Report

Stack Testing Measurements
in the flue gas of kiln no. 9

SECIL, Companhia de Cal e Cimento, S.A.
Fábrica SECIL Outão, Portugal

Co-incineração do Combustivel Sólido Sintético (CSS)

Executive Summary

April, 30th, 2002

Accreditation by the German Authorities (Notification) related to §§ 26, 28 BImSchG, 2. BImSchV, §§ 26,28 of 13.BImSchV, § 10 of 17. BImSchV, Nr. 3.2 TA Luft
Emission- and Ambient Air Measurement, Olfactometry, Calibration and Function Test

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April, 30th, 2002

Ordered by:	Fábrica SECIL-Outão, Apartado 71, 2901-901 Setúbal, Portugal
Order n°	Letter DCIM 3035 Final Program
Date of order:	February 2nd, 2002
Location of measurement	Fábrica SECIL-Outão
Part of plant	Kiln 9
Period of measurement:	February 22nd to March 11th, 2002
ERGO project number:	A-0059-02-200
Project manager:	Dr. U. Düwel, Dipl.-Ing. Schröder
Phone:	(+4940) 69 70 96 – 0
Number of pages:	18

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1 Introduction

SECIL, Companhia de Cal e Cimento, S.A., Fábrica SECIL-Outão, Portugal, instructed ERGO Forschungsgesellschaft mbH, Hamburg, Germany, to perform measurements with regard to concentrations of various components in the flue gas of one cement kiln, located at the Outão plant in Portugal. The tests were carried out at kiln no. 9 to determine the concentrations of dioxins/ furans (polychlorinated-p-dibenzodioxins and polychlorinated-p-dibenzofurans), heavy metals, hydrogen chloride, hydrogen fluoride, sulphur dioxide, nitrogen oxides expressed as nitrogen dioxide, carbon monoxide, dust, and total organic carbon (TOC) in accordance with the EC – Council Directive 2000/76/EC of December 4th, 2000 (Incineration of Waste).

Within the scope of an extensive investigation, first experiences shall be gained with the application of the so called Combustivel Sólido Sintético (CSS) (also known as Combustível Alternativo (CA) in past tests) with regard to their combustion in cement plants. Apart from technical questions concerning handling and dosage, it was most important to examine whether the combustion of CSS results in higher concentrations of hazardous substances in flue gas. In this respect, the compounds of dioxins/furans and heavy metals – such as mercury for example – are of special relevance. The investigations are based on the compounds indicated in the EC – Council Directive 2000/76/EC of December 4th, 2000.

The measurements were carried out in accordance with a measurement plan which had been drawn up beforehand. Many years of experience have revealed that a scattering of values is to be ascertained under repeated conditions, that is to say for repeated measurements of the same operating conditions. The scattering of the values is attributable to variations in the composition of the raw material which cannot be influenced and to necessary adjustments of the operating conditions of the cement plant. When evaluating the data, it is nevertheless necessary to determine a difference between the values in the blank tests and the test runs where CSS was applied. This is the reason why the measurement program consists of a series of three test runs each with identical test conditions. The investigations were initiated with three blank tests (blank test I). Subsequently, three test runs applying 3 t/h CSS and 3 test runs applying 6 t/h CSS were carried out. The investigations were completed by a series of another 3 blank tests (blank test II). When adjusting the new test conditions in each case, equilibrium of the cement plant was established, a period of two days used to achieve this before carrying out the measurements.

The alternative fuel (Combustivel Sólido Sintético, CSS) was applied with a mixture of hazardous industrial waste (Resíduos Industriais Perigosos, RIP) and saw dust (serrim). The content of RIP during the test run applying 3 t/h CSS was approx. 52 % and during the test run using 6 t/h CSS approx. 61 %. The CSS is specified more precisely within the scope of the chemical analysis of the process samples.

2 Plant characterization

The cement plant can be described as a four-stage cyclone preheater kiln equipped with planetary coolers.

The measurements were carried out at kiln no. 9 in the factory of SECIL-Outão from February 22nd to April 11th, 2002.

During the stack testing measurements, alternative fuel (Combustivel Sólido Sintético, CSS) has been injected in the main burner in addition to the regular fuel. The cleaning of the flue gas was carried out using an electrostatic precipitator followed by a fabric filter. The raw mill was operating during all tests.

A short documentation of the key data concerning operating conditions was compiled from recordings from the plant process data system and placed at our disposal. The data listed in the following tables show operating conditions within the limitations of normal productive capacity.

Table 2.1: Operating conditions of kiln 9 during the test period

Kiln 9				
Date 2002	Time Period of investigations	Raw mill feed [t/h]	Kiln feed [t/h]	Clinker production [t/h]
Febr., 22	10:00 to 20:00	327	259	151
Febr., 23	10:00 to 18:00	319	259	151
Febr., 24	10:00 to 18:00	280	259	151
Febr., 27	10:00 to 16:00	315	255	149
Febr., 28	10:00 to 19:00	299	256	149
March, 1	10:00 to 19:00	296	255	149
March, 4	11:00 to 22:00	273 [1)]	241 [1)]	141 [1)]
March, 5	15:00 to 23:00	332	247	144
March, 6	10:00 to 19:00	344	244	142
March, 9	15:00 to 23:00	334	250	146
March, 10	10:00 to 18:00	341	249	145
March, 11	10:00 to 18:00	353	246	144

[1)] Technical interruption between 17:00 to 20.00. During this time the measurements were stopped

As for the test runs with 6 t/h CSS on March 4th and March 5th, the process occasionally could not fully be kept stable due to technical problems during the feeding of pet coke (weighfeeder).

The feeding rate of the alternative fuel (Combustivel Sólido Sintético, CSS) was controlled via a special metering unit. The metering unit was calibrated by separately collecting and weighing the entire waste stream at specific time intervals.

3 Summarized test results

The measurement results are summarized in table 3.1.

In accordance with the EC – Council Directive 2000/76/EC of December 4th, 2000, the concentrations are kept standardized at a temperature of 273 K , a pressure of 1013 hPa of the dry flue gas and related to an oxygen content (dry) of 10 vol%.

Evaluation

By means of the results shown in table 3.1, it shall be examined whether there is a significant difference between the blank test and test runs including the combustion of CSS regarding the compounds mentioned.

For the majority of the measured components, any interpretation is clear because no differences can be ascertained between the 12 test runs with regard to the level of the detection limits res. of the assessment limits (see chapter 4). This applies to the components of total dust, hydrogen chloride (HCl), hydrogen fluoride (HF), sulfur dioxide (SO_2), sum of cadmium (Cd) and thallium (Tl), mercury (Hg), sum of Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V and dioxins/ furans (I-TEQ-value). As far as these components are concerned, it can be concluded that at relevant concentration levels, the use of CSS did not produce negative effects on the emissions of the plant investigated.

