

**Estimation of the Limit of Detection and the Limit of Determination via  
Calibration Curve Procedure in the PCDD/F-Analysis**

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### **Introduction**

The estimation of the limit of determination and the confidence interval is very important in trace analysis. To illustrate this fact different methods are described in literature<sup>1)</sup>.

An often used procedure is to determine the mean blank values and their standard deviation. On these values the limit of determination is estimated. Normally the 5- or 6-fold of the mean blank value is defined as the limit of determination while the 3-fold is the limit of detection.

This procedure does not include inaccuracies which occur during sample selecting, extraction, clean-up and measurement.

Therefore the calibration curve procedure seems to be an effective alternative<sup>2)</sup>.

### **Procedure**

In a first step a five-point calibration curve was recorded. The concentrations were 0.025 - 0.050 - 0,100 - 0.150 and 0.200 pg/μl in dodecane. Each level was measured three times. Based on the mean values of the measured peak areas and the belonging concentrations a regression curve was calculated and the limit of determination was estimated upon these data.

In a second step the signal:noise ratio was calculated from the measurement of the lowest concentration-level. The limit of determination was estimated based on a signal:noise ratio of 6:1.

Both values are compared in Table 1.

In order to proof the linearity of the calibration curve, the theoretical and the measured values were compared. (see Fig.2 and Table 2)

**Tab .1: Limit of determination**

	<b>In dodecane</b> concentration in pg/μl		<b>in human blood</b> concentration in pg/g, fat basis	
	signal:noise ratio 6:1	calibration curve procedure	signal:noise ratio 6:1	calibration curve procedure
2,3,7,8-TCDD	0.010	0.172	0.250	4.300
1,2,3,7,8-PeCDD	0.010	0.078	0.250	1.950
1,2,3,4,7,8-HxCDD	0.020	0.129	0.500	3.225
1,2,3,6,7,8-HxCDD	0.020	0.129	0.500	3.225
1,2,3,7,8,9-HxCDD	0.020	0.069	0.500	1.725
1,2,3,4,6,7,8-HpCDD	0.025	0.123	0.625	3.075
OCDD	0.028	0.120	0.700	3.000
2,3,7,8-TCDF	0.020	0.154	0.500	3.850
1,2,3,7,8-PeCDF	0.005	0.045	0.125	1.125
2,3,4,7,8-PeCDF	0.005	0.082	0.125	2.050
1,2,3,4,7,8-HxCDF	0.010	0.098	0.250	2.450
1,2,3,6,7,8-HxCDF	0.010	0.081	0.250	2.025
1,2,3,7,8,9-HxCDF	0.012	0.086	0.300	2.150
2,3,4,6,7,8-HxCDF	0.015	0.121	0.375	3.025
1,2,3,4,6,7,8-HpCDF	0.022	0.137	0.550	3.425
1,2,3,4,7,8,9-HpCDF	0.025	0.093	0.625	2.325
OCDF	0.030	0.157	0.750	3.925

The differences of the limit of determination derived from the signal/noise ratio and the calibration curve procedure are shown. The higher values achieved by the calibration curve procedure were obtained by the influence of the standard deviation and the interval of confidence of the whole analytical procedure.

The limit of determination in human blood was achieved by transferring the data from dodecane to an analysis of human blood. In order to get more reasonable values for the limit of determination PCDD/F should be added in the reported concentrations to low-contaminated blood.

Yet these values were not available, but will be measured in the bear future.

Data in the table is based on a 5-point-calibration curve in the range of 0.025 - 0.2 pg/μl which was measured three times.

