Determination of Nickel and Cobalt by Atomic Absorption

In the atomic absorption method of analysis, first described by Walsh[1], the solution to be analysed is sprayed into a flame, and with a hollow-cathode lamp which emits the line spectrum of the element being determined as the light source, the absorption of light by atoms of the element is measured at a characteristic wave-length.

To realize the full potentialities of the method, it is obviously important that the strongest absorption line be used. As at the temperature of commonly used flames all but a small proportion of the atoms are in the ground-state, only lines due to absorption by unexcited atoms need be considered, and of these lines it is usually assumed that the strongest absorption line will correspond to the strongest emission line. I have pointed out that while this is so in the simple spectra of the elements in Groups I and II, it is not necessarily the case in the more complex spectra of the heavier elements, and that as oscillator strengths for the various lines of these elements are generally not known, it is necessary to determine experimentally which line is the strongest in absorption[2]. Results were given for manganese and iron, showing that for these elements the strongest absorption lines were at 2794·8 Å. and 2483·3 Å. respectively.

The spectra of nickel and cobalt have now been investigated by the methods described previously. It has been found that the strongest absorption line for nickel is at 2320·0 Å. ($a^3F_4 - y^3G^0_5$), the absorption at this wave-length being about fifteen times that at 3415 Å., the wave-length of the strongest emission line. For cobalt, the strongest absorption line is at 2407·2 Å. ($a^4F_{4\frac{1}{2}} - x^4G^0_{5\frac{1}{2}}$), and this line is about fifty times as sensitive in absorption as is the strongest emission line at 3527 Å.

When these lines are used, the atomic absorption method can usefully be applied to the determination of nickel and cobalt, the sensitivity obtained being about the same as that already reported for iron.

I thank Mr. O. E. Clinton for his assistance with this work, full details of which will be reported elsewhere.

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[1] Walsh, A., *Spectrochimica Acta*, **7**, 108 (1955).
[2] Allan, J. E., *Spectrochimica Acta*, **15**, 800 (1959).

BIOCHEMISTRY

Steric Factors affecting the Specificity of Polyglycosidases

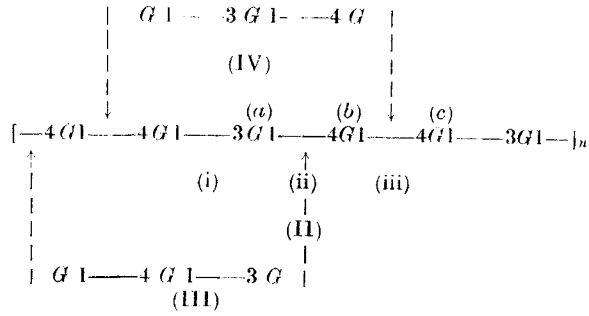
The marked substrate specificity exhibited by enzymes has been related to a steric affinity between the molecule attacked and the attacking enzyme[1]. According to this concept, proper orientation of the substrate in the vicinity of the enzyme permits formation of an activated intermediate in which several points of contact may be established.

Enzymes which hydrolyse simple glycosides exhibit extremely high specificity for the glycosyl radical of the molecule, whereas the structure of the aglycone group usually is important in a quantitative, rather than qualitative, sense[2,3]. Glycosidases that degrade polysaccharides (I) appear to show high specificity for

$$[\text{---}\overset{(a)}{x}G1 \text{ ---- } \overset{(b)}{x}G1\text{---}]_n$$
(I)

a particular type of linkage, as well as glycosyl unit. In evaluating such specificity, the enzyme is tested usually with several polysaccharides each of which contains only one type of sugar component and linkage (or as close as possible to this ideal); this procedure has become general since few polysaccharides of more complex structure are characterized in sufficient detail to be suitable as enzyme substrates. Cellulase, for example, degrades polymeric chains in which β-D-glucopyranose units are linked through positions-1 and 4 (I, G = D-glucopyranosyl; $X = 4$) but not when the linkages are β-(1→3), α-(1→4), etc., and is regarded as a β-(1→4)-poly-D-glucopyranosidase. In common usage, this terminology refers to the linkage cleaved, and implies that its position of attachment to unit I(*b*) has an important bearing on specificity. However, the glycosyl unit (*a*) is itself attached to a third unit (through the X-hydroxyl group), and the location of this linkage also might be expected to affect specificity through its influence on the stereochemistry of (*a*). Clearly, the relative importance of these steric factors is difficult to assess with polysaccharides of homogeneous structure. Recent observations[4] on the enzymolysis of a polysaccharide that contains mixed types of linkages suggest, however, that such questions should be taken into account in classifying polyglycosidases.

The polysaccharide examined is a soluble D-glucan from oats[5,6], the structure of which is represented[4,6] mainly by II, that is, a linear chain of β-D-glucopyranosyl units in which two (1→4) linkages (ii) and (iii) alternate repeatedly with a (1→3) linkage (i). Two different enzyme preparations have been found to degrade the glucan rapidly and extensively under conditions expected to minimize trans-glycosidation side-reactions. One of the enzymes has been classified



as a β-(1→3) D-glucosidase, since it shows high specificity for laminarin and only low activity on other substrates tested[7]. With this polyglycosidase, the major product obtained from the oat glucan is trisaccharide III[4,6], showing clearly that hydrolysis is preferential for linkage (ii), that is, the glycosidic bond of a β-D-glycosyl unit (*a*) attached through positions-1 and -3 to adjacent units, rather than a β-(1→3) linkage (i). (In laminarin, of course, most of the glycosyl units possess this type of 1,3-relationship.)

The second enzyme used, a cellulase from *Streptomyces* sp. *QM B814* [8], degrades the glucan mainly to trisaccharide IV [4,6], showing that the hydrolytic action