

Organic micro-pollutant on-line analysis And detection system: AQUAPOD

KEYWORDS: On-line analysis, organic micro-pollutants, pesticides, hydrocarbons, SPE, UV spectrophotometry.

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The paper presents a new system for the on-line analysis of organic micro pollutants in natural waters, using an SPE technique for sample pre-concentration and cleaning. The apparatus is optimised for different pesticides and phenol compounds, but it can be used for the detection of others compounds like hydrocarbons. Several laboratory tests were made to define the system performance. Results from in situ evaluation and on-line monitoring of pesticides pollution are also reported.

Introduction

Nowadays almost all river basins are disturbed by industrial or agricultural pollutions. Among them organic micro-pollutions constitute a real problem for many water uses. The main focus is of course on drinking water production, but there are others such as fish farming and in some case sea or river bathing.

Current laboratory analysis cannot be an adequate answer to monitor industrial activities like drinking water production. Because they are slow and expensive, chromatographic methods are not suitable for plant process control or 24 hours monitoring. Enzyme-linked immunoabsorbent assays give some interesting and rapid information, but they need people and are dedicated to particular type of compounds (triazines, substituted ureas for pesticides, some PAHs, etc.)

So, there is a need from waterworks' managers to set up analysers which could monitor organic pollutants in natural water.

To meet this need HOCER developed with a French laboratory based in Brest (Pôle Analytique des Eaux) a new general system for the on-line analysis of organic pollutants able to measure at low sensibility levels ($\mu\text{g/l}$) according to the European Water Framework Directive.

This paper presents the technical and scientific basis of the apparatus, some results of laboratory, and in situ validation tests. Records of some pesticide pollutions are also presented.

Technical under laying

UV analysis has long been used for on-line measurement of different compounds mostly nitrates and dissolved organic matter (DOM). Apparatus on the market are frequently based on the analysis at one or two wavelengths but others use multi-wavelength analysis.

Chromophors such as aromatic cycles or carbonyl complexes have high extinction coefficient in UV wavelength. This allows the detection of different families of micro-pollutants like phenols, triazines, substituted ureas, BTEX ... Due to interferences with major compounds in natural waters (Nitrate, humic and fulvic matters) the sensibility reached using direct UV measurement cannot be lower than 1ppm/l. In order to reach the hoped level ($\mu\text{g/l}$), a concentration step is required.

Solid phase exchange technique is currently used in laboratory analysis to prepare samples before the injection into the HPLC. We will use this technique to concentrate the dissolved organic matter and make a fractionated extraction in order to eliminate all the compounds which could interfere during the analysis.

This technique of concentration coupled with direct UV analysis has been patented by HOCER.

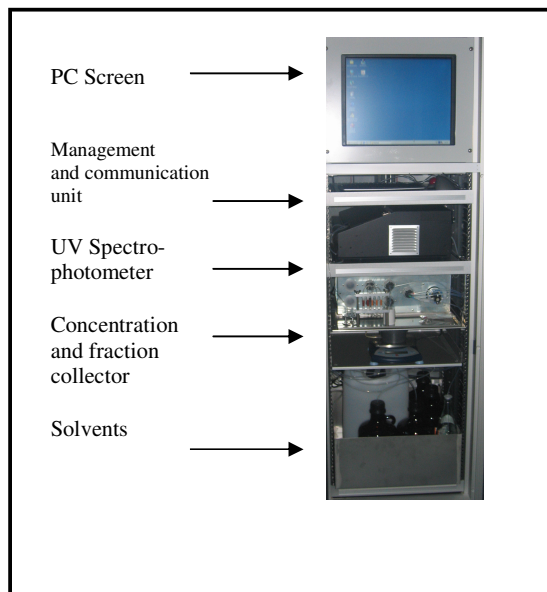
System description

A complete automation of HPLC analysis is rather difficult. Despite the tremendous progress in analysis reproducibility, a great number of factors (column ageing, solvent reproducibility, pressure and temperature variability, etc.) makes sometimes the analyst intervention compulsory, what is possible in waterworks. Moreover, this apparatus remains quite expensive.

The greatest difficulty encountered to set up a completely automated system is due to the chromatographic separation. So, the idea was to avoid this step. De facto, the number of compounds identified during one analysis will be greatly reduced but remains compatible with an objective of detection of a few dominant micro-pollutants.

