1.2. Scope of the thesis

Part I opens with Chapter 1, which comprises a brief introduction, the scope of the thesis, and perspectives and trends, respectively. Chapter 2 reviews most of the more important ‘modern’ sample-preparation techniques which are used today in GC analysis. General principles, instrumental set-up and relevant analytical performance data are provided. Attention is also devoted to the comparison of different techniques. In addition, for each technique, a number of applications for food, environmental and biological analysis is presented and some of these are discussed to demonstrate the versatility of each technique.

In Part II, the focus is on the development of new instrumentation and techniques for sample introduction in GC and on the simplification and/or automation of existing methods for sample preparation. Chapter 3 reports the use of an automated on-line system for SPE–PTV–GC–MS. River water samples are automatically enriched on a DVB-type SPE cartridge and subsequently desorbed on-line into the GC–MS system. A PTV was used as the injection interface because of its reliability in large-volume injection and its robustness when real-life samples have to be analysed. Analyte recoveries were in the range of 70–100% with LODs of 15–50 ng/l and 0.7–10 ng/l with full-scan and SIM MS detection, respectively. Chapter 4 reports the development of an automated procedure for FAME and CTME analysis. For the determination of the fatty acid composition of fats and oils including their cis/trans distribution a simple but, unfortunately, manual and time-consuming sample preparation procedure is available. The proposed novel procedure is much faster (less than 15 min vs. 1 h) and manual sample handling is drastically reduced. The development of an automated liner-exchange system for DTD–GC–MS is reported in Chapter 5. Samples are put into a newly developed liner which is capped with a standard crimp cap. The liners are placed in a sample tray and transported to a thermal desorption device. Both liner transport and liner exchange (which can be performed after each analysis) are automated. The practicability of the device was shown for fatty acid profiling in vegetable oils, chemical analysis of spores and pollen, the analysis of preservatives in wood, as well as for characterizing car exhausts and for the determination of nicotine in tobacco. The new device was also applied for the trace-level determination of pesticides in food, which is reported in Chapter 6. After sample extraction, the samples required very little clean-up and were injected into a micro-, or µ, vial which is held in a liner. Next, the liner is placed in the injector and the contents of the vial are thermally desorbed and led directly to the capillary GC column. After GC–ToF MS analysis, the data are processed automatically by using a peak deconvolution algorithm. For the set of target pesticides, LODs were in the range of 2–40 ng/g, which nicely brackets the 10 ng/g value required for baby food. Chapter 7 reports a novel concentration technique for large-volume injection, AT-column. The technique is based on solvent evaporation in an empty liner with solvent vapour discharge via the split line of a PTV injector. Little or no optimization is required. The only relevant parameter is the injector temperature, which can
easily be calculated using the Antoine equation. AT-column combines the inertness of cold-on-column injection, and the flexibility and robustness of the PTV large-volume technique.

**Part III** focuses on multi-dimensional comprehensive techniques such as GC×GC, LC×GC and LC×GC×GC, where the first- or, first and second dimension(s) of the analytical system act(s) as the sample-preparation step(s) for the next one. In this thesis, these techniques were used for unravelling the composition of very complex samples like mineral and edible oils. GC×GC systems are commercially available already for several years and from various vendors. However, this is not true for the comprehensive coupling of LC and GC. **Chapter 8** discusses the design of an automated on-line comprehensive two-dimensional LC×GC system, and its application to edible oils and fats. Two interfaces were constructed to enable the transfer of large numbers of LC fractions to the GC part of the system. One was based on the use of a six-port switching valve, while the other one used a dual side-port syringe. The actual transfer of the LC fractions to the GC was effected by using a standard split injector to vaporize the analytes of interest and the LC eluent. Gas-phase splitting was applied to match LC mass load and GC column loadability. The reliability of the system was demonstrated by analysing large series of edible oils and fat samples – with the focus on both intact triglycerides and FAMEs – without encountering any technical problems. The information density of the chromatograms could be further improved by coupling the system to ToF MS (LC×GC–ToF MS), which allowed easy identification of individual compounds as well as compound groups. This system was also applied to the group-type characterization of mineral oils, which is reported in **Chapter 9**. Here, LC×GC was found to be an interesting approach for the characterization of complex samples. The addition of ToF MS detection is highly desirable to unravel the composition of a diesel sample and to identify individual compounds or compound classes. **Chapter 10** reports the coupling of multi-step direct thermal desorption with comprehensive GC×GC–ToF MS for the characterization of olive oil volatiles. Oil samples were injected without any sample preparation and thermally treated at temperatures ranging from 70°C to 600°C. The extracted volatiles were transferred directly to the GC×GC–ToF MS for instrumental analysis. Modern software features such as automated peak finding, mass spectral deconvolution and scripts were used for data processing to characterize the samples. Finally, in **Chapter 11**, the characterization of triacylglyceride (TAG) constituents of edible oils and fats by means of various one- and (comprehensive) multi-dimensional chromatographic techniques was studied, such as LC on a Ag(I)-loaded column (AgLC), GC, AgLC×GC, GC×GC, and AgLC×GC×GC. The best characterization of a TAG mixture was obtained by AgLC_{TAG}×GC_{FAME}×GC_{FAME} with ‘chemical modulation’ (in-line TAG-to-FAME methylation) between the first and the second dimensions. On the other hand, the use of GC_{FAME}×GC_{FAME} already provides a much better separation than is available in the literature. It allows an easy classification, in terms of the total concentrations of saturated, mono- and poly-unsaturated, and trans fatty acids. To put it differently, all sample information required in daily practical analysis for food-labelling purposes can be obtained in just a few hours.