TECHNICAL NOTE 10721

Routine, robust analysis of PAHs and PCBs in soil by single quadrupole GC-MS

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Goal

The aim of this study was to demonstrate the robust and routine performance of the Thermo Scientific™ ISQ™ 7000 single quadrupole GC-MS system with ExtractaBrite (EI) source for the analysis of PAHs and PCBs in soil.

Introduction

Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are toxic organic pollutants that can contaminate soils, air, sediments, and water as a result of natural and human processes. PCBs and PAHs are resistant to environmental degradation and can be transported over long distances. PAHs and PCBs from the environment can enter the food chain where they are persistent and can bio-accumulate (vPvB).[1]

PAHs and PCBs have numerous congeners, many of which have identical masses, that require chromatograph separation prior to detection. For this reason, gas chromatography-mass spectrometry is the analytical technique of choice for their separation and quantification. Higher mass PAHs are prone to poor peak shape and resolution, making peak integration challenging. This reduces sensitivity leading to higher limits of detection and quantification. Robust, and routine analysis of PAHs and PCBs in complex soil matrices requires consumables and instrumentation that deliver exceptional degrees of stability in terms of peak areas and response factors so that multiple batches of samples can be analyzed day in and day out without instrument maintenance such as liner change, column trimming, MS maintenance, or tuning.

In this work, the suitability of the ISQ 7000 system was demonstrated for the analysis of PAH and PCBs in complex soil matrices. Sensitivity, robustness, and suitability for routine analysis was assessed by looking at the response factor and ion ratio stability for a low-calibration QC standard interspaced throughout the 320-injection sequence of 250 samples, standards, and blanks. The system robustness was assessed by examining the peak area stability of over 115 injections of a soil QuEChERS extract.

Experimental

Calibration standards containing 45 native PCB and PAHs at twelve concentration levels (full details can be found in a supporting application note, AN10720.[2]), and 14 (^{13}C-labeled) internal standards were acquired from Fisher Scientific, AccuStandards, and Wellington Laboratories Inc. (Ontario, Canada). For the assessment of relative response factor (RRF) stability, a low-level calibration standard (40 pg/µL) was defined as the QC standard and injected directly. The details of the sample and standard preparation can be found in the supporting application note.[2]

An ISQ 7000 single quadrupole GC-MS instrument equipped with an electron ionization (EI) source and vacuum probe interlock (VPI) was coupled to a Thermo Scientific™ TRACE™ 1310 GC with Instant-Connect SSL injector. The ExtractaBrite EI source is fully removeable without the need to break vacuum, enabling source cleaning and column changing. The patented RF lens leads to an excellent level of sensitivity and robustness.

Liquid injections (1 µL) of the QuEChERS soil extracts were performed using a Thermo Scientific™ AI AS 1310 Autosampler with Thermo Scientific™ LinerGOLD™ single taper with glass wool SSL liner (P/N 453A1925-UI). Chromatographic separation was achieved by a Thermo Scientific™ TraceGOLD™ TG-5 SilMS 30 m × 0.25 mm i.d. × 0.25 µm (P/N 26096-1420) film capillary column. Additional details of instrument parameters and consumables used can be found in the supporting application note.[2]

Data was acquired using timed-SIM mode, processed, and reported using Thermo Scientific™ Chromeleon™ 7.2 software, which allows instrument control, method development, quantitative/qualitative analysis, and customizable reporting all within one platform.

Results and discussion

PAH and PCB robustness were assessed based on absolute peak area analyte response for 115 injections of a soil QuEChERS extract containing incurred residues. The system suitability for routine PAH and PCB analysis was then assessed by evaluating the stability of response factors over a 320-injection sequence for low level QC standards. Additional details of chromatography, sensitivity, linearity, and sample analysis can be found in the supporting application note.[2]

Routine GC-MS analysis

Matrix complexity

Due to the diversity of matrices with various degrees of complexity, selectivity can be challenging in routine GC-MS analysis of environmental samples. An example of sample complexity is shown in Figure 1 as TIC of a sonicated unspiked QuEChERS soil extract.