Values within a clearly measurable range were ascertained for the nitrogen oxide expressed as NO_2, carbon monoxide (CO) and Total Organic Carbon (TOC) components. As expected, scatterings of the values were ascertained under repeated conditions, that is to say for repeated measurements under the same operating conditions (see blank test from March 22nd to March 24th and from April 9th to April 11th). The scattering of the values may be attributed to variations in the composition of the raw material which cannot be influenced and to necessary adjustments of the operating conditions at the cement factory. This applies to cement plants worldwide. Within the scope of evaluation, it must be determined whether or not there is a significant difference between the measuring values ascertained within the scope of the blank tests res. during the test runs including the application of CSS.

As for the nitrogen oxide component expressed as NO_2, it may already be concluded by means of the graphics (see Figure 5) that in comparison with the blank tests no higher values were ascertained during the test runs including the application of 3 t/h and 6 t/h CSS. Compared with the blank tests, the mean values of the 4 groups are slightly lower in the test runs where CSS was applied (mean values: blank test I: 1042 mg/m^3, 3 t/h CSS: 956 mg/m^3, 6 t/h CSS: 959 mg/m^3, blank test II: 981 mg/m^3).

A summing up of the single values of the four groups for the component carbon monoxide (CO) results in the following mean values: blank test I: 512 mg/m^3, 3 t/h CSS: 526 mg/m^3, 6 t/h CSS: 626 mg/m^3, blank test II: 492 mg/m^3. When comparing the mean values of the test run including the application of 3 t/h CSS with the mean values of blank test I and II, the values are higher by 14 res. 34 mg/m^3. However, this is not a significant difference, as, with respect to these (proportionally) small differences the uncertainty of measurement of the

Values related to normal conditions (1013 hPa, 273 K, dry) and to an oxygen content of 10% (dry)													
Date		22.02.2002	23.02.2002	24.02.2002	27.02.2002	28.02.2002	01.03.2002	04.03.2002	05.03.2002	06.03.2002	09.03.2002	10.03.2002	11.03.2002
Incineration Status	Unit	Blank test I	Blank test I	Blank test I	CSS 3t/h	CSS 3t/h	CSS 3t/h	CSS 6 t/h	CSS 6 t/h	CSS 6 t/h	Blank test II	Blank test II	Blank test II
Total dust	mg/m^3	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Hydrogen chloride (HCl)	mg/m^3	< 1	1,6	< 1	< 1	1	< 1	< 1	1	< 1	< 1	< 1	< 1
Hydrogen fluoride (HF)	mg/m^3	< 0,2	< 0,4	< 0,2	< 0,3	< 0,2	< 0,2	< 0,3	< 0,2	< 0,2	< 0,2	< 0,3	< 0,2
Sulphur dioxide (SO_2)	mg/m^3	< 9	< 9	< 9	< 9	< 9	< 9	< 9	< 9	< 9	< 9	< 9	< 9
Nitrogen oxides expr. as NO_2	mg/m^3	1.030	1.170	925	851	1.080	937	859	1.050	969	966	1.000	976
Carbon monoxide (CO)	mg/m^3	472	421	644	562	456	559 [1)]	755 [1)]	657 [1)]	465	483	478	514
Total organic carbon TOC	mg/m^3	27	20	27	39	25	28 [1)]	28	34	24	21	21	23
Sum of cadmium (Cd) and thallium (Tl)	mg/m^3	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005
Mercury (Hg)	mg/m^3	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005	< 0,005
Sum of Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V	mg/m^3	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05
Dioxins/ furans, I-TEQ-value	ng/m^3	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01

Table 3.1: Summary of the test results for the investigated components

[1)] Small periods of out of range registration measuring methods has already an important influence. Furthermore, the collected data of blank test I, blank test II and 3 t/h CSS shows the highest value with blank test I with 644 mg/m^3. The lowest value of the test run with 3 t/h CSS remains under all three single values of blank test II.

The numerical comparison of the mean values of blank test I and II with the test run 6 t/h CSS shows greater differences in the case of test run 6 t/h CSS with 114 and 134 mg/m^3. This is attributable mainly to the higher values ascertained for test run 6 t/h CSS dated March 4th and 5th. Operating conditions show that, within the scope of the investigations, optimum operating conditions for the plant including the application of CSS could only be ascertained during practical operation. Experience has shown that this procedure takes a certain amount of time in full-scale plants such as cement plants. This is supported by a time series which shows declining values (755 mg/m^3 on the 4th of March; 657 mg/m^3 on the 5th of March and 465 mg/m^3 on the 6th of March), so that already in the case of the third test run with 6 t/h CSS (6th of March) a result relating to carbon monoxide could be achieved which remained under all three values of blank test II. This shows that the application of CSS does not necessarily lead to higher carbon monoxide emissions.

All measured values for carbon monoxide including those of the test run with 6 t/h CSS are within the normal limitations of cement factories. To be able to draw comparisons, values of measurements carried out in April 2001 at kiln no. 9 [1] are given which are in the range of 520 to 682 mg/m^3 (1/2 h mean values). The Verein Deutscher Zementwerke e.V., German Cement Works Association [2] indicates carbon monoxide values in the range of approx. 2.5 mg/m^3 (detection limit) to approx. 2000 mg/m^3 for the years 1998 and 1999 for 44 res. 30 German cement plants.

A summing up of the single values of the four groups for the Total Organic Carbon (TOC) component shows the following mean values: blank test I: 25 mg/m^3; 3 t/h CSS: 31 mg/m^3; 6 t/h CSS: 29 mg/m^3; blank test II: 22 mg/m^3. As the mean values of blank tests I and II are relatively similar – and as well the mean values of the tests with 3 t/h CSS and 6 t/h CSS -, the next obvious step would be to realize further evaluation on the basis of mean values for all 6 measurements for the blank tests I and II and for all 6 measurements of the tests including CSS (mean value: blank test I and II: 23 mg/m^3; 3 t/h CSS and 6 t/h CSS: 30 mg/m^3). There is a numerical difference of 7 mg/m^3 between blank tests I and II and the test runs with 3 t/h CSS res. 6 t/h CSS. This difference is already influenced significantly by the measurement uncertainty of the measuring method, so that the significance of the findings must be called into question. The higher mean values of the single test runs result from two values (3 t/h CSS: 39 mg/m^3 on February 27th and 6 t/h CSS: 34 mg/m^3 on March 5th). This shall be attributed (as already mentioned when evaluating the carbon monoxide) to the fact that within the scope of the investigations, optimum operating conditions for the plant including the application of CSS could only be ascertained during practical operation. Experience has shown that this procedure takes a time especially with regard to full-scale plants like cement factories. Such an optimization could be achieved: The plant could be operated for two days during the test runs including CSS with values which were below the values of blank test I (3 t/h CSS: 25 mg/m^3 on February 28th; 6 t/h CSS: 24 mg/m^3 on March 6th; blank test I:27 mg/m^3 on February 22nd and 27 mg/m^3 on February 24th). It cannot be concluded from the available data that the application of CSS necessarily leads to higher values of Total Organic Carbon. This statement is supported principally by the fact that no increase with regard to the concentration of Total Organic Carbon can be ascertained between the test run with 3 t/h and the test run with 6 t/h (3 t/h CSS: 31 mg/m^3, 6 t/h CSS: 29 mg/m^3). This, however, would have been the case when combustion of CSS inevitably resulted in higher values for Total Organic Carbon.

