# Exact Mass Desorption Chemical Ionization (DCI) on the GCT

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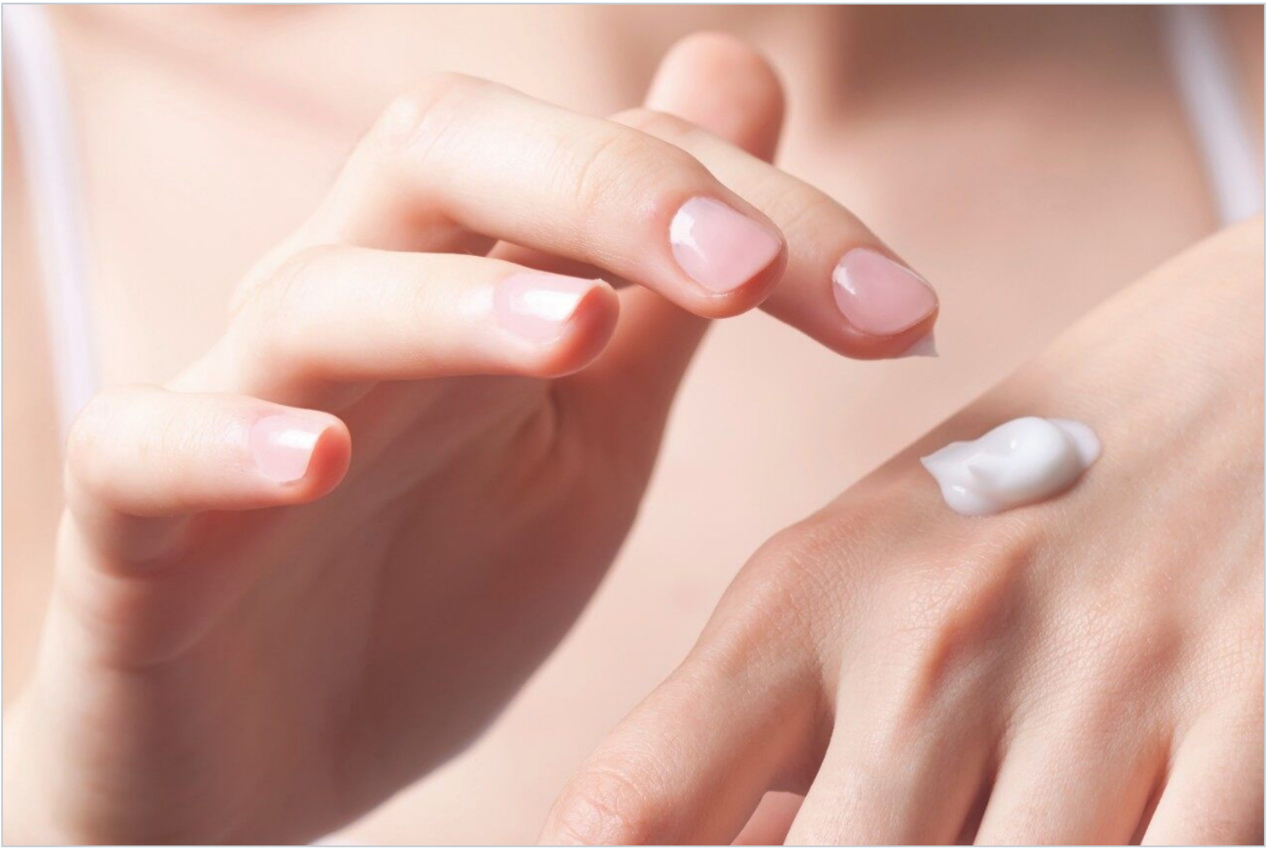

This is an Application Brief and does not contain a detailed Experimental section.

## Abstract

The objective of this brief is to provide examples where a significant increase in pseudo-molecular ion formation was observed between the solids and DCI probes. These objectives were met using the GCT orthogonal acceleration Time-of-Flight (oa-TOF) MS detector operating in CI mode.