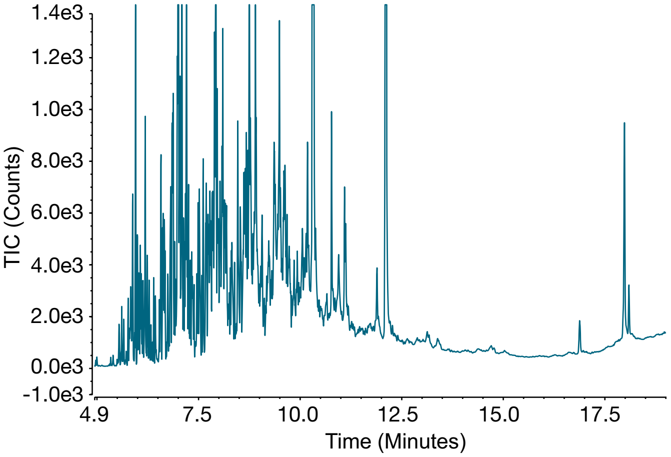


Figure 1. QuEChERS soil extract (unspiked), Full Scan (FS), *m/z*=50-550

Robustness

To assess system robustness, a QuEChERS soil extract containing incurred residues was chosen and injected 115 times and the peak areas were plotted for detected PAHs and PCBs (Figure 2). The amount on column (OC) and in sample, based on the calibration, ranged from 1.0 to 2.5 pg on column (1.0–2.5 µg/kg in sample) and each analyte detected had the ion ratio within tolerance based on the average ion ratio calculated from the calibration. The results demonstrate excellent source robustness with 15% peak area RSD for 115 injections of a complex QuEChERS soil matrix. It is important to note that no liner change, column trimming, MS maintenance, or tuning were performed over the injection sequence (inlet septa were replaced every 100 injections).

Response factor stability in matrix samples

To test the suitability of the ISQ 7000 system for routine GC-MS analysis, a low-level calibration QC standard was injected every 20 injections and the average RRF % RSD was monitored for each PAH and PCB congener (Figure 3). The RRF % RSDs were ≤11% for all the targeted PAHs and PCBs calculated over a 320-injection sequence that took 12 days to complete (which included over 250 sample injections). This demonstrates the excellent system stability over two working weeks with no liner change, column trimming, MS maintenance or system tuning.