All values measured for Total Organic Carbon, even those including the application of CSS are within the normal limitations for cement factories. In order to be able to draw comparisons, values of measurements carried out in April 2001 at kiln no. 9 [1] are shown which are in the range of 22 to 24 mg/m^3 (1/2 h mean values). The Verein Deutscher Zementwerke e.V., German Cement Works Association [2] indicates Total Organic Carbon values in the range of approx. 2 mg/m^3 (detection limit) to approx. 60 mg/m^3 for the years 1998 and 1999 for 42 res. 25 German cement factories.

In addition, a statistical test (t-test) has been carried out with the collected data of the components carbon monoxide and Total Organic Carbon. As is widely acknowledged, the results of such tests may be problematic for small data compilations such as these as they may produce varying results - according to the test conditions. It is for this reason that the evaluation of the measuring results is not based upon the results of the statistical tests. However, the latter are presented here for the sake of completeness.

The tests were carried out using the standard t-test (unilateral) on the 95% and 99% level. Each of the 6 values of blank tests I and II was compared with the 3 values of the test runs with 3 t/h CSS and 6 t/h CSS. The t-test did not reveal a significant difference for the component carbon monoxide (neither on the 95% level nor on the 99% level) between the mean values of the blank tests and the values of the test runs including the application of CSS. As far as the component Total Organic Carbon is concerned, the test does not show a significant difference either on the 99% level between the mean values. A significant difference with regard to the mean values can be stated for the test runs 3 t/h CSS and 6 t/h CSS on the 95% level.

No sulfur dioxide (SO_2) could be measured with a detection limit of 9 mg/m^3. This means that the emissions of this component during the measurements in February / March 2002 were significantly lower than in measurements carried out in April 2001 [1], where values between 68 and 105 mg/m^3 were determined. This shall be attributed to the installation of the fabric filter which was installed in addition to the already existing electrostatic precipitator. It is generally known that acid components like sulfur dioxide, for example, are removed at the basic dust particulate layers of fabric filters. The efficiency of the fabric filter can be verified by means of the measured values of the total dust. Values in the range of 13 to 20 mg/m^3 were ascertained in April 2001 [1] for total dust for an operation of the plant without fabric filter. For an operation of the plant with a fabric filter during the tests in February / March 2002, no dust could be determined with a detection limit of 1 mg/m^3.

The output capacity of the cement plants is almost constant during all 12 test runs with a clinker production within the range of 141 t/h to 151 t/h, such that, in this respect, the test runs are comparable.

Summary

As far as the components total dust, hydrogen chloride (HCl), hydrogen fluoride (HF), sulfur dioxide (SO_2), sum of cadmium (Cd) and thallium (Tl), mercury (Hg), sum of Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V and dioxins/ furans (I-TEQ-value) are concerned it can be ascertained at a relevant concentration level that there is no change with regard to the emissions when comparing blank tests with the investigations including the application of CSS. Likewise, there is no change on the concentration level of normal emissions for the component nitrogen oxide expressed as NO_2. As for the carbon monoxide and Total Organic Carbon components, a comparison between test runs using CSS and blank tests reveals higher mean values for the CSS tests with an increase in the range of approx. 3 % to approx. 30%. These mean values, though, are within the normal limitations of cement factories. However, a detailed evaluation shows (see chapter 3) that probably this increase is not significant for the application of CSS as combustible material: The scattering of the values within the single groups, the course of the values related to time and the observations during the investigations on-the-spot lead to the assumption that variations within the scope of an operation optimization caused the increase of the values in question.

4 Characterization of measurements

Each of the congeners listed in Annex I of the Council Directive 2000/76/EC of December 4th, 2000, is determined for the measurement of dioxins/ furans. The I-TEQ value is evaluated following the procedure described in Annex 1. This procedure also complies with the European Standard EN 1948.

The heavy metal values include particle bounded forms, the gaseous (vapor) forms and their compounds in accordance with the Council Directive 2000/76/EC. Table 3.1 show the sum of groups of elements related to Annex II.1.1 of the Council Directive. In case that the result for the single element was below the detection limit half of the value of the detection limit was set into the sum up calculation.

Dioxins/ furans and heavy metals are detectable even at very low concentrations through use of laboratory procedures based on instrumental analysis. The detection limit, the uncertainty and the blank levels of the measuring procedures - respectively small inevitable process variations - cause a specific range which cannot be used for comparative tests. Therefore, levels within this range are not reported but indicated by “lower than” (assessment level).

For the components total dust, hydrogen chloride and hydrogen fluoride the resultant values show averages over ½ hour measurement period. The values for the components sulfur dioxide, carbon monoxide, nitrogen oxide expressed as NO_2 and Total Organic Carbon (TOC) are mean values for the investigation period of a test run (approx. 7 hours on average). The values for dioxins/ furans are based on an average sampling time of six hours, the values for the heavy metals on an average time of about one hour.

The flow rate of the sampled gas stream is adjusted to isokinetic conditions on the sampling nozzle during sampling of dioxins, dust and heavy metals.

The sampling of dioxins/furans, heavy metals and dust was carried out over the cross-section of the stacks following ISO 9096.

Technical details of the measurements are reported in Annex A, those of the operating conditions in Annex B.

ERGO Forschungsgesellschaft mbH

Hamburg, April 30th, 2002

Dr. Uwe Düwel   Dipl. Ing. Hauke Schröder

References

[1] ERGO Forschungsgesellschaft mbH: Report: Stack testing measurements in the flue gas of the Fábrica de Cimento, Secil Outão, Portugal, kiln 8 and 9, September 2001

[2] VDZ, Verein Deutscher Zementwerke e.V., German Cement Works Association, Umweltdaten der deutschen Zementindustrie, September 2000 und Mai 2001.

