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# Improved routine speciation of organotin compounds in environmental samples by pulsed flame photometric detection

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**Abstract**

The high toxicity of the organotin species requires sensitive analytical methods in order to understand the origins of pollution and perform monitoring programs in the water cycle. The optimisation of a new detection method, pulsed flame photometric detection (PFPD), is reported for the simultaneous determination of butyl-, phenyl- and octyltins. The methodology of the experimental designs at two levels was used. It allows the evaluation of the influence of the three gas flow-rates on the peak heights and resolution between the closest peaks obtained using two different wavelengths of detection (390 and 611 nm). The modelling of these two responses, according to second-order polynomials, leads to the precise adjustment of the operating conditions. PFPD has shown two significant improvements over conventional flame photometric detection: increased sensitivity (absolute detection limits: 0.07 to 2 pg as Sn) and greater selectivity, whatever the wavelength used. This new analytical process was validated by the analysis of certified reference material and spiked river water. It was used in routine analysis of environmental samples (wastewater, sludge, sand and oyster). 

*Keywords:* Pulsed flame photometric detection; Flame photometric detection; Detection, GC; Water analysis; Environmental analysis; Chemometrics; Experimental design; Organotin compounds

## 1. Introduction

Today, the contamination of the environment by organotin compounds is unquestionable [1]. Their severe effects on both aquatic organisms [2] and mammals [3] including humans and their high bioaccumulation potential has led to the control of pollution levels in environmental samples. Untreated wastewater can give rise to pollution of aquatic systems even if organotin contents are low. Sludge used as fertiliser in agriculture contains organotins that could be transferred to soils [4].

To understand the origin of pollution and perform monitoring programs in the water cycle, sensitive analytical methodologies are required.

A procedure based on one-step ethylation–extraction using sodium tetraethylborate ($NaBEt_4$) followed by gas chromatography–flame photometric detection (GC–FPD) has been previously proposed [5]. This procedure has been proved to be convenient for environmental pollution control [6]. Nevertheless, two problems appeared: (1) detection limits (4 to 10 ng Sn $l^{-1}$) were sometimes not sufficient to reach concentrations in waters and (2) interferences can appear from sulphur-containing compounds, which are abundant in environmental samples [7].

In this paper, a new detection method is proposed to remedy to these problems. Pulsed flame photometric detection (PFPD) is the newest member of the

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family of flame-based gas chromatographic detectors [8,9]. PFPD operates with a pulsed flame instead of a continuous one and offers a number of significant improvements over conventional FPD [10]. The present work consisted in optimising PFPD for both Sn–H and Sn–C emissions. The process has been validated by the analysis of certified reference material and environmental samples such as freshwater, wastewater and sewage sludge.

## 2. Experimental

### *2.1. Apparatus*

#### *2.1.1. Chromatographs*

Organotins were determined using: (1) a Varian 3300 gas chromatograph (Palo Alto, CA, USA) equipped with a conventional FPD system and a Varian 1075 split/splitless injector. The FPD operating conditions previously described [5] were as follows: temperature 270°C; flow-rates: 280 (air), 185 (hydrogen) and 30 (nitrogen) ml $min^{-1}$, and (2) a Varian 3800 gas chromatograph (Walnut Creek, CA, USA) equipped with a PFPD system and a Varian 1079 split/splitless injector temperature programmable.

The separation was carried out on capillary columns (30 m×0.25 mm I.D.) coated with methylsilicone (0.25 μm film thickness) (Quadrex, New Haven, CT, USA). Nitrogen was used as carrier gas. The following temperature program was necessary to allow separation of organotin compounds [5]: the column temperature was held at 80°C for the first minute, increased to 180°C at the rate of 30°C $min^{-1}$ and then to 270°C at 10°C $min^{-1}$.

#### *2.1.2. Theory of PFPD operation*

Recently, Amirav and co-workers have developed a new type of FPD based on the use of a discontinuous flame [8,9]. This PFPD has been shown to outperform conventional FPD in detection sensitivity and selectivity.

PFPD is based on a flame source and combustible gas flow-rate that cannot sustain continuous flame operation. An air–hydrogen flame is used. In this system air is divided into two flows: the first one, called ''Air1'' mixed with hydrogen ($H_2$) carries the effluent from the column to the detector. The second one, ''Air2'' is added to this mixture in the detector to adjust the total ratio air–$H_2$ and control the ignition rate. Then, the flame ignites two to four times per second using a continuously heated ignitor coil.

It has been shown that the time emission profiles are characteristic of the species involved [8]. Fig. 1 presents the emission of main potential interferents over tin, i.e., hydrocarbon (combustion products) and sulphur compounds.

