Poster Reprint

ASMS 2019
WP327

Workflow solutions for direct insertion, real-time gas chromatography -mass spectrometry

Angela Henry[1]; Luis Cuadra-Rodriguez [2]; Paul Tripp[2]; Wei Song [1]

[1]Agilent Technologies Inc., 2850 Centerville Road, Wilimington, DE 19808, USA

[2]Agilent Technologies Inc., 5301 Stevens Creek Blvd, Santa Clara, CA 95051

Introduction

The need for fast screening of samples is desired across many fields of study, from crime laboratories analysis of seized drugs, to verifying RoHS compliance of plastic commodities. Conventional screening with gas chromatography-mass spectrometry (GC/MS) requires sample preparation of dissolution, dilution and/or headspace sampling and long GC analysis times. Typical application of direct insertion real-time MS provides quick analysis of various sample types but does not have chromatographic separation of the analytes, causing increased time of human review. Direct insertion GC/MS is an easy-to-use screening technique, and offers fast analysis with GC separation and mass spectral confirmation in under a minute.

Consumables supporting this technology provide various sampling techniques for samples, such as liquids, powders or tablets.

Experimental

Instrument Design

The GC/MS QuickProbe instrument (Figure 1) consists of an inlet with a split helium (He) carrier gas flow, which connects to a fast thermal oven containing a high temperature, short 100% dimethylpolysiloxane capillary column. This column connects inside of the GC oven with an Ultimate Union. The second column is also a short 100% dimethylpolysiloxane capillary column that connects to the inert single quad mass spectrometer. Samples are manually inserted in the inlet and held for a set amount of time.

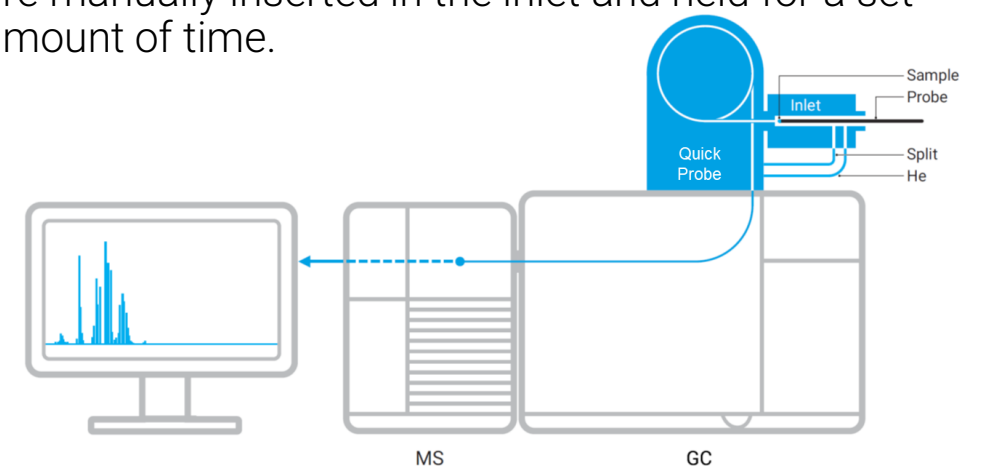

Figure 1. Schematic of direct insertion GC/MS instrument.

System Parameters

Inlet: 250°C Carrier Gas: 5.5 psi Helium, split

Oven Temperature Program: 50°C (hold 2 s), ramp 7°C/s to 310°C (no hold, or 20 s).

MS Source: 230°C MS Quad: 150°C

Run time: 40-60 seconds

Experimental (continued)

Probes

Glass rod probes are utilized to transfer samples into the inlet. Two probe styles were chosen for different sample types: round tip and pocket probes. The round tip probe was used for liquid samples and tablets that were scraped. Pocket probes were used for powder samples to trap a small amount of powder in the cup. Probe holders were designed to hold and protect probes between sampling and insertion into the GC/MS to prevent inlet and probe contamination.

Suggested workflow for sampling

The suggested workflow is: 1) run system blank, 2) run probe blank, 3) run sample, 4) run blank, and 5) run standard, where necessary.

1) System blanks are completed at the beginning of the sequence or day, similar to a normal GC/MS blank.

2) A probe is installed into the probe holder, then inserted into the inlet. Probes are held in the inlet for ~5 seconds and then removed to clear contamination.