Annex I

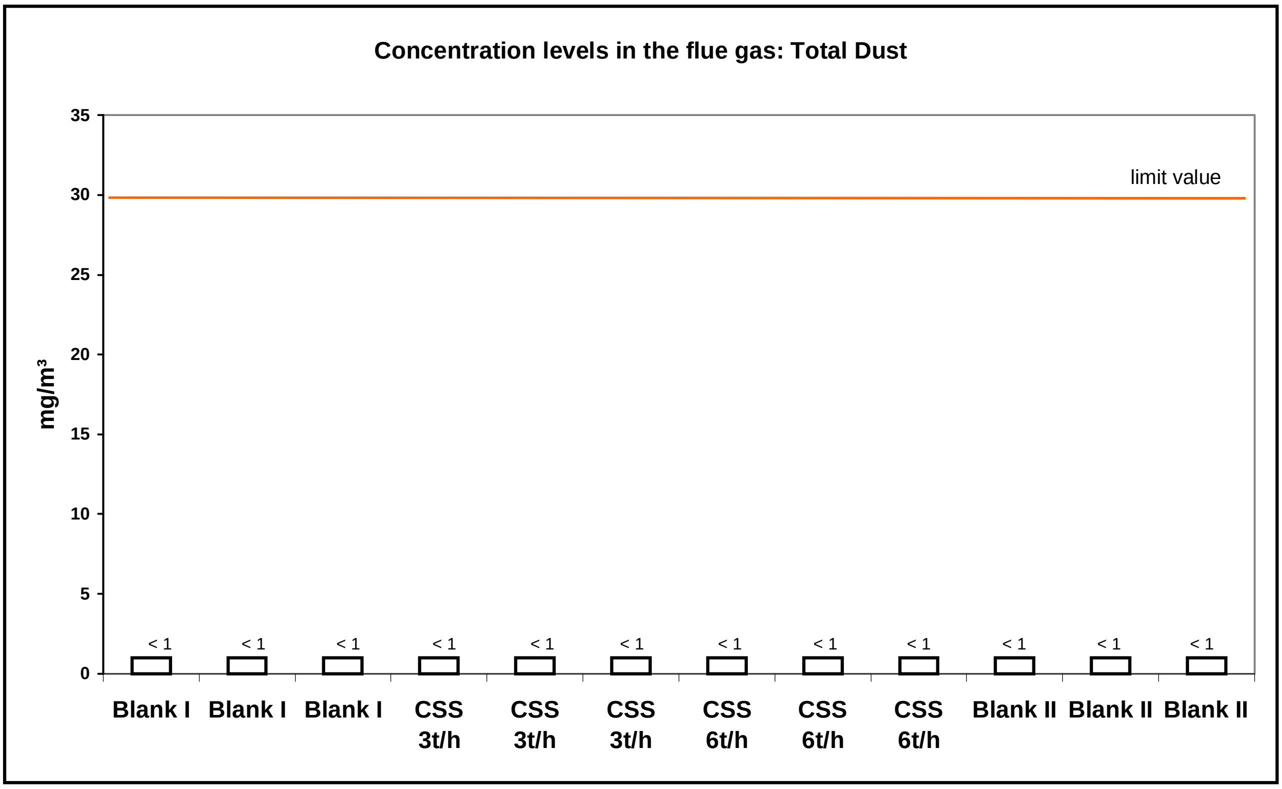


Figure 1

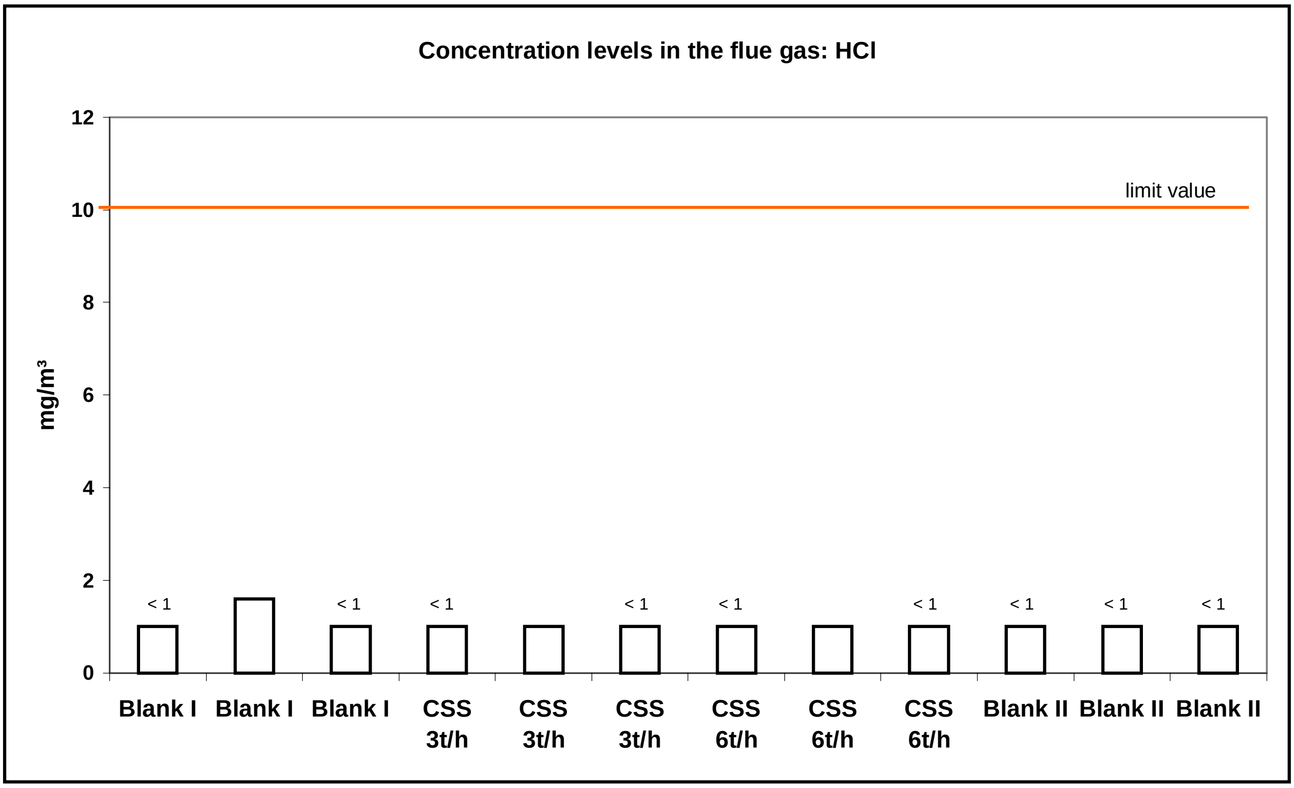


Figure 2

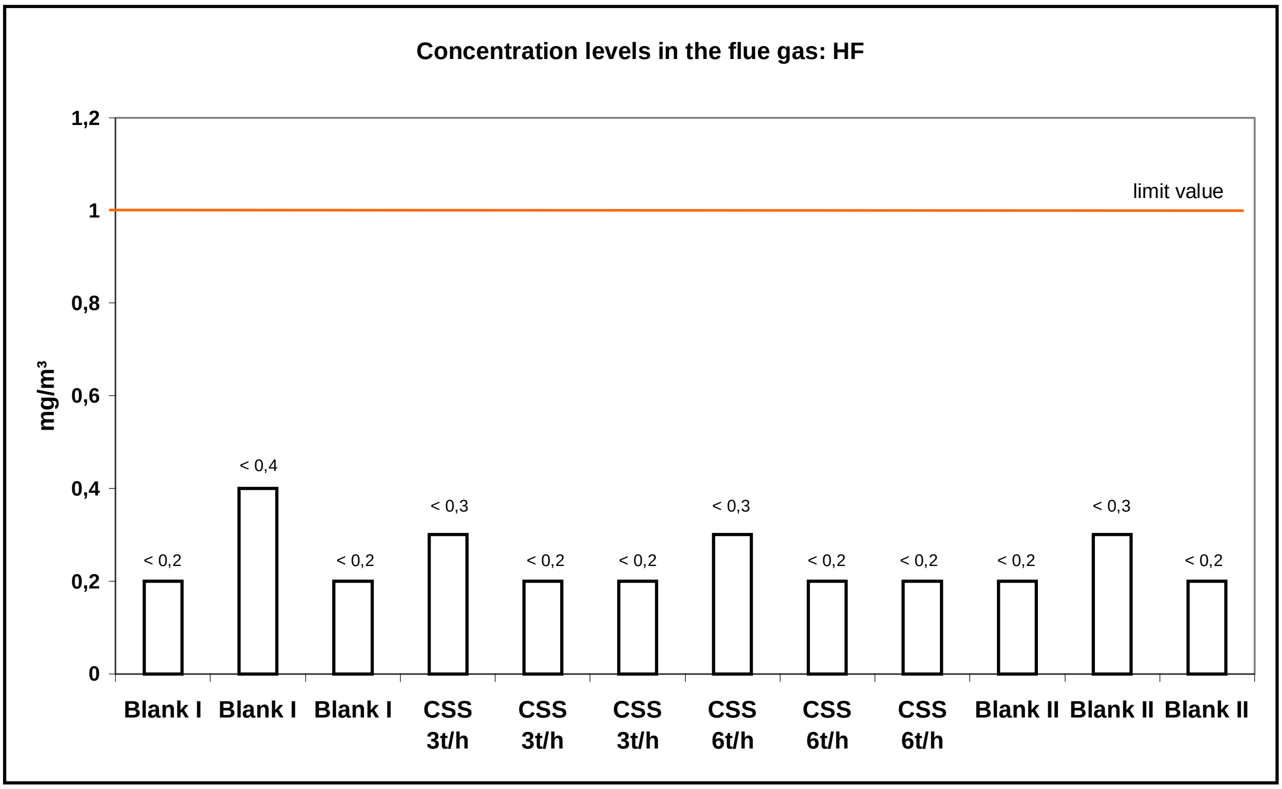