Now, the time period of the emission which has to be integrated to generate the detector signal can be selected by adjusting the start (gate delay) and the duration (gate width) of the detection according to the profile of the species studied. Then, the highest selectivity is obtained for the detection of tin compounds.

In the flame, organotins give rise to: Sn–C bonds, which emit in the blue at 390 nm, and Sn–H bonds, which emit in the red at 610 nm [11].

Sn–C emission is up to 100–1000-times more important than Sn–H emission but at the corresponding wavelength 390 nm the main-interfering sulphur species also emits [12]. So, in conventional FPD, the emitted light is isolated from background emissions by using an interference filter, generally at 610 nm. In PFPD, a passband filter can be now used

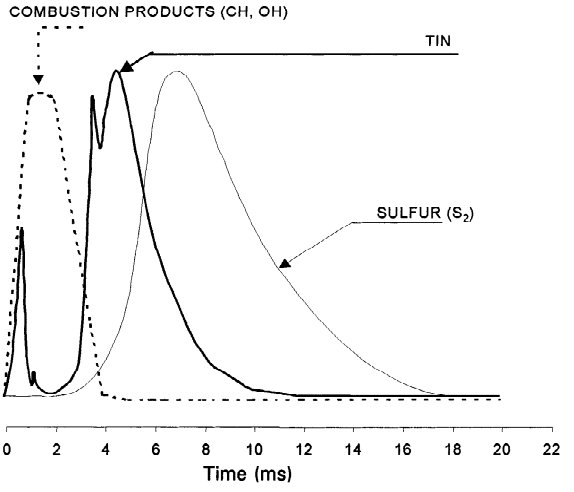


Fig. 1. Emission profiles of tin and potentially interfering elements [22].

at the both wavelengths, owing to the electrometer gate delay and width.

Under these conditions, the optimisation of the three gas flow-rates (Air1, Air2 and $H_2$) was performed for both Sn–H and Sn–C emissions. The detector was operated with 390 nm and 610 nm optical interchangeable filters (Schott, Clichy, France) and an air–hydrogen flame.

### 2.2. Reagents and standards

Methanol and sodium ethanoate were purchased from Prolabo. Hydrochloric, nitric and ethanoic acids were obtained from Merck, and isooctane from Fluka. The deionised water used was 18 MΩ (Millipore system).

Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem. The working solution was made daily by dissolving 0.02 g in 1 ml of deionised water and then storing at +4°C in the dark.

Glassware was rinsed with deionised water, decontaminated overnight in 10% (v/v) nitric acid solution and then rinsed again.

Organotin standards stock solutions (1000 mg $l^{-1}$ as tin) monobutyltin trichloride (MBT, 95%), dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 96%), monophenyltin trichloride (MPhT, 98%), diphenyltin dichloride (DPhT, 96%), triphenyltin chloride (TPhT, 95%), monooctyltin trichloride (MOcT, ≥90%), dioctyltin dichloride (DOcT, ≥90%), trioctyltin chloride (TOcT, 100%) and tricyclohexyltin chloride (TcHexT, 90%) (Aldrich, St. Quentin Fallavier, France) were prepared in methanol. Tripropyltin chloride (TPrT, 98%) was obtained from Strem. Stored at +4°C in the dark, they were stable for 1 year [13,14].

Working standards were obtained by dilution in water (weekly for 10 mg $l^{-1}$ and daily for 100 μg $l^{-1}$). They were also stored in the dark at +4°C.

### 2.3. Reference material and samples

The validation of the method was performed using a certified reference material: PACS 2, sediment from the National Research Council of Canada (NRCC) certified for its TBT and DBT content. It has an indicative value for MBT and was spiked with MPhT, TPhT, TcHexT and TOcT.

Freshwater sediment from Amsterdam (The Netherlands) and different French samples (river water, wastewater, sewage sludge, sand and oyster) were also analysed. For reasons of confidentiality, the sampling locations are not indicated.

### 2.4. Analytical procedure

#### 2.4.1. Derivatisation and analysis

For waters: a 100-ml aliquot of water sample was directly introduced into the derivatisation reactor. Ethylation was carried out using $NaBEt_4$ (0.1 to 0.3 ml of a 2%, w/v, solution) in sodium ethanoate–ethanoic acid buffer (pH 4.8). A 0.5-ml volume of isooctane was added and the mixture was shaken at 420 rpm for 30 min. Then, 2 to 4 μl of isooctane was directly injected into the GC–PFPD system.

For solid samples: the extraction step was previously optimised and described. It was performed before the derivatization step, as follows: (i) 1 g of wet oyster was extracted in 1 ml methanol+5 ml 0.1 *M* HCl in methanol by ultrasonic stirring for 1 h [15], (ii) a 0.5–2 g sample of freeze–dried sediment or sand was extracted in 20 ml of glacial ethanoic acid by mechanical stirring for 12 h [6,16] and (iii) 2 g of wet sewage sludge was extracted in 10 ml of glacial ethanoic acid by mechanical stirring for 12 h [17].