### Benefits

- The oa-TOF mass spectrometer allows full mass range data to be produced with good mass measurement accuracy using a singlepoint internal lock mass correction
- Desorption Chemical Ionisation provides a powerful technique for generating more intense pseudo-molecular ions for samples that are thermally labile via the solids probe

## Introduction

Commonly, solid sample introduction into the chemical ionization (CI) source is achieved using a solids probe. The sample is placed in a glass or quartz crucible situated in the probe tip that effectively acts as an oven, allowing the sample to be indirectly heated.

The Desorption Chemical Ionization (DCI) probe provides an alternative method. The sample is placed on a rhenium wire that is rapidly heated, directly in the CI plasma. Rapid heating and close association with the CI reagent gas ions results in reduced fragmentation extending the range of CI analysis to more thermally labile compounds of high polarity/molecular weight.

The objective of this brief is to provide examples where a significant increase in pseudo-molecular ion formation was observed between the solids and DCI probes. These objectives were met using the GCT orthogonal acceleration Time-of-Flight (oa-TOF) MS detector operating in CI mode.

## Experimental

### Instrumentation

The GCT is an oa-TOF MS detector designed for the characterisation of volatile or semivolatile compounds by exact mass measurement and elemental composition determination. Compounds can be introduced through a GC or alternatively may be volatilised directly from a heated insertion solids probe or from the DCI probe.

The GCT provides elevated mass resolution of 7000 Full Width Half Maximum (FWHM), good mass measurement accuracy to within 5 ppm and excellent full scan sensitivity compared to scanning quadrupole instruments - maximizing the chemical information obtained from a single experiment.

The precise and stable relationship between ion arrival time and the square root of its mass allows good mass accuracy with only a single internal reference mass. The mass scale is first calibrated using a multi-point reference compound injected via a septum into a small reservoir. In this example, the system was calibrated in CI mode using Perfluorotributylamine. Once the calibration had been completed, the $M^+$ ion of Chloropentafluorobenzene, *m/z* 201.9609 was used for single point lock mass correction.

## Experimental

Adenosine, Hydrocortisone, and Tripalmitin were used in the following experiments. Individual solutions (1 mg/mL) were made up in a suitable solvent (Methanol or Dichloromethane).

For the solids probe, a small quantity of each compound (c. 10 µg) was loaded onto the probe and directly inserted into the ion source. The temperature of the probe tip was ramped from 20 to 650 °C at 200 °C/min.

For the DCI probe, a small quantity of each compound (c. 0.5 µg) was loaded onto the probe and directly inserted into the ion source. The current passed through the probe tip was ramped from 0 to 1.5 A at 0.5 A/min.

The ion source was operated in CI+ mode, at an electron energy of 70 eV and a source temperature of 150 °C, with an emission current of 100 µA. For all experiments, ammonia was employed as the reagent gas at a source pressure of, approximately, $1.0 \times 10^{-4}$ mbar. The mass spectrometer was integrating between 50 and 900 Da in a time of 0.9 s with an interscan delay of 0.1s.

The DCI probe current is fully controlled from MassLynx Software, with parameters set and stored in a dedicated DCI method file.

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# Results and Discussion

A combined, single point lock mass corrected spectrum of Adenosine is illustrated in Figure 1a from the solids probe. The spectrum shows a base peak fragment ion at *m/z* 136 and a less intense pseudo-molecular ion at *m/z* 268. The $[M+H]^+$ ion is approximately 4 % of the base peak ion.

This spectrum can be compared to that obtained from the DCI probe, illustrated in Figure 1b. The spectrum shows a base-peak pseudo-molecular ion at *m/z* 268 and a less intense (9 %) fragment ion at *m/z* 136.

