# Fast Quantitative Determination of Organophosphorus Pesticides in Water Samples

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## 1. Introduction

The determination of organophosphorus pesticides (OPPs) in water samples still presents significant problems. To reach the required EU level of 0.1 part-per-billion (ppb) for drinking water, and the 1–3 ppb level in surface water, a significant concentration step and very sensitive detection are required. Properties of the OPPs such as good solubility in water, a wide polarity range, thermolability and chemolability, suggest column liquid chromatography (LC) as the method of choice for the analysis-cum-detection of these compounds. However, the use of LC is not really satisfactory because many OPPs do not have a chromophoric group—let alone that, generally speaking, UV absorption does not provide sufficient selectivity and/or sensitivity in environmental trace analysis. Next, identification with modern mass spectrometric detection suffices due to the low ionisation in the electrospray and APCI interfaces. In actual practice, therefore, capillary gas chromatography (GC) is the preferred separation technique, especially because it can be easily combined with the selective and sensitive thermionic, flame-photometric and MS detectors. In one rather laborious example, described by the Environmental Protection Agency (EPA), the determination is carried out by liquid-liquid extraction of 1 L of water sample with dichloromethane, evaporation of this solvent, exchange to methyl tert-butyl ether and injection of a few microliters on a capillary GC column equipped with an NPD[1]. Solid-phase extraction can solve some of the disadvantages of liquid-liquid extraction, such as laboriousness, the use of large quantities of extraction solvents and sample. Carried out in a miniaturised fashion, the required concentration step does not need any solvent evaporation step[2]. SPE is carried out on small cartridges filled with a polymeric sorbent using 50 mL of sample. After drying by applying a nitrogen pressure, the analytes are eluted with 50 to 100 µL of ethyl acetate. The small sample volume prevents that analytes, among them the relatively polar OPPs show breakthrough during trace enrichment. For identification purposes, MS is required. The slow scanning instruments usually prevent the use of fast GC analysis.

In this note, the GC analysis of extracts by means of fast GC with MS detection is the main objective. Since fast GC often leads to loss of resolution a solution has to be found. Time-of-flight MS (TOF MS) appears to be the MS of choice, because it provides a high rate of acquisition, which enables chemometrical approaches for data analysis. In this paper, real-life water sample extracts—spiked at (sub) ppb-level—have been subjected to fast GC–TOFMS. Special attention has been paid to the acquisition rate and to the similarity of the acquired spectra (absence of skewing). Next analytical data were evaluated with respect to linearity and detection limits.

## 2. Experimental Conditions

An SPE procedure commonly used in fully automated SPE–GC was used[3]. A solvent delivery unit and a Prospekt valve-switching module (Spark Holland, Emmen, the Netherlands) equipped with a 10 x 2 mm i.d. LC-type precolumn packed with 10 µm PLRP-S (Polymer Laboratories, Church Stretton, UK) styrene–divinylbenzene copolymer, was used for automated SPE.

River Rhine (Lobith, the Netherlands) water was filtered through a 0.45 µm BA membrane filtration system (Schleicher & Schuell, Dassel, Germany) prior to extraction.

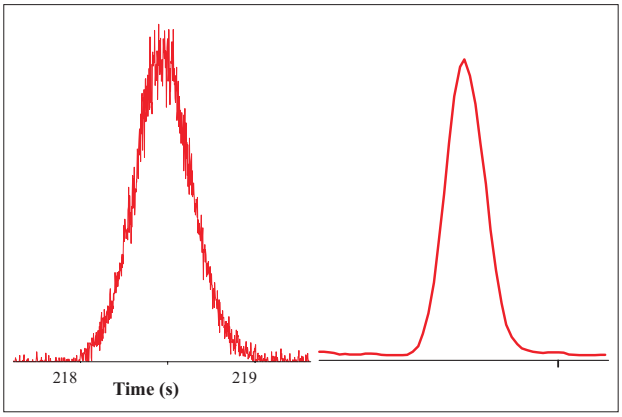


*Figure 1. TIC 500 pg Diazinon at 500 and 20 Hz.*

The PLRP-S precolumn was flushed with 2.5 mL of HPLC-grade water to remove the methyl acetate from the previous run, and next, loaded with a 100 mL water sample (5 mL/minute).

