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## Note

# Analysis of 2,2′-thiodiethanol in aqueous matrices by liquid chromatography with electrochemical detection

P. C. BOSSLE*, S. F. HALLOWELL, D. J. REUTTER and E. W. SARVER
*Analytical Division, Research Directorate, Chemical Research & Development Center, Aberdeen Proving Ground, MD 21010-5423 (U.S.A.)*
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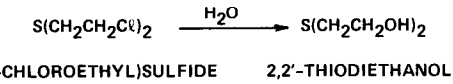
The ability easily to detect, separate and quantitate trace amounts of 2,2′-thiodiethanol in aqueous matrices is of relevance and potential use in environmental studies as well as in general analytical methodology. 2,2′-Thiodiethanol, commonly known as thiodiglycol (TDG), is the major hydrolysate of bis(2-chloroethyl) sulfide (mustard gas):




Because mustard gas is susceptible to hydrolysis, TDG is more likely to be encountered in the natural environment than mustard gas itself.

Gas chromatography (GC) has been employed to analyze TDG in non-aqueous matrices[1]. A lengthy extraction and work-up procedure must be performed, however, before TDG in an aqueous matrix can be analyzed.

By itself, TDG is not amenable to direct spectroscopic or high-performance liquid chromatographic (HPLC) analysis using the conventional ultraviolet (UV) or fluorescence detector. It has been demonstrated that this problem could be circumvented for alkyl sulfides by derivatizing them to chromophore-bearing N-phenylsulfonylsulfilimines prior to HPLC analysis[2]. However, the manual applications involved in precolumn derivatization can be tedious and time-consuming. In addition, side-product formation and incomplete derivatization could complicate the chromatogram and make quantitative analysis difficult.

Nicholson[3,4] demonstrated that alkyl sulfides are electrochemically active and can be irreversibly oxidized at 0.8–1.0 V on a platinum working electrode in 0.1 *M* hydrochloric acid. In this report, we evaluate the suitability of liquid chromatography with electrochemical detection (LC–ED) for the direct analysis of TDG in an aqueous matrix. Optimum electrochemical and chromatographic parameters were determined for maximum selectivity and sensitivity. The application of this technique for the detection of TDG in soil and ground-water is demonstrated.

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## MATERIALS AND METHODS

### *Instrumentation*

HPLC analyses were carried out using a Waters Assoc. liquid chromatograph consisting of a Model 6000A pump, an U6K injector, a 730A data module and a 720A systems controller. The separation was carried out using an Alltech Assoc. 10-$\mu$m $C_{18}$ (600 RPC) column (25 cm × 4.6 mm I.D.). An LC-4B amperometric controller with a LC-17 flow cell equipped with a TL-10 platinum electrode and a RE-1 silver–silver chloride reference electrode was utilized as the detector (Bioanalytical Systems, West Lafayette, IN, U.S.A.).

### *Chromatographic procedures*

Analytical separations were performed under the following conditions: sample size, 5 $\mu$l; flow-rate, 1.5 ml/min; column temperature, ambient; mobile phase, acetonitrile–0.2 *M* sodium phosphate buffer (pH 8.0) (5:95); detector potential, +970 mV; detector sensitivity, 0.5–1.0 nAFS.

A standard solution of TDG was injected onto the column and a retention time of 3.9 min was determined. A peak fraction was collected, and its identity con-

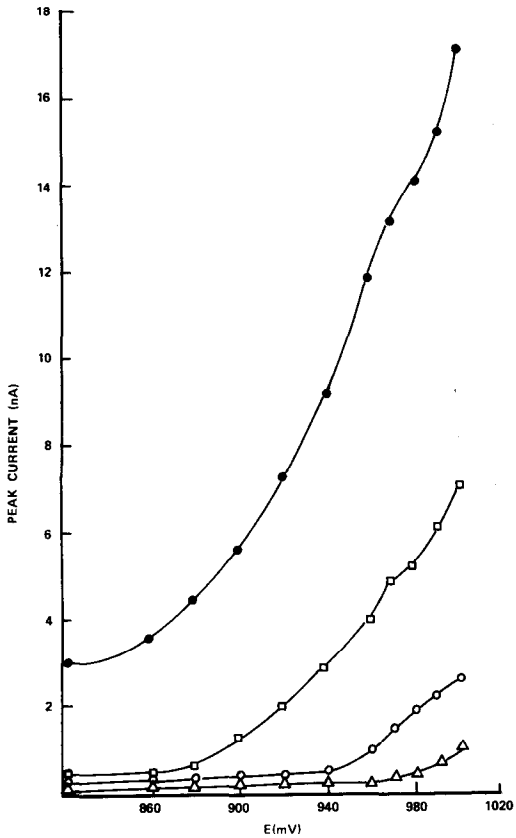


Fig. 1. Hydrodynamic voltammograms of TDG at pH 5.0 (△—△), 6.0 (○—○), 7.0 (□—□) and 8.0 (●—●).

firmed by mass spectrometry. The calibration curve was obtained by injecting 5 μl of a known concentration (10, 20, 40, 100, 200 and 400 ng/ml) of TDG onto the column in triplicate and measuring the detector response in terms of peak height (pA).

