

Characterization of polyfunctional alkoxy silanes using potassium (K^+) ionization of desorbed species mass spectrometry¹

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Abstract

Potassium ionization of desorbed species (K^+ IDS) mass spectrometry has been used to characterize polyfunctional alkoxy silanes and the modes of reaction for 'star gel' precursors and simpler tetraalkoxy silanes. Efficient observation of molecular ions enabled by K^+ IDS can readily establish the purity of molecules such as $Si(CH_2CH_2Si(OEt)_3)_4$ and $cyclo-(Me(CH_2CH_2Si(OEt)_3)_4SiO)_4$, and has been highly useful in determining the extent of intramolecular condensation in the star molecules. K^+ IDS has also established the distributions of polysilicate species and the presence of important reactive intermediates containing $SiOOCH$ groups when $Si(OMe)_4$ reacts with formic acid.

Keywords: Silicon; Alkoxy silanes; Potassium ionization of desorbed species mass spectrometry; Mass spectrometry; Sol-gel; Organic-inorganic materials

1. Introduction

Modern mass spectrometric methods might seem of limited use in characterizing complex reaction mixtures. However, a mass spectrometric technique known as potassium (K^+) ionization of desorbed species (K^+ IDS) has been recently shown to produce potassiumated molecular ions of components in organic polymers and coatings with little or no fragmentation [1–3]. Under K^+ IDS conditions, intact organic molecules are desorbed by rapid heating. In the gas phase, organic molecules are ionized by potassium attachment. The potassium ions are produced by thermionic emission from an aluminosilicate matrix. K^+ IDS is performed with commercial quadrupole mass spectrometers. Using K^+ IDS, one can easily observe and record pseudomolecular ions with values of $[M]K^+$ up to 1800 Da. The experiment takes less than 10 min to perform (often including sample preparation) and the data are quantitative for many oligomeric materials. The technique has been used to

characterize low molecular weight polycarbosilanes [4,5], haloaldehyde polymers [6,7] and a variety of coatings components [3]. We have extended our use of K^+ IDS to characterize the polyfunctional alkoxy silane molecules used to make 'star gel' organic-inorganic hybrid materials [8,9] and to analyze the components of partial condensation of both these polyfunctional silanes and more conventional alkoxy silane precursors such as $Si(OMe)_4$ (TMOS). We have also explored species generated from a newly developed non-aqueous route to silica gel, based on the reaction of strong carboxylic acids with alkoxy silanes [10,11]. We report on these results herein.

2. Results and discussion

2.1. Characterization of polyfunctional organoalkoxy silanes

Star gel precursors are polyfunctional alkoxy silane molecules which can be condensed by sol-gel techniques to form new inorganic-organic hybrid network materials [8,9]. The molecules comprise multiple tri-

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¹ This paper is dedicated to Professor Robert Corriu in recognition of his outstanding contributions to the field of organosilicon chemistry.

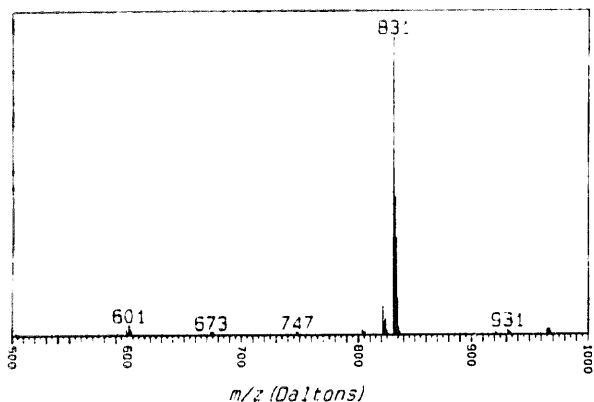
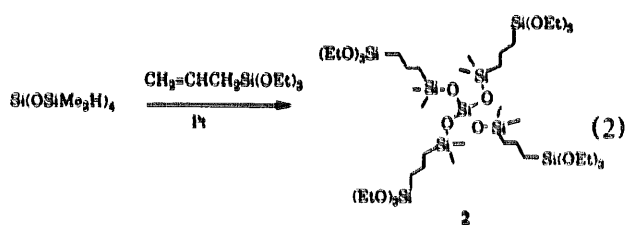
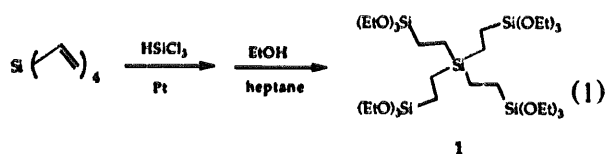


Fig. 1. The K^+ IDS mass spectrum of $\text{Si}(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ (1).

alkoxysilane-terminated arms linked to an organic or organosilane core, and are generally synthesized by hydrosilylation of core and arm segments; two representative examples are shown in Eqs. (1) and (2).



