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# Detectors For Liquid Chromatography

## PREFACE

Liquid chromatography (LC) is, for all practical purposes, a hyphenated technique. Physical separation of components is only one part of LC. Except for preparative LC, where physical separation is the entire goal, some technique for quantitation is needed. In principle, any measurement method can be used. In practice, there are several constraints when a measurement method, that is, a detector, is interfaced to LC. First, good sensitivity is needed to deal with the low concentrations of typical analytes, which are often diluted substantially during the separation. This is not simply because of the general rule that the better the detectability, the broader the scope of application, but also because the injected quantity must be kept below the point of saturation of the stationary phase. Second, the volume of the detector must be small to avoid additional band broadening due to extracolumn effects, to preserve the quality of the separation. This volume includes, for example, the connecting tubings to the end of the column, in addition to the actual volume active in producing the signal. Recent developments in microcolumn LC make this problem even more severe. Third, the detector must be able to function in the presence of a large background—that of the eluent molecules. Unlike gas chromatography (GC) where the mobile phase can be an inert material such as helium, the LC mobile phase often affects the actual detector signal. It is necessary to be able to null out this background signal, and to maintain it at a stable level to reduce noise. Fourth, the time response of the detector must be compatible with the chromatographic event. This is even more important for the new high-speed columns. If multi-dimensional information is to be obtained, for example, recording entire spectra, the detector must cycle rapidly to be useful. Indirectly, time response also affects the detectability, because long time constants cannot be used to average out noise. Last, detector selectivity is much more important in LC compared to GC. Current technology provides separation efficiencies in LC that are inferior to those in GC. The chance of peaks overlapping in LC is then much higher. A selective detector can be used to monitor a subset of all analytes. Effectively, components can thus be resolved without physical separation.

Detectors are not just ancillary techniques for LC. In many situations, analytical measurements can be greatly improved by interfacing the instrument to a liquid chromatograph. What is gained is essentially a simple procedure for



sample preparation and cleanup before the measurement. Interferences can then be reduced or eliminated. It is true that one has to worry about additional problems due to dilution and the presence of the eluent. On the other hand, for analytes in solution, LC allows measurement in a well-prescribed solvent—the eluent—rather than the original, often less predictable, solvent. The presence of the eluent can also be turned into an advantage. Because some species are always present at the detector, a signal can be produced in certain detectors even when analytes are absent. When analytes that give no response at the detector are eluted, displacement of the eluent occurs at the detector cell. A negative signal can thus be generated to provide a means for quantitation of the “inactive” analytes. This indirect mode of detection substantially increases the scope of a given measurement technique. Another application resulting from the dependence of the signal on both the eluent and the analyte is that of quantitation without standards. Finally, the time dependence in LC can be used to improve the accuracy and detectabilities of many analytical measurements. This may be called “sample modulation.” As long as the noise associated with the analytical measurement is not on the same time scale as the chromatographic event, one can reduce the “noise” compared to static measurements by proper signal averaging or base-line correction.

New books on LC detectors appear on the market at regular intervals. I have tried to assemble here a group of authors (all of whom probably regret having succumbed to my heavy arm-twisting) who are noted experts in the fields that have been “interfaced” to LC, but are not necessarily purebred chromatographers themselves. Perhaps a different viewpoint can be offered. Discussions include the basic principles behind the detector response, the instrumentation, and selected applications for the purpose of comparison and evaluation of the potential.

Many thanks to my friends for their fine contributions, and to my co-workers for hours of argument and for the data that led to many parts of this book. I would like to dedicate this monograph to Professor Philip Elving, without whom the Chemical Analysis Series would certainly have had less impact in the field today.

EDWARD S. YEUNG

*Ames, Iowa  
October 1986*

# Detectors For Liquid Chromatography

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## CHAPTER

### 1

## REFRACTIVE INDEX DETECTOR

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### 1. INTRODUCTION

The refractive index (RI) detector has a unique place in liquid chromatography (LC). It is one of very few universal detectors available. Unless the analyte happens to have exactly the same RI as the solvent, a signal is observed. Thus for the initial survey of samples, when the physical and chemical properties of the analytes are not known, the RI detector can provide useful information. The most severe limitation is the poor limits of detection (LOD) that can be achieved compared to other detectors. Moreover, for very complex samples, when components coelute, there is a possibility of mutual cancellation of the signal because both positive and negative RI changes can occur.