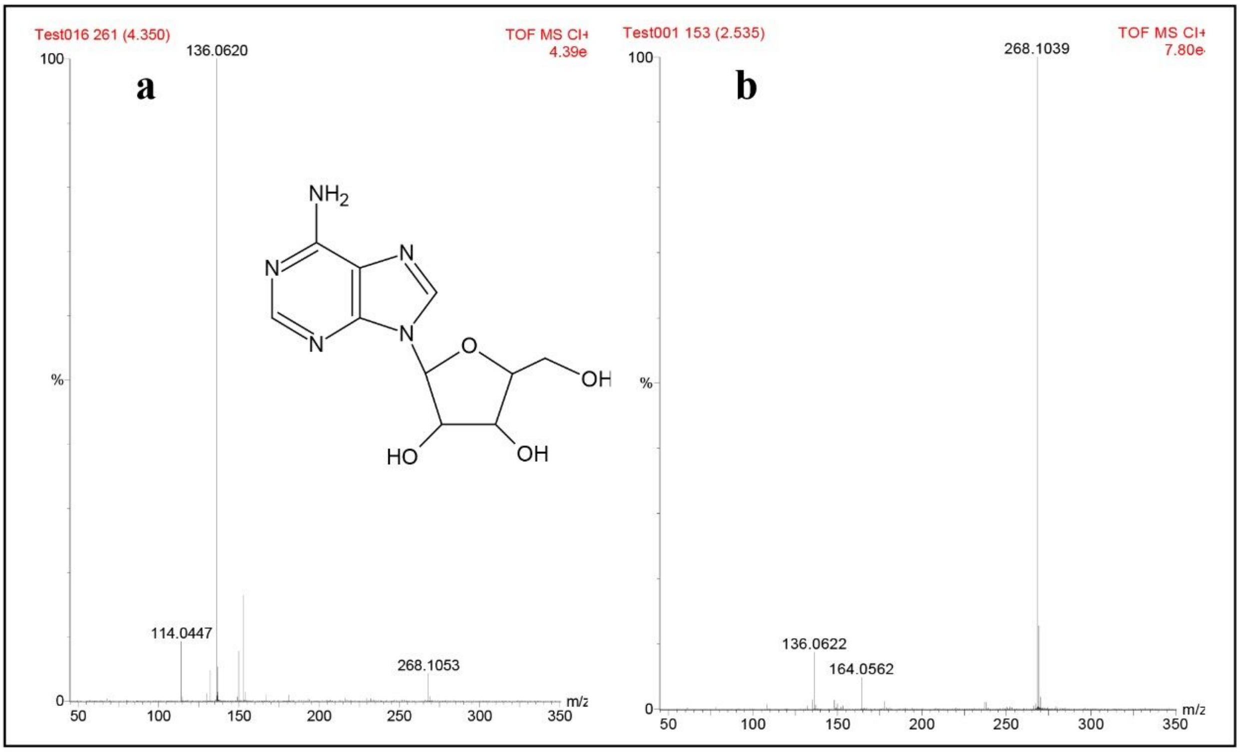

*Figure 1.. Solids probe and DCI probe spectra obtained for adenosine.*

The spectrum for Hydrocortisone is illustrated in Figure 2a from the solids probe. The spectrum shows a base peak fragment ion at *m/z* 303 and a less intense pseudo-molecular ion at *m/z* 363. The $[M+H]^+$ ion is approximately 2 % of the base peak ion. This spectrum can be compared to that obtained from the DCI probe, illustrated in Figure 2b. The spectrum shows a base-peak pseudomolecular ion at *m/z* 363 and a less intense (51 %) fragment ion at *m/z* 303.