K^+ IDS analysis has proved useful for determining the degree of substitution, and thus the purity of the products from hydrosilylation. Fig. 1 shows the K^+ IDS spectrum of the crude product from the Pt-catalyzed hydrosilylation of tetravinylsilane with trichlorosilane, followed by ethanolysis to give $\text{Si}(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ (1). Only the molecular ion ($[M]K^+$) of 1 at 831 Da with the expected isotopic envelope was observed. No ions corresponding to partially-substituted material, such as the trisubstituted $\text{CH}_2=\text{CHSi}(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_3$ (expected $[M]K^+ = 667$ Da) or disubstituted $(\text{CH}_2=\text{CH})_2\text{Si}(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_2$ (expected $[M]K^+ = 503$ Da) were observed. In the synthesis of $\text{Si}(\text{OSiMe}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ (2), complete hydrosilylation of $\text{Si}(\text{OSiMe}_2\text{H})_4$ by allyltriethoxysilane was confirmed by the appearance of a cluster of ions in the K^+ IDS spectrum at 1183 Da (Fig. 2). The cluster is due to the tetrafunctional 2 and its isotopes. The purities of 1 and 2 were also confirmed by ^1H and ^{13}C NMR.

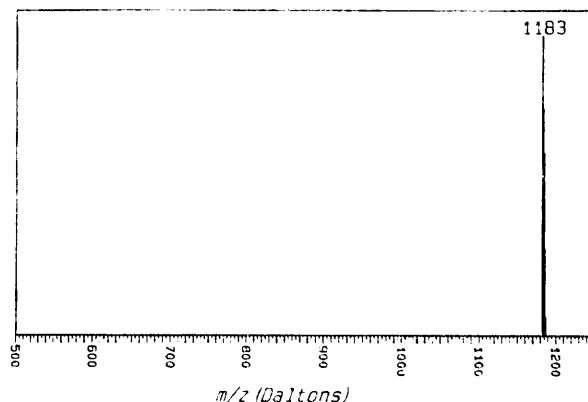


Fig. 2. The K^+ IDS mass spectrum of $\text{Si}(\text{OSiMe}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ (2).

In contrast, an attempted synthesis of cyclo- $(\text{Me}(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4\text{SiO})_4$ (3) from the reaction of cyclo- $(\text{Me}(\text{CH}=\text{CH}_2)\text{SiO})_4$ with triethoxysilane initially gave a number of products, as evidenced by ^1H and ^{13}C NMR spectroscopy. Fig. 3 shows the K^+ IDS spectrum of this crude product mixture. Three major groups of ions were observed corresponding to the molecular ions shown in Scheme 1: 3 ($[M]K^+ = 1039$ Da), trisubstituted cyclo- $(\text{Me}(\text{CH}=\text{CH}_2)(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_3\text{SiO})_4$ ($[M]K^+ = 875$ Da) and a minor amount of disubstituted cyclotetrasiloxane ($[M]K^+ = 711$ Da). Supercritical fluid chromatographic (SFC) analysis of this crude reaction mixture confirmed the presence of three compounds, and was consistent with the results obtained by K^+ IDS analysis. SFC analysis has been utilized previously in conjunction with K^+ IDS to support the quantitative results [12].

