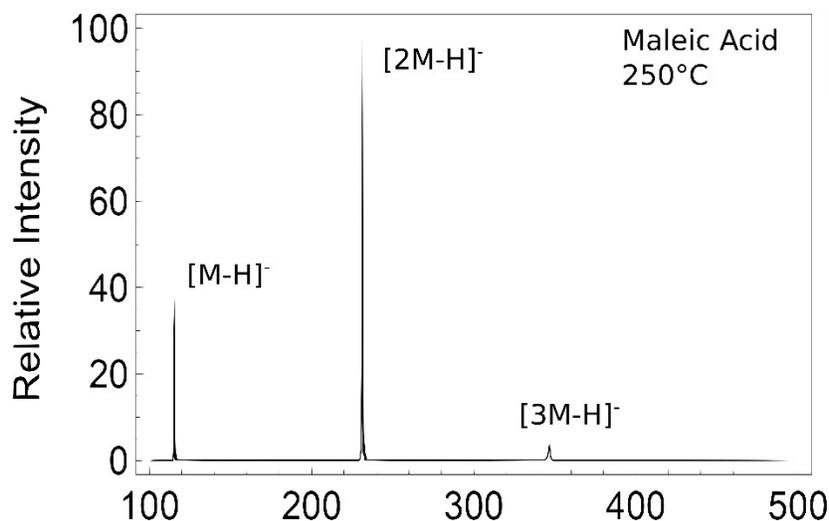


Electronic Supplemental Information

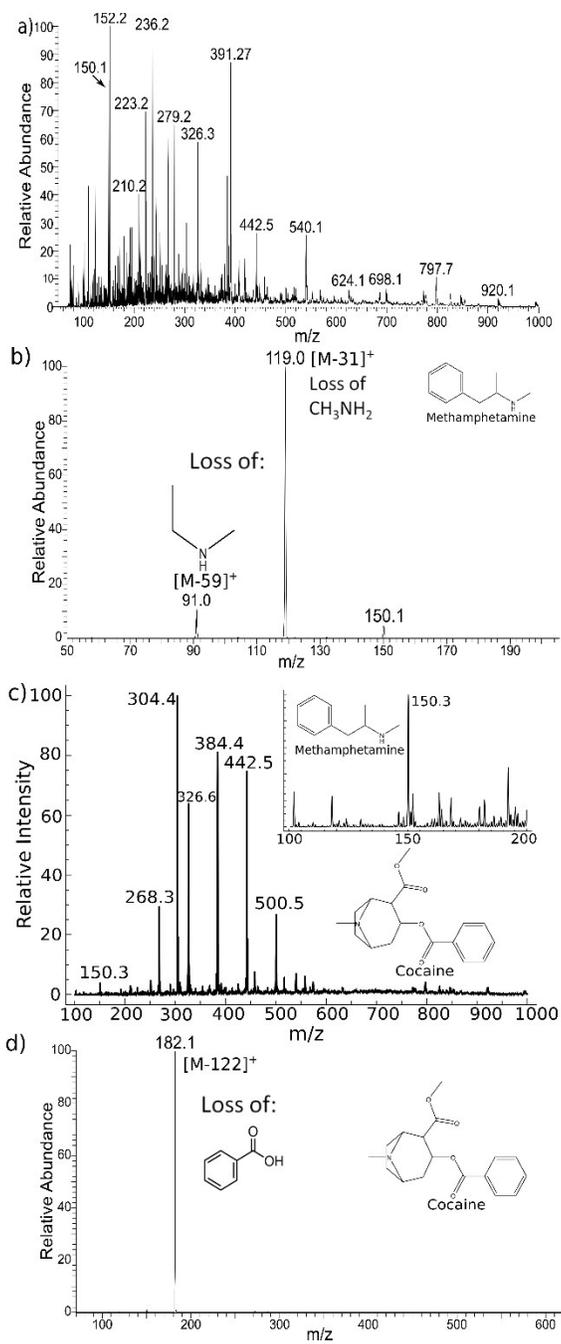
Maleic Acid Data



SI Figure 1 Spectrum of maleic acid in negative mode showing the deprotonated monomer, dimer, and trimer. The temperature refers to the measured heating tape temperature.