#### 2.4.2. Quantitation

Tripropyltin was used as internal standard. The TPrT relative chromatographic responses of butyl-, phenyl-, octyl- and tricyclohexyltin were calculated from standard solutions prepared in deionised water. The internal standard procedure was then applied to two to five aliquots of 100-ml samples or 0.5 to 2 ml of acidic extract (solid matrices).

#### 2.4.3. Optimisation

Optimisation was performed with aqueous standard solutions containing 100 ng Sn $l^{-1}$ of the 12 organotins (four butyl-, three phenyl-, three octyltins, tricyclohexyltin and tripropyltin).

The experimental design method was used as described by Goupy [18,19] and Sado and Sado [20]. According to our analytical experience, complete designs at two levels (noted "−1" and "+1") were used to research the influent factors [17,21].

Each experiment was performed once, except the experiment at the centre (noted ''0''), which was carried out six times. This procedure was used in order to at once determine the experimental precision by the standard deviation ($\sigma$) of the ''0'' and adjust the different sets of results obtained over several days.

The effects of the factors and interactions and their corresponding precision were evaluated by matrix calculation according to:

$$\mathbf{A} = (\mathbf{X}^t\mathbf{X})^{-1}\mathbf{X}^t; \mathbf{Y} \quad (1)$$

$$\delta\mathbf{A} = t[\sigma^2(\mathbf{X}^t\mathbf{X})^{-1}]^{1/2} \quad (2)$$

with: $\mathbf{A}$ = matrix of the effects; $\delta\mathbf{A}$ = matrix containing the precision of each effect; $\sigma$ = standard deviation of the experiment ''0''; $\mathbf{X}$ = matrix of the experiments; $\mathbf{X}^t$ = transpose of $\mathbf{X}$; $\mathbf{X}^{-1}$ = inverse of $\mathbf{X}$; $\mathbf{Y}$ = matrix of the responses obtained experimentally; $t$ = Student coefficient (interval of confidence = 95%).

A factor $i$ or an interaction $ij$ was considered as significant if its effect was higher than its respective precision: $a_i > \delta a_i$ or $a_{ij} > \delta a_{ij}$.

For the optimisation designs, the determination of each model was made by an iterative approach, on the basis of the polynomial equation:

$$Y = a_0 + \sum_{i=1}^{n} a_i X_i + \sum_{i=1,j=1}^{n} a_{ij} X_i X_j + \sum_{i=1}^{n} a_i X_i^2 \quad (3)$$

with $n$ = number of significant factors; $Y$ = mathematical representation of the response studied; $X_i$ = representation of the factor $i$ in the coded experimental field (levels $-1$ to $+1$); $a_0$ = mean of the $N_T$ experiments of the experimental design; $a_i$ = effect of the factor $i$; $a_{ij}$ = effect of the interaction between the factors $i$ and $j$; $a_{ii}$ = square of the effect of the factor $i$.

First-order model (including the only first three terms of Eq. (3)) was firstly proposed and compared with experimental results. Generally, such a multilinear model cannot correctly fit the response $Y$. So, it was necessary to use a composite design. Complementary experiments were made using two levels $\pm\alpha = N^{1/4}$ ($N$ = number of experiments in the initial design, $\alpha > 1$). The $N_T$ (initial + complementary) experiments allows a second-order model (complete Eq. (3)) was proposed. This quadratic model was then adjusted by stepwise (i.e., iterative calculation allowing the progressive removal of low-significant or insignificant effect $a_i$, $a_{ij}$ or $a_{ii}$). Step by step, the analysis of the variance was made according to Snedecor (95%) as previously described [17,19–21]. This statistical approach allows at once the determination of the global significance of each model and the detection of any possible systematic error. The stepwise process gives a precise adjustment of a model to the experimental.

The determination of the optimal operating conditions was made by the combination of two methods of optimisation: from the model previously established, a laboratory-made algorithm of research of the optimal zone is used [17] and then, the plotting of the iso-response curves in this zone is performed. This approach gives a more precise view of the variations of the responses even in case of elevated number of influent factors (i.e., $>2$).

#### *2.4.4. Determination of the analytical performances*

Repeatability is a critical factor to illustrate and evaluate the stability of emissions. It was determined by performing 10 consecutive manual injections of 2 μl of standard solution containing butyltins and phenyltins in deionised water (100 ng Sn $l^{-1}$). Tripropyltin was used as internal standard (100 ng Sn $l^{-1}$). The relative standard deviations (RSDs) were evaluated from the relative peak area measurement.

