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Determination of Environmentally Relevant Compounds Using Fast GC/TOF-MS

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Abstract: The use of GC/MS techniques is crucial to modern environmental trace analysis. However, due to the slow scanning capabilities of common quadrupole detectors, the implementation of fast gas chromatography is restricted. The now evolving Time-of-Flight mass detectors, have fast scanning capabilities and thus can provide the data density necessary to accurately define narrow chromatographic peaks typical for accelerated GC methods.

The applications described herein demonstrate how the analysis of acidic pesticides and acidic drugs can be easily accelerated by a factor of 5 to 10 simply by using smaller column dimensions and higher helium flow rates. The quantitative data recorded with a Leco Pegasus II TOF system were comparable to the results obtained with the original routine methods. In addition to the fast acquisition, special software features allow peaks to be found automatically even when they are buried underneath the baseline, thus enabling an additional screening for unknown components besides the target analysis. A spectral deconvolution algorithm separates overlapping mass spectra and thus helps to deal with coeluting signals which can often be observed using fast GC conditions.

Keywords: Environmental analysis · Fast GC · Spectral deconvolution · TOF-MS

Environmental analysis is an important application area for instrumental trace analysis techniques, especially GC/MS. Due to the timing behavior of scanning quadrupole MS detectors in the range of about 5 to 10 full mass scans per second, there are some restrictions for the improvement and acceleration of the applied chromatographic conditions. The shortening of the analysis time is restricted by the appearance of narrow and coeluting peaks and peak groups, which cannot be resolved with slow scanning detectors. Not only the shape of peaks typical to fast chromatography with widths at base of less than one second can no longer be accurately described when such scan rates are applied, but also the data density required for comprehensive analytical interpretations of those chromatograms cannot be provided using common quadrupole technology. The more complex the analyte mixture is, the slower chromatographic conditions should be applied in order to avoid time-consuming manual processing and interpretation of mass spectra deriving from coeluting peaks. Thus, in order to be able to apply fast chromatographic conditions for MS detection, one needs a fast scanning detector together with a powerful software to be able to process and correctly interpret coeluting substances.

Based on the implementation of a GC/TOF-MS system with an extremely high data acquisition rate of up to 500 full scan mass spectra per second, two environmental applications for such systems were developed. The samples and extracts used for the measurement were provided by the coworkers at the ESWE laboratory and KIWA and were prepared according to the methods already published elsewhere [1][2].

The first application presented deals with the determination of acidic pharmaceuticals in surface waters. As the occurrence of medium polar pharmaceutical compounds in the aquatic environment gained a lot of interest in Europe over the last years [3][4], some routine analysis methods have been established which proved able to deliver accurate and rugged results. One of these routine methods was taken and by use of a shorter GC column with a smaller inner diameter the analysis time was reduced from 55 min originally to less than six min. In order to provide the necessary scanning speed for the mass spectral acquisition, a Time-of-Flight detector (Pegasus II by Leco) was used. The parameters were as follows:

GC-Parameters:

Column:	J&W DB-17 HT; 10 m x 0.1 mm x 0.1 µm
Injector temp.:	270 °C
Injection:	0.5 µl splitless
Heating progr.:	80 °C initial temperature, hold for 0.3 min, with 55 °C/min to 310 °C, hold for 1 min
Flow rate:	0.4 ml/min helium constant flow

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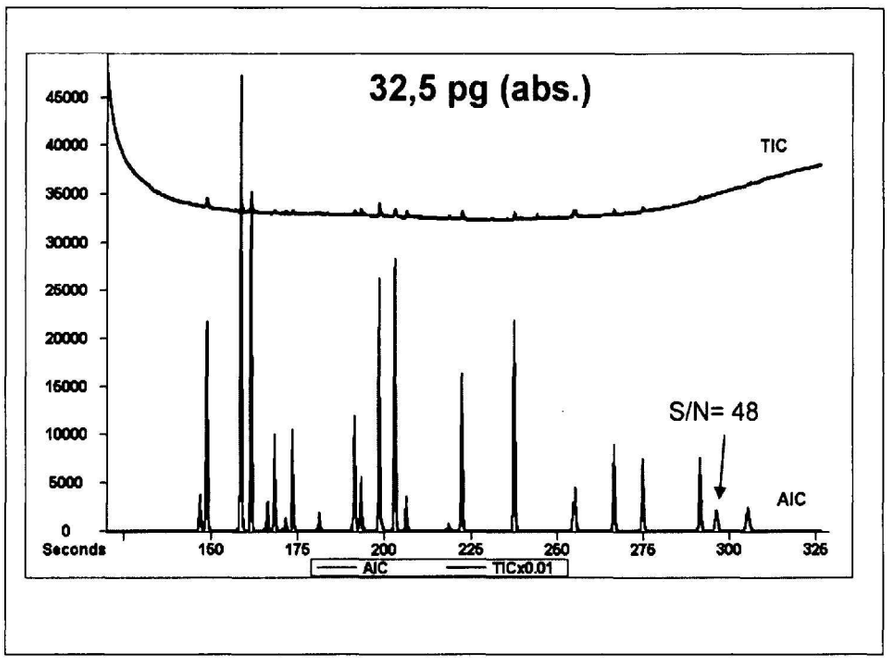