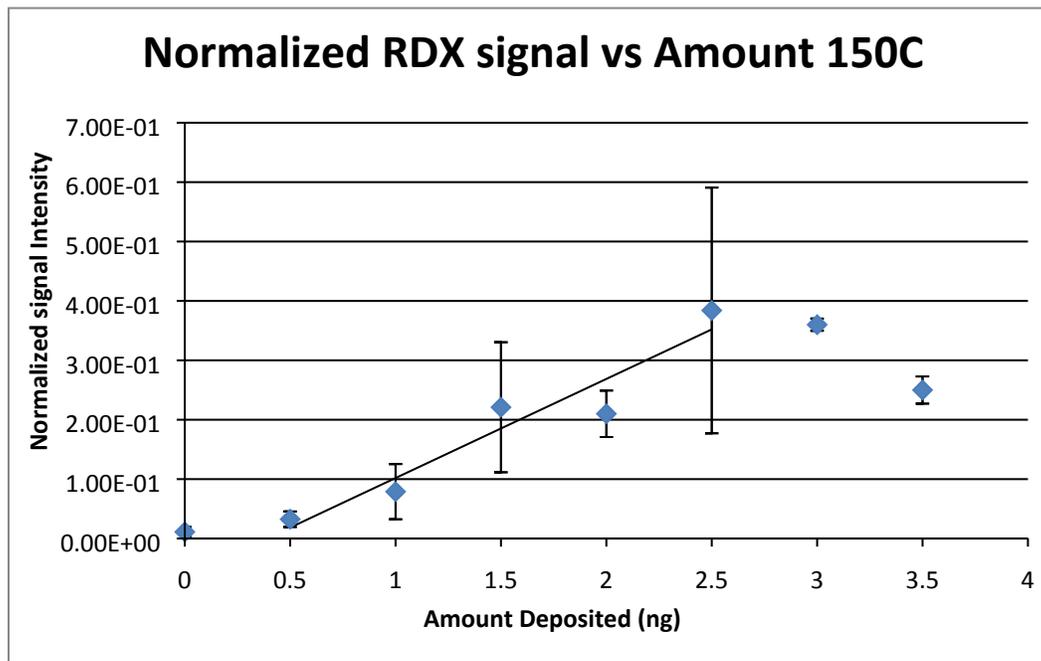
CID data for currency

An EZ-DART spectrum was taken for both fifty (SI figure 2a) and twenty (figure 3 and SI figure 2c) dollar notes, both of which had been in circulation prior to testing. The methamphetamine identification was supported by the CID data for the 150.1 m/z peak,¹ shown in SI figure 2b, from the fifty dollar note. The cocaine identification was supported by the CID data for the 304.4 m/z peak,² shown in SI figure 2d, from the 20 dollar note. Structures for both are shown in SI figure 2c and their respective CID spectra. While the both notes displayed each peak, identification required separate CID spectra due to the relative intensities being insufficient to obtain CID data from a single currency note. Due to the large number of peaks and high amount of background signal observed from the 50 dollar note, additional identifications were not pursued.



SI Figure 2 a) The overall spectrum of the 50 dollar bill. b) CID spectrum for protonated methamphetamine from a 50 dollar bill. The loss of 31 corresponds to a loss of CH₃NH₂ and the loss of 59 to a loss of C₃H₈NH c) The overall spectrum for the 20 dollar bill as shown in figure 3. d) CID spectrum for protonated cocaine from the 20 dollar bill. The loss of 122 corresponds to a loss of benzoic acid. The targeted m/z values for each CID spectra are indicated on the side.

LOD Determination for RDX



SI Figure 3 Calibration curve of RDX used for the determination of the LOD for RDX. Signal response was normalized to the background peak for palmitic acid.

The lower limit of detection calculation for RDX with an R^2 of 0.915. The LOD of 1.1ng was calculated using linear regression analysis.³ 2.5ng was found to be the limit of linearity for the calibration curve.

The calibration's linearity is observed to drop at higher concentrations, possibly due to the signal for the RDX in these data being normalized to the highest background signal. The drop in linearity may be related to increasing ionization of the background normalization ion with the higher concentrations due to increasing amounts of solvent during standard deposition, as well as the overlap between the sample and the DART region of desorption and ionization. A combination of these two effects could account for the observed loss of linearity. While

