PAHS ANALYSIS IN PALM OIL SIGNIFICANT ROBUSTNESS IMPROVEMENTS

Technology Advantage: Agilent JetClean Self-Cleaning Ion Source in a GC/MS/MS System

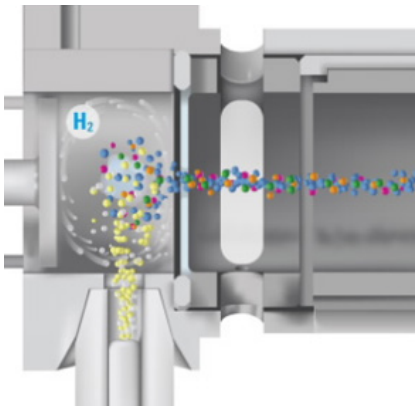

Figure 1. Agilent JetClean Self-Cleaning Ion Source.

Introduction

Regulated limits for polyaromatic hydrocarbons (PAHs) in food have been steadily lowered as the result of increased awareness about their potential carcinogenic impact and their presence in our food supply. The allowed maximum contaminant levels in critical matrices are set as low as 1 µg/kg by European Regulation 1881/2006[1].

To achieve these detection levels consistently in complex food matrices, EI sources typically require frequent cleaning, leading to lost laboratory productivity.

The Agilent JetClean Self-cleaning ion source with automatically controlled hydrogen addition eliminates the need for frequent manual cleaning, and ensures consistent results over many months of operation.

Instrumentation

- Agilent 7000C GC/MS/MS-based PAH Analyzer
- DB-EUPAH column (30 m × 0.25 mm, 0.25 µm) with post-column backflushing
- Agilent JetClean Self-cleaning ion source with continuous H_2 flow

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Sample Preparation

Palm oil, a common food component and challenging matrix, was extracted by toluene without any purification. The extract was spiked at 5 ng/mL of each of the regulated four PAHs, resulting in an equivalence of 1 µg/kg of benzo(a)pyrene (BaP), benzo(a)anthracene (BaA), chrysene, and benzo(b)fluoranthene (BbF) in palm oil. ^{13}C labels of the analytes were added as the internal standard.

Study Sequence

A 5-day evaluation period was designed to determine the system precision and robustness. Table 1 shows the sequence of injections that was carried out each day.

Table 1. Sequence of injections made to evaluate system precision and robustness.

Daily injections (repeated for 5 days)		
1	Blank	Toluene
2-11 (10)	Calibration	0, 1, 2.5, 5, 10, 20, 30, 50, 80, and 100 ng/mL, equivalent to 0, 0.2, 0.5, 1, 2, 4, 6, 10, 16, and 20 µg/kg in matrix
12	Blank	Toluene
13-18 (6)	QC sample	1 ng/mL, equivalent to 0.2 µg/kg in matrix
19	Blank	Toluene
20-25 (6)	Palm oil extract	5 ng/mL, equivalent to 1 µg/kg in matrix
26	Blank	Toluene
27-32 (6)	QC sample	1 ng/mL, equivalent to 0.2 µg/kg in matrix
33	Blank	Toluene
34-39 (6)	Palm oil extract	5 ng/mL, equivalent to 1 µg/kg in matrix
40	Blank	Toluene

Results and Discussion

Calibration

A 10-point linear calibration curve was prepared daily in the 1–100 ng/mL range. Excellent linearity was obtained: the R^2 value for BaP was 0.9976 on the first day, and 0.9972 on the 5th day, virtually identical. The R^2 difference was only 0.0004, indicating that the system conditions remained unchanged despite the injection of over 200 samples between calibrations, many of them the palm oil extract with heavy matrix.

Precision

Table 2 shows the area count for each of the PAHs detected in the palm oil extract for 12 injections on day 1 and day 5. The stable response resulted in a very low area count %RSD for each analyte every day. Even the combined day 1 and day 5 results deliver %RSD below 4 %. Note that this is based only on raw area count, without using the internal standard response to correct for small operational imprecisions that are often encountered when analyzing a complex matrix.

Table 2. Area count for each of the PAHs detected in the palm oil extract for 12 injections at 1 ng/mL level (0.2 µg/kg in matrix).

Areas	Day 1	Day 5	Day 1	Day 5	Day 1	Day 5	Day 1	Day 5
Sample	**BaA**		**Chrysene**		**BbF**		**BaP**	
SPK_OIL-1	124,833	125,119	119,104	118,308	149,500	147,912	167,868	154,471
SPK_OIL-2	122,837	132,562	116,891	127,786	148,031	158,223	171,496	185,316
SPK_OIL-3	126,858	120,574	118,272	109,267	152,958	144,451	174,546	162,590
SPK_OIL-4	124,750	126,248	119,199	122,896	147,486	149,448	166,499	172,664
SPK_OIL-5	126,454	128,350	120,454	118,989	151,083	149,821	174,304	170,538
SPK_OIL-6	125,048	124,918	117,413	116,110	146,604	147,202	169,356	160,305
SPK_OIL-7	126,848	127,236	120,370	121,535	155,079	149,775	168,295	169,821
SPK_OIL-8	128,167	133,703	120,799	128,893	150,774	158,544	174,729	182,656
SPK_OIL-9	121,409	121,916	117,578	115,348	151,576	146,707	168,768	165,262
SPK_OIL-10	122,218	125,474	118,858	124,321	149,693	148,796	170,291	166,748
SPK_OIL-11	125,949	128,717	120,147	122,050	151,454	153,817	175,673	166,051
SPK_OIL-12	129,523	127,455	121,779	121,687	156,374	149,013	172,214	170,050
%RSD Area (12 inj.)	1.8	2.9	1.2	4.3	1.9	2.8	1.7	4.9
%RSD, 24 inj. (day1 + day5)	2.5		3.2		2.4		3.7	

