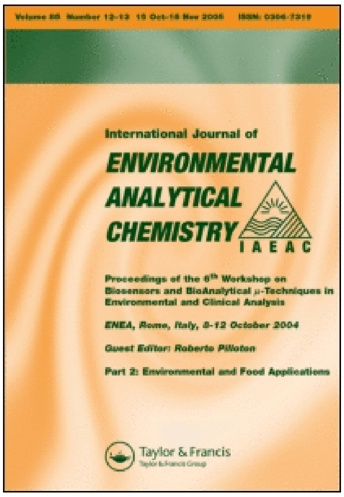

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Evaluation of Non-Linear FPD Response†

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A new model of Flame Photometric Detector (FPD) response has been developed and applied for FPD signal evaluation. It has been shown that the second order polynomial fit quantitatively describes the detection mechanism and that this is the only relevant procedure for detector signal evaluation. Detector characteristics, such as sensitivity, linearity, lower detection limit and selectivity have been quantitatively described and their limited meaning shown. Selectivity of detector depends on its construction and should be selected as high as possible. The same holds for separation efficiency of the gas chromatographic system used. It is not recommended to use FPD as a monitor of the sulphur content in the air.

KEY WORDS: FDP signal evaluation, Sulphur, aie.

INTRODUCTION

Since its introduction in 1961[1] the Flame Photometric Detector (FPD) belongs to standard GC instrumentation. The application field is very broad and covers selective measurements of sulphur, phosphorus, halogens, cyano-group, organo-metallics, etc. (see for example)[2-11].

The constructional development of the FPD is characterized by overcoming problems of high quenching rate and an improvement of selectivity of measurement.

Separation of burning and excitation chambers[12,13] led to the construction of a dual flame FPD, in which quenching effects are significantly suppressed.[14,15]

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The selectivity of measurement was improved by selection of filter wavelength where coincidence with other excited species is very small, and by application of a light guidance rod to suppress light dispersion.[16–18]

But the most critical part of the FPD operation is related to detector signal evaluation. The FPD does not show linear response for sulphur, but response is a power function of effluent concentration. There are many papers relating the power function to a form of chemical boundary of sulphur containing compounds (for example),[2,19,20] as well as phosphorus containing compounds.[21] There are original papers relating exponent value to experimental parameters of FPD operation such as flow pattern[14,20,22,23] and burner configuration.[24,26]

Practical problems with non-linear detector response led to different linearization procedures, such as addition of a certain amount of detector sensitive compound into a make-up gas[27,28] and/or electronically calculating square root of response. Evaluation of all these "linearized" responses lead to significant errors when the parameters are not precisely known.[29–37] It will be shown later that all problems with evaluation of FPD signal originate from inadequate models of FPD response.

The subject of this paper is the formulation and discussion of a new FPD response model for quantitative analysis.

THEORETICAL AND DISCUSSION

Reaction mechanism

The FPD measures the intensity of molecular emission of the fluorescence or chemiluminiscence of hetero-atoms in the effluent molecules. The main process taking place in an FPD under the conditions of a cold flame (excess of hydrogen) can be described by the following schematics:

$$\mathrm{P(S)ORG} + h\nu \rightarrow \mathrm{HPO^*(S_2^*)} + \mathrm{ORG} \qquad (1)$$

$$\mathrm{HPO^*(S_2^*)} \rightarrow \mathrm{HPO(S_2)} + h\nu' \qquad (2)$$

$$\mathrm{HPO^*(S_2^*)} + Z \rightarrow \mathrm{HPO(S_2)} + Z' \qquad (3)$$

where P(S)ORG is effluent compound containing phosphorus or sulphur and $\mathrm{HPO^*(S_2^*)}$ are exited molecular forms of phosphorus and sulphur.

Reaction 1 leads to excitation of hetero atoms. Returning to their ground state can proceed by reactions 2 and/or 3 resp., while for FPD measurement only radiative de-excitation (Eq. 2) is of interest. Reaction 3 leads to non-radiative de-excitation, so-called quenching.