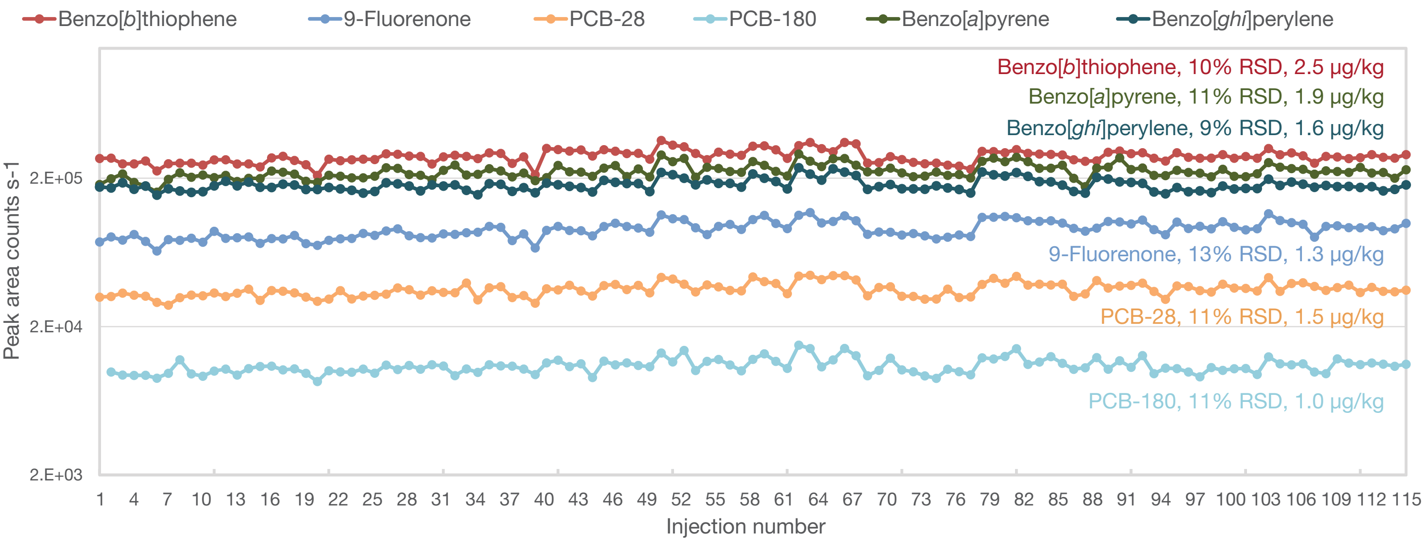
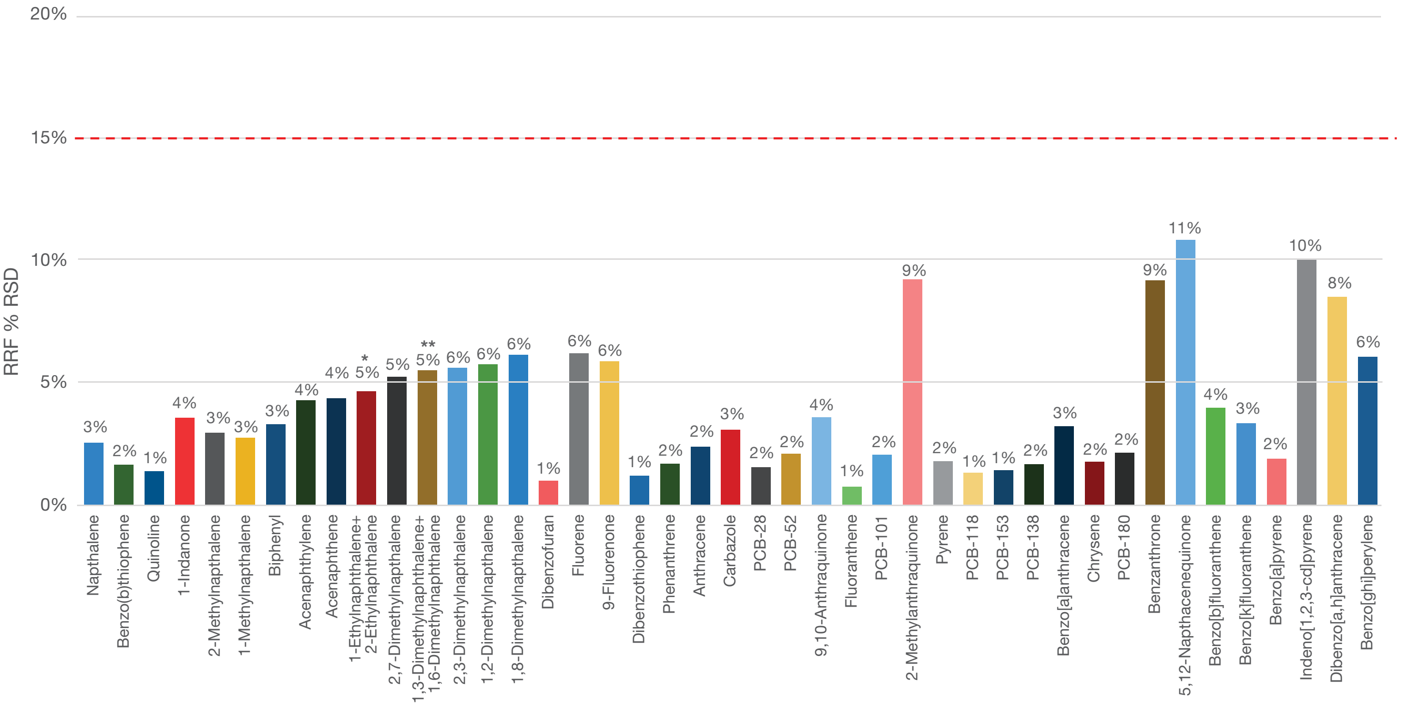