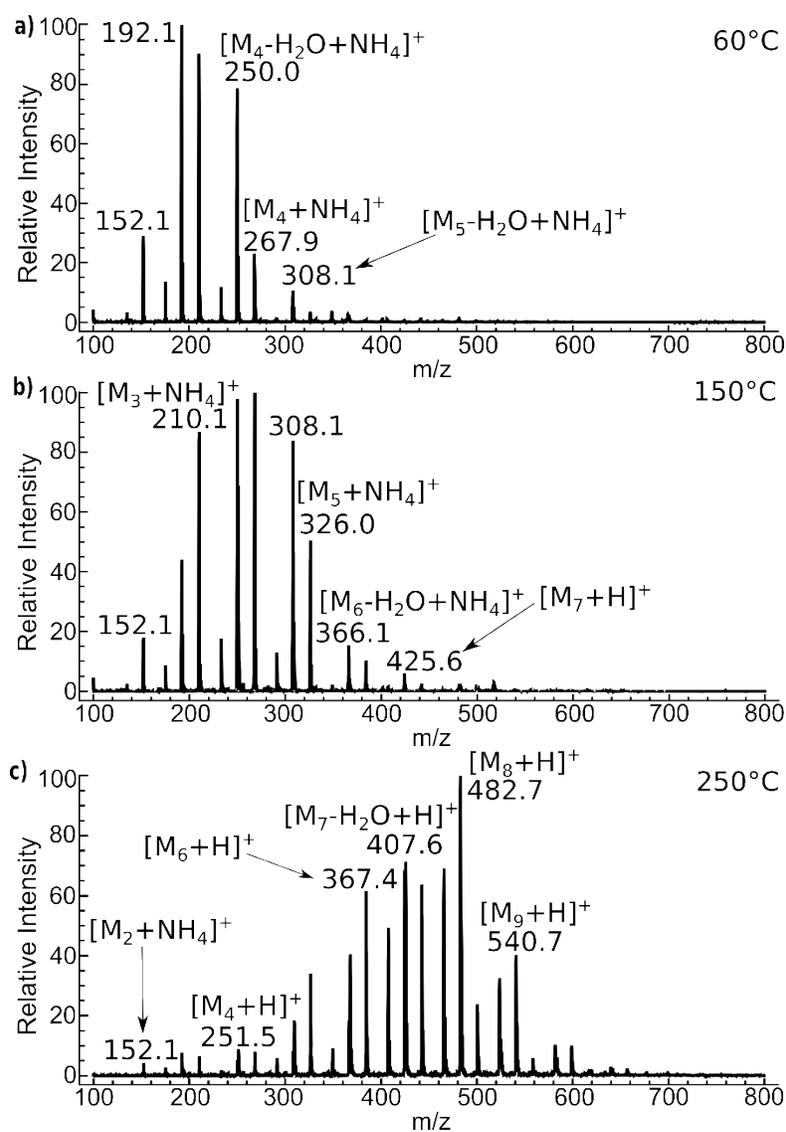
cluster ion formation has been observed with RDX, such clusters were not observed at higher mass for any amount of RDX used in our experiments.

PPG Data and Discussion

In addition to the La Brea Tar Pit hydrocarbon sample described in the text, Poly(propylene glycol) (PPG) was used for a TPD study, due to the high number of possible ion species which follow an easily interpreted pattern. The average mass of desorbed and ionized PPG molecules detected in the EZ-DART spectrum was calculated for a temperature ramped from 60°C to 250°C, showing an overall linear relationship. Since there were few noticeable changes in average mass at and below 60°C, the lower temperatures were not examined in detail. The mass spectra of PPG at 60°C, 150°C, and 250°C are shown in SI Figure 4, highlighting the temperature-dependent shifting of the mass envelope. Identification of the observed ion species was performed using MS³, shown below.

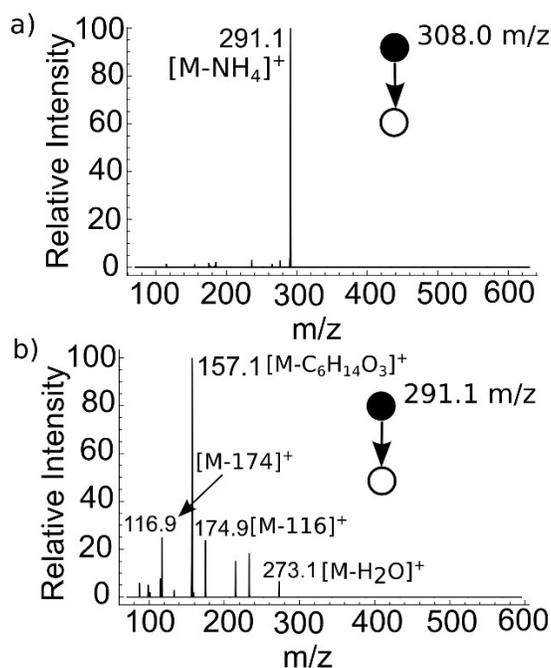
The stability of the ion current during the temperature ramp suggests that the overall ionization efficiency is not significantly impacted by temperature for a more complex sample. Additionally, these data show that even at elevated temperatures, the only observed species are of mass less than 1000 Da. For this PPG sample, where the average mass is 2700 amu, analysis by EZ-DART does not seem to be appropriate for characterization of the entire polymer, but does provide characterization for the lower molecular weight components in the distribution. The effect of temperature on the detected average mass for PPG has implications for the analysis of other complex organic mixtures with varying volatility. The near complete loss of species under 200 Da at a typical DART