### 2. QUANTITATIVE RELATIONSHIPS

The RI detector responds to both the eluent and the analyte. The responses from components in a mixture are not additive. Therefore, quantitation is not as straightforward as in the absorbance detector, for example. Many different rules for predicting the RI of a two-component mixture have been suggested. The simplest is a linear interpolation of the RIs of the components (1),

$$n = n_A C_A + n_B C_B \quad (1)$$

where  $n$ ,  $n_A$ , and  $n_B$  are the corresponding RIs of the mixture, the component A, and the component B.  $C_A$  and  $C_B$  are the fractional concentrations of the components, in units of weight, volume, or mole fraction. Because  $C_A + C_B = 1$ , one also has

$$\begin{aligned} n &= n_A + (n_B - n_A)C_B \\ &= n_A + kC_B \end{aligned} \quad (2)$$

The difficulties associated with Eqs. 1 and 2 are obvious from the arbitrary definition of  $C$ , because a linear interpolation in one concentration unit implies a nonlinear behavior in the other two units. A more complicated form is derived (2), based on the Gladstone–Dale specific refraction:

$$\frac{100(n - 1)}{d} = \frac{w_A(n_A - 1)}{d_A} + \frac{(100 - w_A)(n_B - 1)}{d_B} \quad (3)$$

where  $w_A$  is the weight percent of the solute, and  $d$ ,  $d_A$ , and  $d_B$  refer to the densities of the mixture and the two components.

It is also possible to start from first principles to see how RI depends on the components in a mixture. From the basic relations among the electric field, the electric displacement vector, and the polarization, one obtains the Clausius–Mosotti relation (3):

$$\chi = \frac{3}{4\pi} \frac{M}{N_0 \rho} \left( \frac{\epsilon' - 1}{\epsilon' + 2} \right) \quad (4)$$

where  $\chi$  is the susceptibility per molecule,  $M$  is the molecular weight,  $N_0$  is Avogadro's number,  $\rho$  is the density of the material, and  $\epsilon'$  is the dielectric constant, which depends on the frequency of the electric field. It can be shown that, except at high densities or high field intensities, neither of which is true in LC, the susceptibility of a mixture is additive (3):

$$\chi = \sum_i x_i \chi_i \quad (5)$$

where  $x_i$  is the mole fraction of component  $i$  with susceptibility  $\chi_i$ . It may be noted that for sufficiently low field strengths or high temperatures

$$\chi_i = \alpha_i + \frac{D_i^2}{3kT} \quad (6)$$

where  $\alpha_i$  and  $D_i$  are the polarizability and the permanent dipole moment of the species  $i$ ,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. Now the volume fraction of the component  $i$ ,  $C_i$ , is given by

$$C_i = \frac{x_i(M_i/\rho_i)}{\sum_j x_j(M_j/\rho_j)} \quad (7)$$

The refractive index of component  $i$ ,  $n_i$ , is given by

$$n_i = \sqrt{\mu'_i \epsilon'_i} \quad (8)$$

where  $\mu'_i$  is the permeability of the medium. But because  $\mu'$  is very nearly unity (typically deviating by less than  $10^{-3}$ ), we can replace  $\epsilon'_i$  with  $n_i^2$  in Eq. 4. Combining Eqs. 4, 5, 7, and 8, we have

$$\frac{n^2 - 1}{n^2 + 2} = \sum_i C_i \left[ \frac{n_i^2 - 1}{n_i^2 + 2} \right] \quad (9)$$

Now consider the case of a binary mixture, which is composed of an analyte and an eluent. At any particular instant, the measured RI response is determined by the volume fraction of the analyte (of RI  $n_x$ ) in the flow cell,  $C_x$ , and the volume fraction of the eluent in the flow cell ( $1 - C_x$ ). Using Eq. 9 and the subscript 1 for the eluent, we obtain

