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LAPRW 2019

Poster #113

Agilent
Trusted Answers

Introduction

Today's high throughput food laboratories require reliable and timely pesticide residue analysis of varied food samples. To gain the highest productivity of the analytical instrumentation, the JetClean Self-Cleaning Ion Source was successfully applied to pesticide residue analysis, significantly reducing the need for manual source cleaning and increasing the sample throughput of the GC/MS system.

Similarly, applying the StreamSelect (SS) configuration to LC/MS systems eliminates the idle time of the MS, and increases the LC/MS system throughput. Both the JetClean and the StreamSelect operations are executed automatically using MassHunter SW.

The JetClean Self-Cleaning Ion Source of GC/MS systems eliminates or greatly reduces the need for manual source cleaning and assures consistent results over many months of operation. JetClean will generate additional days of instrument "uptime" yearly, and free up many hours of the operator's time by eliminating/reducing manual source cleaning. JetClean automatically introduces finite amount of hydrogen to prevent or remove matrix deposit buildup.

Rhodamine 6G treated lens:
Before (left) and **After** (right) JetClean applied
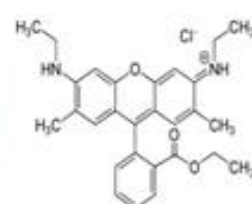
Rhodamine 6G

The JetClean effectiveness is demonstrated by the above figure. The extractor lens was heavily marked with a Sharpie pen, creating a serious Rhodamine 6 "contamination", imitating the accumulation of deposits one would see during normal analysis of samples with heavy matrices. After an automatically initiated cleaning cycle, utilizing prudently controlled hydrogen flows, the deposits from the lens were removed without human interaction.

Analysis with JetClean can be carried out in fully inert environment, where JetClean initiated only after the analysis is complete. This is the "Clean Only" mode of operation. JetClean also offers simultaneous cleaning and analysis, using the "Acquire and Clean mode" when hydrogen is continuously flowing into the source, yet in small enough amount to limit spectral anomalies.

StreamSelect operation for LC/MS systems
During LC/MS analysis of food extracts, the MS detector, the most expensive component of the system is idle while the column is regenerating or waiting for the first analyte to elute once an injection is initiated.

StreamSelect allows the convenient integration of two LC systems to be attached to the same MS, maximally utilizing the detector and increasing sample throughput.

The MassHunter StreamSelect software maintains direct communication between all HPLC and mass spectrometer components. The software seamlessly orchestrates all LC functions and MS acquisition, resulting in:

• Accurate tracking of samples from each independent LC to the MS
• No misidentification of MS data files
• Advanced sample handling/dilutions
• Intelligent error handling
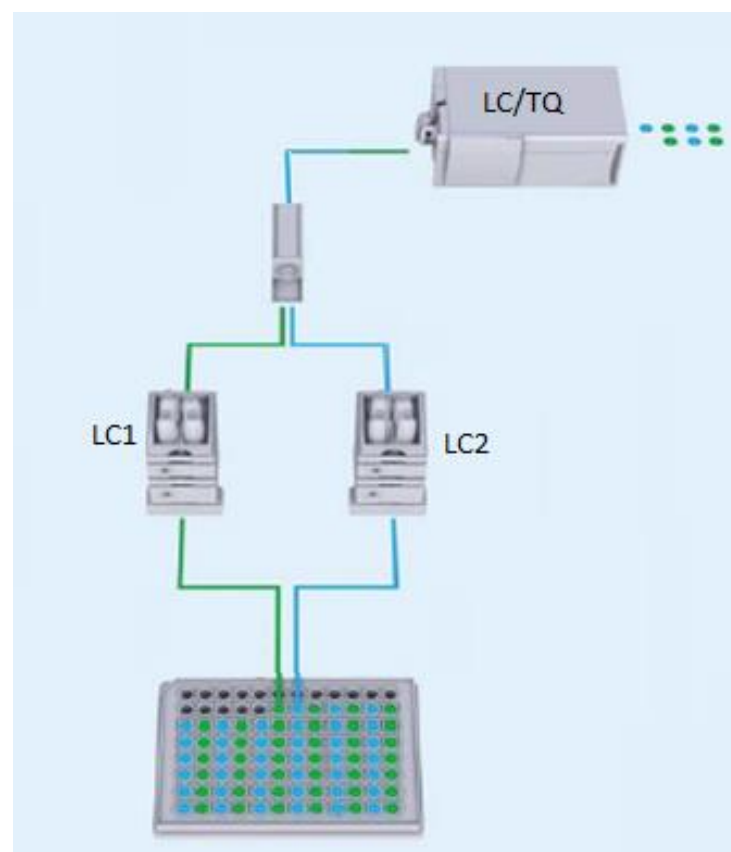
Intuitive automation software controls the system greatly enhancing throughput.