We have characterized approximately 20 polyalkoxysilane precursors of star gels using K^+ IDS mass spectrometry to determine the extent of hydrosilylation and to characterize product purity. The information acquired by K^+ IDS effectively complements that from NMR

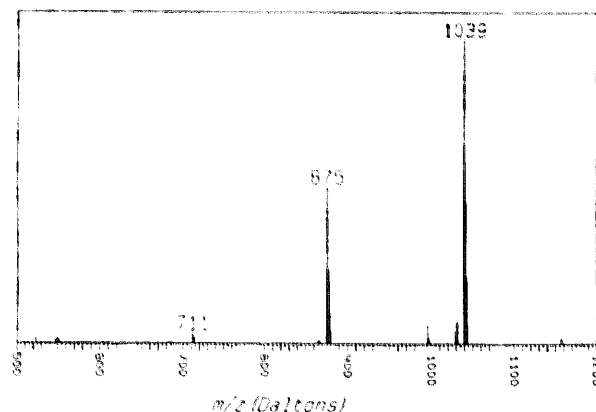
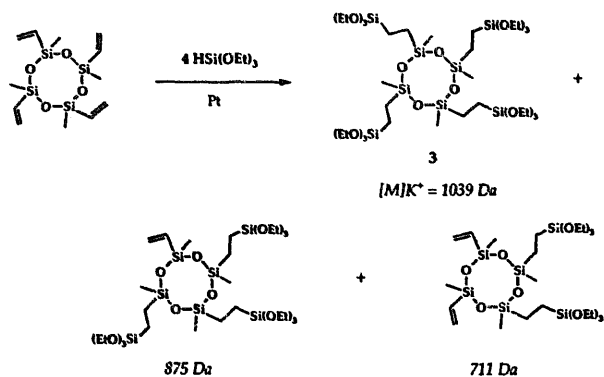


Fig. 3. The K^+ IDS mass spectrum of the products derived from incomplete hydrosilylation of cyclo- $(\text{Me}(\text{CH}=\text{CH}_2)\text{SiO})_4$ with triethoxysilane.



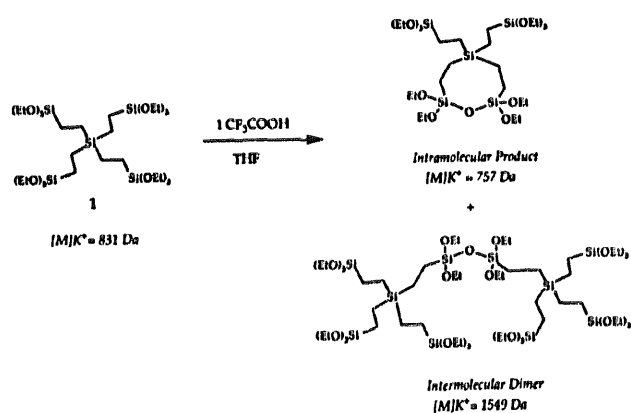
spectroscopy, since the latter can be used to determine isomeric distributions. K^+ IDS can be an invaluable tool to quickly examine complex reaction mixtures of low molecular linear polymers, dendrimers, or species derived from multiple substitutions on a single compound.

2.2. Characterization of partially condensed alkoxy-silanes

Star gel precursors such as **1**, **2** and **3** can be condensed into organic–inorganic networks using traditional aqueous-based acid- or base-catalyzed sol–gel chemistry, or a non-aqueous method using formic acid [10,11] (Eq. (3)).



As well as the usual network-forming condensation reactions leading to organic–inorganic networks which eliminate water, alcohol or formic acid, the condensation pathway for the stars can also include intramolecular cyclization reactions, as shown for **1** in Scheme 2. The distinction between intra- and intermolecular condensation pathways is minimal in ^{29}Si NMR of the



network materials due to overlapping chemical shifts of their characteristic resonances. However, using K^+ IDS mass spectrometry, cyclic and acyclic species can easily be distinguished from one another. Fig. 4 shows the K^+ IDS spectrum of partially condensed **1** where both intramolecular (757 Da) and intermolecular condensation (1549 Da) products can be observed along with unreacted **1**. Their relative abundance indicates a ratio of intra- to intermolecular condensation of about 17:1. A molecular ion corresponding to a minor amount of **1** containing a silanol (Si–OH) group from adventitious hydrolysis is also found at 803 Da. The next higher homolog $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ (**4**) shows a ratio of about 3.3:1, as expected from entropic consequences of formation of a ten-membered ring.