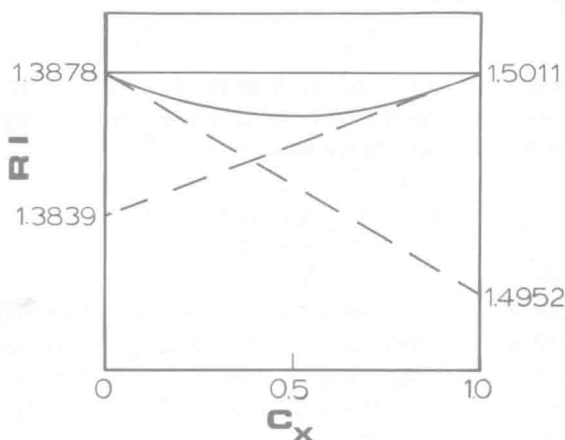
$$\frac{n^2 - 1}{n^2 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} = C_x \left[ \frac{n_x^2 - 1}{n_x^2 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right] \quad (10)$$

Combining the two terms on the left of Eq. 10, we get  $3(n^2 - n_1^2)/[(n^2 + 2)(n_1^2 + 2)]$ , which in turn equals  $3\Delta n_1(n + n_1)/[(n^2 + 2)(n_1^2 + 2)]$ .  $\Delta n_1$  is in fact the experimental observable from any of the differential RI detectors. Note that for low concentrations, errors much less than 0.1% are expected if all  $n$ 's are now replaced by  $n_1$ 's. Rearranging and redefining terms, we get

$$\Delta n_1 K_1 = C_x (F_x - 1) \quad (11)$$

where  $F_i \equiv (n_i^2 - 1)/(n_i^2 + 2)$ , and  $K_i \equiv 6n_i/(n_i^2 + 2)^2$ .

To appreciate the implications of Eqs. 10 and 11, we have plotted the actual dependence of the RI of a mixture of heptane and benzene as a function of the volume fraction of benzene in Fig. 1. The ordinates are shifted on the left compared to the right to facilitate visualization. The solid horizontal line is a linear interpolation of the RIs for the two pure solvents, and is commonly assumed in elementary discussions of applications of refractometry (1). The curved line is the actual dependence from Eq. 10. It can be seen that the linear interpolation does extremely poorly throughout. The dashed lines in Fig. 1 are the tangents to the curve for small concentrations of each of the components. From Eq. 11, the two slopes are given by  $(F_x - F_1)/K'_1$  and  $(F_1 - F_x)/K'_x$ , respectively. Using a standard refractometer, we have independently confirmed linearity and the limiting slope, as specified by Eq. 11, for cases with the minor component present below 5% by volume for a number of binary mixtures involving combinations of hexane, benzene, chloroform, carbon tetrachloride, and carbon di-



**Figure 1.** RI dependence on volume fraction for benzene in heptane; solid horizontal line, linear interpolation; solid curve, true dependence; dashed lines, limiting slopes. Reproduced with permission from R. E. Synovec and E. S. Yeung, *Anal. Chem.*, **55**, 1599 (1983). Copyright 1983 American Chemical Society.

sulfide. It can be seen from Fig. 1 that if the true dependence is plotted without a shift in the ordinate, the curvature is not obvious. Presumably this is why a linear interpolation (1) is used routinely.

Equations 10 and 11 do not hold for all situations. It has been pointed out (4) that the Lorentz-Lorenz term (5),  $(n^2 - 1)/(n^2 + 2)$ , in Eq. 9 can be replaced by the empirical Eykman term,  $(n^2 - 1)/(n + 0.4)$ . Good fit to experiments is also reported using the relationship

$$\frac{n - 1}{d} = \frac{1}{d_A - d_B} \left[ n_A - n_B + \frac{(n_B - 1)d_A - (n_A - 1)d_B}{d_B + C_A(d_A - d_B)} \right] [1 + C_A(1 - C_A)K] \quad (12)$$

where  $K$  is an empirical constant and  $C$  is the concentration in mole fraction. There is also a problem in the case of nonideal solutions. Nonideal mixing changes the implication of the volume fraction  $C_x$ , and in a sense makes the horizontal scale in Fig. 1 nonlinear. Some examples are mixtures of water-methanol and water-acetonitrile (6). In general, polar species interact with each other and nonideal mixing occurs. So Eqs. 10 and 11 are applicable only to mixtures of nonpolar species that do not differ greatly in molecular size.

