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Identification of inorganic anions by gas chromatography/mass spectrometry

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Abstract

Inorganic anions were identified by using gas chromatography/mass spectrometry (GC/MS). Derivatization of the anions was achieved with pentafluorobenzyl *p*-toluenesulphonate (PFB-Tos) as the reaction reagent and a crown ether as a phase transfer catalyst. When PFB-Br was used as the reaction regent, the retention time of it was close to those of the derivatized inorganic anions and interfered with the analysis. In contrast, the retention time of PFB-Tos differed greatly from the PFB derivatives of the inorganic anions and the compounds of interest could be detected without interference.

Although the PFB derivatives of SO_4, S_2O_3, CO_3, ClO_4, and ClO_3 could not be detected, the derivatives of F, Cl, Br, I, CN, OCN, SCN, N_3, NO_3, and NO_2 were detected using PFB-Tos as the derivatizing reagent. The inorganic anions were detectable within 30 ng approximately, which is of sufficient sensitivity for use in forensic chemistry. Accurate mass number was measured for each PFB derivative by high-resolution mass spectrometry (HRMS) within a measurement error of 2 millimass units (mmu), which allowed determination of the compositional formula from the mass number.

In addition, actual analysis was performed successively by our method using trial samples of matrix.

Keywords: Forensic science; Inorganic anion; Pentafluorobenzyl derivatives; Crown ether; Gas chromatography; Mass spectrometry

1. Introduction

The analysis of inorganic anions in forensic chemistry is important for the analysis of powder residue from explosives and contamination of poisons. Generally, analysis of inorganic anions is accomplished by ion chromatography [1,2]. Recently, capillary electrophoresis methods [2–8] have been developed.

Ion chromatography and capillary electrophoresis identify inorganic anions by retention time or migration time. However, a sample contaminated with matrix is often difficult to analyze. Gas chromatography/mass spectrometry (GC/MS) identifies compounds by chromatography retention time and mass spectrum, making the method a highly accurate procedure and an essential method in forensic chemistry. Inorganic anions are not volatile, so analysis by gas chromatography directly is difficult. Therefore, GC methods for inorganic ions require conversion to a volatile derivative such as a methyl [9], ethyl [10], butyl [11], or pentafluorobenzyl (PFB) derivative [12–16]. Among them, PFB derivatives have been used for supersensitive ECD

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(electron capture detector) in GC [12] and GC/MS [13–16]. The conventional synthesis of PFB derivatives of inorganic anions uses a quaternary ammonium salt as a phase transfer catalyst, with the reaction conducted between an organic (salt of anion) and an aqueous (PFB-Br and PFB derivative of anion) phase.

Funazo et al. [12] reported that bromide, iodide, cyanide, thiocyanate, nitrite, nitrate, and sulfide could be converted to PFB derivatives using pentafluorobenzyl *p*-toluenesulphonate (PFB-Tos) as the derivatizing reagent and tetra-*n*-amylammonium chloride as a phase transfer catalyst. The PFB derivatives were analyzed by GC with a flame ionization detector. But this method was not ideal for the identification of unknown ions, because GC discriminated among unknown agents only by retention time.

Kage et al. reported the analysis of PFB derivatives of inorganic anions by GC/MS. Cyanide [13], thiocyanate [13], nitrite [14], nitrate [14], and azide [15] were converted to PFB derivatives using pentafluorobenzyl bromide (PFB-Br) and tetra-decyldimethylbenzylammonium chloride (TDMBA) as a phase transfer catalyst.

In addition, Tsuge et al. [16] reported that cyanide, thiocyanate, nitrite, nitrate, azide, and sulfide could be converted to PFB derivatives using PFB-Br as the derivatizing reagent and TDMBA or polymer-bound tributylmethylphoshonium chloride as a phase transfer catalyst, and then identified by GC/MS. However, when the quaternary ammonium salt was used as the phase transfer catalyst as shown in the case of Kage et al. and Tsuge et al., the anion of the salt (e.g., chloride or bromide ion) was present in the reaction mixture. Therefore, the detection of chloride or bromide was difficult.

This study was designed to develop a method for the discrimination of inorganic anions under a single condition. Crown ethers were used as a phase transfer catalyst because they do not contain inorganic anions. The inorganic anions were derivatized between a solid (salt of anion) and liquid (PFB-Tos and PFB derivative of anion) phase by PFB-Tos, using a crown-ether as the phase transfer catalyst. This resulted in a more convenient reaction process than the previously reported processes. PFB derivatives were detected by GC/MS, and detection limits were determined.

Furthermore, the application of our method to trial samples of matrix was actually performed by using beverages which contained azide and cyanide; because, sodium azide and potassium cyanide become a problem in matters relating to poisoning in Japan.

For low-resolution mass spectrometry (LRMS), the same mass number can indicate different compositions. Because LRMS determines integral mass; it cannot unambiguously identify a compound. Then, accurate mass measurement by high-resolution mass spectrometry (HRMS) becomes important.

Accurate mass measurement of PFB derivatives of inorganic anions to identify compositional formula using high-resolution GC/MS has not yet been reported. Therefore, we determined the compositional formula of PFB derivatives of inorganic anions by measurement of the mass number.

2. Experimental

2.1. Materials

2.1.1. Inorganic anions

Inorganic anions were purchased from Wako Pure Chemical Industries Co. Ltd. (Osaka, Japan) and Kanto Chemistry Co. Ltd. (Tokyo, Japan). The following reagents were used: potassium fluoride (KF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), potassium cyanide (KCN), potassium cyanate (KOCN), potassium thiocyanate (KSCN), sodium azide (NaN_3), potassium nitrate (KNO_3), sodium nitrite ($NaNO_2$), potassium perchlorate ($KClO_4$), sodium chlorate ($NaClO_3$), sodium sulfate (Na_2SO_4), sodium thiosulfate ($Na_2S_2O_3$), and sodium carbonate (Na_2CO_3).

2.1.2. Derivatizing reagent

Pentafluorobenzyl *p*-toluene sulfonate (PFB-Tos, TCI; Tokyo, Japan) was used for the derivatizing regent. PFB-Tos (1.761 g) was dissolved in 100 ml of dichloromethane to give a concentration of 50 mM.

2.1.3. Phase transfer catalysts

The 18-crown-6-ether (18-crown-6, Wako Pure Chemical Industries Co. Ltd., Osaka, Japan) and 15-crown-5-ether (15-crown-5, Aldrich; St. Louis, MO, USA) were used as phase transfer catalysts. 18-crown-6 (264.3 mg) and 15-crown-5 (220.2 mg) were dissolved in 100 ml of dichloromethane to give a concentration of 10 mM.

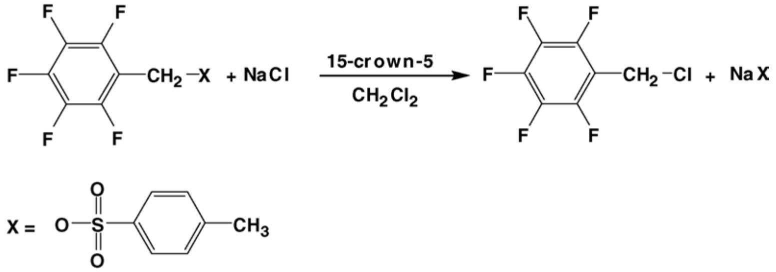

Fig. 1. Formula for the PFB derivatives.