Subsequently, it was flushed with 2.5 mL of HPLC-grade water to displace residual sample and to remove highly polar and ionic compounds. After rigorous drying of the packing material (15 minutes) with a nitrogen purge at ambient temperature, desorption with methyl acetate was performed at a flow rate of 150 µL/minute using a Phoenix 20 syringe pump (Carlo Erba Strumentazione, Milan, Italy). After the void volume of the precolumn and connective tubing was filled, the extract (100 µL) was collected in an autosampler vial. Prior to the next run, the PLRP-S sorbent was cleaned by flushing with methyl acetate. 1.0 µL of extract was introduced in the split mode (ratio 1:5) into the GC–TOFMS system.

*GC Parameters*
Column:
Chrompack CP-Sil 8; 5 m x 0.1 mm x 0.10 µm
Injector: 300°C
Split Rate: 1:5
Heating Program:
50°C initial temperature, with 50°/minute to 320°C, hold for 1 minute
Flow Rate:
1 mL/minute helium; "constant flow mode" on.

*MS-Parameters*
Mass Range: 35 to 435 amu
Scan Rate: 10 to 500 spectra/second from 60 to 360 seconds
Ion Source: 225°C
Transfer Line: 320°C
Total Run Time: 360 seconds

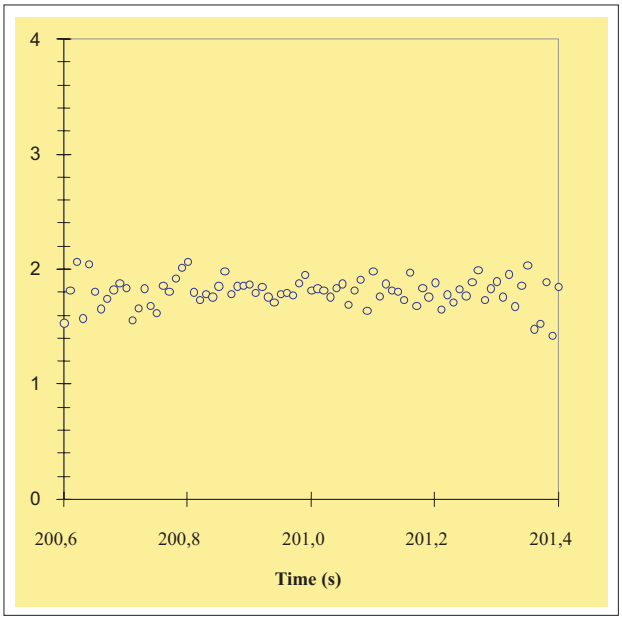


***Figure 2. Mass ratio of m/z 193 and m/z 137 over the peak profile of diazinon at 100 Hz.***

## 3. Results

Figure 1 shows total ion chromatograms obtained for 500 pg of Diazinon with scan rates of 500 and 20 Hz, respectively. The figure clearly illustrates that scanning at a rate as high as 500 Hz is possible. The disk space of 20 MB per minute of spectra recording does not play a role of importance anymore with hard disks of 20 GB and more being commercially available. It should be added, however, that data analysis requires additional RAM.

It can also be concluded that higher scan rates lead to loss in sensitivity. Selection of the appropriate acquisition speed is essential; ten spectra over a complete GC peak usually are sufficient and provide the best sensitivity. High scan rates will be only useful for very narrow peaks, e.g. when using 50 µm internal diameter columns or even less, and for improving the automatic deconvolution.

