air and gas. The flame itself provides a satisfactory criterion when the correct ratio is attained.

The apparatus is essentially a simple tube burner to which a mixture of air and gas in controlled proportions is delivered. The burner is set in an enclosure of which the exit is made sufficiently small to maintain a slight excess of pressure over the external atmosphere and prevent back diffusion of air to the flame. The flame is, therefore, surrounded by its own products of combustion. The enclosure is formed by a tall glass cylinder sealed to a solid base supporting the burner. At the top of the cylinder there is a loosely fitting lid with two small holes.

With excess air the flame, as seen in a darkened room, has a lilac-coloured inner cone surmounted by an envelope of paler lilac shade. At the top of the outer envelope the colour changes to a reddish hue. When the ratio of air to gas is slowly reduced there comes a point where the outer envelope suddenly increases about three-fold in height. Further slight reduction in the air/gas ratio causes the height of the outer envelope to decrease again, and this is accompanied by the appearance of a small violet-blue flame at the base of the main flame, there being a dark space between the two flames. With further

Observations with gases ranging from 347 to 522 B.Th.U. per cu. ft. indicate that the method can be applied to any town gas.

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¹ *Nature*, **156**, 207 (1945).

A New Spectrographic Spark Source

ABOUT a year and a half ago, our attention was directed to the relative instability of the condensed spark sources generally in use for quantitative spectrographic analysis. Consequently, work was carried out with the object of stabilizing the electrical excitation conditions in the analytical gap. The investigation led us to consider two general types of excitation circuits, namely, the high-voltage high-power circuit and the low-voltage controlled A.C. arc. In both these circuits the discharge is initiated by means of a synchronized trigger-circuit employing enclosed auxiliary spark gaps of the 'Trigatron' type (a three-electrode gap enclosed in a high-pressure argon-oxygen mixture).

The control of the main discharge by means of an auxiliary gap was originally suggested by Feussner¹, who used a synchronous rotary spark gap. The attainment of satisfactory operation of the inter-