operating temperature of 250°C indicates that when performing analysis with the EZ-DART on a complex organic mixture, the temperature must carefully be considered if characterization of both low and mid mass species is desired. From these results, it appears that having the ability to perform TPD analysis enables the possible targeting of compounds with variable volatility when performing the analysis of a complex organic mixture with the EZ-DART.



SI Figure 4. Spectrum of PPG with subunit count labeled as M_x and relevant adducts labeled.

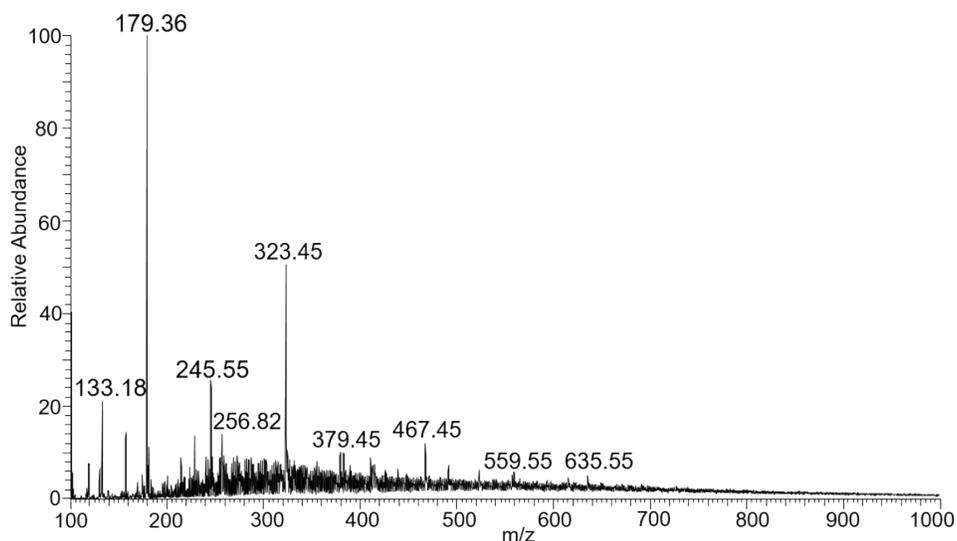
The identification of each species present in the PPG spectra was further supported by the presence of adduct species. The additional possible in-source dehydration reactions and heterogeneous dimerization can make the identification of the specific monomer involved in a peak difficult, especially with unit-mass resolution mass spectral data. To assist with data interpretation the most abundant species in the spectra were targeted for CID analysis. An automated multistep CID program was used, targeting the most abundant species for CID. Initial CID removed the adducting molecule or separated a dimer, and subsequent CID allowed for the confirmation of the species involved, sample spectra for which are shown below. The use of the software based CID procedure allowed for simple identification of each species with changes in temperature.



SI Figure 5 a) The CID spectrum of 308 m/z at 150°C showing only the loss of ammonia b) The subsequent CID of 291.1 from a, showing multiple losses. These losses correspond to the losses of different monomer units. The targeted m/z values for each CID spectra are indicated on the side.

ESI spectrum and method discussion for La Brea Tar pits sample

Approximately 2 grams of tar was mostly dissolved in 20 mL of 50/50 methanol/toluene solution. The solubilized fraction was then diluted by 1:10 in 100% methanol twice serially. This solution was then electrosprayed, providing the spectrum observed below.



SI Figure 6 The electrospray mass spectrum for dissolved tar.

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3. M. M. Sanagi, S. L. Ling, Z. Nasir, D. Hermawan, W. A. W. Ibrahim and A. Abu Naim, *Journal Of AOAC International*, 2009, **92**, 1833-1838.