

Introduction

Domestic waste water must be managed effectively to meet the challenges of increasing population, stringent regulatory requirements, and aging water treatment facilities. To meet these challenges, specific analytical methods are available to monitor chemical compounds in wastewater. However, because of the complexity of the sample matrix, several analytical methods are required to determine polar and non-polar organic compounds in the dissolved and suspended phases that may impact water quality. The proposed method is proved to be a promising one for non-target screening of complex matrix samples with the advantages of higher sensitivity and better repeatability.

An accurate-mass approach in pesticide screening using quadrupole time-of-flight mass spectrometry (Q-TOF) ensures reliable pesticide identification under this approach, and allows for a virtually unlimited number of compounds to be screened simultaneously.

For any unexpected compounds the user can quickly verify the identities of such compounds with high resolution accurate mass data and if subsequent quantitative screening is considered important for future work then they can easily export the critical ion information into a quantitative method, if necessary hundreds of pesticides can be quantified in a single analysis.

Initial compound identification was performed by spectrum comparison with NIST17 EI library and confirmed by retention index (RI) matching when possible.



Figure 1. GC/Q-TOF Data Analysis Workflow Strategy

Experimental

Instrument Analysis

The sample extracts and controls were analyzed by an Agilent 7250 Series GC/Q-TOF system equipped with a low-energy capable EI source (Figure 1).

Table 1 provides the GC and QTOF method parameters for data acquisition. A midcolumn backflushing method was used with a 15 m × 0.25 mm, 0.25 μm HP-5 column connected between the multimode inlet (MMI) and a purged union with a second column (15 m × 0.25 mm, 0.25 μm HP-5MS UI) connected between the purged union and the Q-TOF transfer line (Figure 2).

An injection of n-alkanes was used to calibrate the retention index (RI) of the acquisition method.

Experimental

Water samples were collected from municipal waste water plant Karlsruhe, Germany. In total 6 samples were taken 3 from the Primary intake – Sedimentation stage and from the final effluent

Sample preparation

Each water sample, including the blanks, were extracted through liquid-liquid extraction (LLE). Three milliliters of dichloromethane (DCM) were added to a 30 mL water sample, ultrasonicated for 5 minutes, and the DCM layer was extracted and deposited into 2-mL autosampler vials for analysis.

Data Analysis

- The data processing used Agilent MassHunter Data Analysis Software B.10.00.
- The targeted screening of pesticides (a combined quantitative and qualitative workflow) was based on a commercial GC/QTOF pesticides library [2].
- For the untargeted screening the above mentioned PCDL Library and the NIST 2017 GC/MS Library

