New ionization strategies in particle-beam liquid chromatography–mass spectrometry based on the principle of surface ionization

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ABSTRACT

The potential of surface ionization (SI) as an ionization technique in particle-beam (PB) LC–MS was investigated. Using a laboratory-built surface ionization probe with a platinum tip, several ionization phenomena were observed, *i.e.*, thermal surface ionization (TSI), hyperthermal surface ionization (HSI) and alkali metal addition. Although TSI experiments suggest that kinetic energy is added to the molecules in the PB, the increase in kinetic energy is still insufficient to induce efficient HSI. TSI in combination with LC-PB-MS leads to highly improved detection limits of tetraalkylammonium salts. The use of the SI probe as a thermionic emitter of alkali metal ions for the formation of alkali metal adduct ions leads to sensitive detection of crown ethers and to a considerably extended upper mass limit for polyethylene glycol samples in comparison with standard ammonia chemical ionization conditions.

INTRODUCTION

In 1923, Langmuir and Kingdon [1] described the phenomenon of surface ionization (SI) for the emission of alkali metal ions from metal surfaces. Further research in this field revealed that an atom or a molecule that adsorbs on a surface can be desorbed as either a positive or a negative ion, depending on its ionization potential or its electron affinity, the surface workfunction and the temperature of the surface. Surface ionization appeared to offer the highest possible ionization efficiency, but unfortunately only for compounds with a low ionization potential, *i.e.*, alkali metals [2,3], or compounds with a high electron affinity. Therefore, surface ionization never became a standard ionization technique in organic mass spectrometry. This situation might change because Amirav and co-workers [4–6] demonstrated that the energy barrier for the hyperthermal surface ionization of compounds can be overcome by increasing the molecular kinetic energy. The use of a supersonic or a so-called hyperthermal molecular beam in combination with gas chromatography–mass spectrometry (GC–MS) offers an improved ionization efficiency [4–6].

Because the particle-beam (PB) interface forms a high-velocity beam of molecules and molecule aggregates by expansion of the mobile phase into the momentum separator of the interface [7], the potential of SI in combination with particle-beam mass spectrometry has been investigated in our laboratory. The use of SI in particle-beam liquid chromatography–mass spectrometry (LC–PB-MS) may widen the applicability range of the particle-beam interface and improve its performance in terms of achiev-

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able detection limits as a result of improved ionization efficiencies.

In our experiments it appeared that several ionization phenomena could be observed, i.e., thermal surface ionization (TSI), hyperthermal surface ionization (HSI) and alkali metal addition. Therefore, in our research into the potential of surface ionization as an ionization technique in LC–PB-MS, three strategies were investigated. It is important to realize that all SI data presented here were obtained in the filament-off mode. For the TSI analysis of tetra-alkylammonium (TAA) salts, a comparison was made between TSI and electron impact (EI) ionization with respect to the ions generated and the detection limits achieved. For the analysis of polyethylene glycol (PEG) samples a comparison was made between alkali metal addition and standard ammonia chemical ionization (CI) conditions.

EXPERIMENTAL

Apparatus

The experiments were performed on a Finnigan MAT (San José, CA, USA) TSQ-70 triple quadrupole mass spectrometer. For the LC–PB-MS experiments the mass spectrometer was equipped with a Hewlett-Packard (Palo Alto, CA, USA) HP 59980 particle-beam interface. The particle-beam interface was coupled to the mass spectrometer with a ca. 15 cm laboratory-made stainless-steel transfer tube. A pneumatic nebulizer with helium as a nebulization gas was used. The solvent-delivery system consisted of an LKB (Bromma, Sweden) Model 2150 LC pump, while samples were introduced via a Rheodyne (Cotati, CA, USA) Model 7125 injection valve with a 20-μl sample loop.

