

## CH424 Instrumental Analysis Lab

### <sup>1</sup>H NMR Analysis of Trichloroethane Mixture

(Reproduced from CH 424 Instrumental Analysis Course Manual, spring 1996, written by Jim Peterson; modified by addendum)

#### Introduction

The composition of mixtures can be quantitatively determined by NMR spectroscopy if distinguishable signals from each component can be integrated separately. The use of an internal standard renders the integration an absolute measurement. In this particular experiment the composition of a mixture of 1,1,1-trichloroethane and 1,1,2-trichloroethane is assayed by <sup>1</sup>H NMR spectroscopy. The chemical shifts of interest, in ppm on the  $\delta$  scale, are:

Trichloroethene	:	6.5
1,2-dichloroethane	:	3.7
1,1,1-trichloroethane	:	2.8
1,1,2-trichloroethane	:	3.9 (doublet); 5.8 (triplet)

#### Reagents

Use carbon tetrachloride, 1% (v/v) in as % (v/v) in TMS as the solvent to prepare five standard solutions with composition: 5% (v/v) 1,2-dichloroethane, 15% (v/v) trichloroethane and 10.0, 15.0, 20.0, 25.0, 30.0% (v/v) 1,1,1-trichloroethane. Prepare a second set of five standards using 1,1,2-trichloroethane instead of 1,1,1-trichloroethane. **NOTE:** Dispose of chlorocarbons in an appropriately labeled container.

#### Procedure

Introduce approximately 0.5 mL of a standard solution into an NMR tube and record the <sup>1</sup>H NMR spectrum between 8.0 and 0.0 on the  $\delta$  scale. Then integrate the signals. Continue in the same manner with the other solutions to prepare calibration curves for 1,1,1-trichloroethane and 1,1,2-trichloroethane, using both internal standards (i.e. generate four curves in all).

Obtain from your instructor an unknown consisting of a mixture of 1,1,1-trichloroethane and 1,1,2-trichloroethane in carbon tetrachloride/TMS. Add 1,2-dichloroethane to 5% (v/v) and trichloroethene to 15% (v/v) as internal standards. Proceed to record the <sup>1</sup>H NMR of this solution over the same range as the standards and integrate the signals obtained. Determine the composition of the unknown mixture by comparing the measured integrated intensity ratios (unknown/standard of the signals with those of the calibration curves. Use the data sets generated with each internal standard independently to obtain two results. Report these in terms of composition of the mixture as it was supplied to you (i.e. before the addition of the internal standards) quoting the 95% confidence limits..

## Questions

- (1) Why is it not necessary to use the same NMR tube for all solutions measured?
- (2) Which internal standard should give the most reliable result in this experiment and why?

## References

T. Wallace, *J. Chem. Ed.*, **61**,1074 (1984)  
J. Peterson, *J. Chem. Ed.*, **69**, 843-845 (1992).

## Addendum

A very significant advantage of NMR determinations is that they do not require availability of pure analyte for calibration purposes. The generation of a calibration curve is, therefore, not absolutely necessary for this type of quantitative measurement. The only Requirements are: i) that distinguishable signals from analyte and (internal) standard can be integrated separately; iii) the numbers of nuclei giving rise to these signals are known.

Approximately 5 mL of the unknown solution is carefully weighed in a stoppered vial. After adding several hundred mg of standard, the increase in weight is accurately determined and the number of moles of standard added ( $\text{mol}_i$ ) calculated. After mixing and transferring to an NMR tube, the spectrum and integrals are recorded in conventional fashion. The number of moles of the analyte in the aliquot taken is given by:

$$\text{mol}_a = \text{mol}_i \times \left( \frac{\text{Integral (analyte)}}{\text{Integral (int .std.)}} \right) \times \frac{N_i}{N_a}$$

where  $N_a$  and  $N_i$  are the number of nuclei giving rise to the relevant analyte and standard signals respectively.