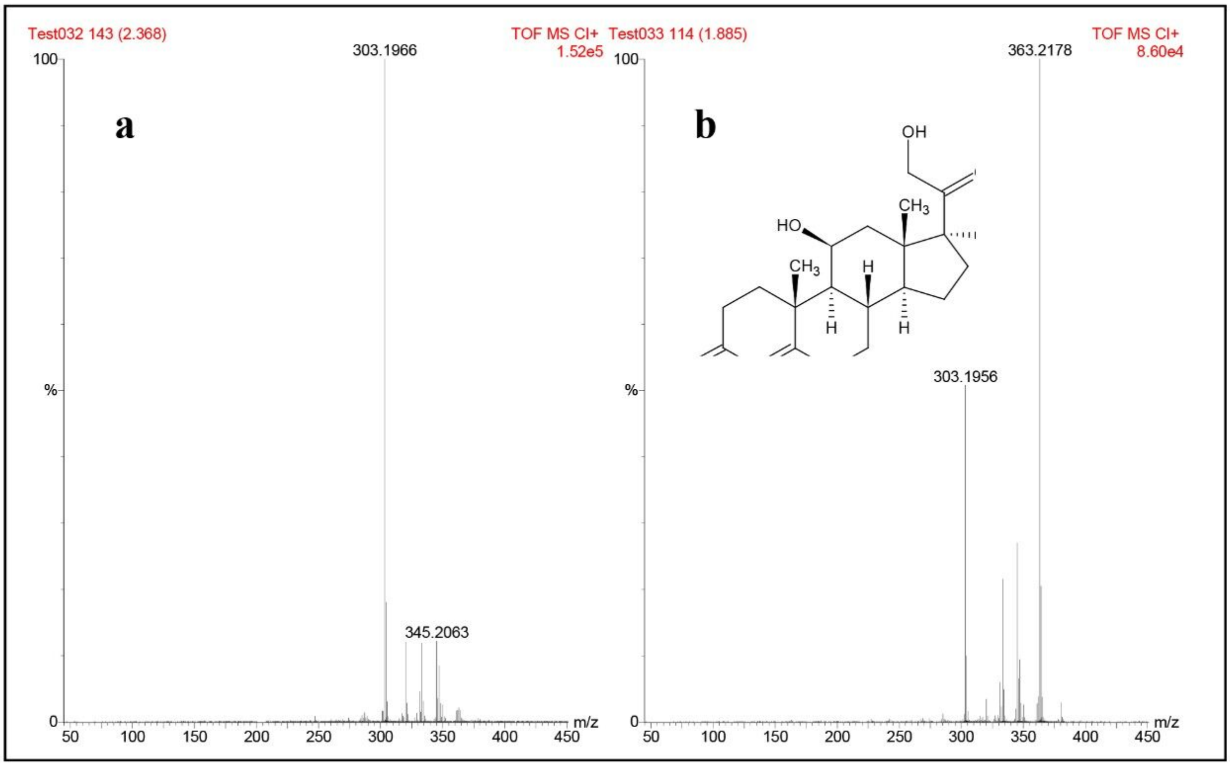

*Figure 2. Solids probe and DCI probe spectra obtained for hydrocortisone.*

The spectrum for Tripalmitin is illustrated in Figure 3 from the DCI probe. There was very little difference between the spectrum acquired with the solids probe and that with the DCI probe. The spectrum shows a base peak pseudo-molecular ion at *m/z* 824.7 and a less intense fragment ion at *m/z* 551.5. The fragment ion is approximately 4 % of the $[M+NH_4]^+$ ion.