Formation of the sulphur excited state goes through a few intermediate states as shown below[32]

$$S+S+M \rightarrow S_2^* + M \tag{4}$$

$$S_2^* \rightarrow S_2 + hv \tag{5}$$

$$S_2 + H + H \rightarrow S_2^* + H_2 \tag{6}$$

and after combustion[33]

$$^1SO_2 + M \rightarrow {}^3SO_2^* \tag{7}$$

$$^3SO_2^* \rightarrow SO_2 + hv \tag{8}$$

It should be kept in mind that the FPD measures chemiluminiscence, thus a low excitation level. This requires low flame temperature, realized for example by effective cooling with an excess of hydrogen and of carrier gas. Thus the FPD signal differs for nitrogen and helium as carrier gas. Excess of hydrogen additionally creates a reduction atmosphere in the flame and thus enables a maximum yield for reactions 4 to 6.

FPD signal

The signal of an FPD to sulphur is determined by the reaction mechanism. Under given conditions the molecular form of sulphur can be excited more than once. This leads to the non-linear response of FPD.

Recently the detector response to sulphur was formulated in the form of power function; $S^{FPD} = ka \cdot C^p$, where C is the concentration of the effluent and p is so-called detector linearity factor. This model is much simplified and does not take into account interactions of sulphur atoms with non-sulphur atoms, simultaneously presented in the effluent and/or burner gases.

The new model of FPD response takes into account the emission of all excited forms (see also).[30] For derivation of the detector signal the following assumptions have been made

—the response to the sulphur atom is quadratic,

—the response to the phosphorus as well as to the carbon atoms is linear,

—under all circumstances the resulting signal is the sum of all contributions, among them those from effluent and from background.

Thus for the sulphur signal of the FPD holds;

$$S_s^{FPD} = k_{ss}(C_{bs} + C_{es})^2 + k_{sc}(C_{bc} + C_{ec}) + k_{sp}C_{ep} \tag{9}$$

where

k_{ss} is the sensitivity for sulphur atom
k_{sc} is the sensitivity for carbon atom
k_{sp} is the sensitivity for phosphorus
all measured in sulphur mode (usually 355 ± 60 nm)

C are the concentrations in background (*b*) and/or effluent (*e*) for sulphur (*s*), carbon (*c*) and phosphorus (*p*) resp. (for example C_{bs} is the sulphur background concentration due to impurities in a carrier gas, stationary phase bleed, etc.).

Since the particular concentrations of atoms in an effluent are interrelated by means of fraction ratio, it follows

$$C_{es} = xC_e \tag{10}$$

$$C_{ep} = yC_e \tag{11}$$

$$C_{ec} = (1 - x - y)C_e \tag{12}$$

Substitution of Eqs. 10–12 in Eq. 9 will result in:

$$S_s^{FPD} = k_{ss}(C_{bs} + C_e)^2 + k_{sc}(C_{bc} + (1 - x - y)C_e) + k_{sp}yC_e \tag{13}$$

Equation 13 can be simplified, knowing the ratio of sensitivities (see below selectivity). If we assume that the impurities concentration (background level) are constant within the analysis, Eq. 13 is transformed in an equation of the second order polynome. It holds

$$S_s^{FPD} = k_{ss}(\varphi_1 C_e^2 + \varphi_2 C_e + \varphi_3) \tag{14}$$

where the parameters have the following meaning:

$$\varphi_1 = x^2 \tag{15}$$

$$\varphi_2 = 2xC_{bs} + (1 - x - y)(k_{sc}/k_{ss}) + y(k_{sp}/k_{ss}) \tag{16}$$

$$\varphi_3 = C_{bs}^2 + C_{bc}(k_{sc}/k_{ss}) \tag{17}$$

Equation 14 demonstrates "problems" of FPD signal evaluation. The plot of Eq. 14 in LOG/LOG coordinates shows the curvature for low effluent concentrations, which significantly depends on carrier gas impurities, bleed of stationary phase, etc. (C_{bs} term). Equation 14 also indicates the so-called sensitized mode of the FPD: it is the increase of sulphur signal in the presence of sulphur in the background (an effect of C_{bs} to parameters φ_2 and φ_3 resp.).