Experimental - JetClean

JetClean operation was tested with two configurations:

	7000D	7010
GC	7890	7890
Injection volume	2 µL	2 µL
Source	Extractor Plus, 9mm extractor	High Efficiency
JetClean	Acquire and Clean, 400µl H$_2$	Clean only, 700µl/min for 2 min during column "bakeout" at the end of each run
Protocol	Japanese protocol[1]	SANTE Guidelines[2]
Calibration	Solvent based with analyte protectants; 1- 200ppb, External standard	Matrix matched with analyte protectants; 0.1-250ppb, Internal standard
Matrix	Spinach	Chard, apple, plum, peppers and spinach
Number of pesticides	Over 200	Over 200

Results and Discussion

The use of JetClean significantly extended the period between source cleaning in both systems: the 7000 in the Acquire and Clean mode and the 7010 in the Clean Only Mode. Even using external calibration mode, without matrix matching, the average R^2 was 0.9997 in the calibration range of 1-200ppb, with a 3.3% RSD precision for 15 spinach samples at 10ppb concentration. The overall accuracy of the spinach samples was 109%, with over 90% of the analytes falling in the 90-125% range.

For visual comparison, the lens photos below were taken from two systems, running the same type of samples. One was a standard system, the other was equipped with JetClean and used in the Acquire and Clean mode of operation. Once the QC results on the standard system started to decline, both systems were shut down for cleaning. As the photos show, the standard system exhibited the common deposits creating the dark ring around the lens opening, which contributed to inconsistent response. The system with JetClean was still meeting the QC criteria, the lens surface did not show any contamination as the deposits were removed by JetClean.
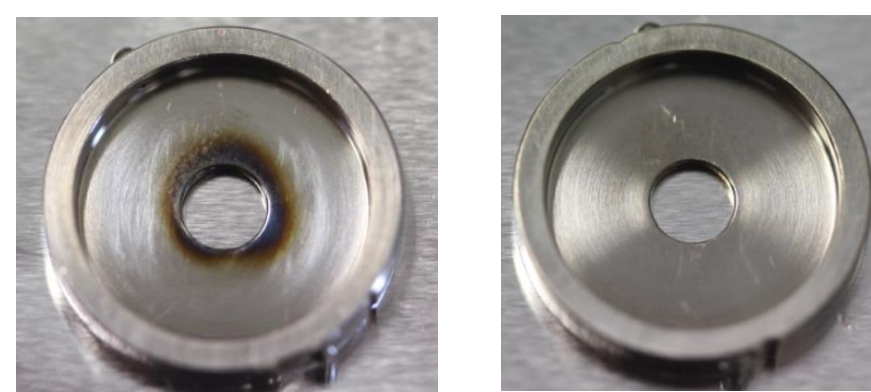
Without JetClean   With JetClean

Lens photos from standard and JetClean equipped systems after the same number and type of samples were analyzed.

Conclusions

QC requirements were maintained and manual source cleaning was significantly reduced by utilizing JetClean, thereby reducing instrument downtime for maintenance and recalibration and increasing productivity. The benefit of JetClean is best summarized by one of the users:

" *We analyzed the EN QuEChERS in various food extracts – e.g. chard, apple, plum, peppers and spinach in the working range of 0.1 – 250 ppb (in vial) using internal standards, analyte protectants and employing the high efficiency source. Without JetClean, manual source cleaning was needed after 200-300 matrix runs. Applying JetClean after each run, manual cleaning was only needed after 600-900 matrix runs, thus, instrument up-time was increased by several-fold and associated cost-savings were realized."*
Dr. Klaus Wilmers, Chemical and Veterinary Analytical Institute, Muenster, Germany.

References:
1. Analytical Methods for Residual Compositional Substances, Department of Food Safety Ministry of Health, Labour and Welfare, Japan, 2006
2. Guidance document on analytical quality control and method validation procedures for pesticide residue analysis in food and feed", Document SANTE/11945/2015
3. Improved LC/MS/MS Pesticide Multiresidue Analysis Using Triggered MRM and Online Dilution, Agilent Application note 5991-7193EN , 2017

Experimental - StreamSelect

LC/MS system with StreamSelect. Sample preparation was based on the AOAC Int. Official method 2007.01 using the acetate buffer QuEChERS extraction and partition steps but without any cleanup. The Agilent 1290 Infinity II LC systems coupled to an Agilent 6490 Triple Quadrupole LC/MS detector was used for the analysis of over 400 globally important pesticides in a short analysis time. The mobile phase gradient was optimized to deliver the best separation. The LC systems used an online dilution setup, ensuring excellent peak shapes of early eluting (more polar) analytes. As a result, acetonitrile extracts (prepared using a QuEChERS-based extraction) are injected directly without a need for dilution with an aqueous buffer/solution prior to the injection.