The observations of pollution events show that in case

of pollution, the number of the present products is tiny.



The concentration method is reduced to a concentration and rinsing step, followed by one (or several) elution which should be efficient enough to gather all the researched pollutants. The analysis is then carried out by UV spectrometry using the deconvolution method developed by the French Ecole des Mines in Alès (South of France).

This process presents several advantages. Firstly, it is possible to work at a relatively high frequency (1 analysis in 45 minutes). The absence of the chromatographic step, which is replaced by a simple fractionated elution, drastically decreases the material costs and requires any calibration for an on-line operating.

The regeneration of the concentration column allows a long-life use of the cartridge thanks to the use of adapted solvents. Laboratory tests in natural river waters have shown that there were any changes of the concentration factors before the 80th analysis. Five columns equipped the apparatus; they are used only 50 times each, giving autonomy for 250 analyses to the Aquapod System.

UV Signal analysis

The UV deconvolution technique is based on the UV spectra deconvolution whose principle relies on two simple hypotheses:

The UV spectrum of a sample can be likened to the total amount of the absorption spectra also called reference spectra;

The combination of a small number of reference spectra allows most of the time to explain the UV spectrum's shape of an unknown sample.

$$S_{sp} = \sum_{i=1, nr} a_i S_{ref_i} + \sum_{j=1, np} b_j S_{polr_j} + Err$$

S_{sp} : Sample spectrum

S_{ref_i} : Water reference spectrum

S_{polr_j} : Pollutants reference spectrum

a_i, b_j : Coefficient of the linear combination

Err : Restoration error

Application to organic micro-pollution analysis

In that case, the natural water samples always possess a UV signature. The spectrum corresponds to the absorption of a certain number of organic molecules naturally present in water. The fractionated elution process allows eliminating a great part of the organic fraction probably corresponding to a lower weight of the molecules which are less stuck on the column; but there remains a fraction which is eluted during the analysis stage.

This UV spectrum is relatively steady and presents any significant differences from one river to another but its intensity rate is unsteady. Yet, it can be less important in groundwaters above all in waters from deep groundwaters (e.g. Evian water) or from drinking waters.

In order to obtain a detailed spectrum, this UV signature must be integrated into the spectrum analysis. The pollutants' signatures are then added to this basic spectrum.

The sample spectrum is then considered as being explained by the combination of a few reference water spectra (empty of pollutants) and of spectrum including polluted products whose reference is known.

For digital stability reasons, the adjustment computation is done from a maximum combination of height spectra:

- Two or three water reference spectra
- Three pollutants reference spectra
- Two constant spectra in order to get rid of some problems due to the baseline fluctuations in presence of small bubbles in the sample.

This limited number of reference spectra is not sufficient to clearly explain the natural water variability. It is also a limitation to Aquapod quantification abilities, because it can detect more than three pollutants.

The algorithm will then test the whole eight-spectrum solutions and analyse the resulted modelling in order to determine the nearest one from the sample spectrum.

The maximum number of reference spectra allowed is twenty for water reference and the same for pollutants. In fact, the number of reference spectra is very often lower.

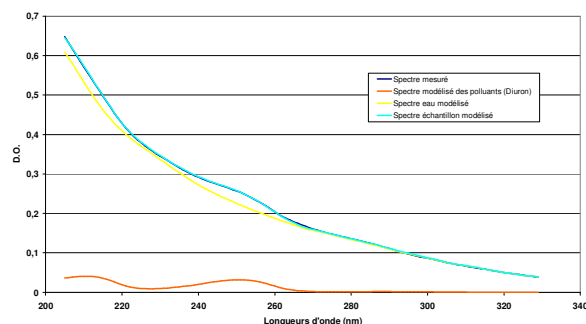


Figure 2: Decomposition of a diuron-polluted river water spectrum

Depending on the modelling quality, a confidence level is defined. Three classes of quality are defined. If the distance of the average difference between the modelled and observed spectra is lower than 0.00003 OD units, then the result is considered as significant and the presence of identified pollutants can be considered as

