

Large-Volume Injections in Hyphenated Systems for Waste-Water Analysis

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Ever more stringent emission regulations issued by the European and Dutch authorities force chemical industries in the Netherlands to reduce the discharge of environmentally hazardous compounds. Apart from offering a challenge to process-development engineers, the more-stringent governmental emission requirements also present a challenge to the analytical chemist. Methods with significantly lower detection limits are required. Large-volume injection is an attractive method for achieving lower detection limits. More and more often, the final method is a hyphenated one. Hyphenation of GC with an identification method is generally required, because of the complexity of the waste streams. In the present research project, two hyphenated GC methods for monitoring industrial waste-water streams were developed.

The first method is used for the element-specific analysis of environmental pollutants and is based on large-volume injection using a programmed-temperature injector (PTV). The second method uses on-column large-volume injection on a pre-column, where the solvent vapour formed during and after sample injection is vented through a solvent-vapour exit, placed between the pre-column and the analytical column. This method is applied for the analysis of oligostyrenes in waste-water streams.

In the analysis of specific classes of pollutants in water, conventional methods based on GC with Atomic-Emission Detection (AED) yield detection limits in the ppm range. However, we are now faced with target values in the ppb range. An added complication is the complexity of the chromatogram. The required quantitation limit of 200 ppb is a sum parameter, *i. e.* it can be spread out over a large number of peaks, each peak representing only a fraction of the total concentration. Gross under-estimates of the total concentration may be obtained if only a few, relatively large peaks exceed the detection limit, while a large number of small peaks are overlooked. Compared with elemental analysis we found this error to be up to 30% for a conventional GC method (1-1 splitless injection). Large-volume injection (LVI) offers a solution to this problem. We have investigated LVI for the analysis of hexane extracts of aqueous samples. By using an Optic-2 PTV injector in combination with an HP-7673 autosampler, we were able to inject volumes up to 50 l automatically. A liner packed with Supelcoport was used in the PTV. Increasing the injection volume by a factor of 50 resulted in an improvement of the detection limit by a factor of 40, *i. e.* almost the theoretical value. This is illustrated in figure 1A and B. Fig. 1A shows a standard 1 l injection. Fig. 1B shows the same sample now at an injection volume of 50 l. With the new PTV-GC-AED method, the results obtained are in close agreement with the total concentrations obtained by elemental analysis, while the GC method evidently offers an improved insight in the nature of solute molecules.

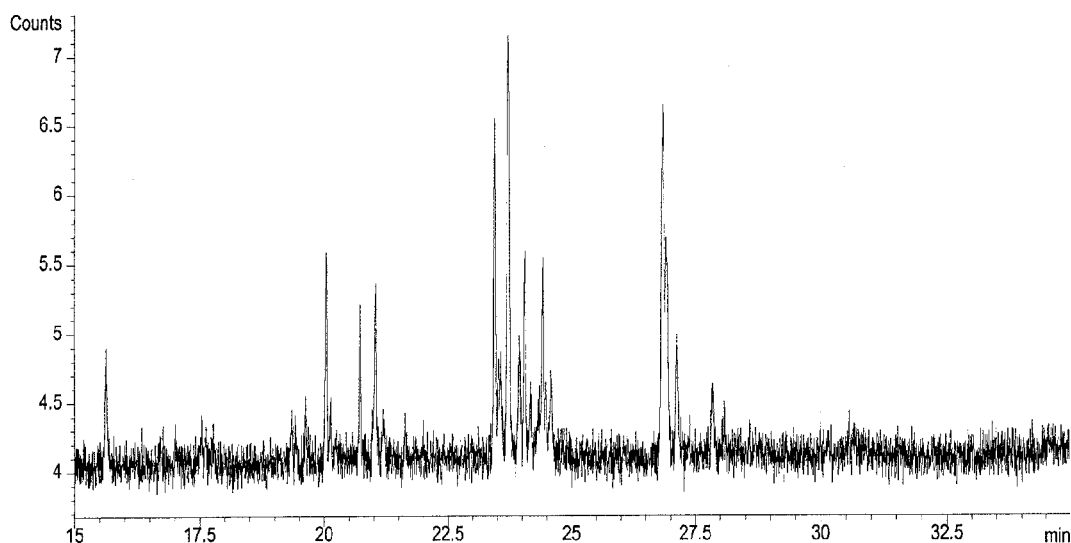


Figure 1A: 1 µl injection of a sample

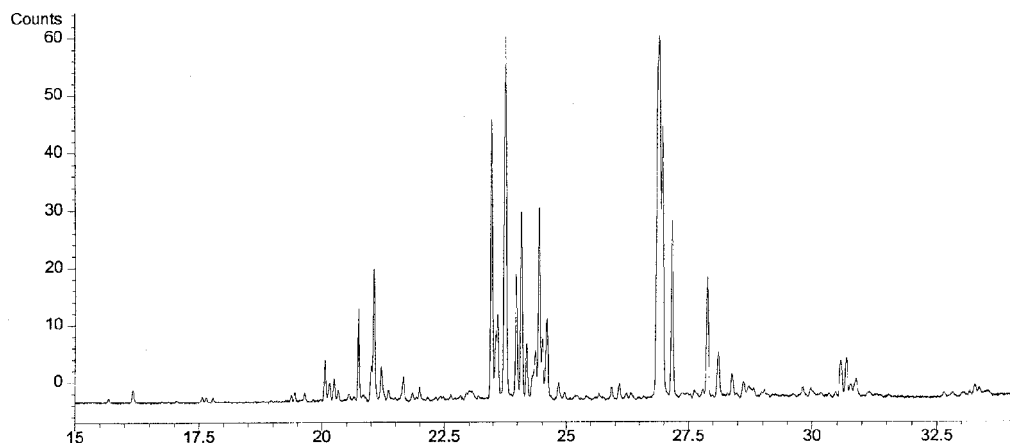


Figure 1B: 50 µl injection of the same sample

A second method developed within the framework of the present project is based on the use of on-column large-volume injection for the analysis of oligostyrenes in waste-water samples. Waste-water streams of certain chemical production plants can contain oligostyrenes. These compounds are under suspicion of being estrogenic. It is therefore important to monitor the concentrations of these oligomers in the various waste streams from the production facilities. The method developed is based on liquid-liquid extraction, followed by GC-mass spectrometry. With the new method the detection limits for (total) oligostyrenes in aqueous samples could be improved to 0.3 ppb. Using a 100- μ l injection the detection limit for individual compounds is in the low-ppt range.

The ever tighter environmental requirements on waste water streams from chemical plants require the development of new, more-sensitive analytical methods. In the development of such

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methods, large-volume injection holds a key position. The injection of 50- to 100-l samples is relatively straightforward using either the PTV or the on-column method. Using large-volume injection, detection limits in the ppt to ppb range can be achieved. Hyphenation with selective detectors such as MS or AED provides the selectivity required for the analysis of complex (water) samples. Both detectors are compatible with large-volume injection methods.

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