The linear range of detection was established by injection of 2 μl standard solution in deionised water using concentrations of 0 to 1000 ng Sn $l^{-1}$. Calibration curves were plotted using the values of relative peak area.

The limits of detection (LODs), defined as the signal equal to three times the standard deviation ($3\sigma$) of the baseline noise were determined for butyl- and phenyltins for both emission modes (Sn–C and Sn–H) and both detection methods (FPD and PFPD).

## 3. Results and discussion

### *3.1. Optimisation of the detection*

Considering the operation of PFPD, the three gas

flow-rates were taken as factors in two composite designs including 15 experiments ($N=8$ experiments of initial design + 1 experiment ''0'' + 6 complementary experiments), each design referring to a detection wavelength (Sn–H and Sn–C). The definition of the experimental field is presented Table 1.

In order to obtain a quantitative and qualitative adjustment of the flame, the following responses were chosen:

(i) The mean peak heights of all the organotins studied, noted, respectively $\bar{h}$(Sn–H) and $\bar{h}$(Sn–C), evaluating the sensitivity of the detection.

(ii) The mean resolution between the closest peaks (i.e., MBT, TPrT, DBT, MPhT and TBT), noted, respectively, $\overline{R_s}$(Sn–H) and $\overline{R_s}$(Sn–C), evaluating the peak tailing and widening. These phenomena are well known in PFPD and are attributed to the limited volatility of the tin combustion products. Raising the temperature of the detector to 350°C and using higher gas flow-rates to help the volatilisation of the organotins can reduce these disturbances [22].

The experiments concerning each initial design were carried out during 2 days. The effects of gas flow-rates and of interactions evaluated using Eqs. (1) and (2) show that the influence of factors on the peak heights and resolutions is the same: when $\overline{R_s}$ is improved, peaks become higher. So, later on, only the resolution is taken into consideration. The three gas flow-rates have significant effects on both the resolutions. Considering experiment ''0'', it is obvious that the studied responses have non-linear variations in the experimental field previously defined (Table 1). So, two composite designs were performed. Their results and those obtained from the initial designs allow the following quadratic models based on Eq. (3) to be proposed:

$$\overline{R_s}(\text{Sn–H}) = 4.02 + 0.05\,(\text{Air1}) + 0.08\,(\text{Air2}) + 0.06\,(\text{H}_2) + 0.20\,(\text{Air1}\cdot\text{H}_2) + 0.11\,(\text{Air2}\cdot\text{H}_2) - 0.08\,(\text{Air1})^2 - 0.13\,(\text{H}_2)^2;\ (R^2 = 0.9945)$$

$$\overline{R_s}(\text{Sn–C}) = 4.75 + 0.67\,(\text{Air1}) + 0.31\,(\text{Air2}) + 0.37\,(\text{H}_2) - 0.64\,(\text{Air1})^2 - 0.58\,(\text{H}_2)^2;\ (\text{R}^2 = 0.9977)$$

The validation step of these models was made according to the comparison model/experimental and study of the variance. The mean differences between experimental and calculated results are, respectively 0.10 [$\overline{R_s}$(Sn–H)], and 0.8 [$\overline{R_s}$(Sn–C)]. They are $\leq 2\sigma$ (with $\sigma$ = the standard deviation of experiment ''0'' made six times; $\sigma$ is, respectively, equal to: 0.05 and 0.4). The correlation coefficient ($R^2$) of each model is higher than 0.994; that means that 99.4% of the variations of the responses can be explained by the models. The analysis of variance in an interval of confidence of 95% also shows that each model is very significant and without any systematic error. Whole of these results allows the validation of the models proposed.

The modelling allows the prediction of the values of resolutions according to the adjustment of the flow-rates. The optimisation step leads to the iso-response curves presented in Fig. 2a (Sn–H) and Fig. 2b (Sn–C). These curves show that the variations of the both resolutions have a maximum clearly located in the experimental field (black areas on the figures).

The different optimal zones are summarised in

Table 1
Optimisation of the detection: experimental field studied and optimal operating conditions[a]

| No. | Factors, Flow-rates (ml min$^{-1}$) | (a) Sn–H | | | | | (b) Sn–C | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Levels | | | Optima, $R_s$ | Operating adjust. | Levels | | | Optima, $R_s$ | Operating adjust. |
| | | $-\alpha$ | 0 | $+\alpha$ | | | $-\alpha$ | 0 | $+\alpha$ | | |
| 1 | Air1 | 8 | 19 | 30 | 27 | 25 | 8 | 19 | 30 | 22 | 22 |
| 2 | Air2 | 6 | 25 | 45 | 39 | 30 | 6 | 18 | 30 | 30 | 30 |
| 3 | $H_2$ | 13 | 32 | 50 | 41 | 30 | 13 | 21 | 30 | 23 | 25 |

[a] $\alpha = 1.68$.

