

3 Techniques used in the analysis of optically active compounds

3.1 Chiroptical methods

Chiroptical methods comprise polarimetry, optical rotatory dispersion (ORD), and circular dichroism (CD). Detection is based on the interaction between a chiral center in the analyte and the incident polarized electromagnetic radiation. Previous applications focused primarily on the elucidation of molecular structures, particularly of natural products for which a technique capable of confirming or determining the absolute stereochemistry was critical. In recent years the application of these techniques has become more and more significant to analytical chemistry.

Among the various requirements of analytical methodologies the properties of analytical selectivity and breadth of application are of prime importance. Analytical selectivity depends on the structural properties of the analyte and the ability of the selected detector to differentiate between the analyte and a potentially high number of interfering compounds. The optimum number of molecular properties necessary to achieve an acceptable level of selectivity appears to be two. If only one property is necessary, separation is essential unless a more sophisticated procedure, which is either time- or phase-sensitive, is used. If three or more properties are necessary, the number of potential analytes is greatly diminished. The most widely used chiroptical method is CD, which measures both rotation and absorbance simultaneously.

Several comprehensive articles on the physical phenomena of chirality and the manifestation of its interaction with polarized light are available [1-5]. For chemical analysis, an elementary understanding of the nature of the interactions and their relationships to each other, as well as the dependence of the experimentally measured parameters on the concentration of the optically active species, is sufficient [6].

3.1.1 *Theoretical background of optical activity*

A molecule will absorb light strongly only if the transition from ground state to excited state involves a translation of charge. This is the basis of linear dichroism. Thus, the lowest energy singlet valence electronic transition in bicyclohexylidene can be shown to be polarized along the double bond, with light linearly polarized along the double bond being preferentially absorbed to light with a perpendicular linear polarization (Figure 3.1.1). For a known transition polarization, linear dichroism measurements can supply information about the orientation of the absorbing group with respect to the axes of the linearly polarized light. Linear dichroism