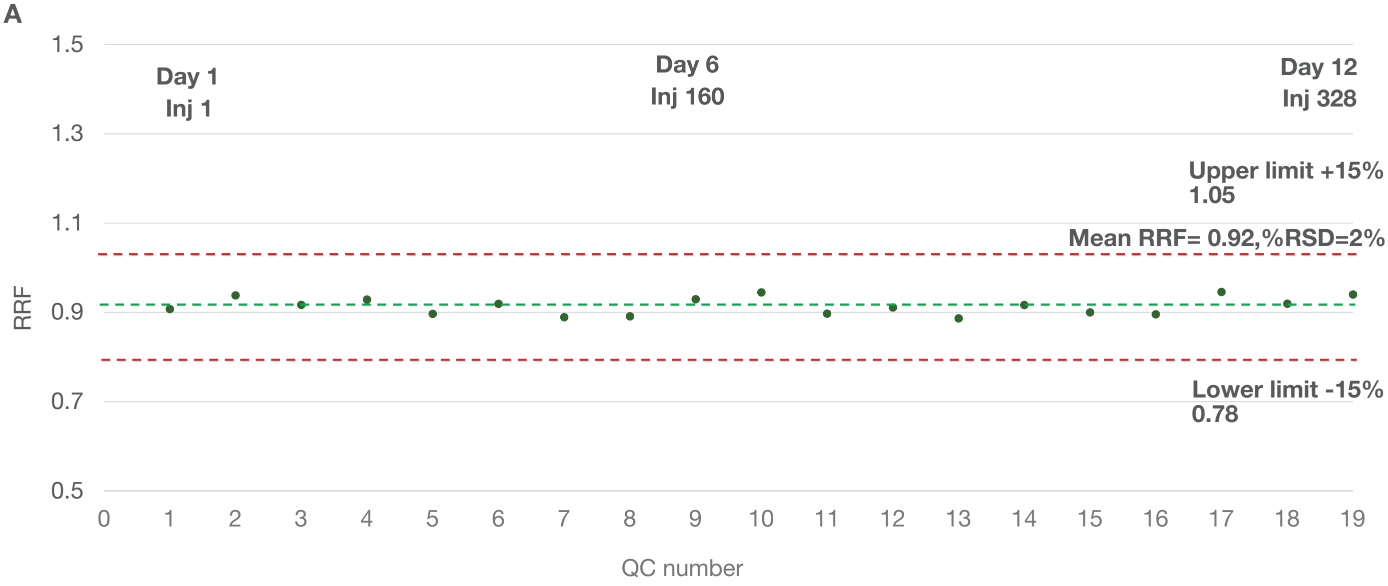
Figure 2. Absolute peak area response (without internal standard adjustment) for PAHs and PCBs detected in 115 injections of a QuEChERS soil extract containing incurred residues. This corresponded to five days of uninterrupted acquisition. Annotated is repeatability as peak area % RSD for n=115 matrix injections as well as the equivalent amount in sample in µg/kg.



Inlet septa were replaced every 100 injections. Apart from this no other inlet maintenance was undertaken.

Figure 3. Response factors % RSD for 19 QC injections performed over a 320-injection sequence containing blanks, standards and over 250 matrix (QuEChERS soil extract) injections. *1-ethylnaphthalene and 2-ethylnapthalene; **1, 3-dimethylnaphthalene and 1, 6-dimethylnaphthalene

RRF values calculated for the QC standards across the batch of 320 injections were within a tolerance window of ±15% compared to the mean calculated from the calibration for all PAHs and PCBs. In the calculated PCB-180 and naphthalene examples (Figure 4) the RRF % RSD for n=19 QC injections were 2% and 3%, respectively.