Figure 3

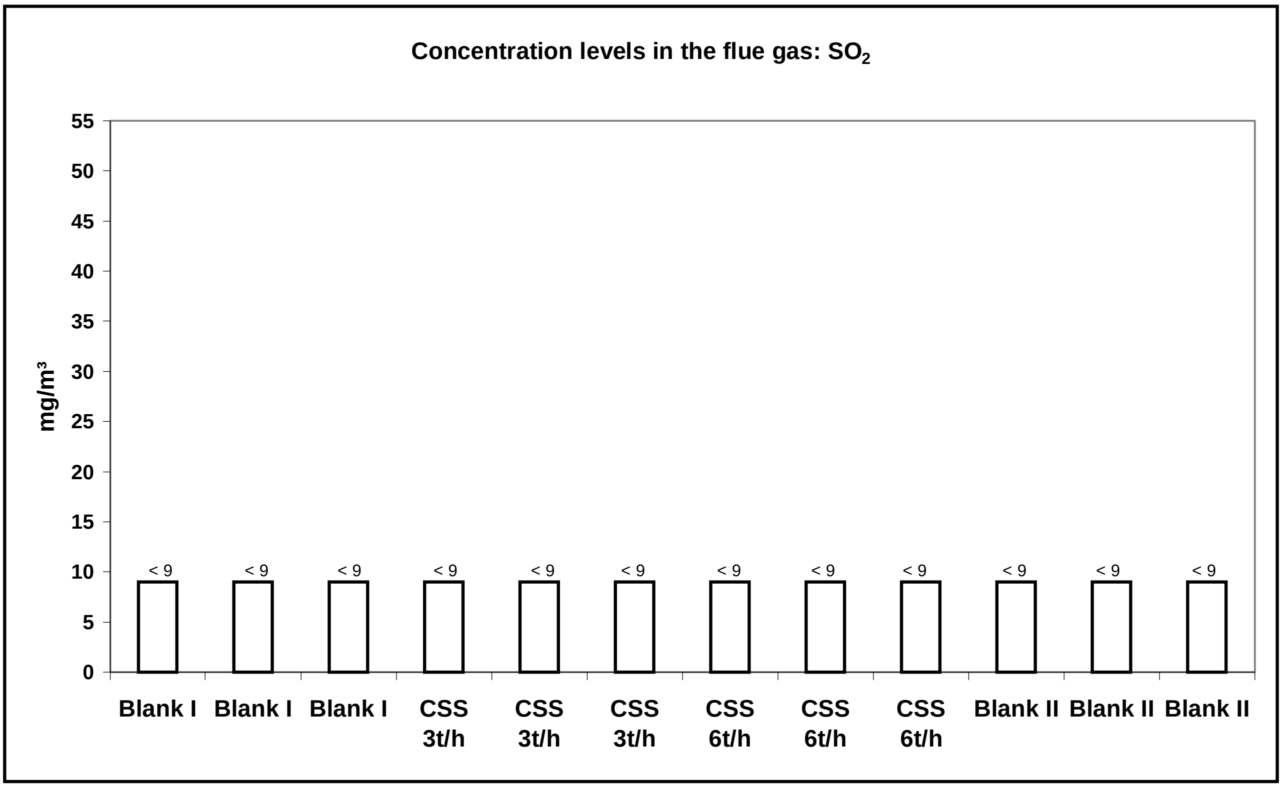


Figure 4 : Limit values set by the competent authority

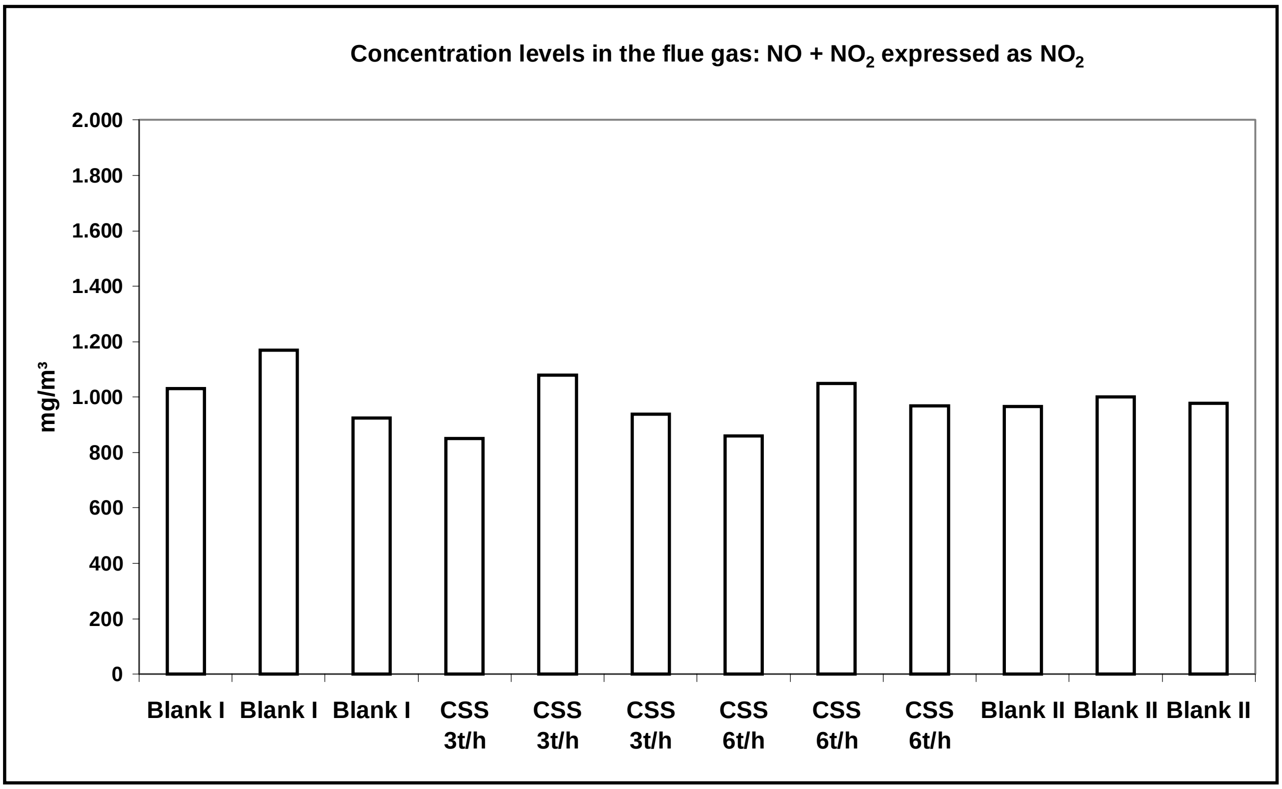