For the surface ionization experiments a special water-cooled surface ionization probe was built, which was inserted into the ion volume of the ion source through the direct insertion probe inlet. Slightly modified source ion volumes were used in order to insert the SI probe. The tip of the probe was made of platinum and was positioned in such a way that the angle between the particle beam and the surface was 45°, as illustrated in Fig. 1. The tip of the probe could
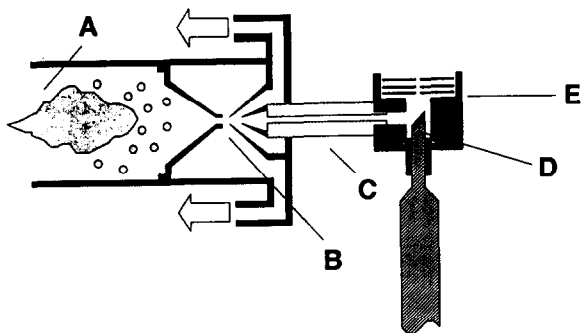

Fig. 1. Schematic representation of the LC–PB-SI-MS system. A = Desolvation chamber; B = momentum separator; C = ca. 15-cm transfer tube; D = surface ionization probe with platinum surface; E = ion source.

be heated to about 1300°C. The surface probe-tip temperature was monitored via a platinum vs. platinum–10% rhodium thermocouple, which was connected to the lens 41 (L41) potential connection in order to bias the probe tip 0–5 V with respect to the ion volume for positive ions. Prior to every experiment the probe bias was optimized for the signal of the molecular species (molecular ion or cationized molecule). All surface ionization experiments were performed in the filament-off mode, monitoring only positive ions. The source temperature for the SI, EI and CI experiments was set at 250°C.

Thermal surface ionization

For the TSI experiments several tetraalkylammonium (TAA) salts were used [8]. EI mass spectra were obtained using a standard GC–EI ion volume at a source temperature of 250°C. The EI experiments were carried out in the filament-on mode, whereas SI experiments were performed in filament-off mode at an oxygen source pressure of ca. 150 Pa using a slightly modified EI ion volume.

For nebulization into the desolvation chamber, 1.5–2.5 l/min of helium was used. Methanol was used as the mobile phase at a flow-rate of 0.1–1.0 ml/min. The temperature of the desolvation chamber was kept at 45°C. All experiments were performed in the flow-injection analysis mode, monitoring the ions either in the single-ion or full-scan mode.

Hyperthermal surface ionization

In the LC–SI–MS experiments, 0.5 ml/min of acetonitrile was used as the mobile phase for the column bypass injection of 280 ng of anthracene ($M_r = 178$) at a surface probe tip temperature of 1100°C. The desolvation chamber was adjusted to 45°C.

For the GC–SI–MS experiments the mass spectrometer was coupled to a Varian (Sunnyvale, CA, USA) capillary GC system equipped with a 0.5-m CP-Sil 5 capillary column. A 1-μl volume of anthracene in acetonitrile was injected in the splitless mode at injector and column temperatures of 200 and 100°C, respectively. The transfer line was set to the highest possible temperature of 350°C for maximum response.

Both LC–MS and GC–MS experiments were performed with a modified EI ion volume. For the oxidation of the platinum probe surface in both the LC–MS and GC–MS experiments oxygen was introduced into the ion source via the CI reagent gas inlet at a source pressure of 150–200 Pa. Most experiments were performed in the single-ion detection mode, monitoring the molecular ion at m/z 178.

Alkali metal addition

Methanol was used at a flow-rate of 0.5 ml/min for the column bypass injection of several crown ethers in NH_3 CI and in combination with the SI probe. The desolvation chamber was adjusted to 45°C. The SI probe tip was inserted into a modified CI ion column. For source pressure experiments both O_2 and NH_3 were introduced into the ion source via the reagent gas inlet.

For the chromatographic separation of PEG samples, a 25 cm × 4.6 mm I.D. Hypersil 5-μm C_{18} column was used. The separation of a 10 mg/ml of PEG 1540 in water was performed with methanol–water (55:45, v/v) as the mobile phase at a flow-rate of 0.5 ml/min, monitoring the alkali metal adduct ions in the full-scan mode. The desolvation chamber was adjusted to a slightly higher temperature of 50°C. Optimum response in LC–SI–MS was achieved at a surface temperature of 1100°C. For the SI experiments the O_2 source pressure was 30 Pa whereas for the CI experiments the NH_3 source pressure was adjusted to 500 Pa.

Chemicals

Tetraalkylammonium (TAA) salts were purchased from Aldrich-Chemie (Steinheim, Germany). Anthracene ($M_r = 178$) was obtained from Merck (Darmstadt, Germany), benzo-15-crown-5 ($M_r = 268$), dibenzo-18-crown-6 ($M_r = 360$) and dicyclohexano-18-crown-6 ($M_r = 372$) from Fluka (Buchs, Switzerland), PEG 1540 from Sigma (St. Louis, MO, USA) and methanol and acetonitrile (analytical-reagent grade) from J.T. Baker (Deventer, Netherlands).