At all scan rates tested (500 to 10 Hz) the spectra acquired over the eluting peak matched very well. As an example, Figure 2 illustrates this aspect for the mass ratio of the well-known ions for diazinon of 193 and 137, respectively. Over the whole elution profile of the peak, mass spectra showed a similarity expressed as relative standard deviation (RSD) of better than 6%. Only when acquisition rates higher than 100 Hz were used, was the RSD value higher than 10%. The uniformity of mass spectra is the essential element for the deconvolution process. Ten OPPs were evaluated in spiked river water samples. Table 1 shows that fast GC provides very accurate retention times. Under the conditions used a scan rate of 20 Hz was sufficient to obtain good reconstruction of the peak profiles (necessary for retention time determination) as well as for deconvolution of the mass spectra. Repeatability of peak areas was excellent for the complete procedure including SPE and fast GC–TOFMS analysis. Regarding analytical data, very low detection limits can be obtained even under split injection conditions. Improvements can still be made when injecting a larger aliquot of the sample, e.g. by means of large-volume injection using either a retention gap or PTV technique. Linear calibration plots were obtained for peak area of the quantitation mass versus the concentration. Finally, all analytes could be identified at the concentration range tested (see linearity range). As an example of river water analysis, Figure 3 shows the analytical ion chromatogram (display of only quantified analytes) with and without spiking at trace level.

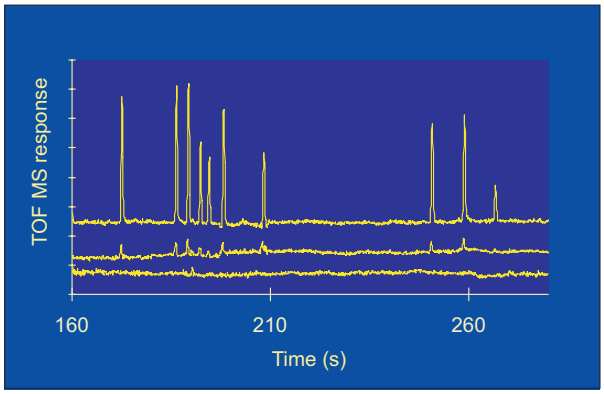


***Figure 3. Time-scheduled reconstructed ion chromatogram using quantification masses of ten OPPs obtained after injection of 1 µL 1000-fold concentrated river Rhine water extract. Lower trace: river water blank; middle trace: same sample spiked at 0.1 µg/L; upper trace: spiked at 1 µg/L. Elution order as given in table 1.***

**Table 1. Analytical data of ten OPPs obtained in spiked river water at concentrations between 0.03 and 5 µg/L.**

| Analyte | Rt (s) | Q. Mass (amu) | Lin. Range (ng/L) | Corr. Coeff. | Det. Lim. (ng/L) | RSD (%) (n = 6) | |
|---|---|---|---|---|---|---|---|
| | | | | | | *Rt* | *Peak Area* |
| Diazinon | 196.6 | 137 | 30–5000 | 0.9999 | 15 | 0.07 | 8 |
| Fenchlorphos | 210.4 | 285 | 30–5000 | 0.9999 | 10 | 0.07 | 9 |
| Fenitrothion | 213.4 | 125 | 30–5000 | 0.9999 | 15 | 0.06 | 8 |
| Malathion | 216.5 | 173 | 30–5000 | 0.9999 | 10 | 0.06 | 9 |
| Chlorpyrifos | 218.6 | 199 | 30–5000 | 0.9999 | 20 | 0.06 | 10 |
| Bromophos | 222.3 | 331 | 30–5000 | 0.9999 | 5 | 0.06 | 11 |
| Bromophos-Ethyl | 232.3 | 301 | 70–5000 | 0.9999 | 30 | 0.06 | 11 |
| Azinphos-Methyl | 274.8 | 160 | 70–5000 | 0.9999 | 20 | 0.05 | 9 |
| Pyrazophos | 283.0 | 221 | 70–5000 | 0.9999 | 20 | 0.05 | 9 |
| Coumaphos | 290.8 | 226 | 70–5000 | 0.9999 | 30 | 0.05 | 8 |

## 4. Conclusions

As demonstrated in this application, the Pegasus is ideal for performing fast, sensitive determination of water analysis. The data processing software detects and identifies the target compounds by comparison of complete spectra (even when the components are buried in the baseline) as well as performing a search for unknown substances after separating overlapping spectra. A proper library identification can also be achieved using derived (background subtracted) spectra. Further acceleration and increase in sensitivity could easily be accomplished by means of higher scan rates, larger injection volume, etc.

Gas chromatographic analyses can be performed within 5 minutes. Regarding quantitative aspects, detection at very low limits (low pg absolute amounts) can be conducted and linear response over a wide concentration, range assures an excellent method for analyzing water extracts.

## 5. References

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