Detection levels

The JetClean source also assured that the chromatographic peak shapes remained Gaussian from day 1 to day 5, delivering strong, easily quantifiable peaks. The 1 pg amount corresponds to 5 times lower concentration than the maximum allowed amount in sample extracts, even in the most demanding matrix such as baby food, easily meeting and exceeding the regulatory requirements.

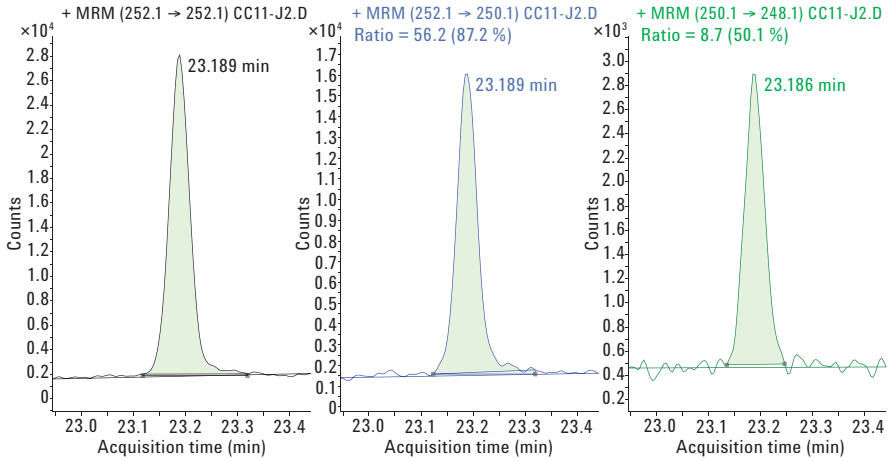

Figure 2. The chromatograms represent the quant and qualifier ion plots of benzo(a)pyrene at the lowest calibration level, at 1 ng/mL, or 1 pg on-column.

The precision and accuracy derived from multiple injections of the QC sample (= 1 ng/mL) is as remarkably good as the results shown in the table for the palm oil extract. The standard deviation (n = 8) of the detected amount for benzo(a)pyrene was 0.0582, resulting in a statistically derived (99 % confidence level, n–1 degrees of freedom) detection limit of 0.175 pg. This measurement should be repeated, as most likely the concentration used for the multiple injections is too high, resulting in an estimated detection limit much higher than the system can actually achieve.

Cleaning Frequency

A system with the same configuration was deployed in a food laboratory. It has delivered similar results and uninterrupted operation since installation, 11+ months ago, eliminating the previously required monthly manual cleaning. The reduced source cleaning frequency provides both increased productivity and convenience. The successful detection of PAHs in environmental samples without manual cleaning for months was also reported[2].

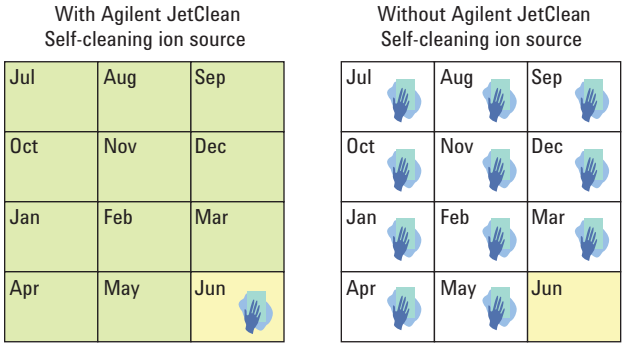

Figure 3. The Agilent JetClean Self-cleaning ion source eliminates monthly cleaning requirements.

Conclusions

The system accuracy, precision, and robustness was demonstrated with exceptional results in the 5-day laboratory test. The GC/MS equipped with an Agilent JetClean source makes it possible to comply easily with the EU regulations in food, even in infant formulas. It delivers detection limits more than 5 times lower than the regulated maximum levels along with outstanding precision and accuracy for extended periods of time. Subsequent field deployment of a similarly configured system in a food laboratory delivered equally outstanding results.

References

1. Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.
2. Anderson, K. A.; *et al*. Modified ion source triple quadrupole mass spectrometer gas chromatograph for polycyclic aromatic hydrocarbon analyses. *Journal of Chromatography A* **2015**, *1419*, 89-98.

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