RESULTS AND DISCUSSION

Thermal surface ionization

The limited sensitivity of ionic compounds in the EI mode, which is related to their low volatility, makes LC–PB–MS less suitable for the analysis of this type of compound. The sample consumption for the EI-MS analysis of tetraalkylammonium salts as described in the literature [9,10] is of the order of 1 mg. As far as we known, only Hsu [11] has reported the combination of ion chromatography with particle-beam mass spectrometry for the determination of organic anionic compounds. However, the full-scan detection limits of *ca*. 100 ng were high.

Thermal emission of cations and anions can be achieved simply by heating a surface on which salts have been deposited [12]. Thermal surface ionization mass spectra for several tetraalkylammonium (TAA) salts have been reported by Schade *et al.* [13] using surface temperatures of at least 500°C.

The use of thermal surface ionization as an ionization technique in LC–PB–MS results in the formation of TAA ions at SI probe temperatures as low as 250°C [8]. In Fig. 2 both the PB-EI and PB-TSI spectra of *ca*. 100 ng of tetrahexylammonium perchlorate are shown. For TAA compounds with the general formula R_4N^+ the $R(CH_3)N = CH_2^+$ and $R_2N = CH_2^+$ fragment ions are the major ions observed in the EI mass spectrum, whereas in TSI no fragmentation is observed and the mass spectrum is determined
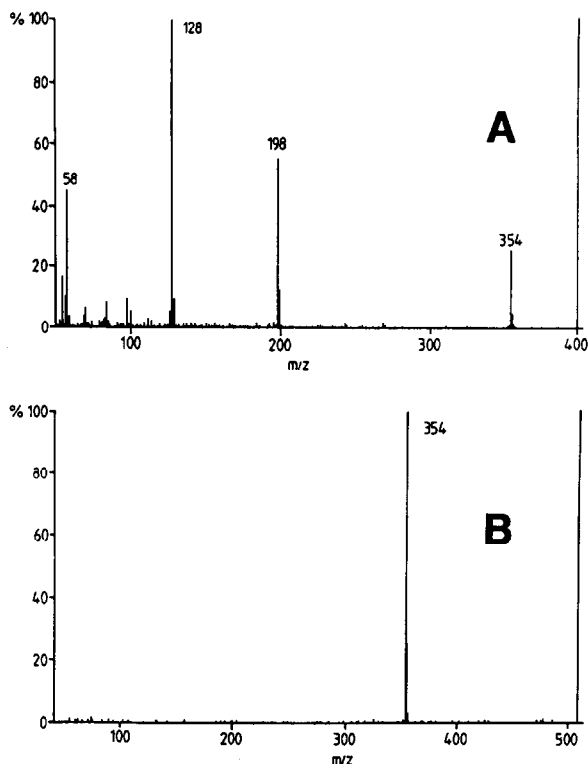
Fig. 2. Mass spectra of tetrahexylammonium (formula mass = 354) perchlorate obtained in (A) filament-on (EI) mode and (B) filament-off (SI) mode at a probe temperature of 250°C.

by an intense signal due to the molecular cation, R_4N^+.

It should be noted that the mass spectra obtained in TSI with the particle-beam interface differ from those reported by Schade et al. [13,14]. They observed considerable fragmentation, whereas in our experiments no significant fragmentation was observed. This indicates a difference in heat transfer to the molecules, which in fact may already be concluded from the differences in the experimental set-up. In TSI with PB the thermal energy is also used for the evaporation of solvent molecules partly clustered to the analyte in the particles. However, it is important to emphasize that soft ionization of ionic compounds can be achieved in this way.

The effect of the probe temperature on the intensity of various TAA salts shows slightly different optima [8]. However, the appearance of TSI at temperatures as low as 250°C, instead

of the 500°C reported by Schade et al. [13], suggests that kinetic energy is transferred to the molecules in the particle beam by the expansion of the mobile phase into the momentum separator of the interface.

The performance of TSI under PB conditions is expected to be determined by two factors: the temperature of the TSI surface and a kinetic component. The kinetic energy of the molecular beam can be influenced by the flow-rates of the mobile phase and of the nebulization gas. A decrease in the liquid flow-rate from 1 to 0.2 ml/min resulted in a tenfold increase in the signal for tetrabutylammonium, whereas an increase in the gas flow-rate from 1.5 to 2.5 l/min resulted in a fourfold increase in signal. These effects are common in particle-beam interfacing, as these parameters affect the transmission through the interface in two ways: a decrease of the droplet size, improving the evaporation rate of the droplets, and an enlargement of the pressure difference between the desolvation chamber and the first pumping stage in the momentum separator, resulting in a higher kinetic energy of the particles [15].