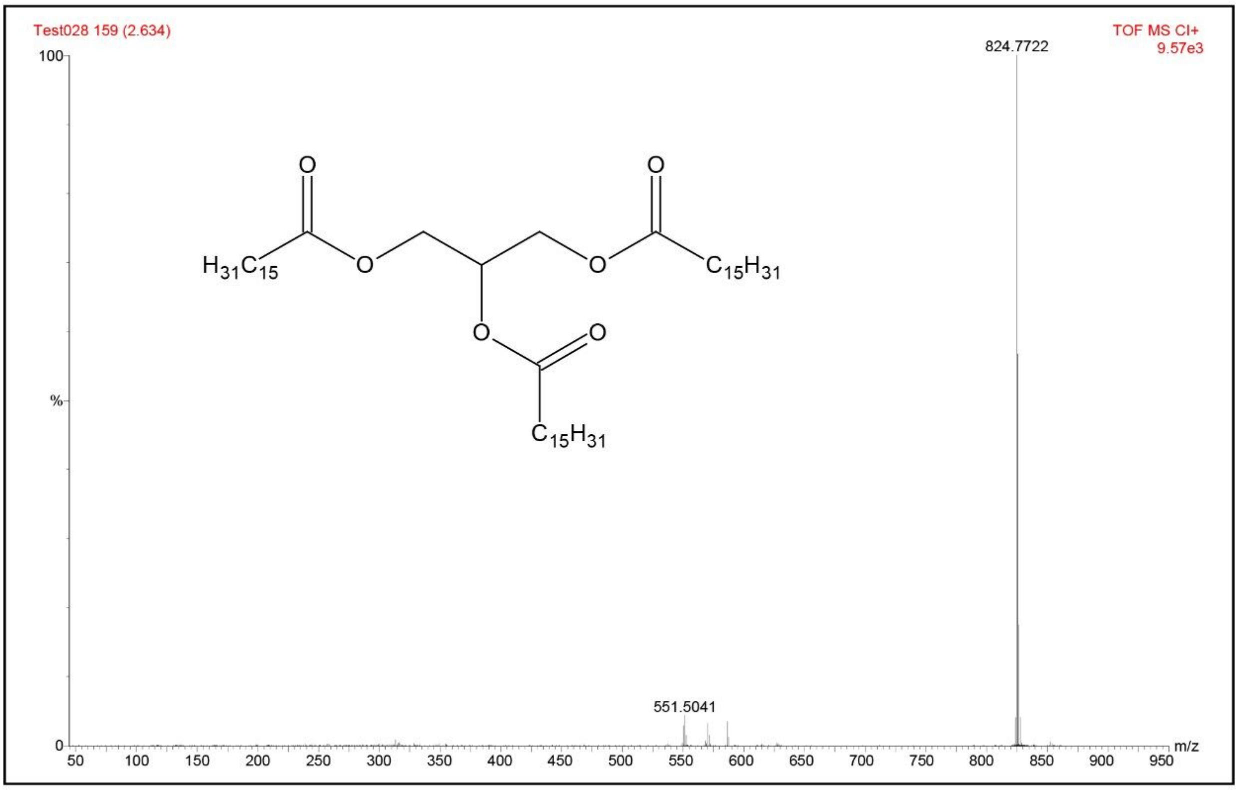

*Figure 3. DCI probe spectrum obtained for tripalmitin.*

This example shows that although the highest ion used for calibration was *m/z* 614 (from PFTBA), the extrapolation of this gives very accurate mass measurement results.

Excellent mass accuracy was obtained for the pseudo-molecular ion and major fragment in each case, see Figure 4.

| | *m/z* | **ppm** | elemental comp |
|---|---|---|---|
| Adenosine | 268 | **2.5** | $C_{10}H_{14}N_5O_4$ |
| | 136 | **0.9** | $C_5H_6N_5$ |
| Hydrocortisone | 363 | **1.8** | $C_{21}H_{31}O_5$ |
| | 303 | **1.4** | $C_{19}H_{27}O_3$ |
| Tripalmitin | 824 | **1.8** | $C_{51}H_{102}NO_6$ |
| | 551 | **0.3** | $C_{35}H_{67}O_4$ |

*Figure 4. Mass accuracy results.*

## Conclusion

The oa-TOF mass spectrometer allows full mass range data to be produced with good mass measurement accuracy using a singlepoint internal lock mass correction. The elevated resolution of the instrument (7000 FWHM) allows nominally isobaric ions to be mass resolved and elemental composition determined.

Desorption Chemical Ionisation provides a powerful technique for generating more intense pseudo-molecular ions for samples that are thermally labile via the solids probe. With these experiments the desorption probe was utilised in CI mode; the probe can also be employed in electron impact (EI) mode.

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