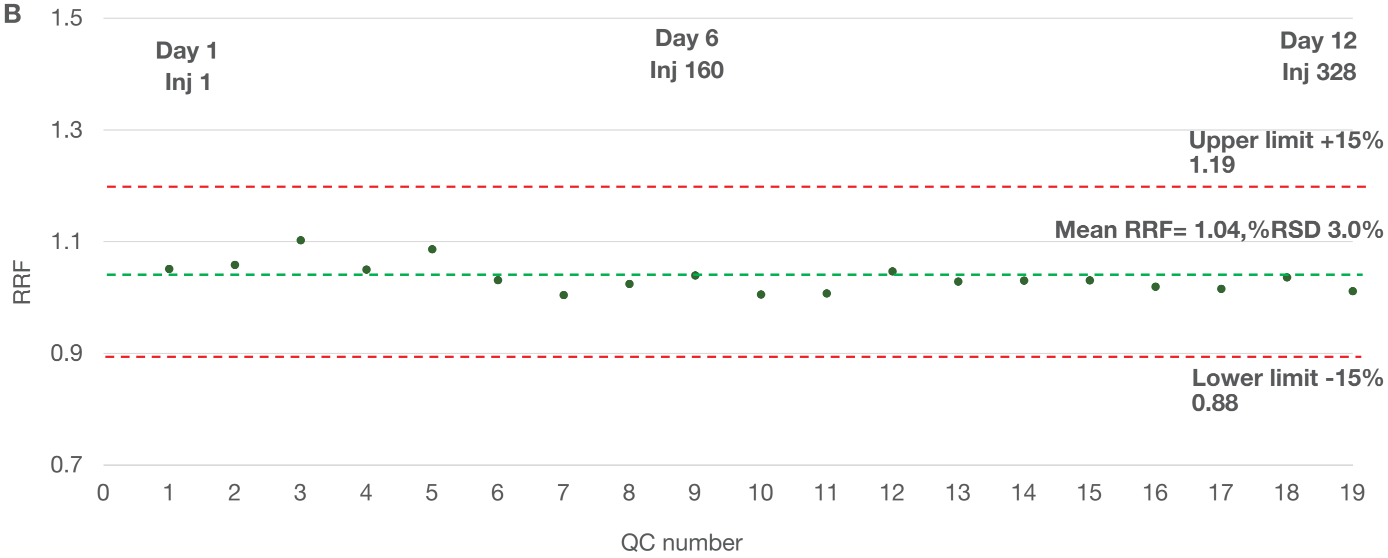


Figure 4. Individual RRF values for PCB-180 (A) and naphthalene (B) demonstrated for low-level standard QCs (40 ng/mL) run throughout the 320-injection sequence. The ±15% tolerance RRF upper and lower limits are annotated using the red dotted lines and the mean RRF for the QCs is displayed by the green dotted line.

Ion ratio stability in matrix samples

Another marker for system stability was assessed by monitoring QC standard ion ratios over two weeks of analysis. The results obtained for all PAHs and PCBs for a low-level QC standard were well within ±15% of the expected values calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in extracted soil). (Figure 5). This demonstrates excellent system stability and applicability for routine analysis.