very probable. If this difference is lower than 0.0007 OD unit the presence of pollutants is possible, but they are probably associated with other molecules. The pollutant is very often not the right one but its spectrum is very closed to one of the reference spectra. When the distance is greater, it means that the pollutant is not in the reference base. In this case an anomaly message is delivered. Only a laboratory analysis will be able to define whether the difference can be explained by the presence of a particular compound or if it is due to a noticeable change in the general organic composition (e.g. fulvic acid). In the first case, if the pollutant is identified, then its spectrum should be integrated into the spectrum base. If a product is detected but any laboratory identification is possible, then the spectra of the product can also be integrated in the reference base as an unknown compound. If there is any pollutant found by the laboratory analysis, then the spectra will be integrated in the water reference spectrum.

Detected products

Aquapod is able to detect a great number of compounds. Nevertheless, two conditions are required: the compound must have an UV spectrum, and it has to be concentrated during the absorbing phase.

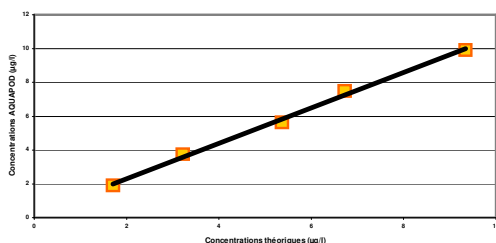


Figure 3: Doping of water from Evian by a stock solution saturated with oil.

Calibration curves have been made for different pure products of different families of pollutants (pesticides, phenols, HAP, ...) but also for some complex compounds that are a uniform and stable mixing of different products (hydrocarbons like oil, unleaded gasoline, kerosene). Figure 3 represents the oil curve.

Table 1 shows the list of the different Aquapod known compounds and the measuring range.

Products	Quantification limit (µg/l)	Measure range (µg/l)
Pesticides		
<i>Triazines</i>		
Atrazine - simazine	0.24	0-10
DEA	0.21	0-10
Terbutam		0-10
<i>Substituted ureas</i>		
Diuron	0.21	0-10
Isoproturon	0.39	0-10
Chlortoluron	0.21	0-10
<i>Pyrethreoids</i>		
Cybermetrim		0-10
Phosphorated		

organic type		
Ethyl-Parathion		0-10
Amids		
Acetochlore,alachlore, ...		0-10
Hydrocarbons (1)		
Heating oil	0-20 /0-500	0-20 / 0-500
oil		0-20 / 0-500
Premium 98		0-20/ 0-500
Premium 95		0-20 / 0-500
Industrial products		
Phenols		
Chloro-phenols		0-10
Para-cresol		0-10
Nitro-phenols		0-10
Complex mixing		
Liquid manure		(2)
Waste water treatment plant release		

Table 1: Listing of the products detected by Aquapod, sensitivity and measure range

⁽¹⁾ Aquapod can be configured to detect at different levels. For global hydrocarbon detection, the sensitivity level is generally set at 10µg/l.

⁽²⁾ For manure detection the concentration notion is difficult to asses, so Aquapod only gives a presence index.

Test results

Performance evaluation tests have been carried out both in laboratory and on site. The objectives were to validate both liability and detection capacities of the apparatus.

Laboratory tests

Test protocol was directly derived from ISO 15839 standard for on-line measurement system validation. The objectives were to characterize the metrological capacities of the apparatus. (Detection and quantification limits, bias, repeatability, etc.)

These tests were realized with artificially doped water. The water used was Evian water known for its low but very stable organic composition. Evaluation was conducted with two reference compounds, indeed Atrazine and Diuron. The doping was directly made in Evian bottle; between each analysis a mock measure is done. Each sample is analysed 5 times. Test solutions are ranging from 0.1µg/l to 10µg/l.

Definitions

Characterization parameters are calculated according to ISO 15839 definitions.

Results

Table 2 summarizes the different results.

Parameters	Atrazine µg/l	Diuron µg/l
Bias	0.17	-0.08
Quantification limit	0.10	0.20
Lower detectable change at 20%	0.09	0.06
Current repeatability at 50%	0.15	0.08

Table 2: characterisation tests of Evian water

On-site tests

Similar tests have been carried out in natural river waters.

The test protocol was exactly the same except that the water used was already filtered at 0.8 µm.