2.3. Characterization of polysilicates

The hydrolysis and condensation of alkoxy-silanes known as sol–gel chemistry has evolved as an important low temperature route to inorganic network materials. There has been interest in the synthesis of low molecular weight polyalkoxy-silanes (polysilicates) as soluble precursors to silica from partially condensed TMOS, $\text{Si}(\text{OEt})_4$ (TEOS) or sodium silicate. NMR studies generally allow only identification of a few of the lowest molecular weight species. Molecular weight information from GPC analysis on species whose silanol groups have been capped via reaction with Me_3SiCl or $(\text{Me}_2\text{Si})_2\text{NH}$ has been reported [13]. However, the standard used for GPC, linear polystyrene, is surely inappropriate for the three-dimensional structure of polysilicates. We wished to see if K^+ IDS could be amenable to the analysis of polysilicate compositions without the need for endcapping. Further, we hoped to establish the existence of the SiOOCH groups in these polysilicates that have been proposed as reactive intermediates in the two-component, non-aqueous sol–gel reactions of tetraalkoxy-silanes with formic acid.

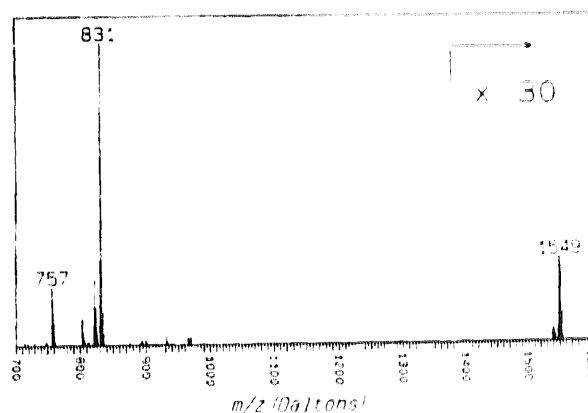


Fig. 4. The K^+ IDS mass spectrum of partially-condensed $\text{Si}(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ (**1**) showing both intra- and intermolecular condensation products.

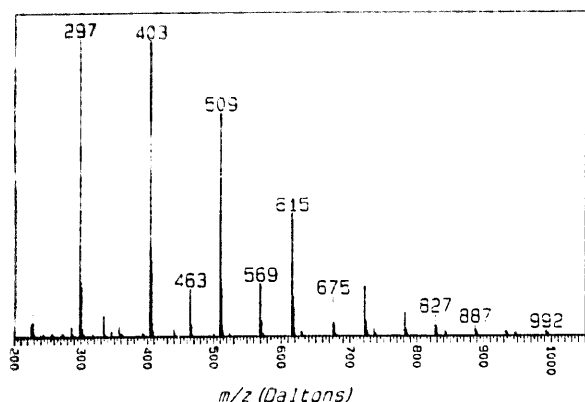
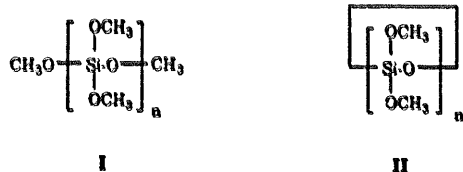


Fig. 5. The K^+ IDS mass spectrum of partially-condensed TMOS.

The polysilicate was synthesized by reaction of TMOS with an equimolar quantity of formic acid. The volatile products, methanol and methyl formate, were removed by distillation during the reaction, and the clear polysilicate was subjected to K^+ IDS analysis. Fig. 5 shows the resulting spectrum. Two main distributions can be observed. The 191, 297, 403, 509, 615, 721, 827 and 933 distribution corresponds to acyclic polysilicates, or their branched isomers, of formula I ($[M]K^+ = 85 \text{ Da} + 106n$), where $n = 1$ to 8. The 357, 463, 569, 675, 781 and 887 distribution corresponds to cyclic polysilicates of the formula II ($[M]K^+ = 39 \text{ Da} + 106n$) where $n = 3$ to 8. Also apparent in lower abundance are ions corresponding to bicyclic species at masses 523, 629, 735, 841 and 947.

The presence of SiOCH substitution on some of the acyclic and cyclic distributions can also be observed in the K^+ IDS spectra in Fig. 5. The substitution of SiOCH for SiOMe appears as molecular ions shifted 14 Da higher than the corresponding completely methoxylated molecular ions. Silyl formates have been implicated as reactive intermediates in the reactions of tetraalkoxysilanes with formic acid, and K^+ IDS provides direct evidence for their existence.