Experimental

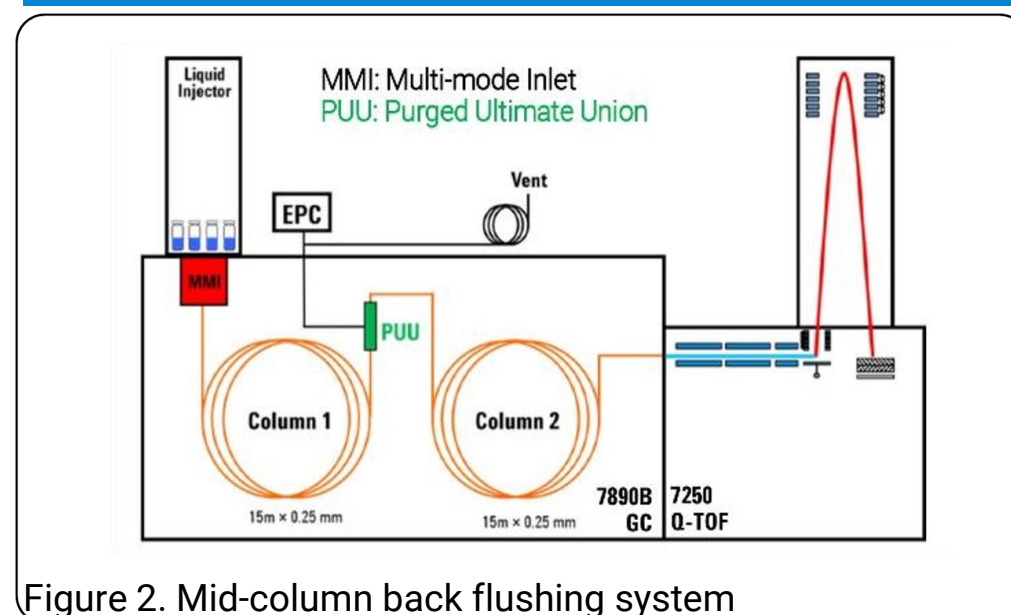


Figure 2. Mid-column back flushing system

Table 1. GC/Q-TOF Operational Conditions

| GC and MS Conditions | Value |
|------------------------|---|
| Inlet | Multimode inlet (MMI), UI liner single taper with glass wool |
| Columns (2 ea.) | 15.0 m x 0.25 mm ID x 0.25 μm HP-5MS UI |
| Carrier gas | Helium |
| Carrier gas mode | Constant flow |
| Column flows | 1.25 mL/min (col. 1) and 1.45 mL/min (col. 2) |
| Autosampler | PAL 3 RTC |
| Retention Time Locking | Chlorpyrifos-methyl locked to 9.143 min |
| Injection mode | Cold splittless |
| Injection volume | 2.0 μL |
| Oven program | 60 °C for 1 min 40 °C/min to 170 °C, 0 min 10 °C/min to 310 °C, 3 min |
| Backflush conditions | 5 min (Post run), 300 °C (Oven) 40 psi (Aux EPC), 2 psi (Inlet) |
| Transfer line | 280 °C |
| Ion source | 280 °C |
| Quadrupole temperature | 150 °C |
| Spectral Acquisition | 45 to 650 m/z, 5 spectra/sec (70eV) |

Results and Discussion

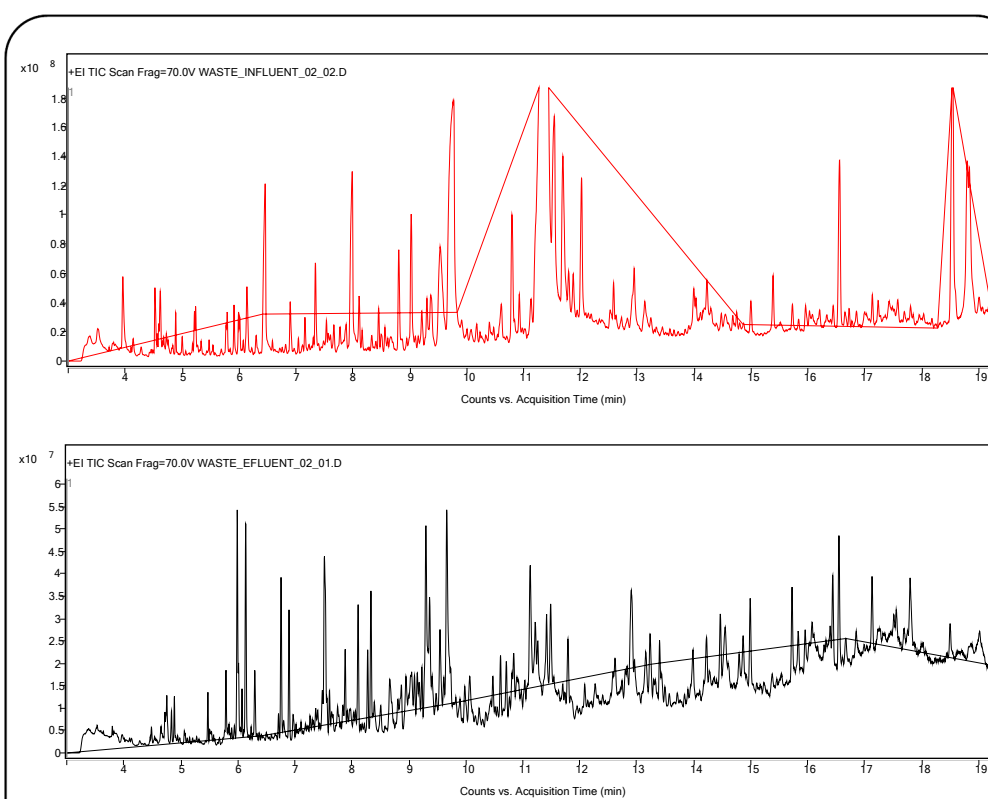


Figure 3. TIC Chromatogram of sewage intake (top) and final effluent (bottom).