Figure 5 : Limit values set by the competent authority

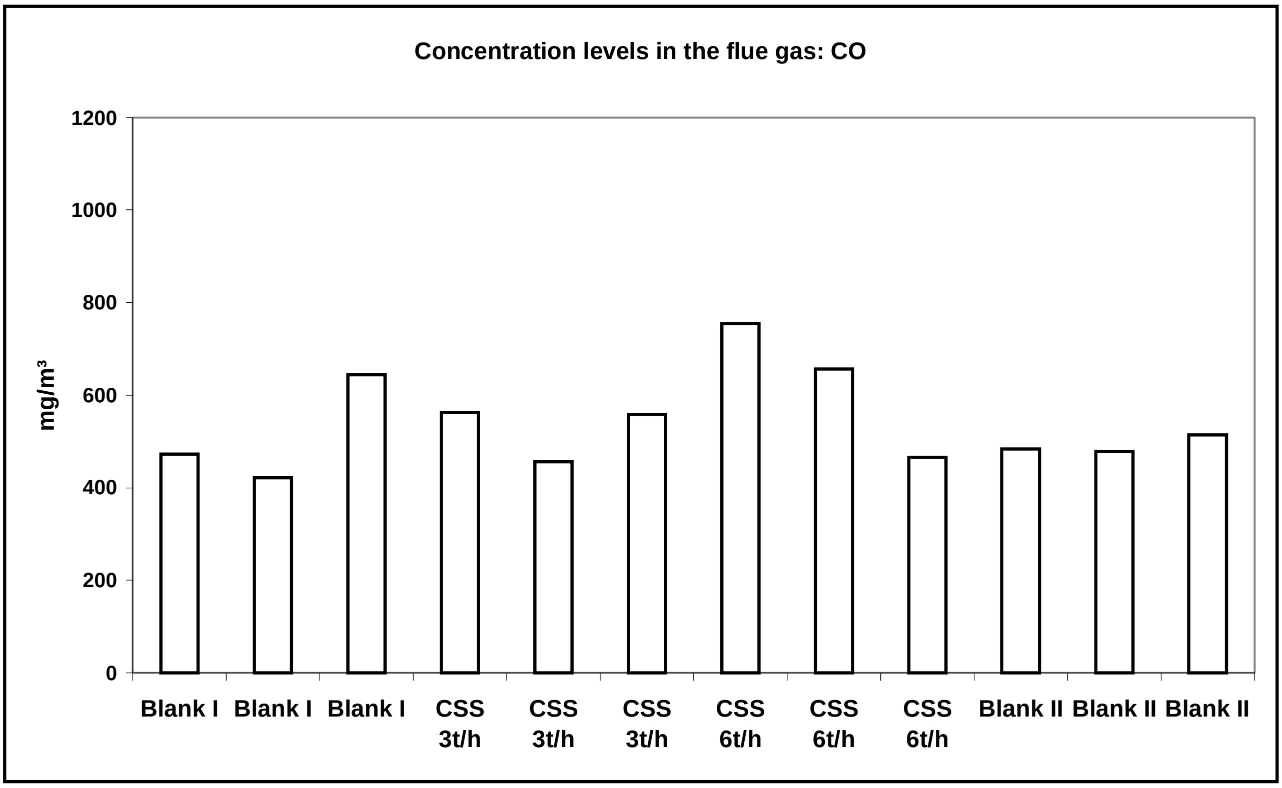
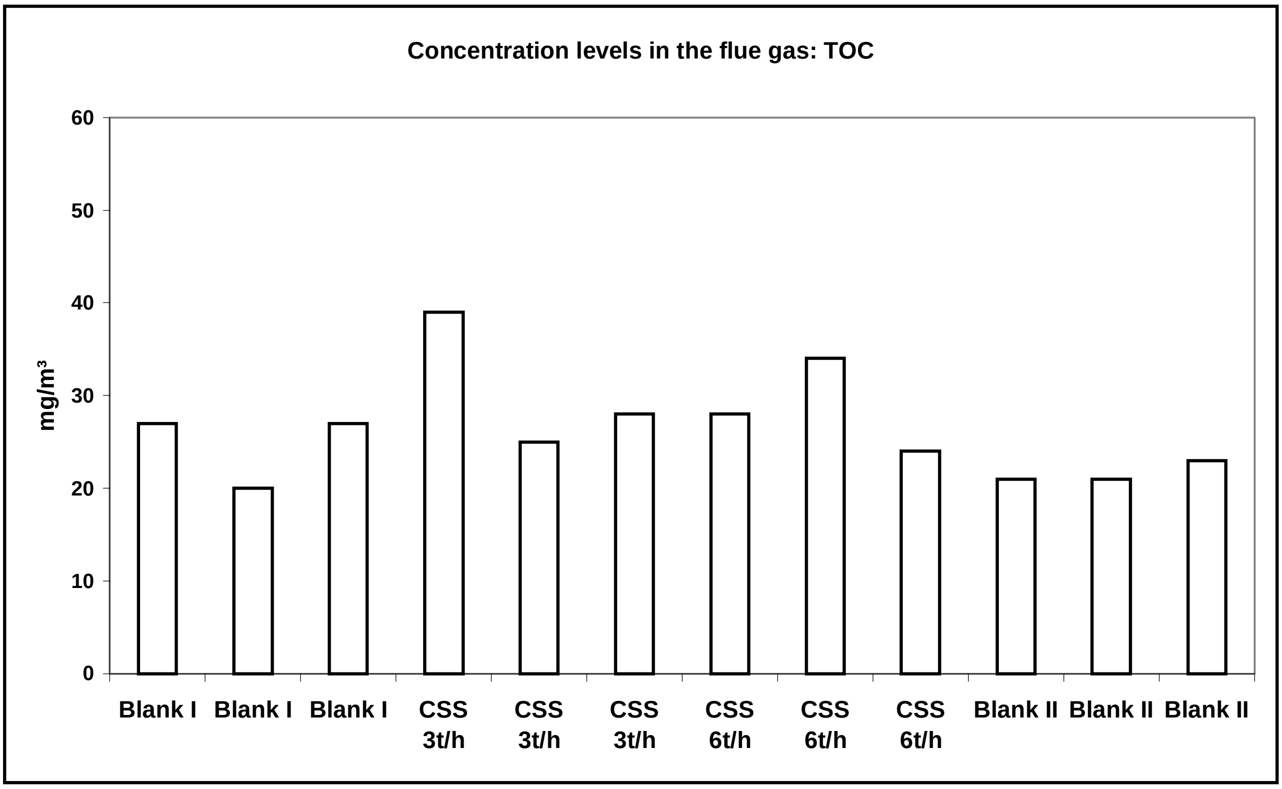