3) When probe blanks are completed, use probe to collect the sample. Round tip probes work best with liquid and tablets and pocket probes were utilized for powders and scraping tablets.

4) Run a system blank to verify no carryover or inlet contamination. A user may run a probe holder blank to verify no contamination on the probe tip.

Peak spectra were compared to NIST14 library in the data analysis software with library match cutoff of 70.

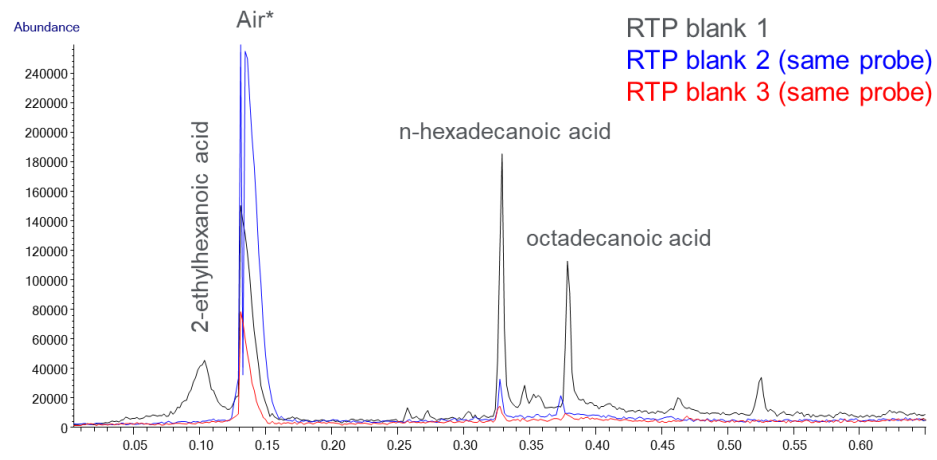

Figure 2. Round tip probe (RTP) blank runs of same probe run back to back.

Probe blanks

Probe blanks are repeated 2-3 times to verify a flat or very low baseline. Typically, contamination is removed within 3 runs. A representative set of probe blank runs is shown in Figure 2. The air peak was from probe holder prototype and has been mitigated in recent probe holder designs.

System blanks

This system blank can be repeated 2-5 times to verify a flat baseline. Typically, the baseline is flat by second run.

Round tip probe workflow: Liquids

Dip probe <5 mm into a liquid sample; allow solvent to completely evaporate. Polar (water, methanol) or viscous (toluene) solvents will take longer to dry, generally >30s. The direct insertion GC/MS system has a fast run time (<1 min) with adequate separation for peaks in the same compound class and retains good peak shapes for compounds that normally tail in GC/MS analysis, such as oxycodone (Figure 3).

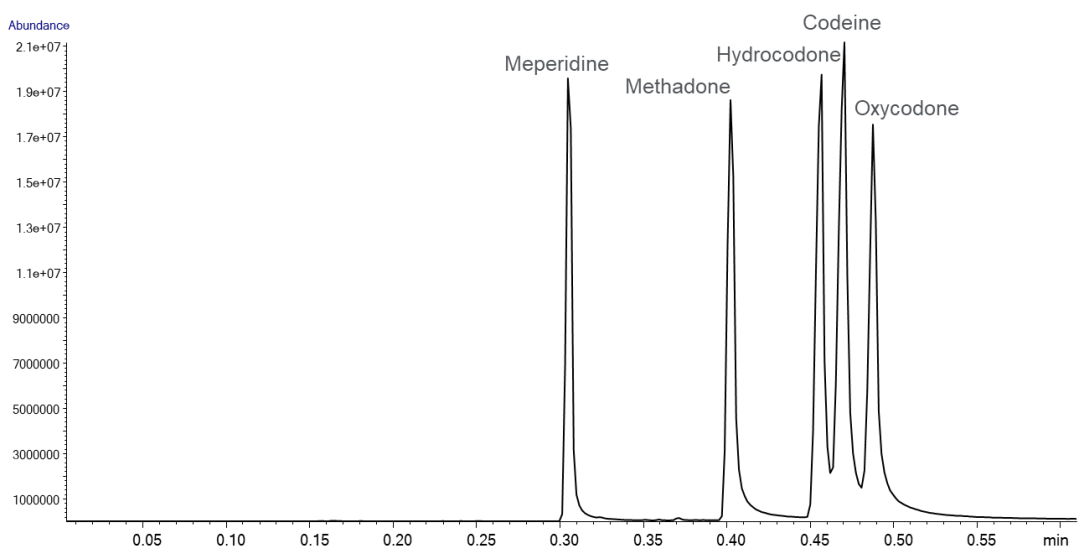

Figure 3. Direct insertion GC/MS total ion chromatogram (TIC) showing fast separation of opiate compounds (250 µg/mL) from liquid sample using round tip probe.

