



Best Practices for Identification and Quantitation

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Volatiles by GC/MS



Four Programs – Multiple Methods

- RCRA – SW 846 Method 8260C
- SDWA – 524.2
- CWA – 624.1
- CERCLA – SOM02.4

Volatiles by GC/MS



Several factors that are looked at in each method with respect to Identification and Quantitation.

- Retention time of target analyte
- Comparison of mass spectrum
 - Characteristic ion
 - Relative intensities of characteristic ions

Retention Time



Method	Criteria
8260 C	Within 0.06 RRT units of the RRT of the Standard Component
524.2 (3,4)	3 SD of the mean RT of the compound in the calibration mixture
624.1	Within 10 sec of the RT of the analyte in the LCS at the beginning of the shift
SOM02.4	Within 0.06 RRT units of the RRT of the corresponding CCV standard

Retention Time



Retention Time

Retention time (RT) is a measure of the time taken for a solute to pass through a chromatography column. It is calculated as the time from injection to detection.

Relative Retention Time

RRT is an expression of a sample's retention time relative to the standard's retention time. The use of the relative retention time (RRT) reduces the effects of some of the variables that can affect the retention time.

$$\text{RRT} = \text{Standard RT} / \text{Sample RT}$$

Mass Spectrum Signals



Method	Criteria
8260 C	Characteristic ions agree within 30% of ions in reference spectrum. Maximize in same scan or within one scan. Ions greater than 30%.
524.2 (3,4)	Characteristic ions agree within 20% of ions in reference spectrum. Primary identification is based on RT. Ions greater than 30%
624.1	Characteristic ions agree within 50% to 200% of ions in reference spectrum. Maximize within the same two consecutive scans. Table 6 in method.
SOM02.4	Characteristic ions agree within 20% of ions in reference spectrum. Within 0.06 RRT units of the RRT of the corresponding CCV standard

Reference Spectra



Method	Criteria
8260 C	Must be generated by laboratory using conditions of the method
524.2 (3,4)	Seems to allow use of lab generated reference spectra or database (NIST)
624.1	Allows the use of either lab generated reference spectra or database (NIST)
SOM02.4	Must be generated by laboratory using conditions of the method

Reference Spectra



- The flexibility allowed between the methods in the generation of reference spectra has been a concern
- With shortened chromatographic runtimes and standard mixes containing many components, laboratory generated reference spectra are not always as “clean” as would be desirable
- Some initiatives to only use reference spectra that refer specifically to a commercial spectral database

Structural Isomers



Method	Criteria
8260 C	Height of valley between peaks less than 50%, otherwise report as isomeric pairs
524.2 (3,4)	Not addressed
624.1	Height of valley between peaks less than 50%, otherwise report as isomeric pairs
SOM02.4	Must be “50 % resolved”

Quantitation



Method	Criteria
8260 C	EICP of primary/quant ion. ICAL \leq 20% use average RRF. Otherwise, calibration curve
524.2 (3,4)	Linear or quadratic calibration curve. Weighting allowed. Cal stds must calculate within 30%
624.1	EICP of primary/quant ion. ICAL \leq 35% use average RRF. Otherwise, calibration curve
SOM02.4	EICP of primary/quant ion. ICAL \leq 20-40%, depending on compound, use average RRF. Two failures allowed.

All methods recommend/require use of internal standard calibration

Library Search - Unknowns



Method	Criteria
8260 C	Guidelines given for qualitative identification of unknowns. Assume RRF of 1 for quantitation.
524.2 (3,4)	Not specifically addressed
624.1	Not specifically addressed
SOM02.4	Very prescriptive requirements for the generation of library search results including differentiating between alkane and non-alkane TICs

Conclusions



- Retention time matching is a critical part of the analysis, even though a mass spec application. All 4 methods use internal standards. The RRT is preferred.
- It would seem that there would be value in broadening the relative abundance criteria but specify the number of scans within which ions maximize.
- If we are not going to specify the requirements for generating reference spectra (RT resolution, etc.) then it would seem that commercial libraries should be used.
- Need some consensus on the quantitation model(s) to be used

Thank you



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