Remarkably, few, if any, silanol groups are evident in the polysilicate spectra. The technique is compatible with silanol detection, since they have been observed in reactions of TEOS with formic acid [14]. It is worth noting that it is difficult or impossible to differentiate between Si-OR and Si-OH in polysilicates with the commonly employed analytical tool of silicon NMR spectroscopy.



3. Conclusions

K^+ IDS mass spectrometry has been shown to generate very high proportions of the molecular ions (with attached potassium) of polyalkoxysilanes and polysilicates. For the polyfunctional 'star gel' precursors, this feature allows characterization of product purity, and an assessment of relative importance of intra- and intermolecular condensation pathways for the resulting organic-inorganic network materials. For polysilicates generated from new non-aqueous sol-gel chemistry, K^+ IDS allows definitive assignment of acyclic, cyclic and bicyclic species and direct observation of mechanistically important silyl formate groups and silanols.

4. Experimental

All reactions were carried out under nitrogen or argon. Solvents were dried prior to use. In the examples that follow, all commercial reagents were distilled prior to use. Triethoxysilane, tetravinylsilane, 1,3,5,7-tetra-vinyltetramethylcyclotetrasilane and tetrakis(dimethyl-siloxy)silane, were purchased from Hüls America Inc., Piscataway, NJ. Allyltriethoxysilane, formic acid and trifluoroacetic acid were purchased from Aldrich Chemical Co., Milwaukee, WI. Platinum divinylsiloxane complex (3–3.5% Pt concentration in xylene, Hüls PC072) was obtained from Hüls America Inc. Proton and carbon NMR were determined in deuterobenzene solvent on a GE model QE-300 instrument. Elemental analyses were performed by Oneida Research Services Inc., One Halsey Road, Whitesboro, NY.

4.1. Synthesis

4.1.1. Synthesis and characterization of $\text{Si}(\text{CH}_2\text{CH}_2\text{-Si}(\text{OC}_2\text{H}_5)_3)_4$ (I)

To a mixture of 12.001 g (0.088 mol) of tetravinylsilane and three drops of Pt catalyst in 50 ml of THF at 0°C was added 38.80 ml (0.384 mol) of trichlorosilane dropwise over a period of 3 h. After the addition, the solution was warmed to room temperature and heated to reflux for 6 h, then cooled and stirred at room temperature for 18 h. The volatiles were removed in vacuo at 60°C leaving 52.89 g (89%) of a white solid identified as $\text{Si}(\text{CH}_2\text{CH}_2\text{SiCl}_3)_4$. ^1H NMR (C_6D_6) 0.36 (m, 2H), 0.76 (m, 2H). ^{13}C NMR (C_6D_6) 1.78 (s, SiCH_2), 17.54 (s, CH_2SiCl_3).

The $\text{Si}(\text{CH}_2\text{CH}_2\text{SiCl}_3)_4$ product from above (52.89 g; 0.078 mol) was dissolved in 100 ml of heptane and the solution heated to 60°C . Dry ethanol (69.50 ml; 1.184 mol) was added dropwise over a period of 3 h with N_2 bubbling through the mixture to remove the HCl produced. The solution was subsequently stirred

overnight at room temperature with continuing removal of HCl. The volatiles were evaporated in vacuo leaving a quantitative yield of pure $\text{Si}(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ as a slightly yellow tinted liquid. ^1H NMR (C_6D_6) 0.79 (m, 2H), 0.90 (m, 2H), 1.18 (t, 6H), 3.81 (q, 9H). ^{13}C NMR (C_6D_6) 2.83 (SiCH_2), 3.68 (SiCH_2), 19.07 (CH_3), 58.93 (SiOCH_2). FTMS (m/e) calculated: 831.381. Found: 831.385 ($M + 39$, 100%).

