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DETERMINATION OF THIOCYANATE, THIOSULFATE, SULFITE AND NITRITE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED WITH ELECTROCHEMICAL DETECTION

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High performance liquid chromatography with an electrochemical detector (Yanaco Model VMD-101) was used to determine SCN^-, $S_2O_3^{2-}$, SO_3^{2-} and NO_2^-. Those anions were separated on a TSK-GEL IEX-520 QAE (anion exchanger) column, with a mobile phase of 0.05 M sodium phosphate buffer (pH 7.5) containing 0.05 M $NaNO_3$ and were detected electrochemically at 0.9 V vs. Ag/AgCl. The minimum detectable amounts of SCN^-, $S_2O_3^{2-}$, SO_3^{2-} and NO_2^- were 0.015, 0.05, 2.5, 0.012 ppm, respectively.

KEYWORDS —— high performance liquid chromatography; electrochemical detector; thiocyanate; thiosulfate; sulfite; nitrite

During the study on the metabolism of cyanide, we have required simple and sensitive analytical methods for the reducing anions such as SCN^-, $S_2O_3^{2-}$ and SO_3^{2-}.

Although ion chromatography[1-3] is a very convenient and useful method for the determination of those anions in environmental samples, complicated pretreatment is usually necessary to remove foreign electrolytes for the analysis of biological materials.

Recently, high performance liquid chromatography combined with an electrochemical detector (HPLC-ECD) has been applied to microanalysis of catecholamines and many other organic compounds,[4-6] and a few applications to inorganic anions have been reported.[7,8]

In this experiment, we tried to develop HPLC-ECD for the determination of those inorganic anions together with NO_2^- which has very high response to ECD.

The optimum supporting electrolytes for ECD (glassy carbon working electrode) were examined to determine the anions described above. Sodium carbonate was not useful as a supporting electrolyte on account of a higher background current, but NaCl, $NaNO_3$, Na_2SO_4 and NaH_2PO_4-Na_2HPO_4 were generally suited.

We tried to utilize those for the eluents to separate SCN^-, $S_2O_3^{2-}$, SO_3^{2-} and NO_2^- on an anion exchanger TSK-GEL IEX-520 QAE (Toyo Soda Co. Ltd.,) column, but complete separation was not attainable in the concentrations higher than 0.2 M for all salts. Four anions were separated excellently in a short time by using 0.1 M $NaNO_3$, and 0.1 M sodium phosphate buffer (pH 7.5) also showed good chromatographic separation compared with other eluents. The effective pH range of the exchanger was from 2 to 8, and decomposition of the anions during the chromatographic separation decreased with increasing pH of the mobile phases.

On the other hand, the responses of four anions increased with increasing salt concentration in the eluents. So the optimum condition of the mobile phase was considered to be 0.05 M phosphate buffer (pH7.5) containing 0.05 M $NaNO_3$.

The applied potential was examined and 0.9 V vs. Ag/AgCl reference electrode was chosen considering the responses of anions and the stability of the base line on the chromatogram.

The schematic diagram of HPLC-ECD and a typical chromatogram are shown in Figs. 1 and 2. The calibration curves for SCN^-, $S_2O_3^{2-}$, SO_3^{2-} and NO_2^- were linear in the range of 0.015-15, 0.05-15, 2.5-80 and 0.012-1 ppm, respectively.

With respect to those reducing inorganic anions, this method is one of the most sensitive methods reported previously, and its application will be described in the near future.

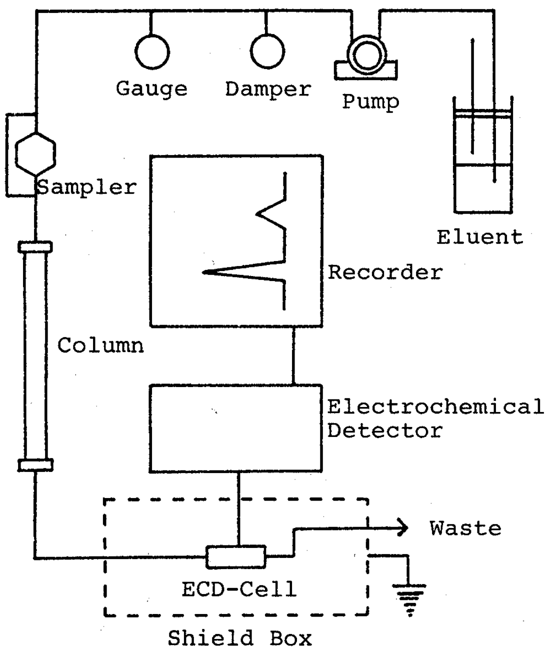

Fig. 1. Schematic Diagram of the Instrument

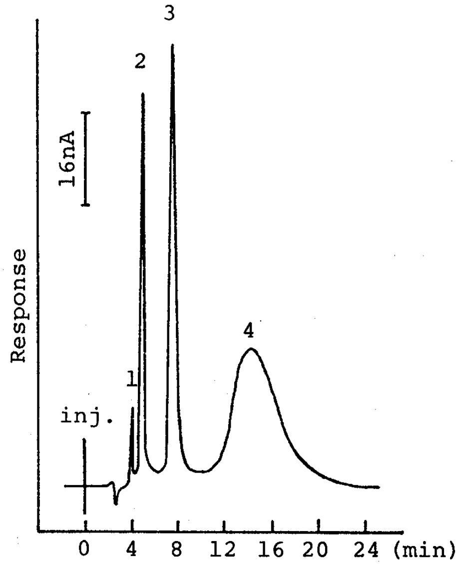

Fig. 2. Chromatogram of Nitrite, Thiosulfate, Thiocyanate and Sulfite
Column: TSK-GEL IEX-520 QAE (4mm i.d.x 150mm).
Mobile phase: 0.05 M sodium phosphate buffer (pH 7.5) containing 0.05 M $NaNO_3$.
Applied potential: 0.9 V vs. Ag/AgCl.
Flow rate: 0.7ml/min.
Sample size: 10μl.
Sample: 1, NO_2^-(0.25ppm). 2, $S_2O_3^{2-}$(3.75ppm). 3, SCN^-(2.5 ppm). 4, SO_3^{2-}(80 ppm).

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