Aerosol spray bottle contents can be tested with probes, whether the probe is dipped into the liquid or the contents are sprayed onto the probe. Nitroglycerin spray bottle was sprayed onto the round tip probe, allowed to dry, and tested in the system (Figure 4). Spraying an aerosol can leave many droplets on and along a long section of the probe. Caution must be taken with aerosols to avoid carryover in the probe holder and overall GC/MS system, such as the liner or column.

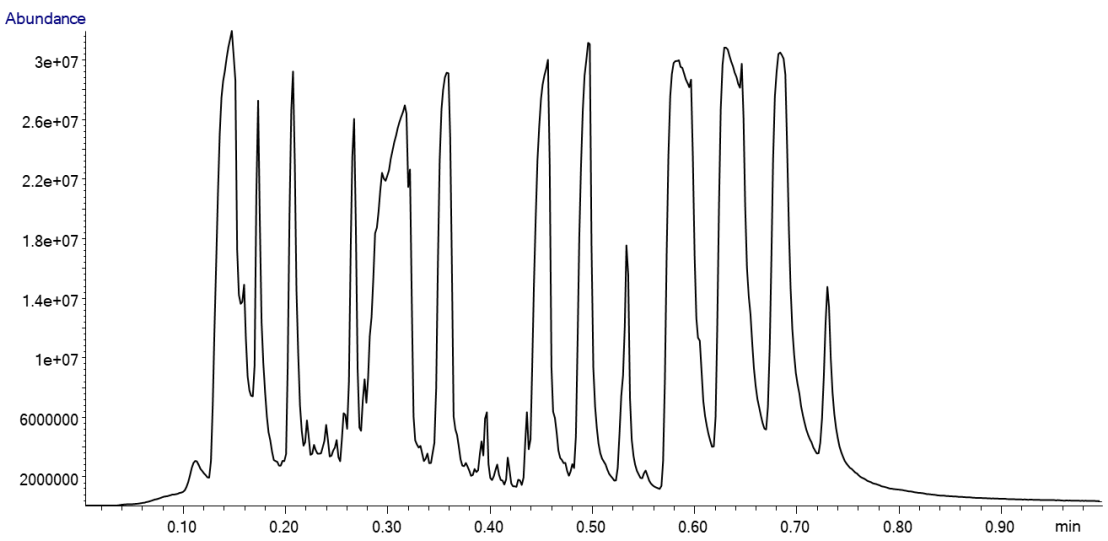

Figure 4. TIC of nitroglycerin spray on round tip probe, where most peaks correspond to esters and alcohols.

Round tip probe workflow: Tablets

Extend the round tip probe ~10mm from end of probe holder (first holder notch). Hold the probe holder near the base and gently scrape the tablet with probe. Depending on tablet, cutting the tablet may be necessary to access the active ingredients. A very small amount of sample is required to detect tablet components (Figure 5).

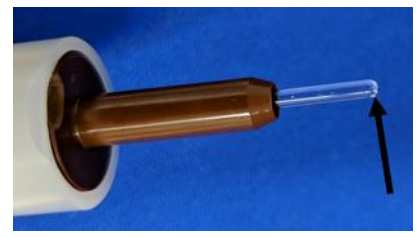

Figure 5. Round tip probe with a very small amount of tablet scrapings on the tip, which is enough for sampling with direct insertion GC/MS.