*Sample preparation*

Two 1-g samples of well mixed soil were weighed out. One sample was spiked with 10 μl of a solution of 100 ppm of TDG in deionized water to give a concentration of 1 ppm TDG. To each sample was added 10 ml of deionized water and the samples were sonicated for 1 h. The soil–water mixtures were then centrifuged at 1640 *g* for 10 min, separation of the aqueous extracts being accomplished using a CF25 centriflow membrane cone (Amicom Corp., Danvers, MA, U.S.A.). The aqueous extracts could then be analyzed directly.

For the ground-water assay, a river-water sample was spiked with 1 ppm of TDG. The spiked sample and an unspiked sample were each successively filtered and injected into the liquid chromatograph.

## RESULTS AND DISCUSSION

To determine the optimum mobile phase pH and electrode potential for the assay of TDG, four different hydrodynamic voltammograms (HDVs) for TDG were performed with the mobile phase buffered to pH 5.0, 6.0, 7.0 and 8.0, respectively, using repetitive injections of 50 ng. Fig. 1 describes the results obtained. The direct

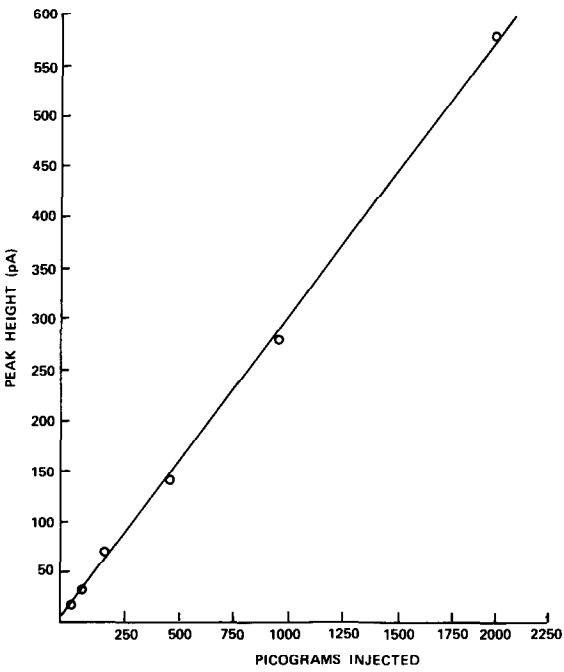


Fig. 2. Linearity of LC–ED for TDG.

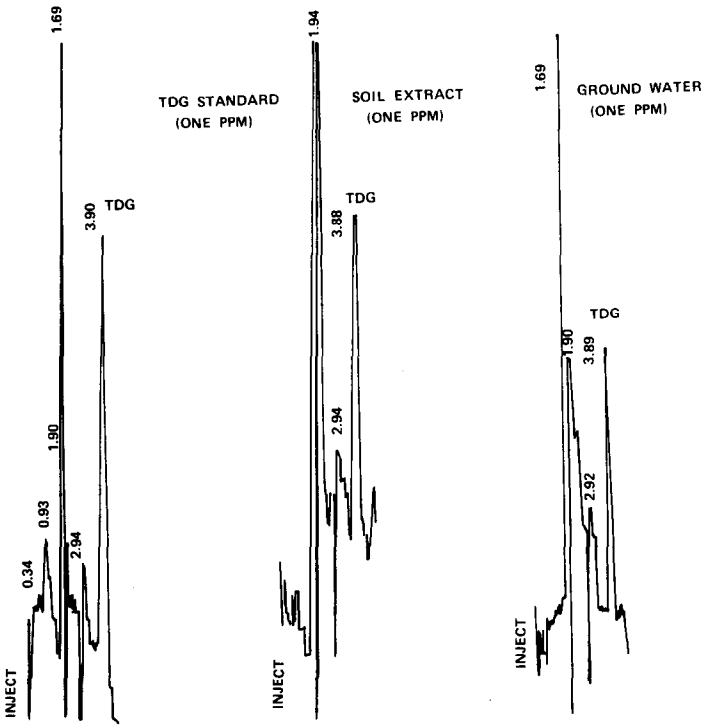


Fig. 3. LC–ED chromatograms for TDG standard, soil extract and ground-water.

relationship between the increasing pH of the mobile phase and detector sensitivity to TDG is quite dramatic. These results are in agreement with Nicholson's findings that the rate of sulfide oxidation is directly dependent on the hydroxide ion concentration[4]. Due to the pH limitations of the silica-based columns, buffers of higher pH were not investigated and a phosphate buffer of pH 8.0 was chosen as the mobile phase for this study. A plateau was not observed for any of the HDVs. An oxidation potential of +970 mV was selected because it provided the sensitivity and chemical specificity desired.

Fig. 2 shows the linearity of the LC–ED assay for TDG over the range of 50–2000 pg injected (slope, 0.285 pA/pg; *y* intercept, 4.16 pA; correlation coefficient, 0.9994). The minimum detectable amount (S/N of 6) was 50 pg.

Chromatograms of a standard 1 ppm solution of TDG, of the spiked soil extract and the spiked ground-water sample are shown in Fig. 3. The chromatograms are clean and free from interference.

Thus, direct electrochemical detection can greatly simplify the assay of trace levels of TDG in real world samples.

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