Online dilution and optimized separation using binary and quaternary pumps

Time (min)	Binary A (%) 10 mM ammonium formate in water-methanol (98:2, v/v) + 0.1 % formic acid	Binary B (%) 10 mM ammonium formate in water-methanol (99:1, v/v) + 0.1 % formic acid	Binary Flow (mL/min)	Quaternary A (%) 10 mM ammonium formate in water-methanol (98:2, v/v) + 0.1 % formic acid	Quaternary Flow (mL/min)	Total Flow (mL/min)
0.00	100	0	0.1	100	0.5	0.6
0.20	100	0	0.1	100	0.5	0.6
0.21	100	0	0.5	100	0.5	1.0
0.40	100	0	0.5	100	0.0	0.5
0.50	50	50	0.5	100	0.0	0.5
2.50	45	55	0.5	100	0.0	0.5
5.50	25	75	0.5	100	0.0	0.5
7.50	15	85	0.5	100	0.0	0.5
8.30	0	100	0.5	100	0.0	0.5
12.00	0	100	0.5	100	0.0	0.5
12.10	100	0	0.5	100	0.0	0.5
14.80	100	0	0.5	100	0.0	0.5
14.9	100	0	0.1	100	0.5	0.6

Matrix-matched standards (typically corresponding to 0.001 to 0.050 µg/mL in the extract) were prepared. Precision and accuracy were tested at 0.01, 0.02, or 0.05 mg/kg in five replicates. For complete analytical conditions see Reference [3].

Results and Discussion

Extracted ion chromatograms of the analytes included in the method, Rt 1-10minutes
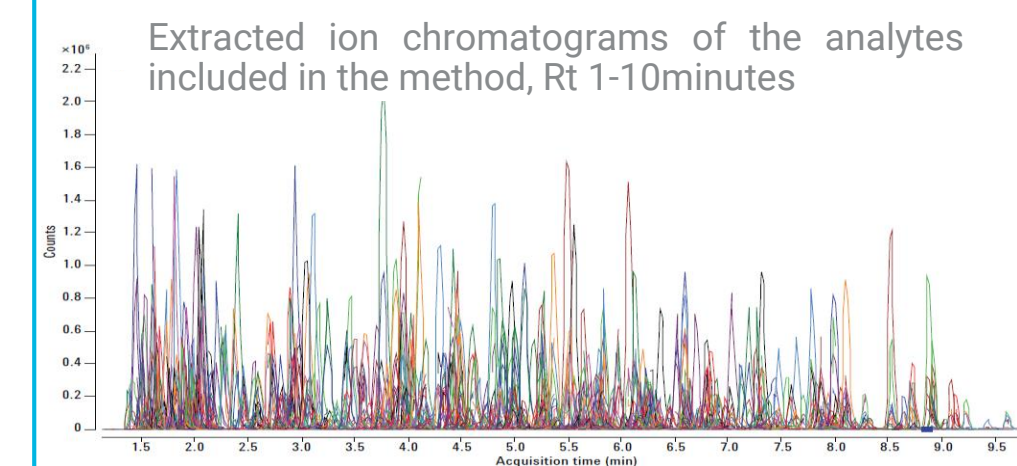
The total cycle time (LC) of the analysis is 15 min., but the MS acquisition time is only 9 min. StreamSelect allowed the staggered introduction of samples from two LC streams, utilizing the MS fully. With the std system 4 samples could be executed in one hour, while with StreamSelect almost 6 samples could be completed, a significant productivity increase.

Standard LC/MS system timeline

StreamSelect LC/MS system timeline

A limit of quantitation (LOQ) of 0.01 mg/kg was achieved for the majority analyte-matrix combinations. The 6490MS excellent sensitivity allowed for easy online dilution setup, which provided excellent peak shapes and retention of early eluting, more polar analytes.

Conclusions

The productivity of the LC/TQ system with StreamSelect increased by 35% compared to the standard system, using the same analytical method with online dilution. Based on the above method, StreamSelect can analyze 12 more samples in an 8 h shift than a standard system.

The StreamSelect systems used the same separation and detection protocols developed for single stream analysis and validated in multiple commodity types/matrices. The generated results successfully met the SANTE guidelines and criteria.