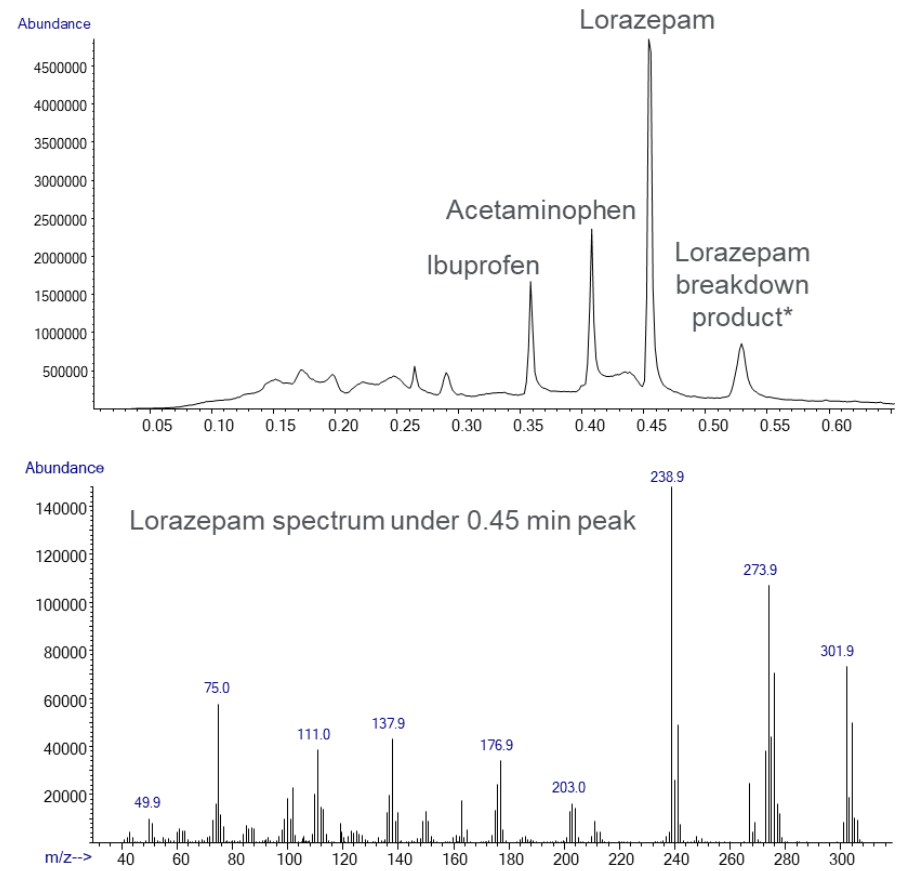

Figure 6. TIC (top) and mass spectrum (bottom) of lorazepam tablet, cut in half, then scraped with round tip probe.

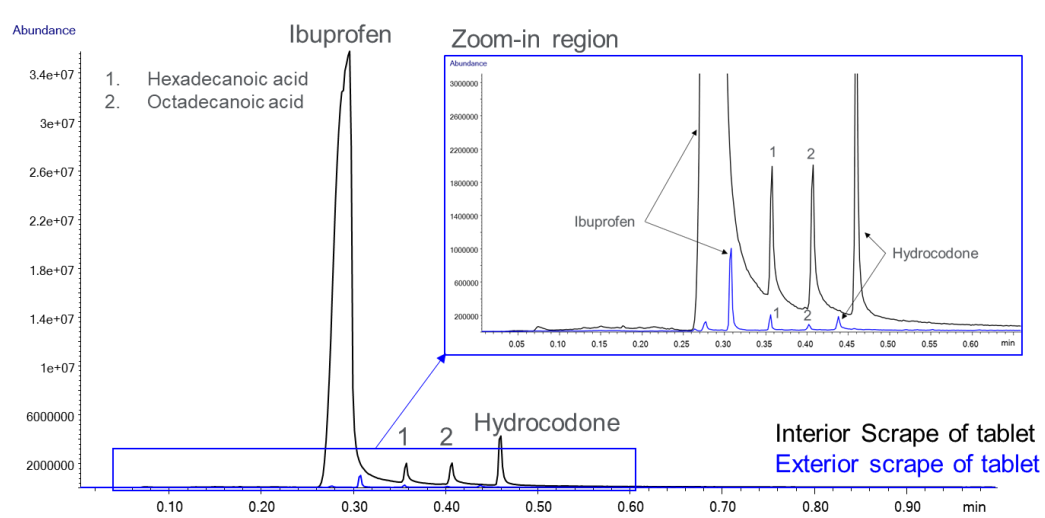

Figure 7. Comparison of TICs for exterior scrape of hydrocodone/ibuprofen tablet and scrape of tablet interior, when cut in half.

Results and Discussion

Pocket probe: Powders and tablet sampling

The pocket probe provides a recessed region to hold powder or tablet scraping. Similar to the round top probe, only very small amount is necessary for testing (Figure 8).