By optimizing the LC–PB–TSI–MS system, a very sensitive method is obtained for the determination of TAA salts. This is demonstrated in Fig. 3, which represents the chromatogram for two injections of 2 pg of tetrabutylammonium bromide. The chromatogram was recorded in the single-ion detection mode at m/z 242, applying a
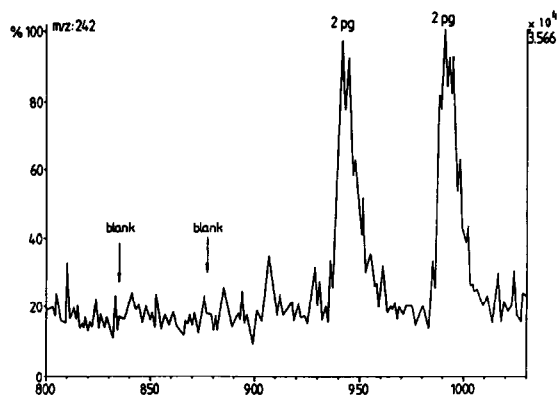

Fig. 3. TSI mass chromatogram for two injections of 2 pg of tetrabutylammonium (formula mass = 242) bromide recorded in the single-ion detection mode at m/z 242, applying a probe temperature of 600°C.

probe temperature of 600°C. The detection limit increases for larger TAA salts. As an example, for tetraoctylammonium bromide a *ca.* fivefold higher detection limit over tetrabutylammonium bromide is observed. These results show that detection limits obtained in particle-beam SI for TAA salts compare well with those obtained using other techniques such as electrospray [16] and ionspray [17]. The calibration graphs for particle-beam TSI show non-linearity at lower concentrations. This is in accordance with PB-EI results reported by others [18]. The observation of this phenomenon under TSI conditions indicates that the non-linearity is caused by decreased transmission in the momentum separator rather than by ionization problems in the ion source. It has been shown that the problem of non-linearity in quantification can be solved by the use of isotope dilution procedures [18,19].

(Hyperthermal) surface ionization

As pointed out in the Introduction, SI as an ionization technique in organic mass spectrometry is suitable for only a very limited class of compounds [20–23]. This is illustrated by the Saha–Langmuir equation for the formation of positive ions [24,25]:

$$\alpha = A \exp[(\phi - IP)/kT] \qquad (1)$$

where $\alpha = n^+/n^0$ is the ratio of the number of positive ions to neutral species evaporating from the surface, A is the ratio of the statistical weights of the ionic and neutral states of the compound, ϕ is the workfunction of the surface, IP is the ionization potential of the compound, k is the Boltzmann constant and T is the absolute temperature of the surface. For an arbitrary compound with a defined ionization potential, the yield of positive ions desorbing from a surface is determined by the surface workfunction and the surface temperature. The highest yield is obtained for surfaces with a high workfunction or at high surface temperatures. Various materials such as tungsten, rhenium, platinum and diamond are often used as surfaces in SI experiments because of their high surface workfunction [5,20]. The theoretical surface workfunction for the platinum probe used in our

experiments is 5.7 eV, which is much lower than the ionization potential of most compounds, explaining the low yield of desorbed positive ions. Additionally, this yield is very much affected by modifications of the surface. As an example, oxidation of the surface increases the surface workfunction [5,20], whereas contamination of the surface with various salts lowers the surface workfunction.

Another way to increase the yield of desorbed ions is to increase the surface temperature. This is illustrated by the fact that an increase in the platinum probe tip temperature results in the emission of larger amounts of sodium, potassium and caesium ions, as illustrated in Fig. 4 for sodium and potassium. The formation of alkali metal ions can be explained by alkali metal contamination, which readily occurs on the tip of the SI probe. The high yield of alkali metal ions is explained by the fact that alkali metals are characterized by a very low ionization potential. The reason why the formation of potassium cations starts at a lower temperature compared with the formation of sodium cations is that the ionization potential of potassium (4.3 eV) is lower than that of sodium (5.1 eV).