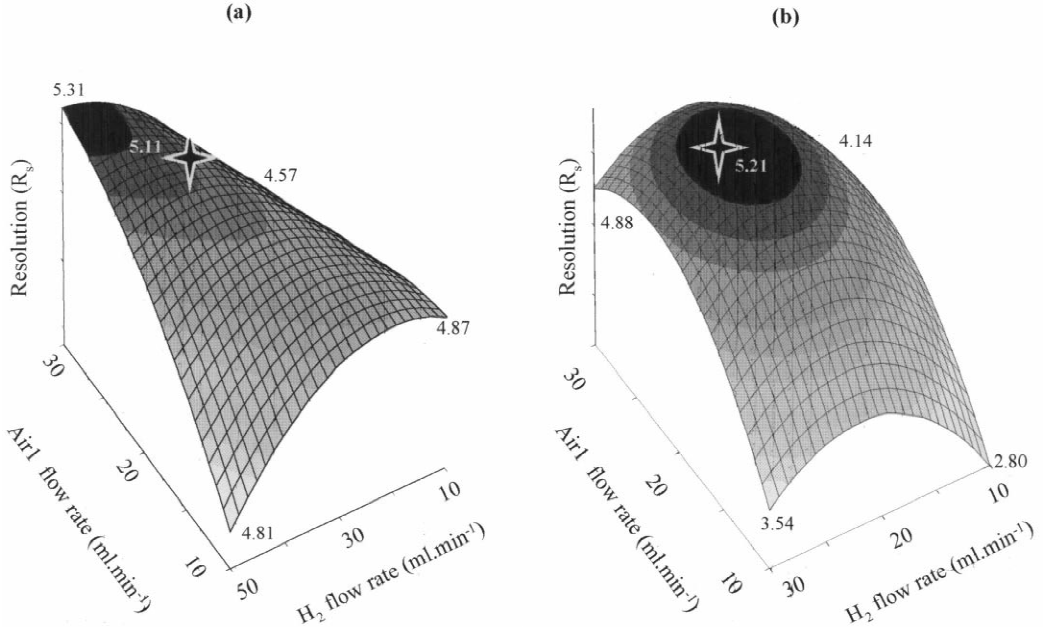


Fig. 2. Optimisation of the detection: response curve of the resolution factor ($R_s$) for (a) Sn–H emission, (b) Sn–C emission.

Table 1. The operating conditions were defined considering these zones (maximum resolutions) but also according to the possible electronic adjustments of $H_2$ and Air2 flow-rates (maximum value: 30 ml min$^{-1}$). They are given in the last columns of Table 1. They correspond to the stars shown on the iso-response curves (Fig. 2).

### 3.2. Analytical performances

The analytical performances are summarised in Table 2. A comparison between the results obtained using classical FPD with a 611±20 nm optical filter and those obtained by PFPD has been made.

#### 3.2.1. Limits of detection, repeatability and linearity

The present LODs obtained using Sn–H emission are 6- to 15-times lower than the FPD ones. Concerning PFPD, compared to Sn–H emission, Sn–C emission LODs are decreased three- to five-times. So, the LODs can be improved by a total of 25- to 50-times, the relative LODs ranging from 0.09

Table 2
Analytical performances

| Compound | Absolute limits of detection (LODs) (pg) | | | Repeatability, RSD (%) ($n=6$) | | Linearity from LOD to (pg) | |
|---|---|---|---|---|---|---|---|
| | FPD, Sn–H | PFPD | | FPD | PFPD | FPD | PFPD |
| | | Sn–H | Sn–C | | | | |
| MBT | 5.5 | 0.48 | 0.10 | 5 | 3 | 500 | 600 |
| DBT | 5.1 | 0.35 | 0.07 | 8 | 7 | 600 | 800 |
| TBT | 4.3 | 0.30 | 0.07 | 8 | 7 | 600 | 800 |
| TeBT | 3.3 | 0.57 | 0.14 | 7 | 8 | 600 | 800 |
| MPhT | 9.9 | 1.61 | 0.38 | 8 | 9 | 500 | 600 |
| DPhT | 4.1 | 0.30 | 0.07 | 10 | 6 | 600 | 800 |
| TPhT | 5.9 | 0.38 | 0.11 | 12 | 8 | 600 | 800 |

(DBT, TBT and DPhT) to 0.48 (MPhT) ng Sn $l^{-1}$ in water. Fig. 3 presents typical chromatograms obtained for an oyster sample, using FPD and PFPD; this comparison, made from a complex environmental sample, illustrates the high PFPD sensitivity.