Fig. 1. Total ion chromatogram (TIC) and background corrected, so-called analytical ion chromatogram (AIC) of a standard extract.

MS-Parameters:
Mass range: 50–380 amu
Scan rate: 40 spectra/sec
Ion source temperature: 165 °C
Total run time: 325 sec

The respective analytes were: 2,4-dichlorobenzoic acid, bezafibrate, clofibric acid, diclofenac, fenofibric acid, gemfibrozil, ibuprofen, indometazin, ketoprofen, meclofenamic acid, naproxen, tolfenamic acid, internal standard: heptadecane nitrile. All analytes except the internal standard were measured as their methyl esters.

A typical fast chromatogram is shown in Fig. 1 where an equivalent of 75 ng/l water concentration was injected. The detection limits lay in a comparable range as the original method (about 10 to 20 ng/l) and the calibration curves had excellent linearity. To further compare the original and accelerated method, some spiked surface water samples were extracted and determined using either method. The results for some representative analytes are shown in Fig. 2.

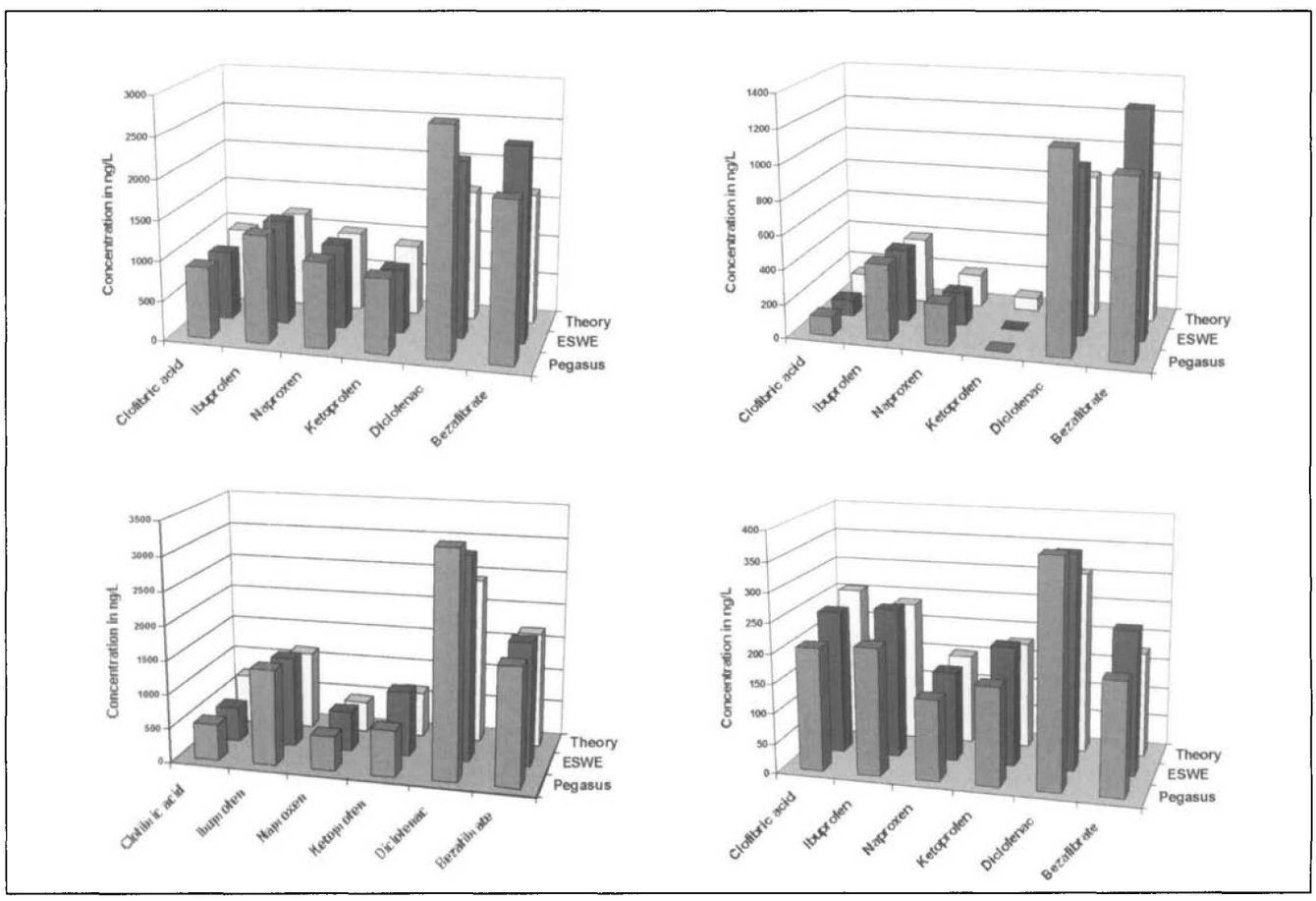

Fig. 2. Comparison of spiked surface water extracts using original and accelerated method.

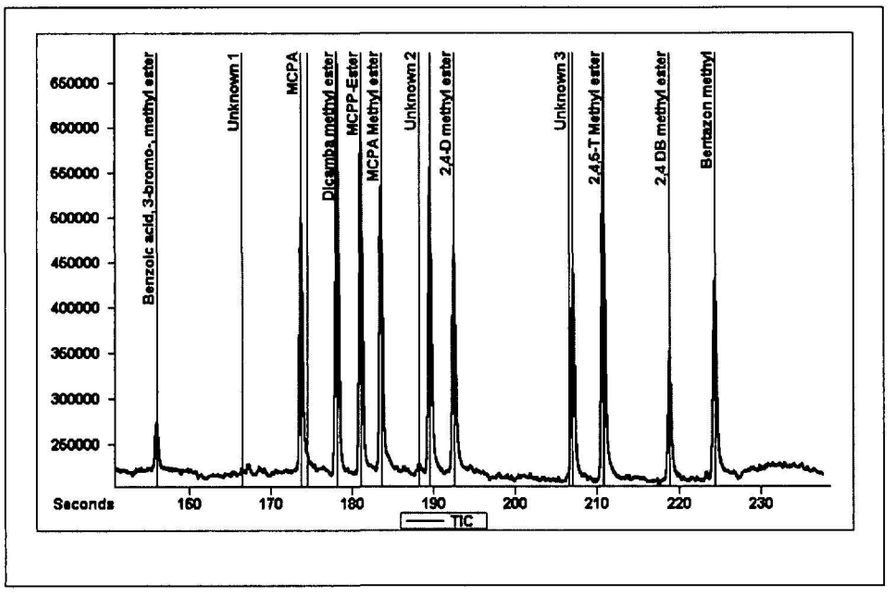

Fig. 3. Total ion chromatogram of a pesticide standard mixture.

Table. Analysis of a surface water sample using both methods

Analyte	Original method	Pegasus method
MCPP	0.17	0.17
Dicamba	0.24	0.25
MCPA	0.02	'not found' (mass 214 was present but spectrum did not match at all. When integrating, the result would be 0.01)
2,4-DP	0.44	0.44
2,4-D	0.18	0.16
MCPB	0.21	0.20
2,4-DB	0.12	0.11
Bentazon	0.27	0.26