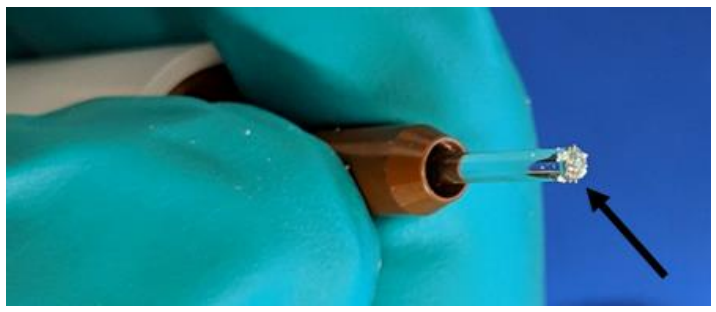

Figure 8. Pocket probe with powder sample.

Sampling powders: Place powder in a weigh boat, if possible. Extend probe holder from holder to second notch. Gently tap the probe tip into the powder, taking care to avoid powder from getting up the sides of the probe. Then, tap the probe on the side of the weight boat to remove loosely held powder; the goal is to avoid carryover or contamination of the probe holder and inlet.

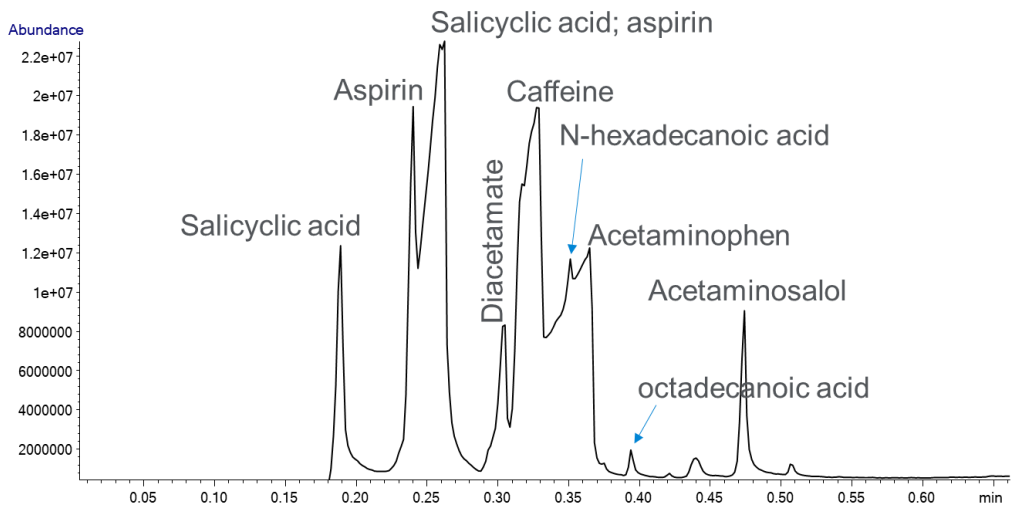

Figure 9. TIC of crushed tablet with main ingredients of acetaminophen, aspirin, and caffeine.

Tablets can be sampled in same manner as round tip probes, where probe is extended to the first notch of the holder. Sampling both interior and exterior of a tablet can provide information about tablet components, handling, and surrounding environment (Figures 6, 7 & 9).