4.1.2. Synthesis and characterization of $\text{Si}(\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ (2)

To a stirred mixture of 10.04 g (0.0491 mol) of allyltriethoxysilane and 14 drops (ca. 0.4 ml) of Pt catalyst was added 3.17 g (0.0096 mol) of $\text{Si}(\text{OSiMe}_2\text{H})_4$ over a period of 1 h. The solution was heated to 90°C for 4 h, cooled, and stirred at room temperature for 18 h. The excess of $(\text{CH}_2=\text{CHCH}_2)\text{Si}(\text{OEt})_3$ was removed in vacuo, and workup, as described previously, yielded 8.84 g of a liquid identified as $\text{Si}(\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$. ^{13}C NMR (C_6D_6) -0.14 ($(\text{CH}_3)\text{Si}$), 15.04 (SiCH_3), 16.74 (SiCH_2), 17.80 (CH_3), 22.13 ($-\text{CH}_2-$), 58.86 (SiOCH_2). K^+IDS MS (m/z) 1183 ($M + 39$, 100%). Anal. Found: C, 46.28; H, 9.55. $\text{C}_{44}\text{H}_{108}\text{O}_{16}\text{Si}_5$. Calc.: C, 46.11; H, 9.50%.

4.1.3. Synthesis and characterization of $((\text{CH}_3)(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{SiO})_4$ (3)

To a stirred mixture of 2.85 g (0.0083 mol) of $((\text{CH}_3)(\text{CH}_2=\text{CH})\text{SiO})_4$ and 8.15 g (0.0496 mol) of triethoxysilane was added 14 drops (ca. 0.4 ml) of Pt catalyst. The solution was heated at 100°C for 2.5 h, cooled, and stirred at room temperature for 18 h. The excess of $\text{HSi}(\text{OEt})_3$ was removed in vacuo and workup, as described above, yielded a clear liquid that was identified as mainly $((\text{CH}_3)(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{SiO})_4$. Impurities were mainly the di- and tri-substituted products as noted by K^+IDS MS. ^{13}C NMR (C_6D_6) -0.901 ($(\text{CH}_3)\text{Si}$), 2.98 (SiCH_2), 9.30 (SiCH_2), 19.01 (CH_3), 58.99 (SiOCH_2). K^+IDS MS (m/z) 1039 ($M + 39$, 100%), 875 (3-arm product + 39, 52%), 711 (2-arm product + 39, 3%).

4.1.4. Partial condensation of 1

A solution consisting of 0.406 g of $\text{Si}(\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3)_4$ and 0.061 g of trifluoroacetic acid ($r = 1.05$) in 0.432 g of tetrahydrofuran was stirred for 20 h and then stirred at 60°C for 3 h. The solution was cooled and the volatiles were removed in vacuo leaving a clear liquid. This liquid was subjected to K^+IDS analysis.

4.1.5. Partial condensation of TMOS using formic acid

Equimolar quantities (0.20 mol) of TMOS and 96% HCOOH were combined in a 50 ml flask. The mixture was kept at room temperature for 30 min, then heated

until the products, methanol and methyl formate, could be distilled out. Reaction was continued until the collection of distillate became very slow (about 2 h). The remaining polysilicate was then examined by K^+IDS .

4.1.6. K^+IDS experiment

The detailed experimental procedure to perform K^+IDS has been described elsewhere [1], but an abbreviated version is given below. The K^+IDS mass spectrometry experiments were performed with a Finnigan 4615B GC/MS quadrupole mass spectrometer (San Jose, CA). An electron impact source configuration operating at 200°C and a source pressure of 1.0×10^{-6} Torr were used. Commercially available Finnigan direct-exposure probes were coated with a 10% w/w slurry of Al_2O_3 , 2KNO_3 , and SiO_2 in acetone. The coated filaments were dried and conditioned by heating the filament to approximately 500°C under vacuum. Neat samples were deposited onto a stainless steel ribbon adjacent to the conditioned filament. The filament and sample were inserted into the ion source and a 1.3 A current applied to the filament. The current causes resistive heating of the filament with subsequent K^+ emission. The sample, which is in close proximity to the filament, is radiatively heated and intact organic molecules are vaporized. The gas phase organic molecules collide with K^+ and are cationized. The mass spectrometer was scanned at a rate of approximately 1000 Da s^{-1} . Under these conditions we obtained about five scans per sample that were averaged to yield the reported spectra. Ions are recorded as $[\text{M}]\text{K}^+$, the mass of the analyte, plus 39 Da, the mass of potassium.

Acknowledgements

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