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Gas chromatography negative ion chemical ionization mass spectrometry: Application to the detection of alkyl nitrates and halocarbons in the atmosphere

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ABSTRACT

Alkyl nitrates and very short-lived halocarbon species are important atmospheric trace gas species that are present in the low to sub parts per trillion concentration range. This presents an analytical challenge for their detection and quantification that requires instrumentation with high sensitivity and selectivity. In this paper, we present a new in situ gas chromatograph negative ion chemical ionization mass spectrometer (GC/NICI–MS) coupled to a non-cryogen sample pre-concentration system. This instrument, with detection limits of <0.01 ppt, is capable of detecting and quantifying a large suite of alkyl nitrate and halocarbon species with high sensitivity and precision. The effects of ion source temperature and reagent gas pressure on the ionization efficiency of the NICI mode are investigated and the results are used to optimize the sensitivity. The NICI mode is compared to the more frequently used electron impact (EI) ionization and the enhancements in sensitivity are presented for all the calibrated compounds.

1. Introduction

Alkyl nitrates are produced photochemically in the atmosphere through the reaction of nitric oxide with peroxy radicals derived from hydrocarbon oxidation [1]. They act as temporary reservoirs of nitrogen oxides (NO_x) and are chain terminators in photochemical ozone production. As a result of their relatively long atmospheric lifetimes they are important for the redistribution of NO_x [2].

Halocarbon gases are important for both tropospheric and stratospheric chemistry through their catalytic destruction of ozone. A range of halogenated “very short-lived substances” (VSLS), and their degradation products have recently been estimated to contribute significantly (10–40%) to stratospheric bromine and, to a much lesser extent, stratospheric chlorine [3]. Halogenated VSLS are thought to be regionally and/or globally important sources of reactive halogens in the troposphere, e.g., bromoform ($CHBr_3$) [4] and methyl iodide (CH_3I) [5,6], and have been linked to the autocatalytic halogen cycles that deplete surface ozone and deposit mercury to the snow pack in polar regions [7].

Alkyl nitrates and many short-lived halocarbons are present in the atmosphere with concentrations in the low or sub parts per trillion (ppt) range, which provides a significant measurement challenge. For low concentrations, cryogenic pre-concentration of up to a few liters of air has routinely been employed to lower detection limits [8,9]. This has often involved using liquid nitrogen and a sampling loop that can subsequently be thermally desorbed and injected on to the chromatographic column. However, the use of liquid cryogens can be a severe disadvantage at remote field sites, which makes the use of adsorbent polymers, e.g., Tenax^{TM}, and carbon molecular sieves a more desirable method for a more versatile field instrument. These adsorbents can often be used at ambient temperatures or can be chilled through the incorporation of water chillers, fans or with a peltier oven device.

Gas chromatography with electron capture detection (GC/ECD) has previously been used to measure both alkyl nitrates and halocarbons in the atmosphere [10,11] due to its excellent sensitivity to compounds with high electron affinities. However, co-elution interferences between some alkyl nitrate and halocarbon species reduces the usefulness of this approach [12,13]. Negative ion chemical ionization (NICI) is selective for the same compounds as the ECD but as a result of single ion monitoring (SIM) with a mass spectrometer (MS) these co-elution issues are substantially reduced, if not completely eliminated. The NICI technique has previously been employed as a confirmatory technique in the measurement of atmospheric alkyl nitrates [14,15] and has been used to make in situ measurements of various peroxy acetyl nitrates [16,17] and aromatic nitrates [18] in the atmosphere.

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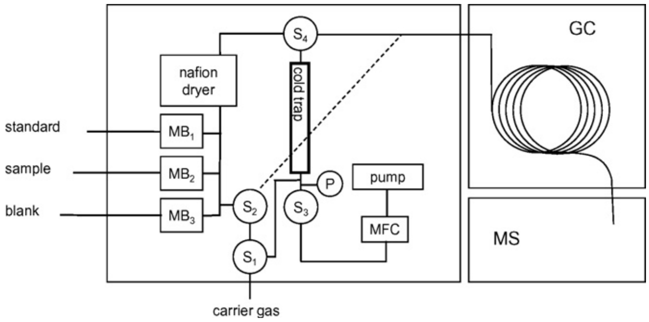

Fig. 1. Schematic of the GC/NICI–MS system with the online automated pre-concentration system (Markes International Ltd.). MB$_x$ = air actuated metal bellows valve, S$_x$ = two or three-way solenoid valve, P = pressure gauge, MFC = mass flow controller. The dashed line indicates the path of the carrier gas during sampling.

In this paper, we present a new in situ instrument that combines a cryogen free adsorbent based pre-concentration system with GC/NICI–MS for the in situ detection and quantification of a suite of atmospheric alkyl nitrates and halocarbon species with high sensitivity and selectivity.

2. Experimental

2.1. Instrumental set-up

A schematic illustrating the instrumental set-up is shown in Fig. 1 and incorporates an online air pre-concentrator (UNITY$^{\text{TM}}$ and Online Air Server; Markes International Ltd.) coupled to a gas chromatograph–mass spectrometer (Agilent Technologies GC 6890/MS 5973N) operating in NICI mode.