For the phosphorus signal of flame photometric detector the similar derivation (Eq. 9) could be carried out. It holds

$$S_p^{\mathrm{FPD}} = k_{ps}(C_{bs} + C_{es})^2 + k_{pc}(C_{bc} + C_{ec}) + k_{pp}C_{mp} \tag{18}$$

where

k_{ps} is the sensitivity for sulphur atom
k_{pc} is the sensitivity for carbon atom
k_{pp} is the sensitivity for phosphorus
all measured in phosphorus mode (usually 525 ± 15 nm).

Substituting for particular atom concentrations the effluent concentration (Eqs. 10 to 12), equation for phosphorus signal is as follows

$$S_p^{\mathrm{FPD}} = k_{pp}(\alpha_4 C_e^2 + \alpha_5 C_e + \alpha_6) \tag{19}$$

where parameters of Eq. 19 are

$$\alpha_4 = x^2(k_{ps}/k_{pp}) \tag{20}$$

$$\alpha_5 = 2xC_{bs}(k_{ps}/k_{pp}) + (1 - x - y)(k_{pc}/k_{pp}) + y \tag{21}$$

$$\alpha_6 = C_{bs}^2(k_{ps}/k_{pp}) + C_{bc}(k_{pc}/k_{pp}) \tag{22}$$

From the Eq. 19 it can be seen that because parameter α_4 (Eq. 20) is much smaller than one $\alpha_4 \ll 1$ (sensitivity to phosphorus in phosphorus mode is much higher than sensitivity to sulphur in phosphorus mode $k_{ps}/k_{pp} \ll 1$), the curvature of the phosphorus signal will be generally small, but significantly for compounds with high sulphur content ($x \rightarrow 1$) and for detector constructions with low selectivity.

DETECTOR CHARACTERISTICS

Detector sensitivity

The detector sensitivity is defined as the ratio of detector signal to effluent concentration (output/input ratio). Applying Eq. 14, the sulphur sensitivity in sulphur mode is described according next equation.

$$k_{ss}=\frac{S_s^{\mathrm{FPD}}}{\varphi_1 C_e^2+\varphi_2 C_e+\varphi_3} \qquad (23)$$

Equation 23 expresses the dependency of FPD sulphur sensitivity on experimental parameters, such as used compound (fraction x in φ_1), purity of operational gases and background level during detection (φ_2 and φ_3), column packing (φ_3), etc. As it can be seen, the specification of the sensitivity of FPD is meaningless, if the experimental conditions and thus values of parameters φ_1 to φ_3 are not specified.

Only under the condition $\varphi_2=0$ and $\varphi_3=0$ (it corresponds to pure sulphur compound and zero background signal) the detector sensitivity k_{ss} can be evaluated in graphical form of LOG/LOG coordinates. Only under these conditions is the intercept equal to ($\log k_{ss}$). Because these conditions are never fulfilled, the specification of FPD sensitivity should be omitted.

The FPD sensitivity for the phosphorus mode is derived from Eq. 19 and has a form similar to Eq. 23. Because of the selectivity ($k_{ps}/k_{pp}\ll 1$), the quadratic terms in Eqs. 19, 20 and 22 are very small and the phosphorus signal will follow quasi linear dependency on effluent concentration. Under these conditions the LOG/LOG plot could be used for sensitivity evaluation, but the value obtained does not have general meaning.

Detector linearity

Detector linearity has been understood as an exponent of power function. This understanding of the linearity led to different linearization procedures and construction of hardware or software linearizers for FPD. But this concept is not relevant for flame photometric detector.

