

**INDICATOR PARAMETERS FOR PCDD/PCDF - PLANT SPECIFIC MODELS****Öberg, T.<sup>A</sup>, Bergström, J.<sup>B</sup>**<sup>A</sup> Tomas Öberg Konsult AB, Gamla Brov. 13, S-371 60 Lyckeby, Sweden<sup>B</sup> Miljökonserterna i Studsvik AB, Box 154, S-611 24 Nyköping, Sweden**Introduction**

Multivariate calibration using PLS-regression has been proved to be very useful in many chemometric applications. Since 1987 we have ourselves used this method for multivariate dataanalysis to develop indirect measurement methods for polychlorinated dioxins (PCDD) and dibenzofurans (PCDF) emitted from different thermal processes. Previously presented results have shown that the emissions of PCDD/PCDF can be modelled and predicted from less costly and more precise isomer-specific analyses of different chlorinated benzenes and phenols<sup>1-4</sup>. The new results we report here comes from a study aimed to further utilize these possibilities and develop specific models for each plant to accomplish maximum precision and accuracy in the calibration process.

**Methods**

Multivariate calibration using PLS have been extensively described in the literature<sup>5-6</sup>.

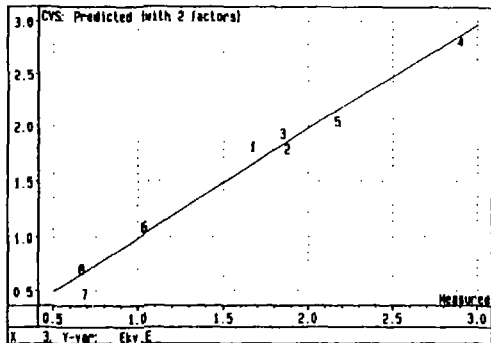
All flue gas sampling was done according to the recommended Nordic method<sup>7</sup>. Chlorinated benzenes and phenols as well as PCDD/PCDF were analyzed using HRGC-MS/SIM as described in an earlier paper<sup>8</sup>. The amounts in each sample have been calculated from the recoveries of labelled surrogates added prior to extraction and clean-up.

**Results and discussion**

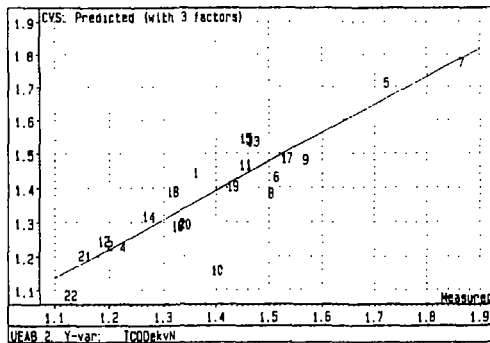
Plant specific models have been developed for two municipal waste combustion (MWC) facilities and one metallurgic industry. In figure 1-3 we show the predictions in each cross-validation segment as a function of measurement results for TCDD-equivalents. By using cross-validation we also get a conservative estimate of the likely spread in future samples.

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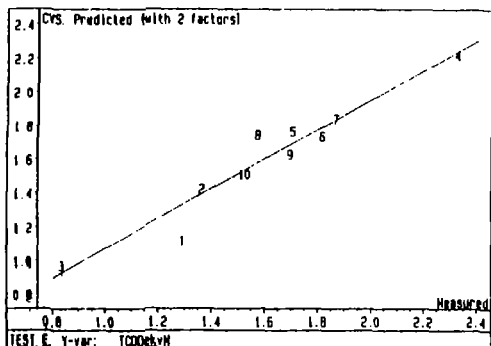
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**Figure 1**  
*Predicted vs analytical results for TCDD-equivalents (Eadon), log-scale 3.2-1000 ng in sample. Plant-specific model for a metallurgical industry.*