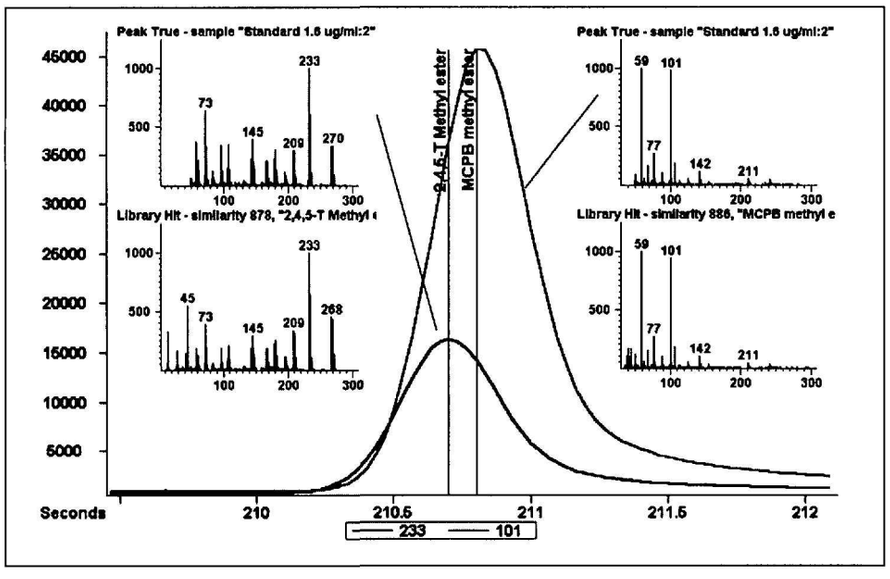

Fig. 4. Coelution and deconvoluted spectra of 2,4,5-T and MCPB.

The second application dealt with the analysis of phenoxy alkane carbonic acid pesticides, comprising compounds such as 4-Cl-phenoxyacetic acid, dicamba, MCPP, MCPA, 2,4-DP, 2,4-D, 2,4,5-TP, MCPB, bentazon, internal standard: 4-bromobenzoic acid. All compounds were also measured as their methyl esters.

The original GC method, which usually takes 30 min for completion was translated into fast GC conditions as follows:

GC-Parameters:

Column: J&W DB-5 MS; 20 m x 0.18 mm x 0.18 µm
Injector temp.: 180 °C
Injection: 1 µl split 10:1
Heating progr.: 70 °C initial temperature, hold for 0.3 min, with 60 °C/min to 270 °C, hold for 1 min
Flow rate: 1.2 ml/min helium constant flow

MS-Parameters:

Mass range: 50–300 amu
Scan rate: 30 spectra/sec
Ion source temperature: 165 °C
Total run time: 230 sec

A chromatogram acquired with the Pegasus II system is shown in Fig. 3. To evaluate the Pegasus performance in comparison to the original method, a native surface water extract was analyzed. The results obtained with both methods are shown in the Table.

As fast GC conditions often cannot provide the same resolution as slow acquisitions, one often observes coeluting peaks. The lower chromatographic resolution on the other hand can be supported by a high analytical resolution, thus giving the possibility to handle such overlapping signal. The Pegasus II software incorporates unique peak find and spectral deconvolution routines, which allows overlapping signals to be accurately handled and interpreted. In the fast chromatogram of this method two of the analytes do coelute, as can be seen in Fig. 4. The deconvolution algorithm extracted the correct spectra of both compounds, even masses present in the both spectra are represented in the correct ratios *e.g.* mass 59.

Besides sensitivity in terms of target analysis capability, the Pegasus II system software has two important algorithm features that allow for fully automated sample characterization. An automatic peak finding routine searches every re-

corded mass trace for maxima indicating the presence of a peak. As a following step, overlapping mass spectra of coeluting compounds are mathematically separated by use of a deconvolution algorithm developed by Leco. This generally produces better spectral quality and information than using simple background subtraction. Thus, not only target analytes can be found, identified and quantified but also other compounds present in the sample can be identified by means of a standard library search, as the instrument always acquires full scan spectra. An example is shown in Fig. 5, where in addition to MCPP at a concentration of 30 ng/l a number of other compounds are visible represented by some of their characteristic mass traces. The deconvoluted spectrum of 30 pg absolute amount of MCPP together with the library spectrum is shown in Fig. 6.

Further experiments in order to compare the two methods in a more detailed and quantitative way are presently underway.

To conclude, it could be shown that environmental analysis can be relatively easily accelerated using the same GC oven but different chromatographic conditions. Fast separation is supported by fast acquisition speed and thus often allows a method acceleration by a factor of ten. Although sample preparation remains the overall time determining step in the presented applications, fast analysis together with the possibility of fully automated data processing including peak finding and deconvolution of coeluting substances not only speeds up the whole quantification process but also gives access to additional information as unique software features can identify compounds well buried underneath the baseline.