It generally holds that FPD is a non-linear detector and its signal linearization on a power fit base should be omitted. Figure 1 shows detector signals for selected combinations of interfering concentrations, as given in Eq. 9. Table I shows values of correlation coefficients and exponent values of forced power functions over 2.5 decades. The exponent values have been calculated downward, starting at highest concentration value (50) and adding point after point (exponent and corr. coeff on line

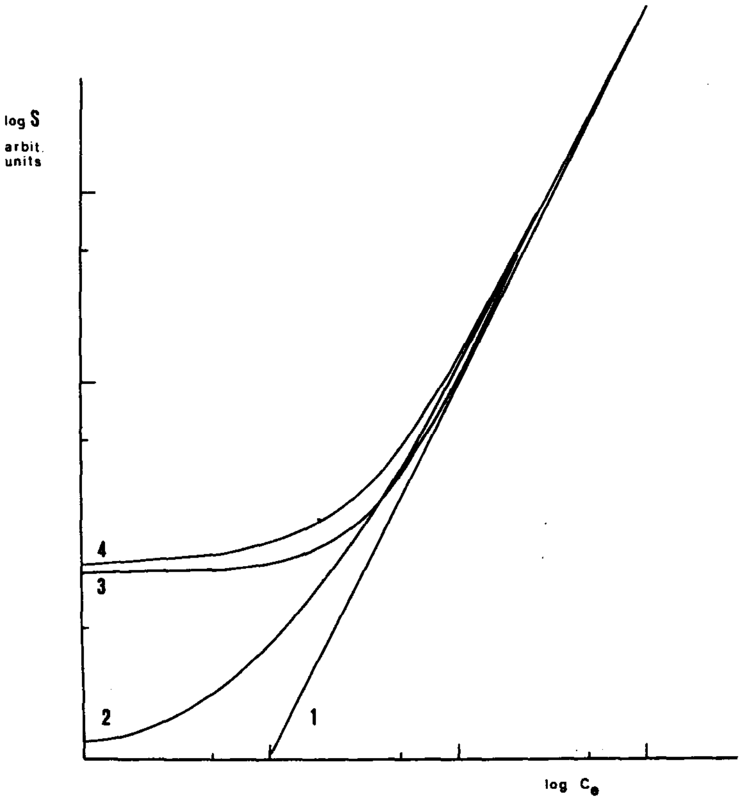

FIGURE 1 FPD sulphur chanel response for different interaction levels (see comments Table I).

10 corresponds to the power fit between points 50 to 10, line 0.01 to the points 50 to 0.01). The curve 1 (column 1 in Table I) simulates the elution of pure sulphur compound with 1% contribution of non-sulphur compound. As shown, the evaluation of this type of signal could be reduced to the power function. It should be mentioned that in practice there would not be such conditions.

The curve 2 (column 2 in Table I) simulates detection of sulphur on a constant sulphur background (for example make-up gas dropped with SO_2). The response curve is significantly curved for small effluent concentrations and the exponent changes between 2.0 and 1.5.

Curve 3 (column 3 in Table I) shows an example of sulphur measurement on relatively high background of non-sulphur compounds (for example monitoring of air pollution). It is evident that the detector

TABLE I

Exponents ρ ("linearity factor") and regression coefficients r of forced power fit for different signals (1 to 4); see text.

	1		2		3		4	
amount	ρ	r^2	ρ	r^2	ρ	r^2	ρ	r^2
0.01	1.940	0.99935	1.504	0.96286	1.239	0.88946	1.215	0.89764
0.02	1.963	0.99974	1.615	0.97777	1.380	0.92243	1.348	0.92774
0.05	1.980	0.99994	1.729	0.99031	1.548	0.95724	1.503	0.95904
0.10	1.988	0.99998	1.810	0.99552	1.695	0.97867	1.640	0.97800
0.20	1.993	0.99999	1.876	0.99820	1.833	0.99266	1.770	0.99093
0.50	2.000	1.00000	1.930	0.99960	1.944	0.99934	1.885	0.99845
1.00			1.955	0.99987	1.980	0.99993	1.936	0.99966
2.00			1.972	0.99996	2.000	1.00000	1.965	0.99992
5.00			1.985	0.99999			1.983	0.99999
10.00			1.990	1.00000			1.989	1.00000
20.00								
50.00								

1) $S_s^{FPD} = C_e^2 + 10^{-2} C_e$

2) $S_s^{FPD} = (C_{bs} + C_e)^2; C_{bs} = 0.1$

3) $S_s^{FPD} = C_e^2 + 10^{-2} C_{bc}; C_{bc} = 10$

4) $S_s^{FPD} = (C_{bs} + C_e)^2 + 10^{-2}(C_e + C_{bc}); C_{bs} = 0.1, C_{bc} = 10$

response becomes curved already at high concentration levels. The detector signal becomes much higher than the corresponding sulphur content and if not properly corrected, the sulphur content will be seriously over estimated.

