

## Field Evaporation of Octadecanethiol

T.J. Prosa, S. Kostrna Keeney,\* and T.F. Kelly

Imago Scientific Instruments, Madison, WI 53711 USA

\*Prairie Technologies, Middleton, WI 53562 USA

Our group has reported atom probe tomography (APT) results for poly(3-alkylthiophene)s deposited on metal carrier tips previously [1,2]. The tip topology and mass fragment distributions were found to be dependent on both incident laser energy density and the deposition method. Mass peaks clearly identifiable as sulfur-containing were difficult to assign, but the alkane signature peaks were abundant and very easy to identify. Because sulfur has two isotopes of reasonable abundance (95%  $S_{32}$ , 4.2%  $S_{34}$ ) the potential for sulfur-containing fragments can be assessed by looking for pairs of peaks with an appropriate intensity ratio. In order to broaden our understanding of the pulsed-laser APT effects on the analysis of sulfur-alkane-containing organic systems, we prepared and analyzed metal carrier tips with deposits of octadecanethiol (C18) ( $SH-(CH_2)_{17}-CH_3$ ). This molecule is commonly used to form self-assembled-monolayers on a number of different metal surfaces [3] and as such, has been studied by APT [4,5]. By heating C18 above its melting point to 50° C and dipping sharp metal carrier tips into the liquid for a period of hours, we were able to prepare bulk material specimens to see how analysis of an oligomer compares to that of related polymer specimens. Greater than 6.7 million ion fragments were collected in laser- and voltage-pulsing modes for a variety of laser energy densities all from a single specimen.

Fig. 1 shows a 900k-ion mass spectrum collected during APT analysis of C18. Integer mass peaks dominate the spectrum while some weak ½-integer peaks (*i.e.* 35.5, 42.5, and 49.5 Dalton) are observed indicating the presence of doubly-ionized evaporation events. Surprisingly, no peaks identifiable as atomic carbon or sulfur can be identified, but the series of peaks labeled  $n=1-18$  in black are identifiable as singly charged alkane fragments,  $C_nH_{-2n}$ . The peaks labeled 2.5-4.5 in brown are potential doubly-charged alkane fragments; although no peaks corresponding to doubly-charged ions for the first 3 alkane fragments are observed. Fig. 2 shows the low-mass region of the same data in linear scale. The insets in Fig. 2 help assess sulfur-containing ion peaks. The peak at 35 Dalton is likely  $C_3H_{10}^{++}$  because of the lack of a peak at 37, while the peaks at 49 and 63 Dalton are likely  $SOH^+$  and  $SOH(CH_2)^+$  because of the corresponding peaks at 51 and 65.

Fig 3 shows 500k ions acquired at 20% pulse fraction under voltage-pulsing conditions. A significant increase in background due to between-pulse evaporation events is observed as well as degradation in mass peak resolution, perhaps contributing to the lack of any peaks beyond 60 Dalton. Nevertheless, many of the primary low-mass fragments in Fig. 2 are also observed here. New peaks are observed at 31, 32.5, 37, and 45 Dalton. Here, limited resolution and intensity do not allow for sulfur peak assessment based on  $S_{34}$ , but it is also difficult to assign these as singly- or doubly-charged alkane fragments as well. Assuming these peaks are either sulfur-containing or some other commonly observed background peak, the chemical identification of these peaks is proposed to be  $SHC_2H_5^{++}$ ,  $SHO_2^{++}$ ,  $(H_2O)_2H^+$ , and  $SHC_4H_9^{++}$  respectively.

### References

- [1] T.J. Prosa, S. Kostrna Keeney, T.F. Kelly, *Mat. Char.*, (submitted).
- [2] T.J. Prosa et al., *Microsc. Microanal.* 13 (Suppl. 2) (2007) 190.
- [3] C.J. Love et al., *Chemical Reviews*, 105 (2005) 1103.
- [4] B. Gault et al., *Microsc. Microanal.* 15 (Suppl. 2) (2009).
- [5] T.J. Prosa, S.L.P. Kostrna, T.F. Kelly, *IFES Technical Digest*, (2006) 533.
- [6] This work was supported by NSF SBIR Grant #0216620.