Figure 6 : Limit values set by the competent authority



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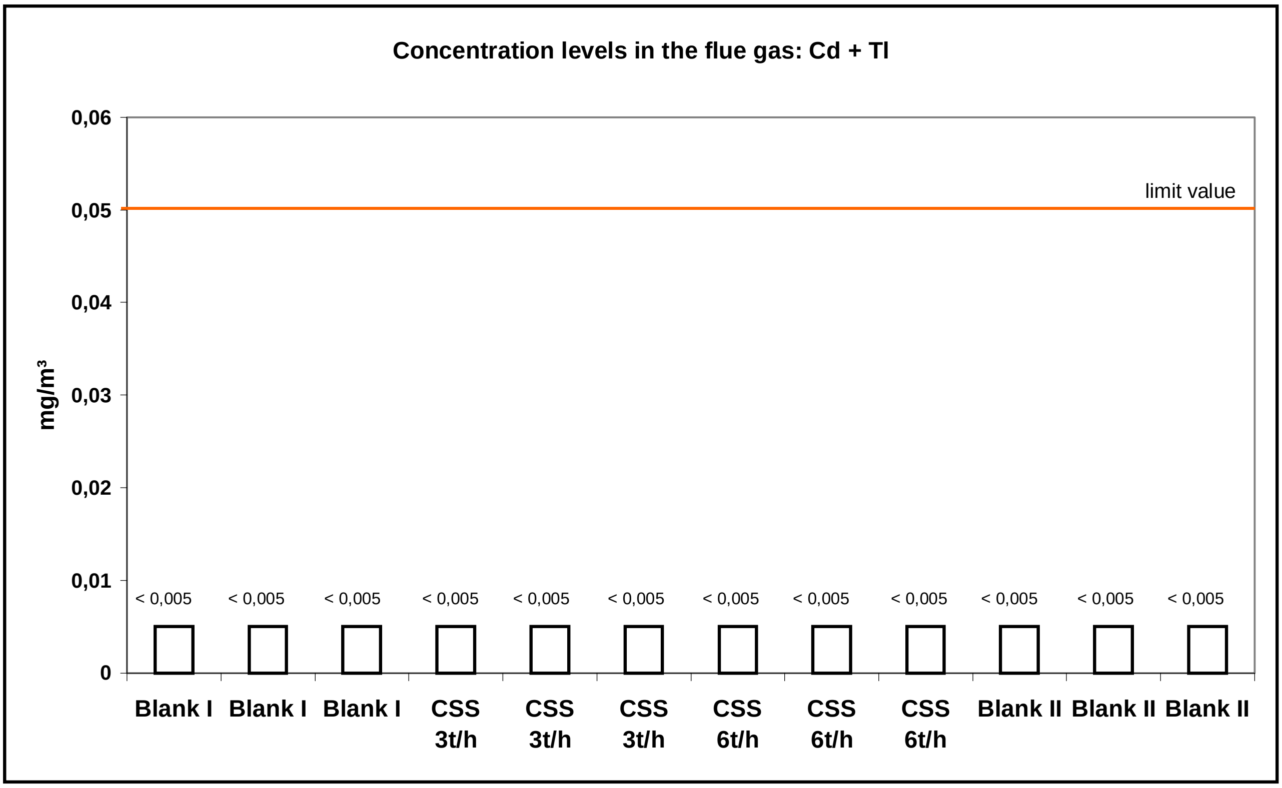


