Waters Lab Highlights

An Internal Communication of Applications and Techniques

LAH 0294 2/86
DP/OS/MD/FE/OT

NO. 108 SOLID SUPPORTED DERIVATIZATIONS FOR ALKYL HALIDES AND EPOXIDES FOR IMPROVED DETECTION IN HPLC

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Solid phase derivatizations to be used in conjunction with HPLC have recently gained a considerable amount of popularity and this area has been recently reviewed (1). Most of these approaches already described involved a chemical reaction of the analyte in which a particular functionality was masked or altered. If done in the pre-column mode, these types of reactions change the chromatography of the analyte which resulted in a more specific analysis, but did not necessarily increase the final sensitivity or decrease detection limits of that analyte.

Our current interests involve pre-column labelling reactions, wherein a substrate with poor or non-existent detection properties in HPLC is labelled with a reagent that yields a derivative with desirable detection properties. Picric acid (2,4,6-trinitrophenol) salts adsorbed onto silica gel were reacted with a variety of alkyl halides including ethylene dibromide (EDB) and an epoxide (2,3). The picryl ethers formed in the derivatization reaction were monitored using UV, reductive electrochemical, and/or photolysis/oxidative electrochemical detection. Significant improvements in both sensitivity and selectivity were achieved through this derivatization approach. The effect of picrate's counter ion on reactivity was studied. Solution vs solid phase reactions were also compared.

Of particular interest was EDB which was converted to its monopicryl and/or dipicryl derivative as a function of reaction time or temperature. The ratio of these derivatives may be specific for EDB and was used to distinguish EDB from other similar compounds such as ethylene diiodide and ethylene dichloride. The combined specificity of the product ratio, the chromaography of these products, and the ability to use three different detection modes provided an extremely specific HPLC method for this compound. In addition to the high degree of specificity, this approach was also very sensitive. For low levels of EDB, the reaction conditions were engineered to convert EDB mainly to the dipicryl derivative. Percent conversions to the dipicryl derivative were as high as 82%. Under these conditions, the limit of detection was below 1 part per billion (ppb) if the photolysis detector was used. Detection limits for EDB after derivatization using UV or reductive electrochemical detection were both below 10 ppb.

One of EDB's current uses is as a lead scavenger in leaded gasoline. This derivatization approach was used to monitor the EDB concentration in a commercial supply of regular gasoline and the results were verified by gas chromatography with electron capture detection (GC/ECD). The method was further validated by a single blind study of spiked EDB in gasoline.

1. S. T. Colgan and I. S. Krull, "Solid Phase Reaction Detectors for HPLC," invited chapter in Post-Column Reaction Detectors for HPLC, ed. by I. S. Krull, Marcel Dekker, Inc., in press, 1986.

2. S. T. Colgan, I. S. Krull, U. Neue, A. Newhart, C. Dorschel, C. Stacey, and B. Bidlingmeyer, J. Chromatogr. 333, 349 (1985).

3. S. T. Colgan, I. S. Krull, C. Dorschel, and B. Bidlingmeyer, Anal. Chem., submitted for publication (1985).