REFERENCE MATERIALS FOR DIOXIN AND DIBENZOFURAN ANALYSIS: PREPARATION AND CERTIFICATION IN THE BCR FRAMEWORK.

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Introduction.

An effective control of analytical quality, especially in the field of dioxin and dibenzofuran analysis, requires the availability of appropriate and certified reference materials. Since 1985, the BCR, a department of the European Communities which is largely dedicated to the problems involved in measurement and testing, has been putting a lot of effort into the fulfilment of this general and worldwide need.
Municipal waste incineration was, and still is, one of the main known dioxin sources. In view of the legislative and technical efforts aiming at the reduction of these emissions, it seemed normal to direct the first project towards the improvement of the analytical methodology for controlling municipal waste incinerator emissions and to the preparation and certification of a representative municipal waste incinerator fly ash. For toxicological reasons and following the requirements of several international laws (The Netherlands, Austria, Germany, Swedish Guideline), it was decided to restrict the certification to the 17 most toxic congeners.

Experimental results and discussion.

The dioxin project started with the analysis of a series of synthetic dioxin mixtures of different chromatographic complexity. Each of the participants, all together 24 laboratories from 8 European contries (1), used combined GC - MS, applying its

own instrumental parameters, standards and calculation procedures.
A detailed evaluation of all results (Table I) indicated the occurrence of systematic errors probably due to the use of inaccurate calibrants and to the application of inadequate integration and calculation procedures.

Table I: summary of the results, in ng/ml, on synthetic dioxin mixtures.

Test No	Range	Mean	CV in %	Test No	Range	Mean	CV in %
1	34 - 73	44	23	10	30 - 53	42	16
2	17 - 42	29	23	11	24 - 123	70	43
3	16 - 36	28	20	12	19 - 56	31	28
4	30 - 91	60	30	13	13 - 25	20	18
5	26 - 43	34	16	14	30 - 67	49	25
6	18 - 56	32	30	15	18 - 32	27	17
7	9 - 39	20	38	16	23 - 43	33	18
8	33 - 64	46	20	17	31 - 51	42	13
9	41 - 62	49	15	18	24 - 42	34	15

Following these findings, the BCR made available a primary, gravimetrically prepared standard solution, against which the working standards had to be referenced, and stressed the need for manual instead of automatic integration. Taking just these precautions, the analysis of a new set of unknown synthetic mixtures showed the improvements listed in table II. After the elimination of the data out of the 99 % confidence limit, the test resulted in the 95 % confidence intervals summarized in table III, which looked very promising in view of a later certification.

Table II: results, in ng/ml, obtained for synthetic dioxin mixtures when taking special precautions regarding calibration and integration.

Test No	Range	Mean	CV in %
19	43.2 - 52.7	49.2	5.5
20	43.9 - 55.5	49.8	6.4
21	37.4 - 67.5	52.2	13.7
22	37.1 - 64.7	53.1	13.4
23	39 - 66.3	50.6	10.5

Table III: 95 % confidence intervals of the mean of means after the elimination of the data out of the 99 % confidence limit (in ng/ml).

Test No	95 % confidence interval of mean of means	CV at 95 % confidence level
19	49.6 - 50.6	1.0
20	48.8 - 51.0	2.1
21	50.0 - 53.6	3.4
22	49.7 - 53.7	3.9
23	49.1 - 50.7	1.6

The next logical step was the analysis of a real, though cleaned-up fly ash extract. Again, analysis was limited to dioxins only. The clean-up was performed by atmospheric pressure liquid chromatography on silica gel, acid/base modified silica gel and basic alumina.

The results showed a relatively small number of outliers, all of which could be traced back to chromatographic separation problems. It was clear that, at the actual state of column technology and from the point of view of certification, all of the dioxin isomers of interest had to be analysed on a good quality polar capillary column. After elimination of the outliers, the coefficients of variation of the mean of means at the 95 % confidence level, were between 2 % and 6 % except for 2,3,7,8-T4CDD, which was present at a level too small in order to allow accurate measurement by low resolution mass spectrometry, the technique used by the majority of the participants. As a consequence a coefficient of variation of 14.4 % at the 95 % confidence level should be considered an excellent result.