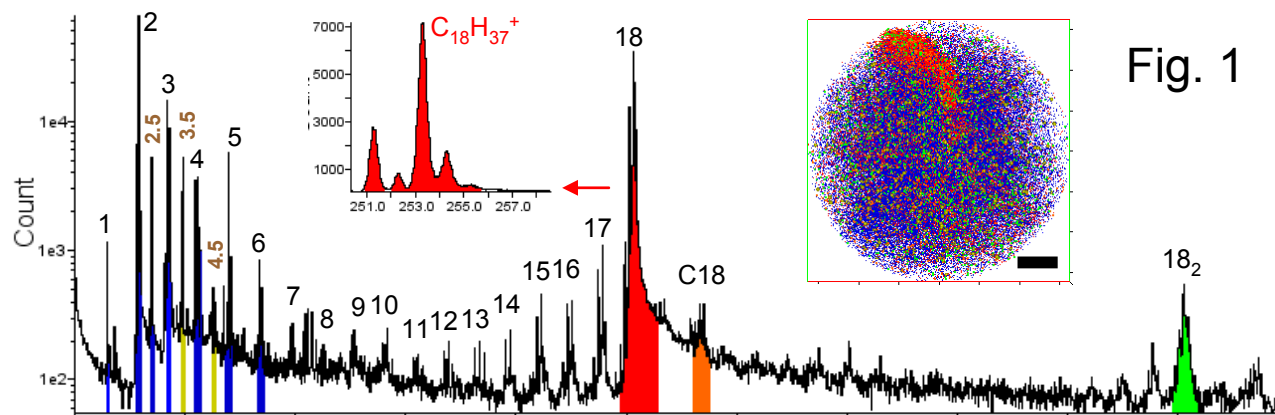


Fig. 1

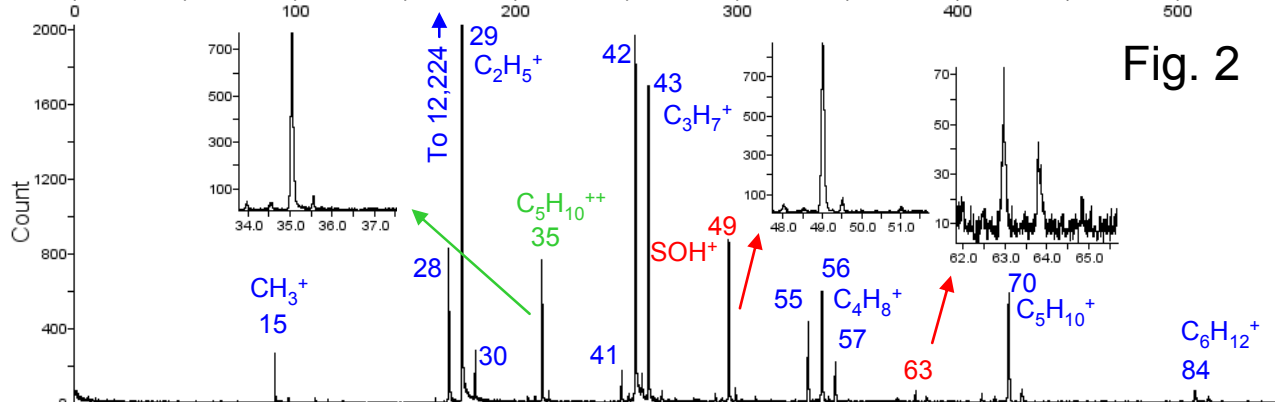


Fig. 2

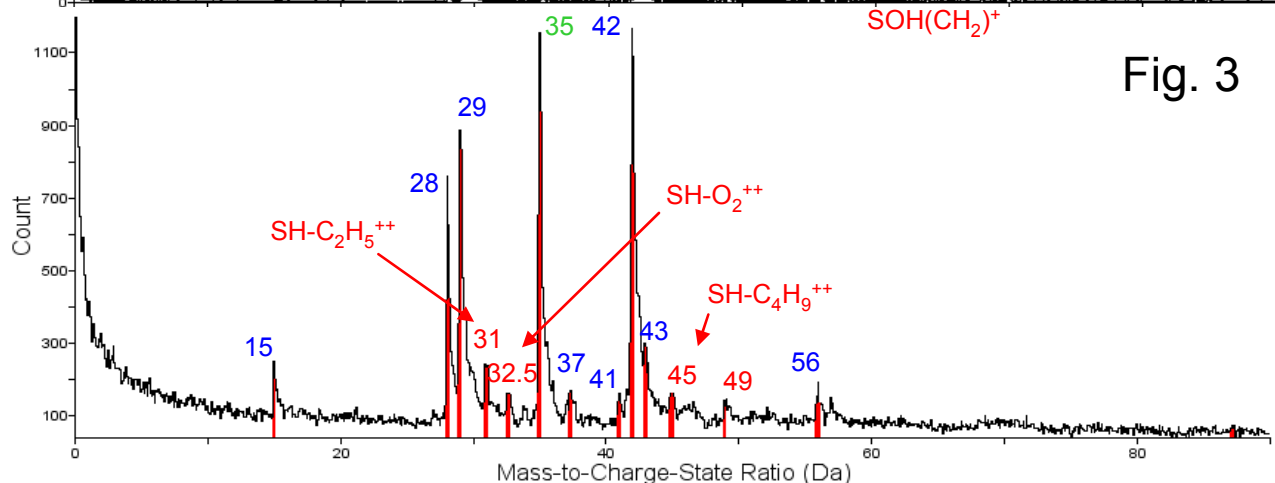


Fig. 3

FIG. 1. Log-scale mass spectrum of *C18* analyzed at  $0.05\text{ nJ}$ . Two series of peaks, enumerated in black (1-18) and brown (2.5-4.5) with a  $14\text{ Dalton}$  ( $\text{CH}_2$ ) repeat are observed. High mass peaks labeled *C18* and  $18_2$  are identified as complete *C18* oligomer less a hydrogen ( $\text{SH}-(\text{CH}_2)_{18}$ ) and clusters of 36 alkane fragments ( $(\text{CH}_2)_{36}$ ) respectively. (Inset-left) Linear-scale  $(\text{CH}_2)_{18}$  region showing expected  $\text{C}_{13}$  isotopic distribution. (Inset-right) Atom map color coded by mass range indicated on mass spectrum. Except for a region rich in large fragments, all ion species have uniform volume distribution throughout as expected. (Note: Scale bar  $10\text{ nm}$ .)

FIG. 2. The  $0\text{-}90\text{ Dalton}$  range from Fig. 1. Each peak is labeled with its mass number and prospective chemical identification. Insets provide added detail for peaks at 35, 49, and 63 Dalton.

FIG. 3. Linear-scale mass spectrum for same sample analyzed under pulsed-voltage conditions analyzed at 20% pulse fraction. Many of the same peaks are observed in the pulsed-laser spectrum. New peaks at 31, 32.5, and 45 Dalton likely come from doubly-charged sulfur-containing ions.