It is difficult to establish other comparisons concerning LODs of PFPD because only one report by Jacobsen et al. on organotin compounds measured by this new detection method is available in the literature [10]. Moreover, these authors gave only absolute LODs for tetrasubstituted compounds: 0.3, 0.4, and 0.2 pg Sn for tetrapropyltin, tetraphenyltin and tetrabutyltin, respectively, using Sn–C emission. These values are similar to ours.

The mean repeatability of the detection remains similar when FPD or PFPD (Sn–H and Sn–C) is used: 8 and 7%, respectively. However, it can be noted that in case of DPhT and TPhT the peaks obtained are more repeatable when PFPD is used.

The range of linearity seems a little larger when

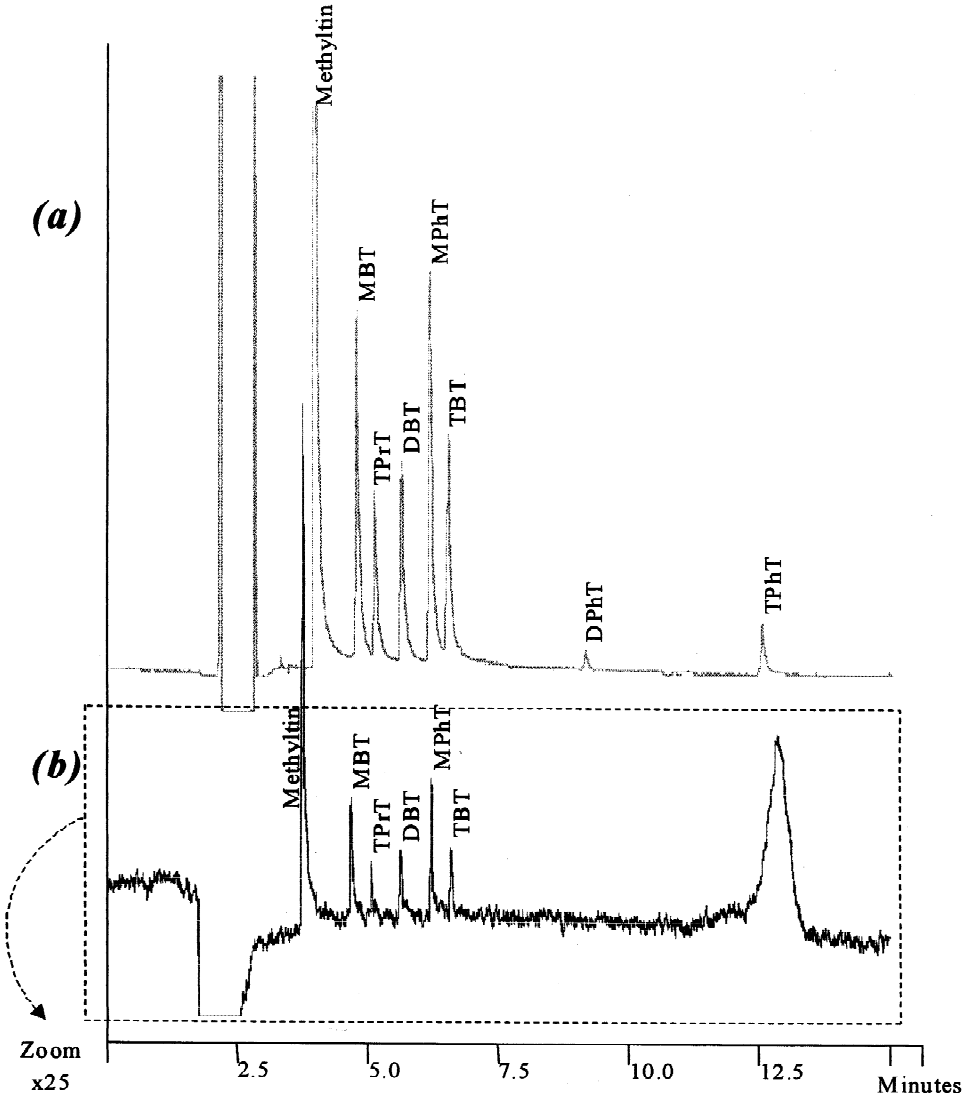


Fig. 3. Typical chromatograms of an oyster sample obtained using (a) PFPD (Sn–C: optical filter at 390 nm, temperature 350°C) and (b) FPD [interferential filter at (611±20) nm, temperature 290°C].

PFPD is used (LOD 600 or 800 pg). However, there is no significant difference between these two flame photometers. Although this range remains shorter than those of other detection methods such as atomic emission spectrometry or inductively-coupled plasma mass spectrometry [23], it is sufficiently large to perform organotin determination at very different pollution levels, as the different examples show, later on.

