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Separation and Quantitation of Monovalent Anionic and Cationic Species in Mainstream Cigarette Smoke Aerosols by High-Performance Ion Chromatography

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Why MeOH? ∴ Reaction of Nox with MeOH → MeNO2 !

Abstract

A simple method has been developed to separate and quantitate monovalent ionic species in mainstream cigarette smoke aerosols based on ion chromatography (IC) with conductivity detection. The method entails collecting the smoke aerosol particulate phase by electrostatic precipitation, dissolving the smoke condensate in methanol (MeOH), and separating the ionic species on either a cation- or anion-exchange column. The method has been applied to the analysis of smoke aerosols from two cigarettes, 1R4F Kentucky Reference cigarettes and a new cigarette that heats but does not burn tobacco. The predominant cations in smoke aerosols from 1R4F Kentucky Reference and the new cigarettes are sodium (Na^+), ammonium (NH_4^+), and potassium (K^+) ions; the predominant anions are acetate (AcO^-) and formate ($HCOO^-$). Trace amounts of chloride (Cl^-), nitrite (NO_2^-), and nitrate (NO_3^-) ions are also present.

Introduction

The mainstream smoke particulate phase produced by burning tobacco is a complex matrix composed predominantly of water, nicotine, and organic molecules. Much research has been devoted to the chemical characterization of the tobacco smoke particulate phase, especially with regard to its organic and nonionic constituents. Some studies have addressed characterization of its inorganic, metallic, or ionic composition. Past studies have been concerned with analyses for metallic constituents and have utilized spectroscopic techniques, such as atomic absorption (1–4), spark source mass spectroscopy (5–7), and neutron activation analysis (5–14). Moreover, determinations for nonmetallic neutral or ionic constituents in tobacco smoke condensates are generally based on activation analysis (5–14) or mass spectroscopy (5–7).

We have found no reports in the literature of the use of high-performance ion chromatography (IC) for analysis of tobacco smoke particulate phase or condensate. This is probably because smoke produced by burning tobacco is largely insoluble in water and most samples for ion chromatography are aqueous or are solubilized into an aqueous medium. In this correspondence, a method is presented to determine monovalent cations and anions in smoke condensates by high-performance ion chromatography with conductivity detection. The method involves precipitating smoke aerosols electrostatically, dissolving the particulate mass in methanol (MeOH), and analyzing the methanolic solutions by IC. The method has been employed for analyses of monovalent cations and anions in 1R4F Kentucky Reference cigarette smoke and in smoke from a new cigarette that heats rather than burns tobacco. The use of IC and a nonaqueous solvent, methanol, to separate and analyze the ions on ion-exchange columns distinguishes the method from previous reports. Recently a report on the separation of sodium (Na^+), potassium (K^+), and ammonium (NH_4^+) ions in another nonaqueous solvent, propanol, has been described (15).

Experimental

Reagents. All chemicals used to prepare standards, samples, eluents, and suppressor solutions were of reagent-grade quality or better. The reagents were used as received without further purification. The suppliers of the reagents and the purity of the reagents were as follows: acetic acid, sodium salt (NaOAc), 99+%, reagent grade, Aldrich; ammonium chloride (NH_4Cl), A.C.S. reagent, Aldrich; 2,3-diaminopropionic acid monohydrochloride (DAP·HCl), 99%, Aldrich; formic acid, sodium salt (NaOOCH), 99+%, reagent grade, Aldrich; hydrochloric acid (HCl), A.C.S. reagent, Fisher; potassium hydrogen carbonate ($KHCO_3$), 99+%, A.C.S. reagent, Aldrich; sodium carbonate, monohydrate ($Na_2CO_3 \cdot H_2O$), 99+%, A.C.S. reagent, Fisher; sodium hydrogen carbonate ($NaHCO_3$), 99+%, A.C.S. reagent, Fisher; sodium chloride (NaCl), 99+%, A.C.S. reagent, Fisher; sodium nitrate ($NaNO_3$), A.C.S. reagent, Aldrich; sodium nitrite ($NaNO_2$), 97+%, A.C.S. reagent, Aldrich; sulfuric acid (H_2SO_4), 95%, A.C.S. reagent, Fisher; tetramethylammonium hydroxide, pentahydrate ($Me_4NOH \cdot 5H_2O$), 97+%, Aldrich; and zinc chloride ($ZnCl_2$), 98%, A.C.S. reagent, Aldrich.

Sample preparation. Mainstream particulate phase condensate samples were obtained by smoking twenty cigarettes of each cigarette type on a Heinreich Borgwaldt (HB) 20-port rotary smoking machine (Model RM 20/CS). The particulate phase was collected by electrostatic precipitation with an HB High Tension Generator (Model 251), an HB Electrostatic Precipitation (EP) Trap, and glass EP tubes. For all samples the Federal Trade Commission (FTC) puffing regimen, i.e., a 35-cc puff of 2 s

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