Anthracene has an ionization potential of 7.5 eV, which is relatively low. However, when 280 ng (14 ng/μl) of anthracene is injected into the LC–PB-SI-MS system at a probe temperature of about 1100°C, a full-scan spectrum is obtained with a signal-to-noise ratio of only 20. Increasing the surface workfunction by oxidizing the platinum surface, realized by introducing oxygen
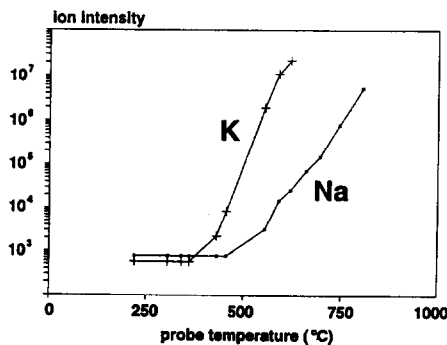

Fig. 4. Potassium and sodium background intensity as a function of the surface probe tip temperature. No liquid was introduced into the particle-beam interface.

into the ion source at a source pressure of 150–200 Pa, results in an improvement in the signal-to-noise ratio. Still, under these experimental conditions sensitive detection of anthracene was not achieved. Improvement of the ionization efficiency and the resulting detection limits for anthracene and other compounds can theoretically be achieved by increasing the probe-tip temperature. However, too high surface temperatures result in serious thermal degradation of many organic compounds.

In order to approach more sensitive HSI conditions [5] in combination with GC–MS, a capillary GC system with a short column and a splitless injector was coupled to the mass spectrometer. With this set-up the solvent is easily separated from the analyte and retention times are low. The analyte expanding at the end of the capillary column into the vacuum of the ion source collides with the surface, as illustrated in Fig. 5. A 1.4 ng (1.4 ng/μl) injection of anthracene resulted in a spectrum (Fig. 6) with a much better signal-to-noise ratio than was the case for the 14 ng/μl sample solution in the PB-SI experiments, even when it is taken in account that the transmission of the particle-beam interface at high concentrations of *ca.* 20% [8] results in a loss of analyte. The increase in the temperature of the transfer line from 250 to 350°C resulted in a more than tenfold improvement in detectability, because of a more pronounced expansion at the end of the capillary column. The signal-to-noise ratio for anthracene under GC–HSI-MS conditions is at least a factor of 1000 better than under LC–SI-MS conditions. A
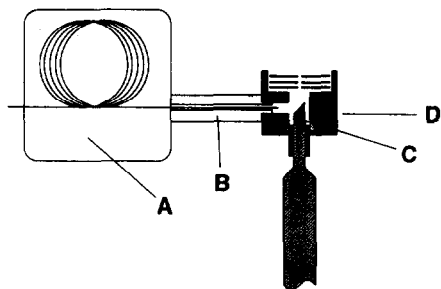

Fig. 5. Schematic representation of the GC–SI-MS system. A = Capillary GC system with splitless injector and a 0.5-m column; B = heated transfer line; C = surface ionization probe with platinum surface; D = ion source.
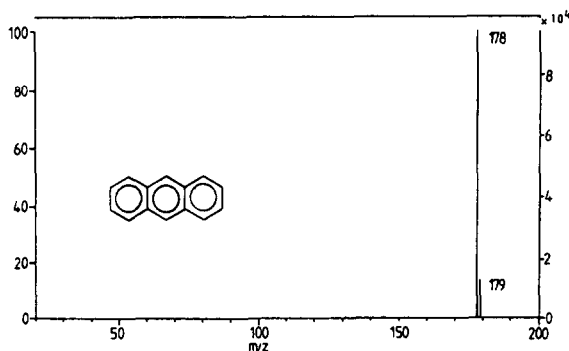

Fig. 6. GC–HSI mass spectrum of 1.4 ng of anthracene ($M_r = 178$) after splitless injection at a surface temperature of 1100°C.

lower GC–HSI-MS sensitivity is observed for compounds with an ionization potential of >7.5 eV, *i.e.*, the ionization potential of anthracene, which can be explained by differences in the experimental setup. An important difference with the GC–HSI-MS system as described by Amirav [5] is that the use of a nozzle–skimmer arrangement by the latter and of H_2 as an expanding gas instead of He result in a much higher kinetic energy of the molecular beam up to 30 eV.