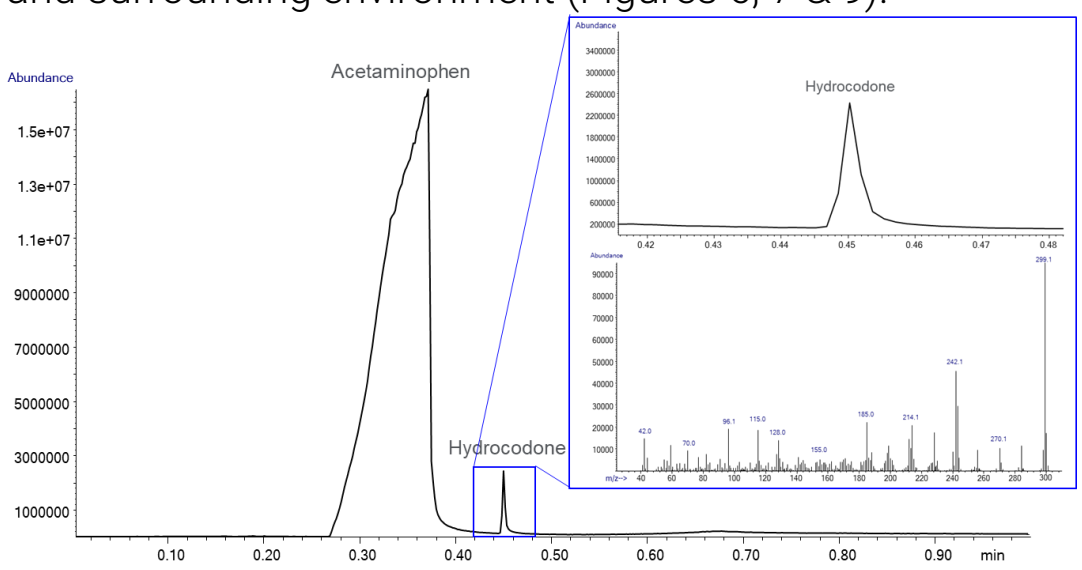

Figure 10. TIC of acetaminophen/hydrocodone tablet scraping; inset: zoom-in of hydrocodone peak and the corresponding mass spectrum under the peak.

Minimizing carryover

Carryover was observed in select powder experiments, liquid experiments, and the nitroglycerin spray.

To mitigate carryover in probe holder and inlet (liner):

- Use the probe holder for sample collection & injection.
- Wipe glass rod with lint free cloth to remove excess.
- Place powder in weight boat for sampling, touch powder gently with probe, then tap against side of weigh boat to remove excess.
- Rinse probe with solvent to remove excess (may not be feasible in all labs).

What happens if there is carryover?

- Determine if carryover is on probe holder or in system (e.g. liner).
- If probe holder is contaminated, the tip can be cleaned or replaced.
- If liner is contaminated, cool system and replace liner (Figure 11).

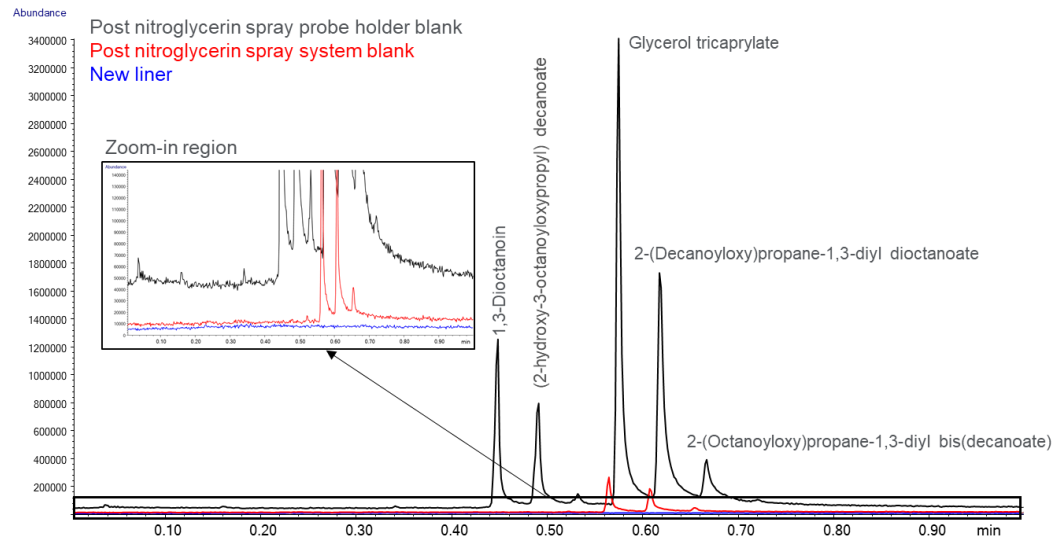

Figure 11. Carryover from nitroglycerin spray in blank chromatograms and clean system blank with new liner; inset: zoom-in of baselines.

Conclusions

The suggested workflow for the QuickProbe GC/MS system is: 1) run system blank, 2) run probe blank, 3) run sample, 4) run blank, and 5) run standard, where necessary.

- Use round tip probes for liquids or scraping tablets.
- Use pocket probes for powders or scraping tablets.
- Fast run time allows accelerated, qualitative screening of samples and retains good peak shapes.

For Forensic Use.

Published in USA, June 2, 2019

Agilent
Trusted Answers