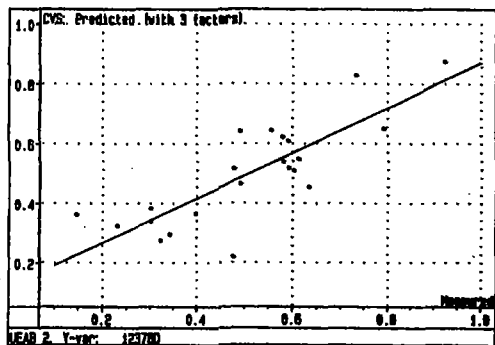
**Figure 3**  
*Predicted vs analytical results for TCDD-equivalents (Nordic), log-scale 6.3-250 ng in sample. Plant-specific model for MWC plant B.*



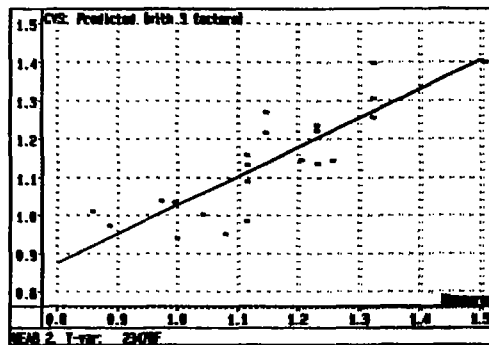
**Figure 2**  
*Predicted vs analytical results for TCDD-equivalents (Nordic), log-scale 6.3-250 ng in sample. Plant-specific model for MWC plant A.*

The samples with the narrowest variation range, figure 3, are particularly interesting to study. In these samples we can predict 2378-substituted isomers with much higher precision than for the groups of congeners, figure 4-7. The specific 2378-substituted isomers are of course analyzed with higher accuracy and precision due to the availability of  $^{13}\text{C}$ -labelled surrogates.

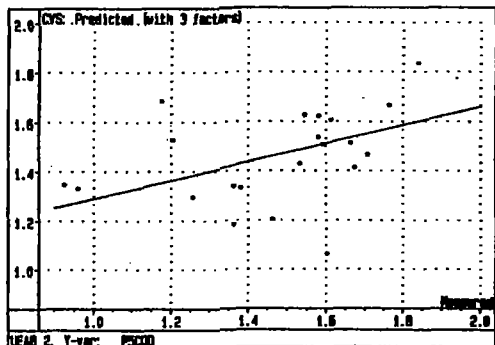
Our interpretation of these results are that the overall measurement precision and accuracy for PCDD/PCDF sets the limits how far we can go in improving the calibration models.



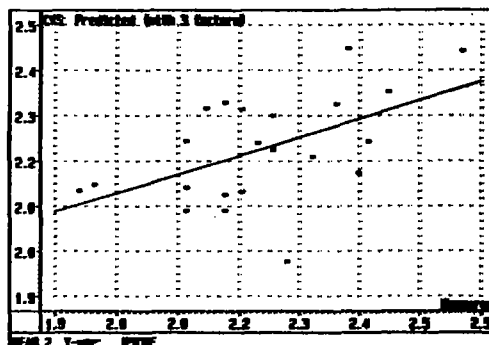
**Figure 4**  
*Predicted vs analytical results for 12378-P5CDD, log-scale 1.3-10 ng in sample. Plant-specific model for MWC plant B.*



**Figure 6**  
*Predicted vs analytical results for 23478-P5CDF, log-scale 6.3-32 ng in sample. Plant-specific model for MWC plant B.*



**Figure 5**  
*Predicted vs analytical results for ΣP5CDD, log-scale 13-100 ng in sample. Plant-specific model for MWC plant B.*



**Figure 7**  
*Predicted vs analytical results for ΣP5CDF, log-scale 79-320 ng in sample. Plant-specific model for MWC plant B.*

### **Future applications**

**Plant specific multivariate calibration models can simplify flue gas sampling procedures since the levels of chlorinated benzenes and phenols are much higher than the levels of PCDD/PCDF. Furthermore, the cost of the analysis is reduced and therefore a greater number of samples can be used as a basis for calculation of the annual emissions.**

**The main source of error for calculation of annual "dioxin" emissions is not uncertainties in the performed analyses, but the lack of representativity. Predicting PCDD/PCDF from plant specific models, with an increased number of test points, will give much better estimates than single-shot conventional measurements. Simplified sampling and analysis also facilitate optimization of both combustion processes and flue gas cleaning equipments.**

### **References**

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