### 3. INSTRUMENTATION

There are essentially four main types of RI detectors. They are grouped based on the physical principles used in the instruments, although variations in the optical arrangements are common, depending on the manufacturer. They all share a common feature, such that the output reflects the *difference* in refractive index between a sample flow cell and a reference flow cell. This is because (in contrast to an absorption detector) the chromatographic solvent also contributes to the signal. A differential measurement can then compensate for the solvent contribution to enhance detection of the analyte. Thus even though the Abbe refractometer is commonly used for RI measurements, it is of little value as an LC detector.

#### 3.1. Deflection Type

Snell's law governs the angles of incidence and refraction at an interface, so that

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad (13)$$

where  $\theta_1$  is the angle of the beam with respect to the normal of the interface in the medium with RI of  $n_i$ . Figure 2 shows the dual-cell arrangement used in the commercial instruments. There are actually three glass cell walls to contain the liquids. If these are thin, their contributions to beam deflection can be neglected. Even if they are thick, they will provide a constant deviation if the cell walls

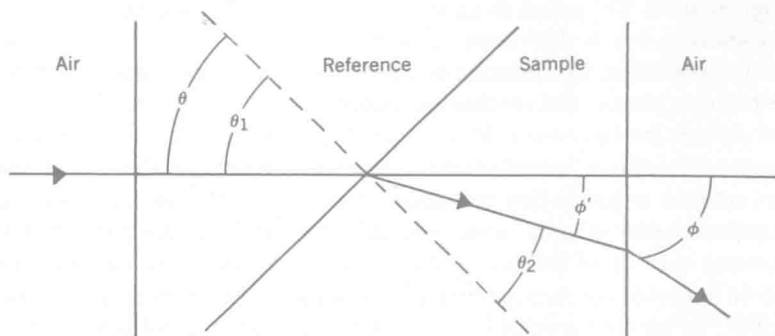


Figure 2. Propagation of light beams through the reference and sample flow cells in a deflection-type RI detector.



are pairs of parallel faces. For simplicity, we have assumed that the light beam enters normal to the first cell wall.  $n_2$  is simply  $n_1 + \Delta n$ , where  $\Delta n$  is the contribution due to the presence of the analyte, according to Eq. 11. Equation 13 then becomes

$$n \sin \theta = (n + \Delta n) \sin(\theta - \phi') \quad (14)$$

At low concentrations, that is, those typical of LC after the column,  $\Delta n$  and  $\phi'$  are both small, so

$$\phi' = \frac{\Delta n}{n} \tan \theta \quad (15)$$

If we further assume that the RI of air is unity, Snell's law gives

$$\begin{aligned} \phi &= (n + \Delta n)\phi' \\ &\approx \Delta n \tan \theta \end{aligned} \quad (16)$$

Actually, the commercial instrument uses a rear mirror to fold the light beam through the same cell a second time, doubling the net deflection. If the deflection is measured as a displacement of  $\Delta x$  at a distance  $X$  away from the cell, then

$$\Delta x = 2 \tan \theta \Delta n X \quad (17)$$

It can be seen that the sensitivity is best when  $\theta$  is maximized. In practice, a compromise of  $\theta = 45^\circ$  has to be used to maintain a small cell volume. If  $X$  is 13 cm, then  $\Delta x = 26 \Delta n$  cm. Because the dual-diode position sensor can detect a change of about  $10^{-4}$  cm on its most sensitive setting (full scale), the maximum RI sensitivity is  $3.8 \times 10^{-6}$  units full scale.

The limitations on the commercial unit include beam collimation, sensitivity of the position sensor, and mechanical rigidity of the system. A slit formed by a mask defines the light beam from a tungsten lamp. If a laser is used instead, the beam collimation is improved and a longer optical lever can be used. Position sensors are now available that can detect deflections to  $10^{-9}$  rad, or three orders of magnitude better than the ones used in commercial RI detectors. However, the pointing stability of the laser and the mechanical rigidity of the system will have to be improved substantially to take advantage of these new position sensors.

Finally, an interesting feature of the commercial RI detector is a mechanical null adjustment. Even though Fig. 2 shows no deflection whenever  $\Delta n$  is zero for any solvent RI, there is actually a deflection that depends on  $n$  because the incidence angle on the cell is not zero degrees. So, a glass plate is put in the