Figure 4. Unknowns Analysis B.10.00 and spectrum comparison with NIST17.

Results and Discussion

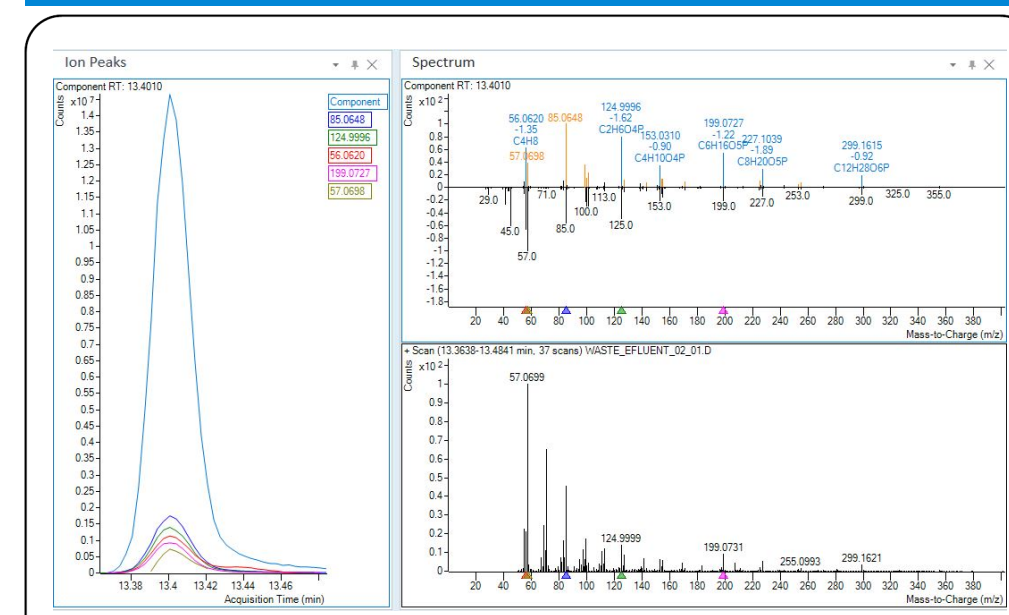


Figure 5. Deconvoluted compound and comparison with library spectra and mass error calculation for extracted ions.

In the two samples groups on average 656 compounds could be found for the influent and 533 for the effluent, respectively.

The compounds extracted and automatically tentatively identified (Figure 4) using a library match score of 70, RI difference of 30 and with at least 3 ions with a low mass error (<5 ppm) (Figure 5). On Average 75% of all deconvoluted compounds could be automatically tentatively can be divided into two groups:

Compounds of natural origin and synthetic substances. The majority of compounds extracted from the sewage waters composed of natural compounds derived from human excrements, nutritional remains, and products of their decomposition.

Among VOCs detected in the samples substances of natural origin were:

- Simple and branched alkanes, e.g. decane, undecane
- Terpenes and terpenoids, e.g., phellandrene, 3-carene

Synthetic substances present in the samples are less susceptible to biodegradation than natural compounds:

- Alkylbenzenes, e.g., mesitylene, xylenes components of solvents, synthetic oils, greases, bitumen masses
- Chlorine-containing substances: chloroform and methylene chloride - organic solvents, benzene chloride -intermediate product of pharmaceutical industry and component of dyestuffs, bromodichloromethane, and dichloroethenes – by-products of water disinfection
- Remains of hygiene articles used in the house- hold: limonene and menthol - aromatizing agents for washing-up liquids and toothpastes
- Plasticizers—diethyl phthalate, diisooctylphthalate, dibutyl phthalate, phthalic anhydride
- Butylated hydroxytoluene—popular antioxidant added to food, cosmetics, drugs, rubber, etc.
- Benzophenone—sunscreen agent;
- PAH, e.g., naphthalene—used as an intermediate product in the production of dyestuffs, solvents, synthetic resins, and insecticides.

Conclusions

A comprehensive workflow that includes suspect screening as well as a non-targeted approach was applied to screen for environmental pollutants in water samples.

An accurate mass GC/Q-TOF library was used to successfully screen pesticides and environmental contaminants.

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