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ANALYSIS OF NITRITE ION IN WATER BY ELECTRON CAPTURE GAS CHROMATOGRAPHY

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A new gas chromatographic procedure for the analysis of trace amount of nitrite ion in water has been developed. The procedure involves the conversion of nitrite ion into 3,4-dichlorobromobenzene which is subsequently determined by electron capture gas chromatography. The coexistence of chloride ion in a large amount with nitrite ion gives rise to the production of 1,2,4-trichlorobenzene in addition to 3,4-dichlorobromobenzene.

Procedures for the colorimetric determination of nitrite ion (NO_2^-) in water have been based on the diazotization of sulfanilic acid by NO_2^- and subsequent coupling with an agent such as α-naphthylamine. Saltzman published a wet chemical technique for the determination of nitrogen dioxide and nitrogen oxide (NO) by the use of the analytical procedure of NO_2^- 1). A gas chromatographic method for the determination of NO_2^- was also presented2)3). This method was based on the nitration of benzene by nitrate ion (NO_3^-) to which NO_2^- was oxidized and the determination of the resulting nitrobenzene by electron capture gas chromatography (EC-GC).

In the previous paper4) we reported a new gas chromatographic detection of NO, in which NO was converted into arylhalide according to the reaction published by Brackman et al.5) and the resulting arylhalide was determined by EC-GC. This method was extended to the analysis of NO_2^-; NO_2^- in aqueous solution was made to react with aromatic amine in the presence of copper(II) halide (CuX_2: X=Cl, Br) to form arylhalide which was subsequently determined by EC-GC. The reactions are seemed to be formulated as follows:

$$\mathrm{Y\text{-}C_6H_4\text{-}NH_2} \; + \; \mathrm{NO_2^-} \longrightarrow \mathrm{Y\text{-}C_6H_4\text{-}\overset{+}{N}{\equiv}N} \; + \; \mathrm{2OH^-}$$

$$\mathrm{Y\text{-}C_6H_4\text{-}\overset{+}{N}{\equiv}N} \xrightarrow{\mathrm{CuX_2}} \mathrm{Y\text{-}C_6H_4\text{-}X}$$

In this work the analysis of NO_2^- in water by EC-GC was investigated by modifying the above reactions in which 3,4-dichloroaniline and copper(II) bromide were used.

Ten ml of $CuBr_2$ aqueous solution (5.0×10^{-2} M) was added to 10 ml of a known concentration of sodium nitrite. Then 5 ml of the toluene solution was added and the mixture was shaken for 2 h. This toluene solution contains 3,4-dichloroaniline (1.0×10^{-2} M) and p-bromochlorobenzene (2.0×10^{-6} M) as an internal standard. At the end of the reaction period, the organic layer was separated from the aqueous layer and the former (1 μl) was directly injected into the gas chromatograph. The reaction product of 3,4-dichlorobromobenzene was determined by an internal standard method. The gas chromatograph used was Shimadzu GC-4BM equipped with a ^{63}Ni-ECD. The column (2 m × 3 mm i.d. stainless steel packed with 10 % OV-17) and detector temperatures were 150 and 250 °C, respectively. The flow rate of nitrogen was 50 ml/min.

Because of the direct injection of the organic layer into the gas chromatograph, the peak of a large excess of 3,4-dichloroaniline appears after a long interval from the three peaks (i.e. toluene, p-bromochlorobenzene, and 3,4-dichlorobromobenzene). In order to avoid the troubles due to entering of 3,4-dichloroaniline into the ECD cell, 3,4-dichloroaniline was discarded out of the gas chromatographic system through the cock installed between the separation column and the ECD cell.

The calibration curve (Fig. 1) is linear in the range of 0.1-1.0 μg $NaNO_2$ in 10 ml of water sample ($\times 10^2$ ppb). The detection limit for $NaNO_2$ is 0.1 μg in 10 ml of water sample. It can be expected to detect NO_2^- at the lower concentration than 0.1 μg/10 ml by the use of aniline derivatives with substituents which yield higher response to an ECD than 3,4-dichloroaniline. The calibration curve does not pass through the origin, the reason of which is presumably due to the small unknown peak given by the blank without NO_2^-. This peak is not separated from the 3,4-dichlorobromobenzene peak.

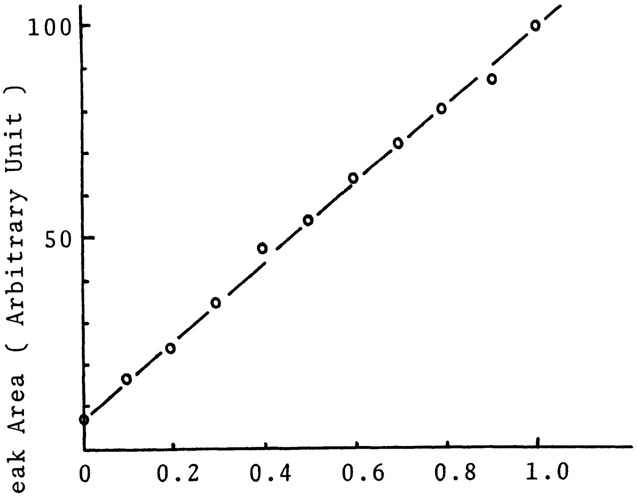

Fig. 1 Calibration Curve for NO_2^-

The influence of cosolute, NO_3^- or Cl^-, was investigated. NO_3^- did not react with aniline as NO_2^- did: NO_3^- does not interfere with this analysis of NO_2^-. Cl^- may be contained in a large amount such as in sea water. Then NaCl is added to be 2.5 % to the sample solution of NO_2^-. The decrease of peak area of 3,4-dichlorobromobenzene to about 50 % results from the addition of NaCl and the small peak of 1,2,4-trichlorobenzene appears on the chromatogram. The use of $CuCl_2$ instead of $CuBr_2$ will be able to avoid this interference of Cl^-. The details of this phenomenon is under investigation.

It is probable that by reacting with the diazonium ion prepared from $NaNO_2$ and the aniline derivative halide ions are converted into the corresponding arylhalides in the presence of copper ion (not halide salt) and determined by EC-GC in much the same way as NO_2^-.

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