### *3.2.2. Selectivity*

The two main potentially interfering elements of tin detection are sulphur and phosphorus [24,25]. Previously, studies have shown that only sulphur compounds have been identified as interfering during GC–FPD analysis [7,26]. In most of cases, this interference was not a problem for butyl- and phenyltin determination in environmental samples. Unfortunately, when sludge or sediments (sampled close to an urban sewer) were analysed, the simultaneous presence of many different organotins (methyl-, butyl-, phenyl-, octyl- and hexyltins) and sulphur compounds appeared as a drawback. The selectivity of FPD is then not sufficient.

PFPD is presented as a very highly selective detection methods. Moreover, the possible use of two different wavelengths associated with gate delay and width of detection significantly decreases the potential risk of interference. A monitoring of organotins in urban sewage sludge performed during some months allowed the control of the selectivity: no interfering peak was ever observed on GC–PFPD chromatograms. From other environmental samples such as oysters, underground waters or freshwater sediment, the same conclusion could be established. From Fig. 3, the presence of an interfering peak at the same retention time as TPhT, on the FPD chromatogram can still be noted, whereas no interference appears when PFPD is used. So, the first applications carried out seem to demonstrate the effective highest selectivity of PFPD compared to classical FPD. This is important especially considering that Sn–C emission was systematically used for these analyses.

## *3.3. Applications*

After optimisation, this new analytical optimised process was validated by the analysis of a certified reference material and environmental samples.

### *3.3.1. Certified reference material and spiked river water*

The PACS 2, sediment certified reference material, was analysed by GC–PFPD. This sediment is certified for its TBT and DBT contents: tributyltin ($0.98\pm0.13$) μg Sn $g^{-1}$ dry mass and dibutyltin ($1.09\pm0.15$) μg Sn $g^{-1}$ dry mass.

It contains also 0.30 μg Sn $g^{-1}$ dry mass as monobutyltin (indicative value). Validation of the analytical method for phenyl-, octyl- and hexyltin compounds was investigated by spiking this sediment. Table 3 shows the results obtained using the two emissions. The concentrations found satisfactori-

Table 3
Determination of organotin compounds in PACS 2 spiked with MPhT, TPhT, TOcT and TcHexT and in river water spiked with different organotin compounds

| Compound | PACS 2: Concentrations (μg Sn $g^{-1}$ dry matter) | | | Spiked river water (ng Sn $l^{-1}$) | | |
|---|---|---|---|---|---|---|
| | Found with GC–PFPD | | **Certified** or spiked | GC–FPD | GC–PFPD, Sn–C | Spiked (±10) |
| | Sn–H | Sn–C | | | | |
| MBT | 0.33±0.02 | 0.28±0.04 | 0.30±0.01 | 124±14 | 147±21 | 145 |
| DBT | 1.09±0.12 | 1.19±0.03 | **1.09±0.02** | 120±4 | 130±3 | 120 |
| TBT | 1.09±0.12 | 0.95±0.09 | **0.98±0.01** | 163±21 | 194±30 | 180 |
| DPht | | | | 130±47 | 140±18 | 120 |
| MPhT | 0.53±0.06 | 0.54±0.10 | 0.50±0.01 | | | |
| TPhT | 0.20±0.01 | 0.21±0.01 | 0.20±0.01 | 200±50 | 243±58 | 180 |
| TcHexT | 0.31±0.07 | 0.24±0.02 | 0.30±0.01 | 196±9 | 187±29 | 180 |
| DOcT | | | | 119±32 | 124±6 | 120 |
| TOcT | 0.31±0.01 | 0.25±0.05 | 0.30±0.01 | 164±21 | 180±33 | 180 |

ly correlate with the spiked and certified concentrations.

A river water, spiked with 120 to 180 ng Sn $l^{-1}$ of several organotins, was also studied. The water was sampled in an urban area. The analysis was performed, under routine conditions, using both GC–FPD and PFPD in order to compare the performances of these two methods. Table 3 summarises the results. The concentrations found using both photometers correlate well. The standard deviations, calculated from four different analyses made by two different analysts, evaluate the precision of the whole analytical process (i.e., from derivatization to GC analysis). So, the RSDs obtained using PFPD ranged from 2.5 (DBT) to 24% (TPhT) and the respective mean RSDs [12% (PFPD) and 17% (FPD)] are logically equivalent. This precision is very satisfactory considering the routine operating conditions.