Figure 8

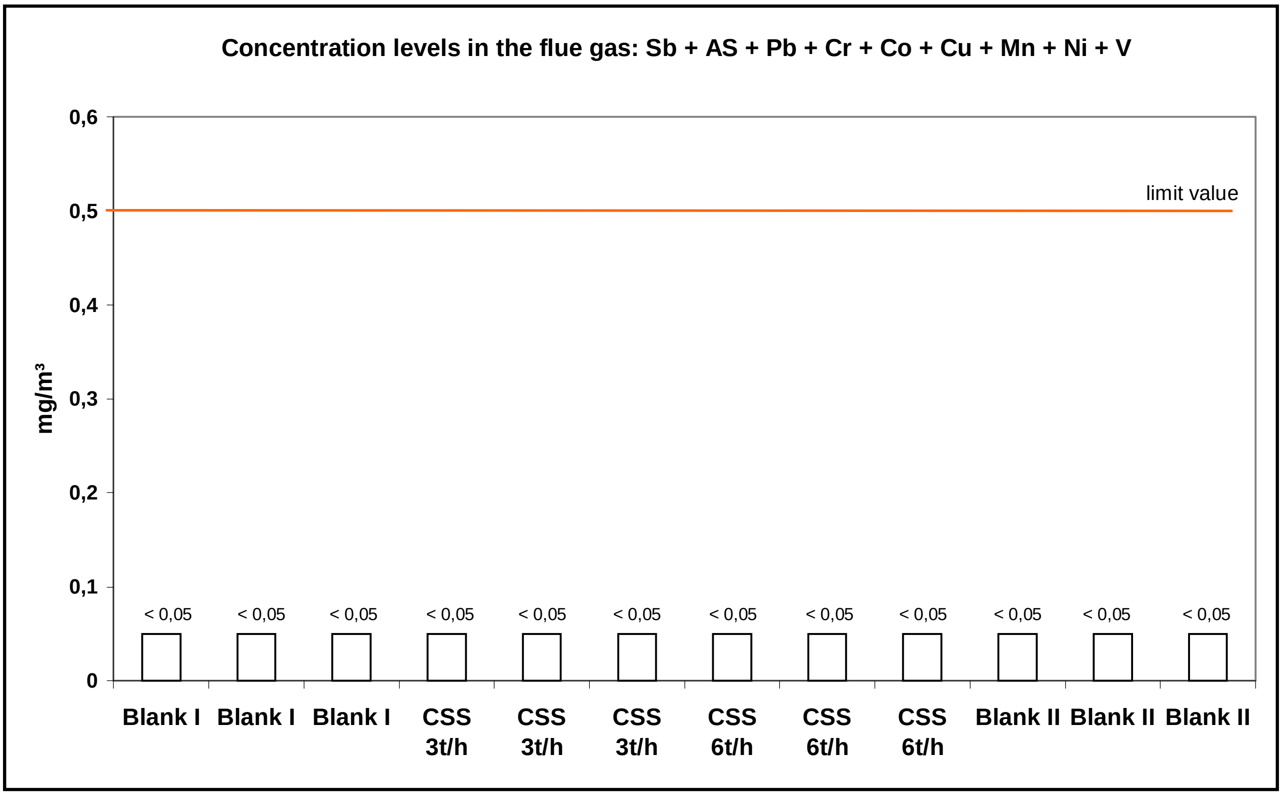


Figure 9

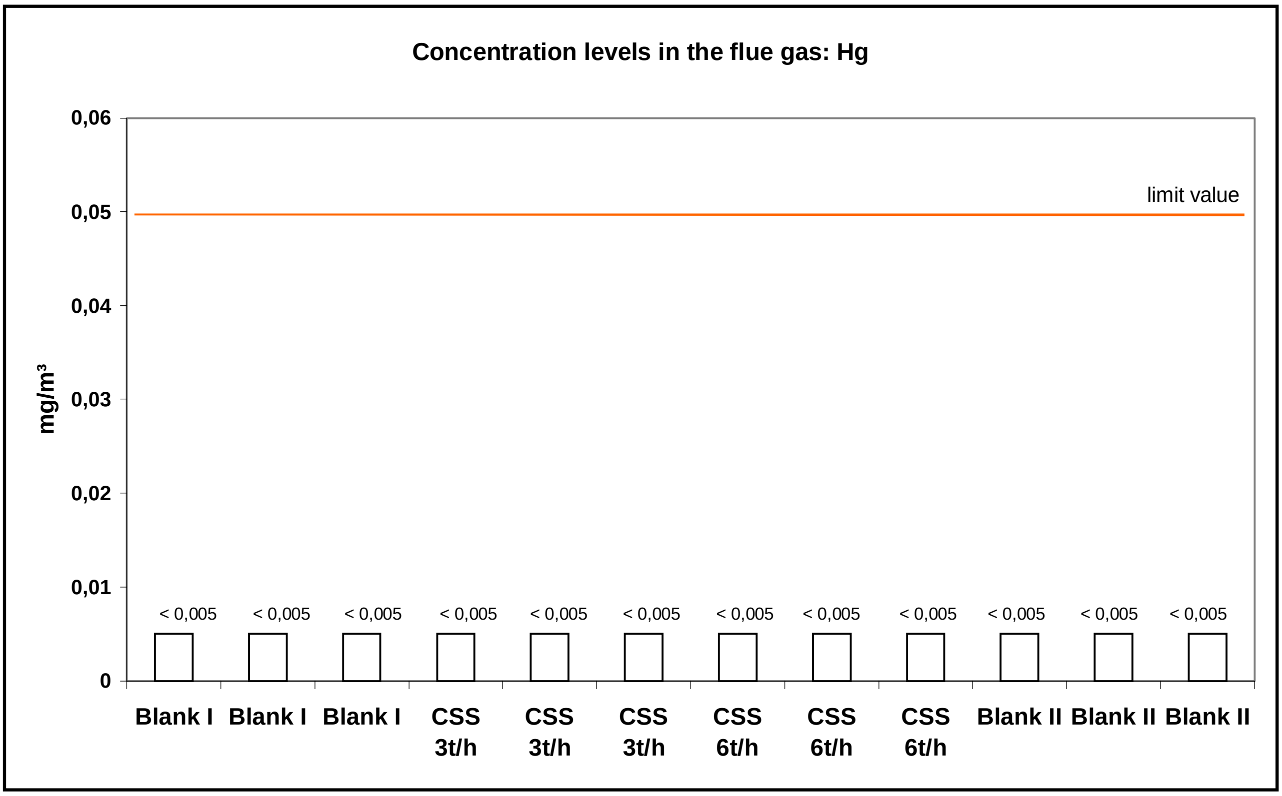
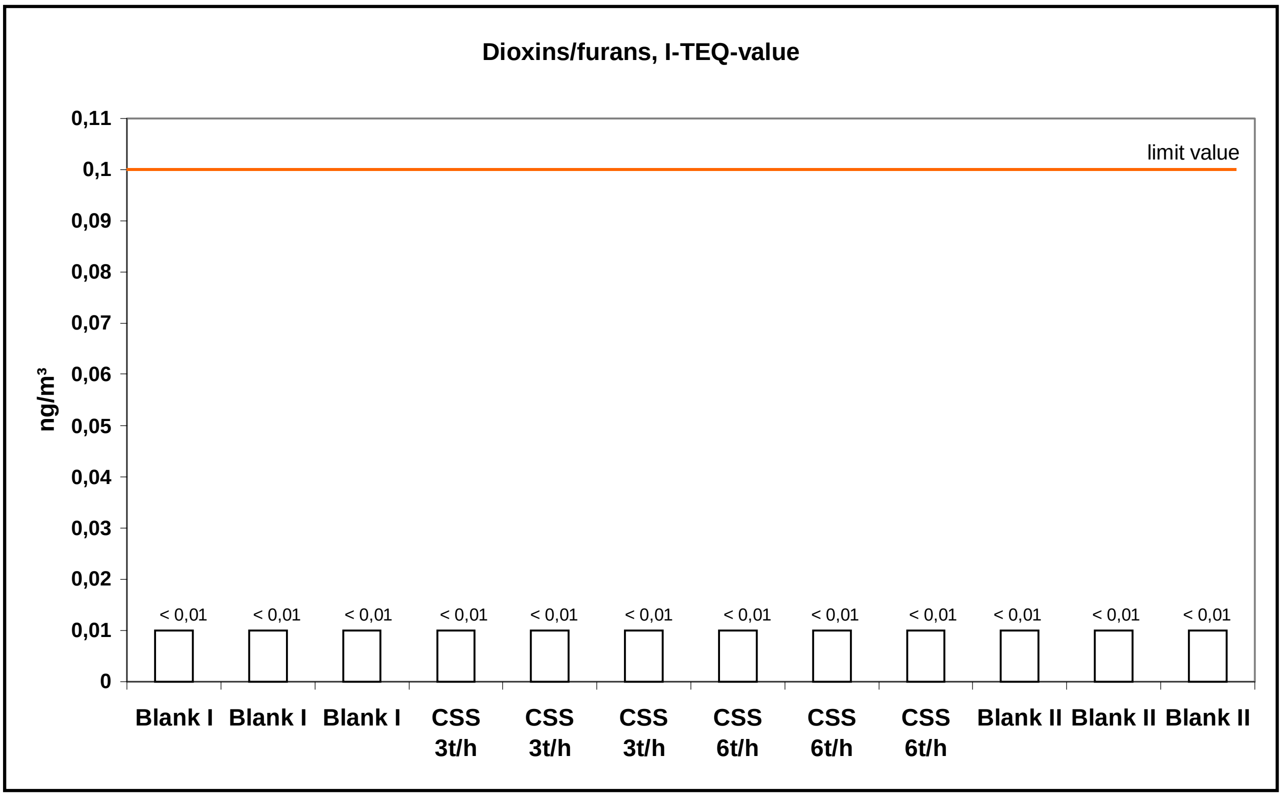


Figure 10


Dioxins/furans, I-TEQ-value
ng/m³
0,11
0,1
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
limit value
< 0,01
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CSS 3t/h
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Figure 11