Air samples (accurately measured ~1000 ml, flow rate 50 ml/min) are dried by a nafion dryer (Permapure$^{\text{TM}}$) with a 100 ml/min counter flow of dry clean nitrogen prior to collection and pre-concentration on a packed (Carbograph-TD$^{\text{TM}}$ and Carboxen-1000$^{\text{TM}}$) capillary cold trap at −15 °C using a two-stage cascade peltier. The thermal desorption of the analytes occurs through controlled resistive heating (>60 °C/s) within the peltier oven. The adsorbents are arranged in order of the strength with the weakest at the front and the strongest at the back and the cold trap is back flushed with carrier gas during heating to avoid permanent retention of analytes by the stronger sorbents. The desorbed analytes are transferred to the analytical column via a heated deactivated silica transfer line (T~120 °C, 0.25 mm OD, 1 m).

The analytes are separated on an RTX-502.2 capillary column (105 m, 320 μm OD, 1.8 μm film, Restek$^{\text{TM}}$ Corporation) using helium (research grade, purity ≥99.99999%) as the carrier gas and by temperature-programmed gas chromatography (30 °C hold 2 min, 8 °C/min to 150 °C hold 16 min, 20 °C/min to 220 °C hold 5 min). The column effluent was subjected to ionization by NICI in the presence of a reagent gas (research grade methane, purity ≥99.9995%), prior to separation and detection by a quadrupole mass selective detector operating in SIM and monitoring m/z 46 for alkyl nitrates, m/z 35, 37 for chlorinated, m/z 79, 81 for brominated and m/z 127 for iodinated compounds. The system was fully automated with a time resolution of 1 h and was capable of switching between ambient, standard and blank runs. The system was also capable of analysing up to six canister samples, standard and blanks in an automated sequence by using an array of additional metal bellows valves (not shown in Fig. 1).

Compounds were identified through a combination of matching retention times to known standards and matching mass spectra, obtained while operating the instrument in full scan EI mode, to the best available mass spectral library data.

2.2. Negative ion chemical ionization

NICI is a soft ionization method that generates less fragmentation than the more routinely employed electron impact (EI) ionization. The MS employed in this work (Agilent Technologies 5973N) has been designed such that it can be operated in either EI or NICI modes simply by changing the source and the polarity of the ion lenses and detector dynode. This allows us to evaluate the NICI mode relative to EI without significantly modifying the instrumental set-up. The CI source is similar to its EI equivalent but possesses much smaller holes in the ion source body for the entrance of the primary ionizing electrons allowing the source to be pressurised (20–50 times relative to the surrounding vacuum chamber) with a reagent gas (e.g., methane). The relatively high partial pressure of reagent gas in the source is crucial in ensuring a sufficiently high number of ion–molecule collisions during the dwell time of the reactants in the ion source. The interface between the chromatographic column outlet and the ion source inlet is tightly connected using a ceramic seal and the reagent gas flows directly into the ion source to ensure maximum pressure with minimal losses to the vacuum chamber.

The excess reagent gas also shields the analyte molecules effectively from the high energy (~230 eV) primary electrons, which is critical in suppressing the competing EI reactions. The energy of the primary electrons is higher than those used for EI (~70 eV) and is necessary in order for the electrons to penetrate through the reagent gas. The primary electrons are emitted through thermo ionic emission from a heated filament and are decelerated through interaction with the reagent gas to form low energy thermal electrons (<15 eV) and positively charged reagent ion radicals (Reaction (1))

$$CH_4 + e^-_{(230\,\text{eV})} \rightarrow CH_4^{\bullet+} + 2e^-_{(<15\,\text{eV})} \qquad (1)$$

Methane is the most common reagent gas and yields practically no negative ions, ensuring a low background signal, while effectively moderating the energetic electrons to thermal energy. The thermal electrons can be captured by a variety of species, similar in essence to those detectable by ECD. Methyl bromide and methyl chloride have been observed during this work to show very low responses as a result of poor electron capture, e.g., for methyl bromide detection limits in NICI mode are a factor of 10 higher than in EI (Table 2).

Alkyl nitrates and halocarbons form anions through the process of dissociative electron capture whereby the capture of the thermal electron is followed almost instantaneously by dissociation to form an anion and a neutral radical (Reactions (2) and (3))

$$\begin{aligned} RONO_2 + e^- &\rightarrow NO_3{}^- + R^\bullet \\ &\rightarrow NO_2{}^- + RO^\bullet \\ &\rightarrow RO^- + NO_2{}^\bullet \end{aligned} \qquad (2)$$

$$RX + e^-_{(<15\,\text{eV})} \rightarrow X^- + R^\bullet\,(X = Cl,\ Br,\ I) \qquad (3)$$

The alkyl nitrates yield several anions while the halocarbon gases only yield the corresponding halogen anion. Previous work by Sato et al. [19] showed the detection of three anions following the fragmentation of C_1–C_6 alkyl nitrates (Reaction (2)). The observed anion fragment for those halocarbons that have more than one halogen atom is predominantly though not exclusively the one with the lower ionization energy.

2.3. Observed fragmentations

Fig. 2 shows two selected regions of a chromatogram from an analysis of a long-term running standard (ambient air filled in Mainz, Germany; April 2004). It is clear that the identified bromo-