### 3.3.2. Environmental samples

Sewage waters and sludge were monitored in an urban treatment plant. The values obtained are presented in Table 4. The systematic presence of butyl- phenyl- and octyltins in sewage water and sludge can be noted. The concentrations can vary from 1 to about 100 ng Sn $l^{-1}$ in water and from 6 to about 250 ng Sn $g^{-1}$ dry matter (which corresponds to 1–50 ng Sn $g^{-1}$ wet matter) in sludge. This range of concentrations shows the interest in having a sensitive analytical method for monitoring studies. This is particularly important considering the project of international standard requiring the analyse of butyl-, phenyl- and octyltins from 5 ng $l^{-1}$ in waters.

Table 5
Routine analyses of organotin compounds in industrial wastewater using GC–PFPD

| | ng Sn $l^{-1}$ | | |
|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 3 |
| MBT | 3.9±0.3 | 2.15±0.09 | 1.92±0.09 |
| DBT | 0.7±0.2 | 0.42±0.08 | 0.4±0.1 |
| TBT | 1.3±0.2 | 0.20±0.06 | nd |
| TeBT | 4.0±0.9 | 6.6±0.9 | 11±2 |
| MPhT | nd | 2.8±0.2 | nd |
| DPhT | 0.7±0.1 | 0.5±0.1 | 0.30±0.03 |
| TPhT | 0.6±0.1 | 0.5±0.1 | 0.49±0.06 |
| MOcT | 0.25±0.06 | 0.49±0.05 | nd |

nd: Not detected, i.e., <LOD.

Other examples of routine analyses performed using GC–PFPD are presented Tables 5 and 6.

Low organotin pollution levels are detected (0.2–11 ng Sn $l^{-1}$) in industrial wastewater samples. Nevertheless, the most toxic trisubstituted butyl- and phenylated species are present. In the same way, sands and oysters appear contaminated. The TBT concentration in oysters is high and can be a potential risk for humans by consumption. The analytical precision is satisfactory (7–22% RSDs for concentrations <5 ng Sn $l^{-1}$ or 5 ng Sn $g^{-1}$) considering at once the low concentrations found and the complexity of the samples. These results underline the necessity of regular organotin control. In this

Table 4
Monitoring of organotin compounds in an urban treatment plant

| | ng Sn $l^{-1}$ | | Sludge[a], ng Sn $g^{-1}$ dry matter |
|---|---|---|---|
| | Influent (raw water) | Effluent | |
| MBT | 77±7 | 41±5 | 239±2 |
| DBT | 12.6±0.4 | 2.7±0.2 | 81±8 |
| TBT | 8.9±0.9 | 1.4±0.1 | 54±5 |
| TeBT | 1.0±0.1 | 3.0±0.2 | 23±1 |
| MPhT | 2.6±0.3 | 3.6±0.4 | – |
| DPhT | 2.1±0.3 | 3.2±0.3 | 54±2 |
| TPhT | nd | nd | 6±1 |
| MOcT | 15±2 | 4.8±0.4 | 5.7±0.8 |
| DOcT | 4.5±0.4 | 3.1±0.3 | 19.0±0.5 |
| TOcT | nd | nd | 12.4±0.2 |

[a] Mean moisture content: 90%.
nd: Not detected, i.e., <LOD.

Table 6
Routine analyses of organotin compounds in sands and oysters using GC–PFPD

| | ng Sn $g^{-1}$ dry matter (1)[a] | | ng Sn $g^{-1}$ dry matter (2)[a] | |
|---|---|---|---|---|
| | Sand 1 (estuarine) | Sand 2 (estuarine) | Oyster (estuarine) | Oyster (port) |
| MBT | 18±3 | 30±1 | 291±30 | 138±5 |
| DBT | <0.45 | 2.0±0.3 | nd | nd |
| TBT | 12±3 | 3.0±0.5 | 57±7 | 132±20 |
| MPhT | nd | 3.0±0.6 | nd | nd |

[a] Mean moisture content: (1) 23%, (2) 87%.
nd: Not detected, i.e., <LOD.

way, considering the highest sensitivity of PFPD compared to FPD, routine analyses become more reliable by GC–PFPD.

## 4. Conclusion

The experimental designs have allowed the accurate determination of the influence of the three gas flow-rates on PFPD. According to the emission used (Sn–H or Sn–C), the modelling and optimisation of the resolution and peak areas have lead one to precisely adjust these flow-rates. These operating conditions are quite different from the recommended conditions given by Varian. Optimised PFPD allows the LODs to be decreased 25- to 50-times compared to those of classical FPD. So, it is possible to quantify organotins below 1 ng Sn $l^{-1}$ in waters and up to 1 ng Sn $g^{-1}$ in more complex solid matrices. The first applications performed show that PFPD is a both a highly sensitive and selective detection method. Considering its low cost and the reduced consumption of hydrogen and air in the flame, this new generation of flame photometer appears suitable for routine organotin analysis in the environment and monitoring in the water cycle.

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