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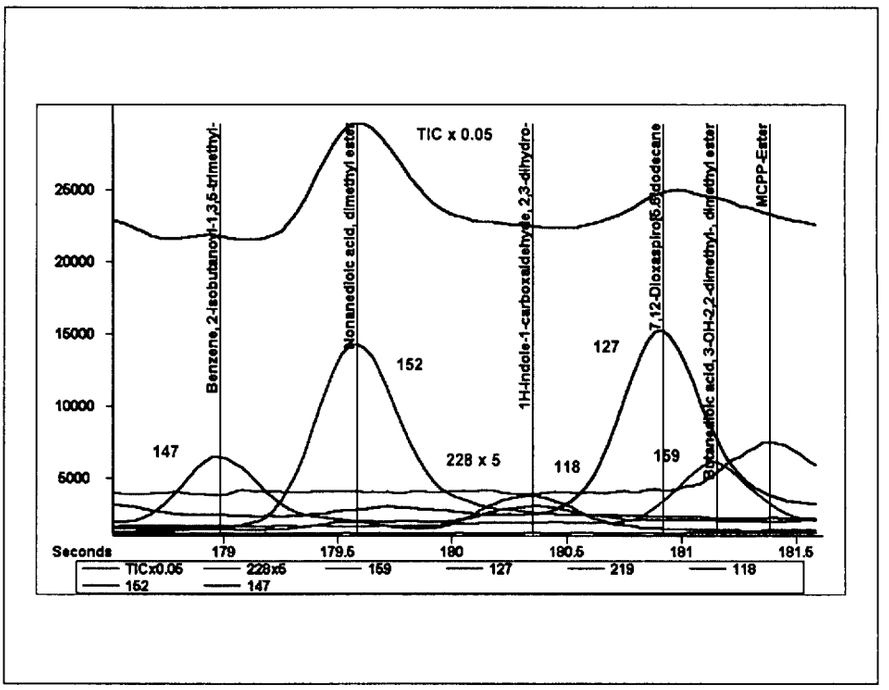

Fig. 5. Detection of MCPP in a surface water extracts together with other present unknown compounds.

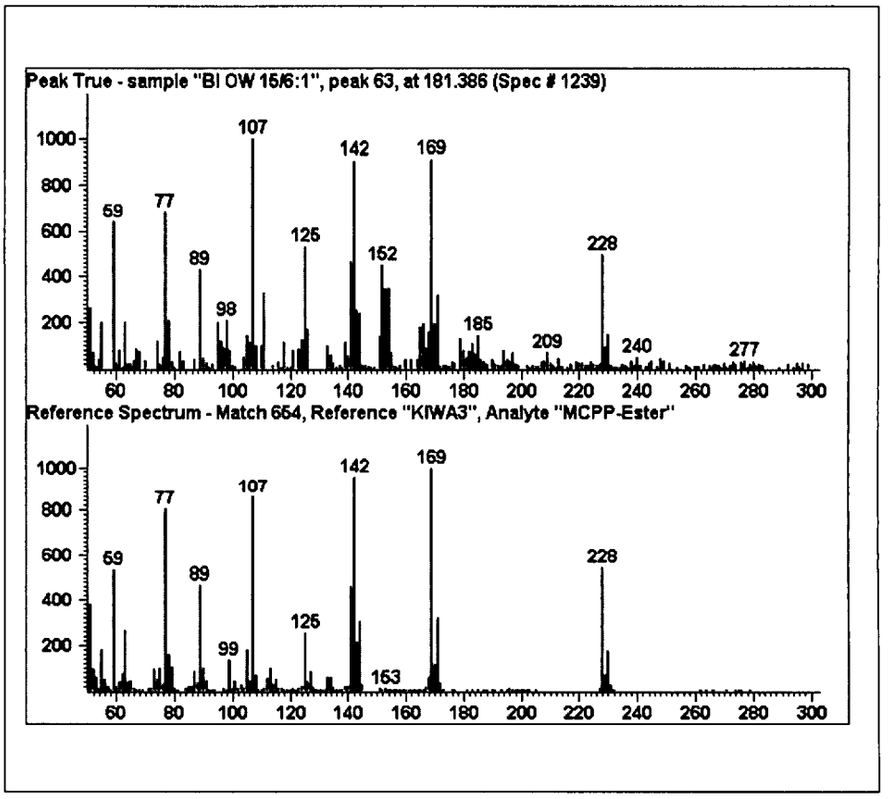

Fig. 6. Deconvoluted and library spectrum of MCPP at a 30 ng/l level.