A very important conclusion that can be drawn from these experiments is that the increase in kinetic energy in case of the PB-SI experiments, caused by the expansion of the mobile phase into the momentum separator of the interface, is too low to overcome the energy barrier for increasing the ionization efficiency. Additionally, contamination of mobile phases with various salts and the resulting permanent delivery of surface-contaminating compounds to the probe surface in particle-beam MS will lower both the surface workfunction and the ionization efficiency. Experiments are currently being performed to improve the nozzle–skimmer part of the interface in order to create supersonic molecular beams in LC–PB-MS.

Alkali metal addition

Alkali metal cations are easily formed by so-called thermionic emitters [26]. They cationize most compounds containing π- or n-donor sites to produce alkali metal adduct ions. Various

studies have been performed using alkali metal ions as reagent ions under atmospheric pressure CI [27] and under normal CI conditions [28,29] and in combination with laser desorption mass spectrometry [30,31]. The use of metal ions as special reagents in analytical mass spectrometry has been reviewed by Teesch and Adams [32]. Alkali metal addition is assumed to be a three-body process, in which a neutral molecule collides with an ion–molecule complex and removes an excess amount of energy, thus stabilizing the alkali metal adduct ion. On the basis of this model, the cationization process would be especially efficient in a high-pressure environment, as the major component gas molecules serve as the third body in the analyte addition reaction with alkali metal ions. Bombick et al. [29] reported the addition of potassium to various compounds at helium and acetone source pressures varying between 1 and 100 Pa.

In this section, the applicability of alkali metal metals as a source of CI reagent ions in combination with the use of the SI probe in LC–PB-MS is discussed. Several crown ethers were used as model compounds. Liou and Brodbelt [33] reported the relative alkali metal ion affinities of various crown ethers. Injection of 200 ng of dicyclohexano-18-crown-6 at a probe temperature of 750°C leads to a spectrum that is mainly characterized by $[M + Na]^+$ and very small $[M + K]^+$ ions. It is remarkable that, despite the ca. twofold higher affinity of 18-C-6 crown ethers [33] for potassium and the ca. fifteenfold higher potassium background over sodium under the experimental conditions, the $[M + Na]^+$ ion is the base peak in the spectrum.

Several studies have been carried out of the exact mechanism of the alkali metal adduct formation [30,31]. Purely thermal desorption of $[M + Na]^+$ ions has been reported for a mixture of a crown ether with sodium iodide [12]. The $[M + Na]^+$ ions are observed at temperatures below the onset for thermionic emission of Na^+, thus excluding a gas-phase ionization mechanism by ion–molecule reactions. The thermal desorption of alkali metal adduct ions was ascribed to the high stability of the $[M + Na]^+$ complex and to a low Coulomb binding energy between the alkali metal and halogen ions. However, for

sucrose Stoll and Röllgen [31] reported a gas-phase ionization mechanism via ion–molecule reactions without any contribution from direct evaporation of preformed cationized molecules.

In Fig. 7, the sodium background intensity and the peak area for the sodiated species of several 200-ng injections of dicylohexano-18-crown-6 ($M_r = 372$) are plotted as a function of the probe tip temperature. It is clearly demonstrated that the optimum for the sodium adduct formation lies well below the minimum temperature required for thermionic emission of sodium ions. This observation corresponds with the former theory, that the alkali metal adduct formation for crown ethers is a surface ionization process, which excludes a direct relationship to the background intensity of the various alkali metal ions in the spectrum. Variation of the source pressure between 10 and 200 Pa had only a slight influence on the alkali metal adduct intensity, suggesting that the alkali metal adduct formation is a surface process rather than a three-body gas-phase process. Additional experiments were performed by contaminating the probe surface with lithium acetate. Despite the lack of lithium in the mobile phase, $[M + Li]^+$ ions were observed in the spectrum. This phenomenon seems to prove that the alkali metal adduct formation is the result of surface cationization rather than thermal desorption of preformed alkali metal adduct ions.