Curve 4 (column 4 in Table I) demonstrates a "real" system with background formed by sulphur as well as non-sulphur containing compounds and simultaneously eluted effluents. It can be seen that linearization of this system by means of a power function is meaningless, the exponent value changes in a broad range from 2 to 1.2.

Practical examples of the above discussed are shown below. Figure 2 demonstrates FPD responses to SO_2 introduced via a logarithmic dilution flask. The response curve does not exhibit large curvature because of the lack of interfering compounds, and is comparable with the curve 1 of Figure 1 as discussed above.

Figure 3 shows an application of FPD in the analysis of oil, with parallel FID detection. Two columns have been used; 1 and 3 meter resp. Because of a bad separation on a 1 m column the elution of sulphur

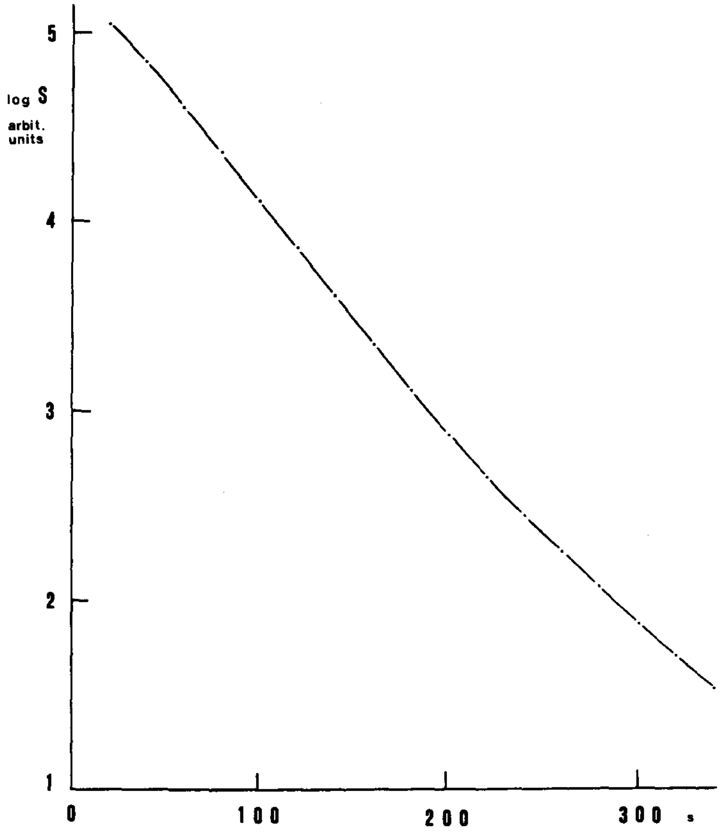

FIGURE 2 FPD sulphur chanel response to SO_2 introduced via logarithmic dilution flask.

containing compounds occurs on much higher background and consequently signals should be higher. This could be seen on different patterns of groups A, B and C. While on 3 m column the main peaks are at the front of the group, on a 1 m column the situation is reversed. Thus in "real" systems (such as curve 4 of Figure 1) the FPD response is a function of separation efficiency and, depending on the conditions, could result even in different patterns.

It has been shown that it is meaningless to specify a linearity factor for FPD. It also follows that using a linearizer with a constant exponent value for the sulphur channel will lead to significantly biased data. It can be said that forcing the polynomial function with power fit is the main reason for so many different values of linearity factors reported in the literature.

