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GAS CHROMATOGRAPHIC DETERMINATION OF NITRITE ION IN WATER USING THE SANDMEYER REACTION

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An improved gas chromatographic method is presented for the determination of trace amount of nitrite ion (NO_2^-) in water. The method is based on the Sandmeyer reaction, i.e., the diazotization of p-bromoaniline by NO_2^- followed by reaction with CuCl in hydrochloric acid to form p-bromochlorobenzene. The derivative is determined by gas chromatography, employing an electron capture detector. The detection limit for NO_2^- is 0.5 ng/ml (ppb).

In recent years, gas chromatographic methods for the determination of NO_2^- have been developed.[1-4] Funazo et al. reported a new gas chromatographic method,[3-4] in which NO_2^- in aqueous solution was made to react with aromatic amine in the presence of copper (II) halide and the resulting arylhalide was subsequently determined by gas chromatography, employing an electron capture detector (GC-ECD). However, the reaction time in this method is too long (i.e., 2-4 h). Their papers have prompted us to report an improved analytical technique for NO_2^-. The procedure involves the Sandmeyer reaction, i.e., the diazotization of p-bromoaniline by NO_2^- followed by reaction with CuCl in hydrochloric acid to form p-bromochlorobenzene, and quantitative determination by GC-ECD.

Two ml of the benzene solution containing p-bromoaniline (1×10^{-2} M) was added to 2 ml of water sample in a 10-ml test tube, and the mixture was cooled well in an ice-water bath. Then 0.5 ml of 3 N HCl was added, and the mixture was shaken for 10 sec and left to stand for 10 min in an ice-water bath. Two ml of CuCl (2×10^{-1} M) in 12 N HCl was added and the mixture was shaken for 15 min at room temperature (20 °C). This CuCl-HCl solution was prepared freshly before use; CuCl was obtained commercially. The organic layer was separated from the aqueous layer and dried with about 0.5 g of anhydrous Na_2SO_4. Two or 5 µl of the organic layer was injected into a gas chromatograph (Shimadzu GC-6AM equipped with a ^{63}Ni-ECD). The analyzing column (2.5 m x 3 mm i.d., glass) was packed with 80-100 mesh Chromosorb W coated with 2 % OV-17. The GC operating conditions were: carrier gas; nitrogen (30 ml/min), temperatures; detector and injector 250 °C, column 130 °C, pulse frequency; 5 or 20 KHz. The concentration of NO_2^- was determined by comparing the peak height of the reaction product with the calibration curve prepared by the same procedure for a series of solutions of known concentration.

A typical ECD chromatogram is shown in Fig. 1. The reaction product was

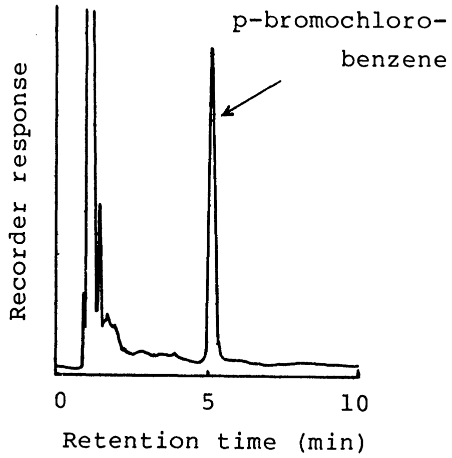

Fig. 1 Typical ECD chromatogram (sample solution obtained from 66 ppb solution of NO_2^-).

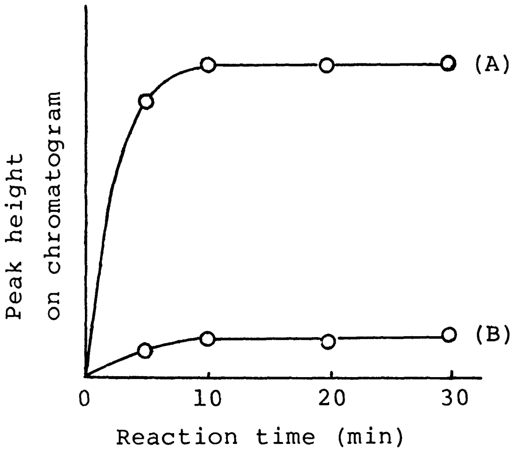

Fig. 2 Dependence of the product yields on the reaction time after addition of the CuCl-HCl solution.
(A) 66 ppb solution of NO_2^- (final yield, 95 %)
(B) 6.6 ppb solution of NO_2^- (final yield, 90 %)

identified as p-bromochlorobenzene by GC-mass spectrometry using a JEOL Model JMS-D 300 mass spectrometer coupled with a JMA-2000 mass data analysis system. 1,2,4-Trichlorobenzene, if desired, could be used as an internal standard (retention time, 7 min). As shown in Fig. 2, the reaction was completed within about 10 min after addition of the CuCl-HCl solution, and p-bromochlorobenzene was formed in good yield. The calibration curve (peak height vs. NO_2^- concentration) was linear in the range of 1-30 and 30-650 ppb NO_2^- in water sample. Blank tests usually showed the presence of about 1 ppb NO_2^- in distilled water and hence it was necessary to correct the calibration curve at a low concentration region for the blank value. The detection limit was 0.5 ppb. The detection limit was calculated from the formula $3\sqrt{2}\ s_{bl}$ where s_{bl} is the standard deviation of blank measures. There were no apparent interferences with this method by NaCl (10 %), NO_3^- (0.03 %), NH_4^+ (0.2 %), SO_4^{2-} (0.1 %), and PO_4^{3-} (0.1 %) in water samples.

As mentioned above, we succeeded to establish a procedure which was found to be rapid and sensitive for the routine determination of NO_2^- in water sample.

The applications of this method to environmental samples, e.g., natural water samples and foods, are in progress.

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