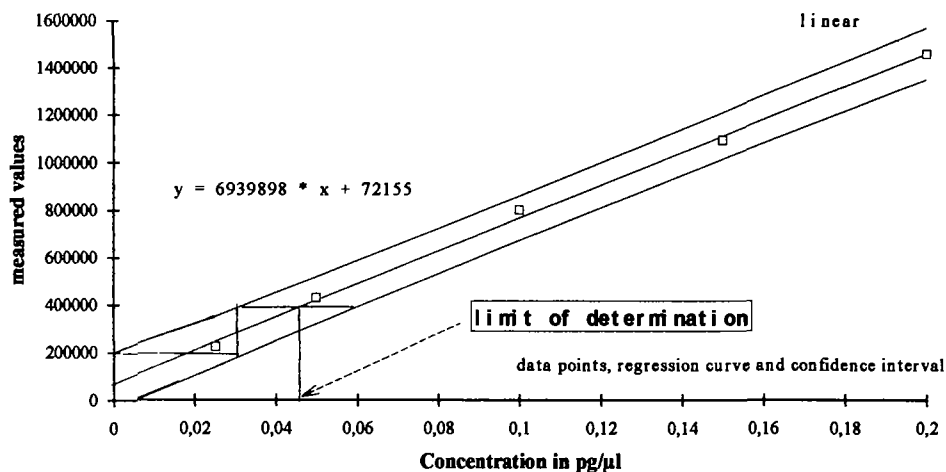


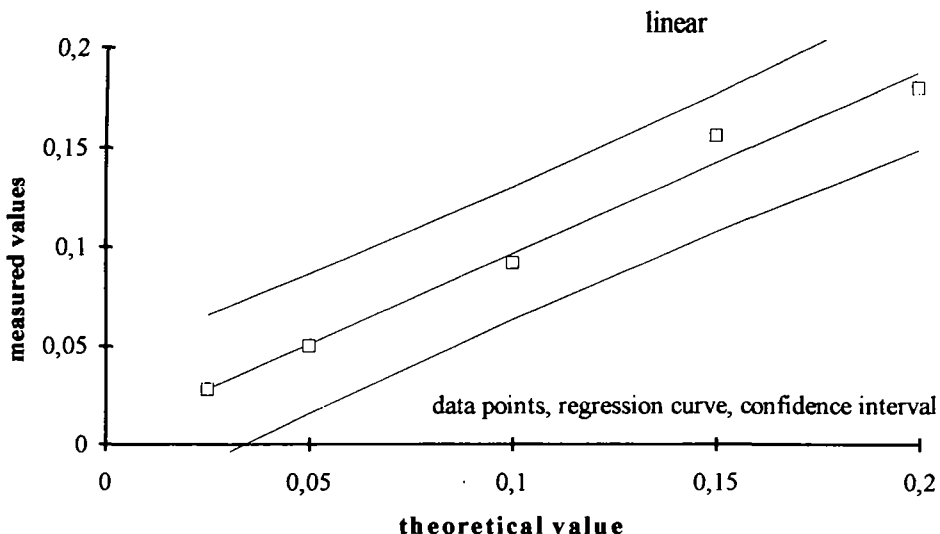
Figure 1: Calibration curve for 1,2,3,7,8-PeCDF in dodecane

Tab. 2: Calibration curve PCDD/F - comparison theoretical/measured values

Concentration in pg/μl

theoretical value	0.025	0.050	0.100	0.150	0.200
2,3,7,8-TCDD	0.028	0.042	0.100	0.160	0.200
1,2,3,7,8-PeCDD	0.028	0.050	0.092	0.152	0.180
1,2,3,4,7,8-HxCDD	0.030	0.056	0.090	0.158	0.170
1,2,3,6,7,8-HxCDD	0.028	0.046	0.078	0.136	0.148
1,2,3,7,8,9-HxCDD	0.028	0.048	0.090	0.152	0.172
1,2,3,4,6,7,8-HpCDD	0.030	0.058	0.092	0.160	0.174
OCDD	0.034	0.054	0.092	0.168	0.194
2,3,7,8-TCDF	0.024	0.038	0.100	0.160	0.180
1,2,3,7,8-PeCDF	0.028	0.050	0.092	0.156	0.180
2,3,4,7,8-PeCDF	0.030	0.054	0.094	0.162	0.178
1,2,3,4,7,8-HxCDF	0.028	0.052	0.090	0.154	0.172
1,2,3,6,7,8-HxCDF	0.026	0.050	0.092	0.160	0.178
1,2,3,7,8,9-HxCDF	0.034	0.058	0.104	0.170	0.190
2,3,4,6,7,8-HxCDF	0.026	0.054	0.090	0.156	0.170
1,2,3,4,6,7,8-HpCDF	0.028	0.048	0.092	0.154	0.186
1,2,3,4,7,8,9-HpCDF	0.028	0.054	0.088	0.160	0.184
OCDF	0.032	0.058	0.102	0.164	0.184

The correlation between the measured and theoretical values of the calibration curve are shown. The measured values are the mean values of three measurements.



**Figure 2:** Calibration curve for 1,2,3,7,8-PeCDF, comparison measured/theoretical value

## Results:

The estimation of the limits of detection and determination via calibration curve procedure is a first approach to get data about the efficiency and precision of the analysis of PCDD/F in low-level-concentrations.

Our considerations show that the values for the limit of determination is remarkable higher when derived from regression analysis by the calibration curve procedure (see Table 1). The reasons are the influence of the standard deviation and confidence interval of the measured values.

Further analysis, especially for the finding of the lowest fortification level and the width of the intervals, are still to be done.

## Literature:

- 1) *Vogelsang, J.*: Limit of detection and limit of determination: application of different statistical approaches to an illustrative example of residue analysis, *Fresenius Z. Anal. Chem.* **328**, 213-220 (1987)
- 2) *Walter, H.-F., K.-H. Holtz, H. Frehse, S. Gorbach u. H.-P. Thier* in : Deutsche Forschungsgemeinschaft: Rückstandsanalytik von Pflanzenschutzmitteln. VCH Verlagsgesellschaft, Weinheim, 11. Lieferung 1991, Kapitel XI-A: Ableitung von Nachweisgrenze und Bestimmungsgrenze nach dem Eichkurvenverfahren