Table IV: results, in ng/ml, for a cleaned up fly ash extract (outliers eliminated)

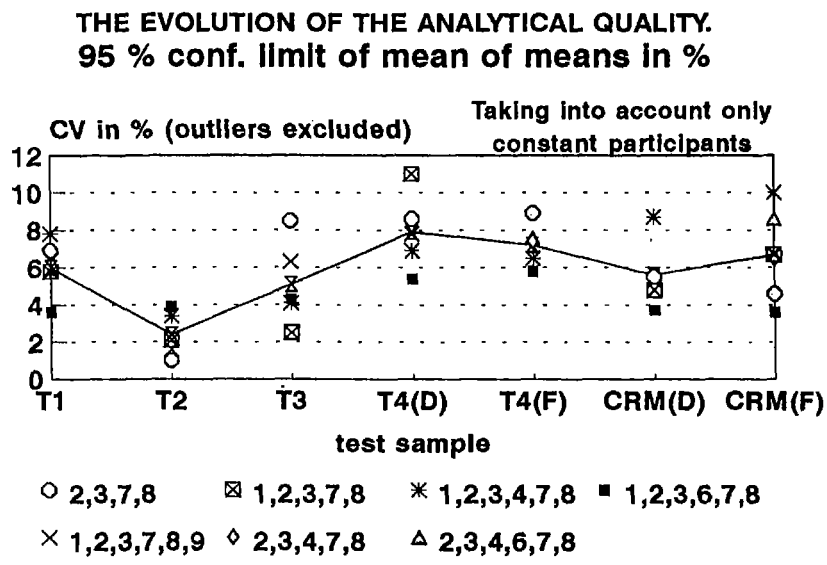
PCDD-isomer	95 % confidence interval of mean of means	CV at 95 % conf. level
2,3,7,8	8.9 - 11.9	14.4
1,2,3,7,8	87.8 - 93.2	3.0
1,2,3,4,7,8	78.5 - 87.9	5.6
1,2,3,6,7,8	204.7 - 223.3	4.3
1,2,3,7,8,9	163 - 183	5.8

In the subsequent test on a raw fly ash extract, both dioxins and dibenzofurans were analysed. Multiple sets of sample clean-up procedures were used. These ranged from a single chromatography on basic alumina, activity grade super I from ICN, to the consecutive application of silicagel, acid/base modified silica gel, $AgNO_3$ modified silicagel, CsOH modified silica gel and finally basic alumina. The resulting data were quite good for most congeners analysed (Table V, figure 1), but problems occurred for 1,2,3,7,8-P5CDF and 1,2,3,7,8,9-H6CDF for which quantitation was found to be impossible on a polar phase but rather easy on a non polar phase.

Table V: overall statistical results, in ng/ml, for the raw fly ash extract.

Group	Isomer	95 % conf. interval of mean of means	CV at 95 % conf. level
Dioxins	2,3,7,8	32.1 - 39.3	10
	1,2,3,7,8	26.5 - 32.3	10
	1,2,3,4,7,8	32.2 - 36.4	6.1
	1,2,3,6,7,8	138.1 - 151.9	4.8
	1,2,3,7,8,9	91.9 - 107.3	7.8
Furans	2,3,7,8	12.1 - 14.5	9.0
	1,2,3,7,8	----------	------
	2,3,4,7,8	41.7 - 48.5	7.4
	1,2,3,4,7,8	76.5 - 87.1	6.5
	1,2,3,6,7,8	81.9 - 91.9	5.8
	1,2,3,7,8,9	----------	------
	2,3,4,6,7,8	121 - 141	7.6

These results were very promising in view of the certification of a raw fly ash extract, provided that the analysis was performed on both polar as well as non polar capillary columns and that a set of rather strict guidelines for quality control purposes was followed. These guidelines included the execution of five independent replicate analyses, a procedure blank control, a detector linearity check for each isomer in the concentration range of interest, a recovery determination, alternating analysis of a calibration standard, a syringe blank and the sample, and finally, calculation of the concentrations in each sample on the basis of the embracketing calibration runs.



The certification was successful for eleven members of the group of the dirty dozen (Table VI). Indeed, the use of a DB-Dioxin column, a newly developped column which was available for only two of the participating laboratories, revealed the presence of an interference in the 1,2,3,4,7,8-H6CDF peak as eluting from the regularly used polar columns. Nevertheless, when taking into account also these latest findings, the future certification of a raw fly ash must be feasible.

Table VI: certification data for the fly ash extract reference material CRM 429.

Group	Isomer	Mean of means (ng/ml)	SD 95 %	CV 95 %
Dioxins	2,3,7,8	4.80	0.39	8.1
	1,2,3,7,8	24.8	1.6	6.5
	1,2,3,4,7,8	66.1	5.9	8.9
	1,2,3,6,7,8	145	4.5	3.1
	1,2,3,7,8,9	78.7	3.7	4.7
Furans	2,3,7,8	16.2	1.1	6.8
	1,2,3,7,8	40.8	2.8	6.9
	2,3,4,7,8	70.8	5.0	7.1
	1,2,3,4,7,8	----	---	---
	1,2,3,6,7,8	165	17	10
	1,2,3,7,8,9	15.2	1.7	11
	2,3,4,6,7,8	299	29	9.7

References.

(1) T. Rymen, J. Hinschberger, E. Maier and B. Griepink, " The quantitative determination of PCDD and PCDF: improvement of the analytical quality up to a level acceptable for the certification of certified reference materials ", report EUR 14357, 1992.