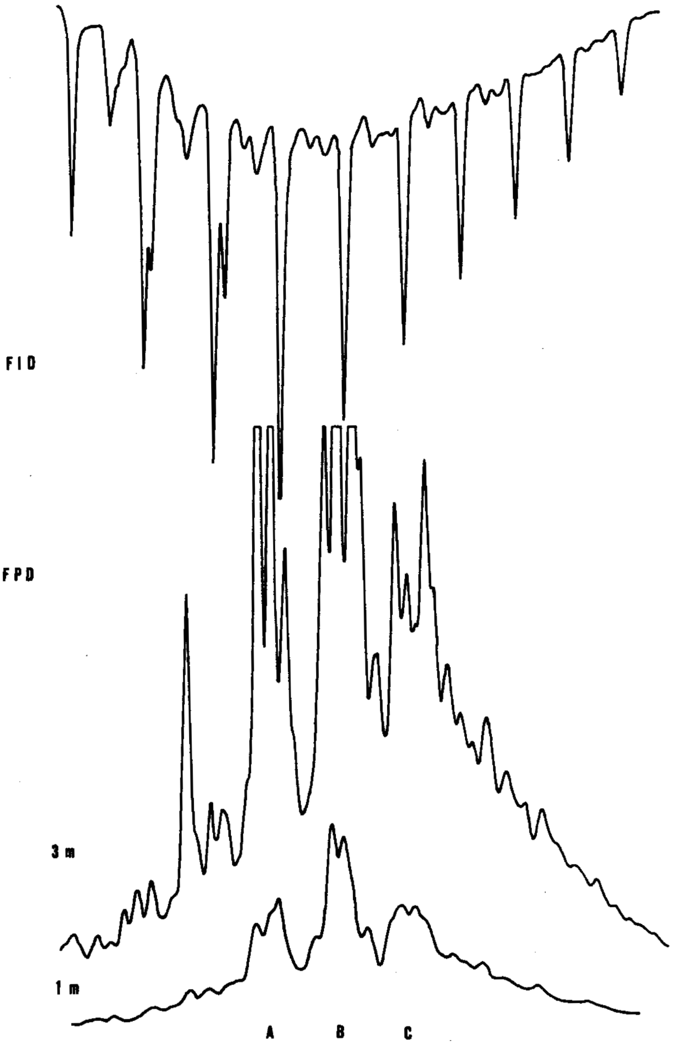

FIGURE 3 Analysis of a crude oil on 1 and 3 meter column packed with 10% OV-101 on Chromosorb W HP80-100 mesh, with parallel FID, FPD sulphur chanel indication (end split 1/1).

TABLE II

Comparison of calibration curve evaluation methods; 1-power function fit, 2-second order polynomial fit.

measured		calculated			
		1		2	
a ng	h mm	h mm	error %	h mm	error %
6	13	12.1	−6.9	12.0	−7.7
12	36	40.5	12.5	37.8	5.0
18	79	82.1	3.9	79.6	0.8
24	140	135.6	−3.1	137.4	−1.7
30	210	200.1	−4.7	211.2	0.6

1-$h = 0.53\ a^{1.7445}$
corr.coeff. 0.9975
2-$h = 0.22\ a^2 + 0.30\ a + 2.2$
corr.coeff. 0.9998

With respect to this discussion the question should be asked of how to best evaluate the FPD signal.

The correct way is to determine the parameters of a second order fit. In experimental work the calibration curve should be checked very often even for a narrow concentration range. As shown in Table II for calibration curves of a pesticide analysis the second order polynome is better correlated with the experimental data and the interpolated values are much more precise than for power fit. But it should be pointed out that this function can be used only for interpolation.

An other aspect of quantitative work with FPD is the question of the signal (peak height) or the response (peak area) evaluation. The peak area is an integral value of detector signal, defined according to Eq. 9. Because of undefined and simultaneously unknown values of particular concentrations during effluent elution, the peak area is less correlated with an effluent amount than the peak height. An example of the analysis of methyl parathion is shown in Table III. We can state that a non-linear FPD response should be preferably evaluated by the measurement of peak height.