Parameters	Atrazine µg/l	DEA µg/l	Diuron µg/l	Isoproturon µg/l	Chlor- toluron µg/l
Bias	-0.05	-0.04	0.00	-0.0	0.00
Quantification limit	0.24	0.35	0.21	0.39	0.21
Lower detectable change at 20%	0.19	0.20	0.23	0.24	0.11
Current repeatability at 50%	0.60	0.08	0.11	0.05	0.07

Tableau 3: characterisation tests in river waters

In situ measurements

River waters analysis

Results shown here were recorded during the first Aquapod evaluation campaign. These data are really interesting because we had at the same time a great number of laboratory results at our disposal. It is then possible to compare Aquapod results with those issued from UV/HPLC measures.

The system prototype was put up at the Elorn River, next to the Bay of Brest in north-west of France. It was decided to set up the equipment at the waterworks of Brest. At that time, this site presented a known risk to pesticide products; that is why HPLC/UV analysis was made every day. During this campaign we also used an automatic water sampler (glass bottle) during two rainy events, in order to have high frequency analysis (one per hour) at time of supposed pesticide pollutions. HPLC/UV analysis was performed by Brest analysis laboratory.

During this campaign we observed several pollution events. Aquapod value fit quite closely with laboratory results. Atrazine measurements (Figure 5) correspond quite well with high frequency laboratory result. Diuron major pollution (Figure 4), at the end of July, is perfectly detected and quantified.

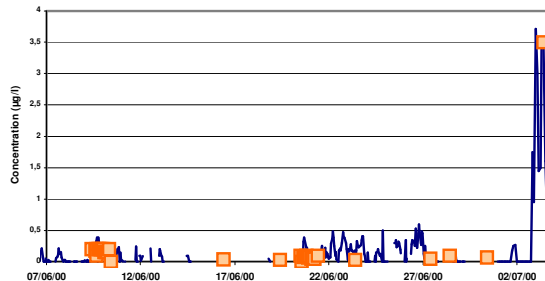


Figure 4: Evolution of the Diuron in the Elorn River on June and July 2000

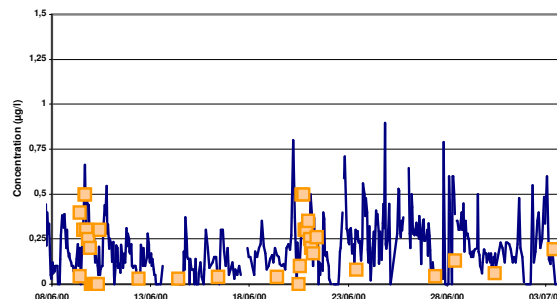


Figure 5: Evolution of the Atrazine in the Elorn River on June and July 2000

Use with another type of water

Aquapod was originally designed to work in natural river waters, and, until now, it has mainly been used in this context, but it can also work with other kinds of water.

Drinking water and water at low organic content

As these waters are less charged with organic matter, the residual interference with natural organic matter is lower. That is why it is possible to concentrate a greater sample volume and to improve the system's sensitivity level.

Marine waters

The concentration method does not react to the presence of salt. That is why the use of Aquapod is possible in marine waters. In Summer 2004, an apparatus was installed along the estuary in the south of Brittany within the framework of the draft for the monitoring of oyster pollutions. In this part of France, the main difficulty came from the great variations between the organic contents in fresh and salted water. Even if the calibration phase had been longer to establish, we proved the possible use of Aquapod in marine waters.

Aquapod general characteristic

The apparatus has a maximum analysis frequency of one frequency every forty five minutes at the rate of one analysis every two hours, carried out within 10 days without a break.

The system can work in an autonomous mode; indeed, it stores the results on the computer disk and can be remotely controlled using a MODBUS protocol.

For maintenance purpose remote connexion can be established using PC-Anywhere software.

Current exploitation tasks come down to the replacement of solvent bottles and concentration column every 10 days ore more depending on the analysis frequency.

Conclusion

AQUAPOD detection system is able to detect, quantify and identify organic pollutants in all types of water. Sensitivity reached and the great range of detected products make this apparatus a very efficient tool to monitor the quality waters and to detect accidental or chronic pollutions with pesticides, industrial products or hydrocarbons for instance.