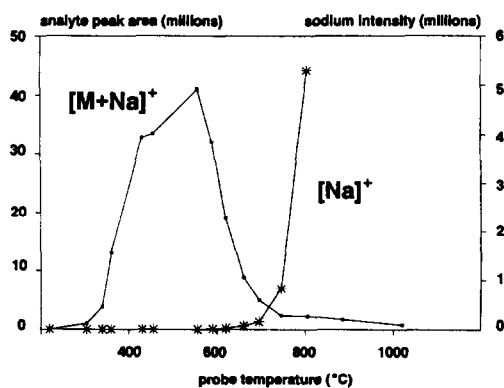Repetitive injections of some crown ethers

Fig. 7. Sodium background intensity and peak area for the sodiated species of several 200-ng injections of dicyclohexano-18-crown-6 ($M_r = 372$) plotted as a function of the probe-tip temperature.

result in reproducible peak areas for a long period of time, because the permanent contamination of mobile phases results in a permanent delivery of alkali metals to the surface. Therefore, no sodium or potassium needs to be added to the mobile phase. Addition of 0.5 mM of lithium acetate to the mobile phase results in the onset of lithium cations in the background spectrum. Under these conditions the spectrum of dicyclohexano-18-crown-6 is now dominated by the $[M + Li]^+$. It takes almost 1 h to condition the probe surface before optimum ionization conditions are obtained. A minor disadvantage of the addition of alkali metal salts (>0.1 mM) to the mobile phase is the serious contamination of the first skimmer in the PB interface. At a probe temperature of 600°C and with addition of 0.5 mM lithium acetate, the minimum detectable amount for dibenzo-18-crown-6 after some minor optimization is *ca.* 200 pg, as is illustrated in Fig. 8. This minimum detectable amount can be lowered significantly by improving the linear dynamic range of the particle-beam interface as a result of the simultaneous injection of a large amount of a carrier [18,34]. For instance, for 100 ng of benzo-15-crown-5 ($M_r = 268$) with simultaneous injection of 20 μg of dibenzo-18-crown-6 ($M_r = 360$), a fifteenfold improvement in response for the 15-C-5 crown ether is obtained.
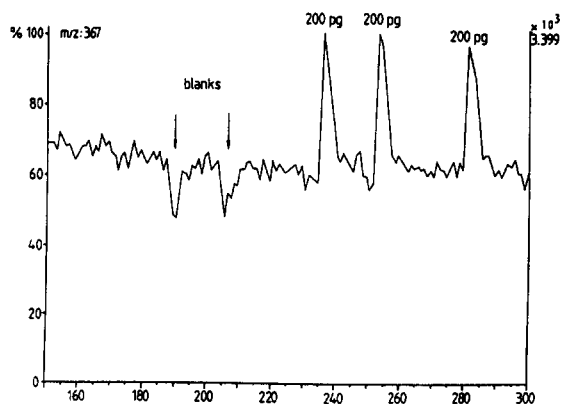
The influence of the probe temperature on the alkali metal adduct formation was investigated for various PEG samples. It appears that a higher probe temperature is needed for molecules with a higher molecular mass. For a PEG 1540 sample maximum sensitivity is obtained at a probe temperature of *ca.* 1000°C. Optimum ionization conditions far above the onset temperature for thermionic emission of sodium ions seem to prove that the alkali metal adduct formation for PEG molecules is a gas-phase process, in contrast to the crown ethers for which the alkali metal addition is SI process (see above).

Fig. 9 shows the spectra that are obtained for a PEG component of a PEG 1540 sample after