Lower detection limit

The lower detection limit is related to detector noise and it should be pointed out that only the noise frequency interfering with the measuring

TABLE III

Comparison of an evaluation of peak area (A) and peak height (h) for methyl parathion measured by FPD in sulphur mode

x amount	A measured	A calculated	A error	h measured	h calculated	h error
1	22.18	15.75	−28.9	2.4	1.9	−20.8
2	57.65	60.59	5.1	9.0	9.3	3.3
4	188.43	197.33	4.7	30.6	31.2	2.0
8	665.50	659.04	−1.0	104.0	103.5	−0.5
16	2334.33	2335.37	0	361.6	361.7	0

$A = 7.843\,x^2 + 21.312\,x - 13.401$
$h = 1.183\,x^2 + 3.871\,x - 3.180$

frequency is relevant (see [29]). The method generally used for the determination of noise by maximum amplitude gives a value, which is about twice that of the filter systems.

The lower detection limit on the FPD could be improved by a so-called sensitized mode of operation. This is realized by dopping of gases with SO_2. Under such conditions the signal becomes larger because of enhanced background signal (see Eq. 13 and Figure 1). The detector performs under the conditions where small changes in the measured signal will cover a broad concentration range.

The significance of the measured value is related to the precision of measurement by means of the confidence interval. If we assume that only the noise is responsible for the precision of the measurement and that it is increasing with the square root of the background current, then for 99% significance level we get

$$\overline{S_2^{FPD}} - \overline{S_1^{FPD}} = 2\ \text{noise}\left(1 + \sqrt{\frac{bc_2}{bc_1}}\right) \tag{24}$$

where $\overline{S^{FPD}}$ are the mean values of the detector signal 1 and 2 resp.

The procedure of the sensitized mode of FPD will lead to a successful solution only if the noise level stays low. Thus all components, such as PMT, light transfer assembly, flame geometry, gas flow stability etc. must be optimized.

One can generally assume that the lower detection limit depends on the background signal of FPD and without precise specifications of experimental conditions its value is doubtful.

Detector selectivity

The selectivity is defined as a ratio of signals of investigated interfering atoms at the same concentration and under the same conditions (constant wavelength). This leads to the following equation:

$$\Phi_{S/C}=\frac{S_{ss}}{S_{sc}}\approx\frac{k_{ss}(xC_e)^2}{k_{sc}C_c}\approx\frac{k_{ss}(xC_e)}{k_{sc}} \tag{25}$$

where Φ is the selectivity, C_c is the hydrocarbon concentration.

The selectivity of the phosphorus mode is

$$\Phi_{P/C}=\frac{S_{pp}}{S_{pc}}\approx\frac{k_{pp}(yC_e)}{k_{pc}C_e}=\frac{k_{pp}}{k_{pc}} \tag{26}$$

From Eq. 25 it follows that the selectivity of FPD in the sulphur mode is a function of effluent concentration and not of hardware configuration only.

Application of selective detectors in GC rose originally from the need to measure complex samples for which the separation efficiency of the GC column was low. In other words, the FPD was used to detect sulphur containing compounds from complex patterns of many overlapping peaks (see Figure 3). From our discussion it follows that just the opposite is required if the FPD is used for quantitative work. Separation systems of high efficiency are required in applications with FPD to overcome high background signal and peak overlap.

Conclusions

Measured FPD response is a sum of all interactions of S, P and C molecular forms in detection mechanism of FPD. The polynom of second order is the best fit regarding the above detection mechanism.

It was shown that evaluation of detector characteristics such as sensitivity, linearity etc. could not be carried out in a log/log plot and calculated values are of limited significance, if the experimental parameters are not specified in detail.

The selectivity of FPD is determined by its construction. Generally it should be as high as possible, because of its active role for detector signals (see Eqs. 16, 17, 20–22). The detector selectivity influences the "curvature" of the signal/concentration plot and thus results in a lower detection limit. It is the parameter, which could "linearize" the phosphorus response of FPD.

Quantitative evaluation of FPD response is very problematic. Generally, peak height should be used for evaluation and second order fit for interpolation. Because the FPD response is a function of background current, carrier gas purity, stationary phase bleeding, resolution achieved, etc. the results should be very carefully interpreted. It can be expected that the actual sulphur content in the environmental samples (especially in the air) is lower than calculated, because of changing background (e.g. hydro carbons emission during rush hours).

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