Introduction
Polychlorinated dibenzo-p-dioxins (PCDDs) and polybrominated dibenzofurans (PCBs) have been characterized by the US EPA as likely to be carcinogenic to humans. Consequently, accurate detection and quantification of PCDDs in the environment, food and animal feed, is important.

Legislation in the European Union (EU) previously required the confirmation and quantification of PCDDs by GC-MS/MS instruments. However, recent technological advances in GC-MSMS/MS triple-quadrupole technology have allowed high sensitivity and selectivity to be achieved. These improvements have led to GC-MSMS being considered a reliable tool that can be used to control the maximum levels for PCDD/Fs in food and feed as a full confirmatory method.

According to new EU regulation, when using GC-MSMS the following specific performance criteria should be fulfilled. 1. Resolution for each quadrupole to be set up to at least 2000. Minutes. 2. Ten specific precursor ions should be used. 3. Maximum permitted tolerance of relative ion intensities of ±15% for selected transitions.

In this work, the performance of a new triple quadrupole GC-MS/MS system for the analysis of PCDD/Fs was assessed. Both solvent standards, and food/feed samples were used to evaluate the instrument performance against the new criteria for dioxin confirmation. Additionally, a direct comparison of the results obtained using the new GC-MSMS system and a GC-HRMS was made.

Instrument and Method Setup
PCDD/Fs were analysed in the standards and matrix samples using the Thermo Scientific instruments and column: TSG-8000 Eco Triple Quadrupole GC-MS/MS, TRACE 1310 GC, TriPlus RSH autosampler and TraceGold TG-ESB510 m + 0.25 mm i.d. x 0.25 µm film capillary column. Additional instrument parameters used to acquire data are listed in Table 1 and Table 2.

Table 1: GC and ion trap conditions. Table 2: Mass spectrometer conditions.

Resolution of each quadrupole was set to unit mass as specified in the new EU Commission criteria for dioxin confirmation by GC-MS/MS (Tab. 2). The TSG 8000 Eco was operated in MS/MS mode using EI+. For data acquisition, two SRM transitions per compound were selected, meeting the 2000 µs criteria for GC-MSMS confirmation of dioxins. Data was acquired using timed-SRM with a minimum of 12 points/chromatographic peak. Selected SRM transitions and their collision energies were automatically optimized using the AutoSRM software application, and the results of this are listed in Table 3. Data processing was performed with Thermo Scientific TargetQuan 3.1 software, designed specifically to co-process a few MS analyses, GC/MSMS and HRMS data, for routine quantification of persistent organic pollutants (POPs) in a regulated environment.

Sample Preparation
Extraction and cleanup of the matrix samples were performed either by PowerPrep™ SPE system (food/feed) or by a manual clean-up with multi-layer silica, followed by basic alumina and a final carbon column (tisk and fish samples). The FoodSafe Extracted samples 3x dry fish samples (previously used in inter-laboratory studies), one feed sample (internal reference material), one milk powder sample (certified reference material), and PCDD/Fs standards containing the native and the 13C-labelled compounds were used.

Results and Discussion
Timed-SRM uses a completely different analytical strategy than the ‘classical’ segmented setup, allowing data acquisition for a target compound in a defined window around the known compound retention time, and not in a wide retention time segment. Using timed-SRMs, the compound’s acquisition window can be individually set to cover closely eluting isomers, such as H/OCDD/Fs.

Chromatography of PCDD/Fs was assessed with the lowest calibration standard (0.5 pg/l) and the highest calibration standard (1.0 pg/l). All native congeners and corresponding 13C-labelled isomers were easily detected, excellent peak shape was obtained for all compounds (Fig. 3), and 5% replicate variation was achieved for HOCDD/Fs (Fig. 2).

Reaching the level of interest
From data acquired on GC-MSMS/matrix quadrupoles, the LOD of an individual congener may be calculated from the lowest concentration point (i.e., CLS), taking into account the recovery of internal standards (SD-120%), ion abundance, and chromatography of the sample. The instrument LOD was assessed by repeatedly (n = 10) injecting the CLS and three subsequent serial dilutions of this standard.

Calculation of the LOD for each native compound took into account I values (95% confidence), the concentration, and the %RSD. LOQs were between 0.01–0.05 pg/l, corresponding to CSL 1.5 and 1.0 diluted. These results demonstrated that TSG 8000 Eco GC-MS/MS can detect and confirm PCDD/Fs at low femtogram levels, thus meeting the detection limit requirements (Fig. 3).

Quantification of Dioxins in Sample Extracts
PCDD/Fs were quantified in the sample extracts and an example of the chromatography is shown for 2378/TCDD (Fig. 5).

The data shows excellent agreement between the results obtained using the TSG 8000 Eco GC-MS/MS and those obtained using GC-HRMS (Figures 6–8).

Conclusions
The results of this evaluation demonstrate that the TSG 8000 Eco GC-MSMS system is:

• Effective tool for routine analysis of PCDD/Fs meeting all the new European Commission requirements for the confirmation of dioxins in food and feed samples.

• Highly sensitive and selective analytical system that can be confidently used for PCDD/Fs detection and confirmation in food/feed samples.

• Comprehensive system solution for dioxin and furan analysis in complex samples, together with the TRACE 1310 GC and TargetQuan 3.1 data processing and reporting software.

• Provide excellent reproducibility, linearity, sensitivity, and selectivity for the analysis of standards and sample extracts.

• Recommended for routine and confirmatory analysis of PCDD/Fs as the calculated PCDD/Fs TEQ values for the matrix samples were in very good agreement with those derived from the sector instrument.

References
3) US EPA Method 1311, Data through inlet dilution-ESI-HRMS (Revision B), 1986.

Acknowledgements
The authors wish to thank Bruce A. Chadie from Wellington Laboratories Inc. for providing the EPA 1013 calibration standards.