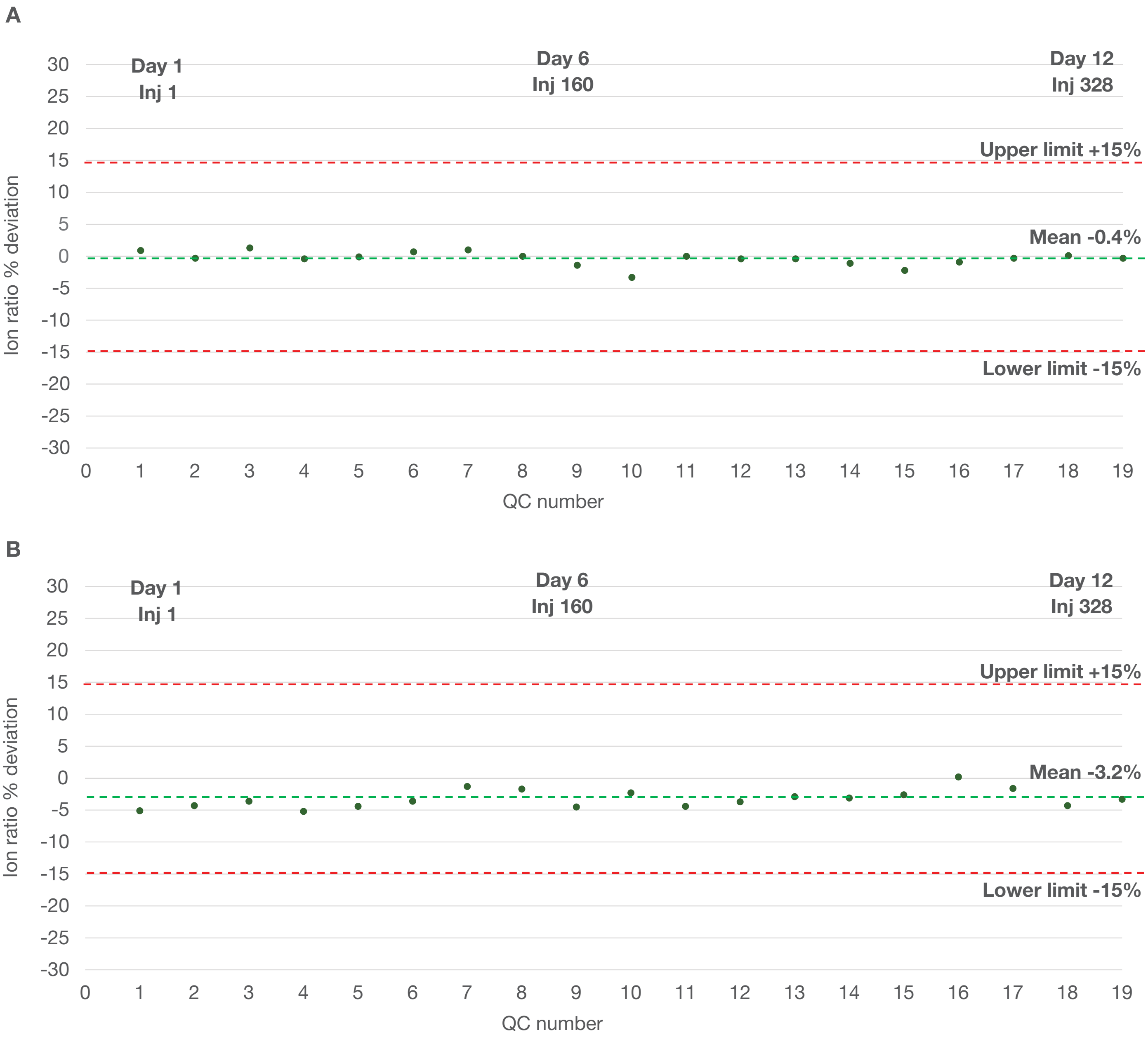


Figure 5. Example of ion ratio stability for PCB-180 (A) and naphthalene (B) demonstrated for low-level standard QCs (40 ng/mL) run throughout the 320-injection sequence. The ±15% tolerance ion ratio upper and lower limits are annotated using the red dotted lines and the mean ion ratio for the QCs is displayed by the green dotted line.

Conclusions

The results of these experiments demonstrate the following:

- Excellent system repeatability in routine use when analyzing QuEChERS soil extracts, with peak area repeatabilities for the incurred residues were <15% RSD over 115 injections.
- High RRF stability at low concentration levels over a 320-injection sequence containing 250 sample injections was demonstrated with the RRF % RSDs for all compounds being ≤11%.
- Outstanding RRF agreement of QC standards over two weeks of continual analysis with the measured RRFs % RSD of the n=19 injected QC standards were all within ±15% of the measured value across the calibration curve with no liner change, column trimming, MS maintenance, or instrument tuning.
- Stable compound ion ratios over two weeks of analysis were achieved, with values within ±15% of the expected values, calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in extracted soil).

In conclusion, these results demonstrate that the ISQ 7000 VPI GC-MS system provides the consistent uninterrupted performance needed in fast-paced, routine environments looking at increasing productivity, reducing instrument downtime, and the cost per sample.

References

1. Guidance on information requirements and chemical safety assessment, part C: PBT/vPvB. [Online] https://echa.europa.eu/documents/10162/13643/information_requirements_part_c_en.pdf (accessed May 8, 2018).
2. Thermo Scientific Application Note 10720: Simultaneous routine GC-MS analysis of PCBs, PAHs, and their derivatives in soil using modified QuEChERS methodology, 2019.

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