Fig. 8. Mass chromatogram for three 200-pg injections of dibenzo-18-crown-6 ($M_r = 360$) with 0.5 mM lithium acetate in methanol as the mobile phase at a probe temperature of 600°C, obtained by single-ion monitoring of the $[M + Li]^+$ intensity at m/z 367.
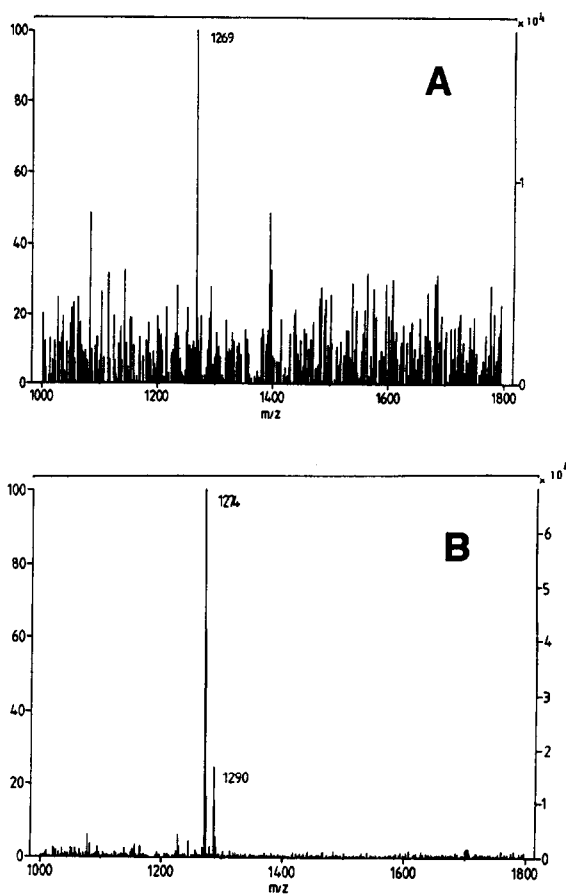
Fig. 9. Spectra from the PEG component $HO[C_2H_4O]_{28}H$ ($M_r = 1251$) of a PEG 1540 sample after chromatographic separation. (A) Obtained under CI conditions at an NH_3 source pressure of 500 Pa; (B) obtained under SI conditions at a probe temperature of 1100°C at a O_2 source pressure of 30 Pa.
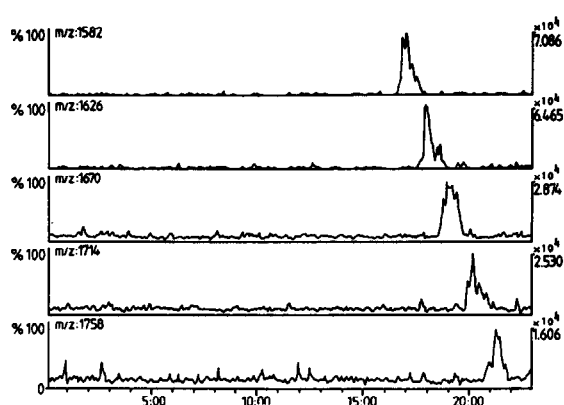
Fig. 10. Partial representation of the chromatogram for the separation of a PEG 1540 sample (200 μg) using methanol–water 55:45 (v/v) as the mobile phase at a flow-rate of 0.5 ml/min and a 25 cm × 4.6 mm I.D. Hypersil 5-μm C_{18} column.

chromatographic separation. In combination with the surface ionization probe, much better sensitivity can be obtained compared with standard CI conditions with NH_3 as the reagent gas. In fact, the $[M + NH_4]^+$ peak at m/z 1269 is the largest ammoniated molecule observed in PB-CI. Additionally, the upper mass limit for LC–PB-MS combination with the heated probe is higher compared with CI conditions, as is shown in Fig. 10. The chromatogram was recorded in the full-scan mode at a probe temperature of 1100°C, while no alkali metal salts were added to the mobile phase. Under these conditions the highest mass that could be observed was the $[M + Na]^+$ ion at m/z 1758. This upper mass limit for the polar PEG 1540 sample is close to the highest reported upper mass limit for the LC–PB-MS detection of non-polar styrene oligomers [35].

CONCLUSIONS

Owing to the expansion of the mobile phase into the momentum separator of the particle-beam interface, a certain amount of kinetic energy is added to the molecules in the beam of particles. However, this increase in kinetic energy is insufficient to induce efficient hyperthermal surface ionization. Thermal surface ionization appears to be a soft ionization technique

for the sensitive detection of tetraalkylammonium ions. For tetrabutylammonium bromide, detection limits as low as 2 pg can be achieved. Introduction of O_2 into the ion source leads to improved sensitivity for various compounds, probably owing to the increase in the workfunction as a result of oxidation of the SI probe tip. The formation of alkali metal adduct ions for crown ethers is probably the result of surface cationization, rather than thermal desorption of preformed alkali metal adduct ions. Because the alkali metal contamination of mobile phases results in a permanent delivery of sodium and potassium to the probe surface, for alkali metal addition experiments no alkali metals have to be added to the liquid. The alkali metal adduct formation can be influenced by adding other alkali metal salts such as lithium acetate to the mobile phase. At a probe temperature of 600°C and with addition of 0.5 mM lithium acetate to the mobile phase, the minimum detectable amount for dibenzo-18-crown-6 is ca. 200 pg. For the analysis of PEG samples the upper mass limit for LC–PB-MS in combination with the heated probe is much higher compared with standard NH_3 CI conditions. The highest mass that could be observed for a PEG 1540 sample was the $[M + Na]^+$ ion at m/z 1758. Improvement of the nozzle–skimmer configuration for the creation of supersonic molecular beams in LC–PB-MS in combination with the surface ionization probe will offer a wider applicability range for this type of LC–MS.

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