Ambient air PCDD/Fs and PCBs determination according to UNI EN 1948-1-3-4: uncertainty and instrumental control limits for preliminary evaluation parameters such as flow velocity, water vapor, oxygen and carbon dioxide concentrations

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Introduction

According to UNI EN 1948-1[1] method, the characterization of the gaseous effluent must be carried out prior to sampling. In particular is necessary to measure velocity and volume flow[2], water vapour[3], temperature, oxygen[4] and carbon dioxide[5]. Those parameters need to be kept under control during all the phases of the sampling, in order to evaluate both the system abnormalities and the final calculations. The aim of this study is to determine the uncertainty of the parameters mentioned above and establish values for parallel measurements in order to verify the performance of the used equipment and to avoid redundant controls.

Materials and methods

The determination of the above parameters was carried out according to the following methods: the velocity of the gaseous stream was determined, in accordance with UNI EN 169112, using pitot tubes, suction pumps (Tecora, Corsico, Milano, Italy, and Mega System, Bareggio, Milano, Italy) and flow tests (Testo,Nova Milanese, Milano, Italy). The water vapour in the ducts was carried out according to UNI EN 14790:2006 (Gravimetric method); the gas flow is passed for about 1 hour through an accurately weighed amount of dried silica gel in a stove at 140 °C. The absorbed water vapour was determined by difference with the dried silica gel measured over a certified field balance (Mettler Toledo, Nova Milanese, Milano, Italy)

The oxygen concentration (v/v) in the fumes was carried out according to UNI EN 14789:2006, which provides the needed instructions for the use of paramagnetism as a measurement technique. It was performed with instruments from two different.

The carbon dioxide was determined according to UNI EN ISO 12039:2001, which leverages the usage of the infrared spectrophotometry; Smoke analyzers were provided from two different suppliers (Horiba – STA, - Sedriano, Milano, Italy and Mega System, Bareggio, Milano, Italy)

The intercalibration organized by ARPAT for two consecutive years was made possible thanks to the availability of the COLACEM plant, a cement plant in the municipality of Rassina in the province of Arezzo (Italy). At this plant a large enough platform is available; it allows 5 teams (about 15 operators) to connect contemporary up to 5 pickup nozzles and perform the tests with the necessary space to allocate all the equipment. Instead, routinely sampling is performed in double by each single team at incinerators and other industrial facilities in agreement with certified internal ARPAT's procedures. In addition, simulated sampling tests were conducted at a pilot plant in Milan (Italy). All the instruments used have been calibrated and monitored constantly, even in the field, with the use of certified reference gases (SIAD, Milano, Italy).

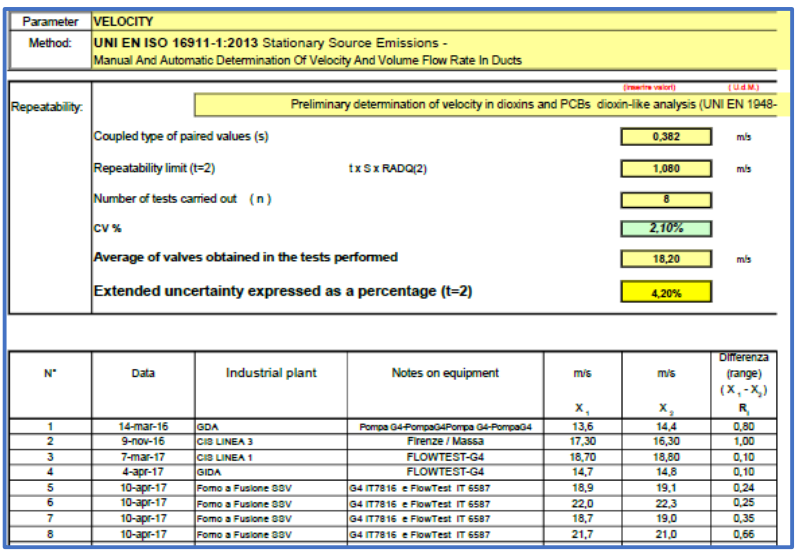
The ISO 5725-2:1994[6] method for calculation of the internal variability assumes the use of a reference material.

In emission sampling the flue gas concentration is time dependent and cannot be assumed to be constant. Therefore in EN 1948-3:1996 the calculation approach used is:

$$s = ((\Sigma X_{i1}-X_{i2})/2n)^{1/2} \quad (Eq.1)$$

where ***s*** is standard deviation, ***n*** is number of confirmed test, ***X*** is the measurement result. This same mode of calculation has also been extended to the parameters covered by this study.

Results and discussion



Parameter	VELOCITY
Method:	**UNI EN ISO 16911-1:2013** Stationary Source Emissions - Manual And Automatic Determination Of Velocity And Volume Flow Rate In Ducts

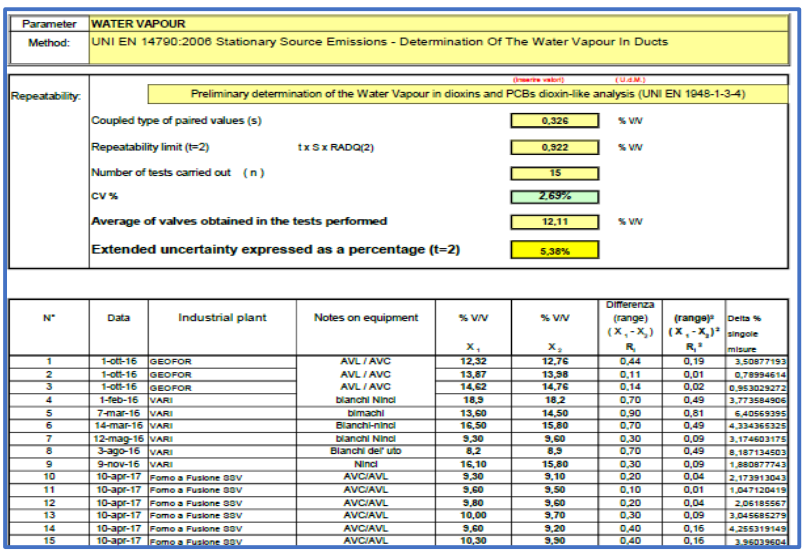
Repeatability:

Preliminary determination of velocity in dioxins and PCBs dioxin-like analysis (UNI EN 1948-

Coupled type of paired values (s)	0,382	m/s
Repeatability limit (t=2) t x S x RADQ(2)	1,080	m/s
Number of tests carried out (n)	8	
CV %	2,10%	
Average of valves obtained in the tests performed	18,20	m/s
Extended uncertainty expressed as a percentage (t=2)	4,20%	

N°	Data	Industrial plant	Notes on equipment	m/s X_1	m/s X_2	Differenza (range) $(X_1 - X_2)$ R_i
1	14-mar-16	GDA	Pompa G4-PompaG4Pompa G4-PompaG4	13,6	14,4	0,80
2	9-nov-16	CIS LINEA 3	Firenze / Massa	17,30	16,30	1,00
3	7-mar-17	CIS LINEA 1	FLOWTEST-G4	18,70	18,60	0,10
4	4-apr-17	GIDA	FLOWTEST-G4	14,7	14,8	0,10
5	10-apr-17	Fomo a Fusione SSV	G4 IT7816 e FlowTest IT 6587	18,9	19,1	0,24
6	10-apr-17	Fomo a Fusione SSV	G4 IT7816 e FlowTest IT 6587	22,0	22,3	0,25
7	10-apr-17	Fomo a Fusione SSV	G4 IT7816 e FlowTest IT 6587	18,7	19,0	0,35
8	10-apr-17	Fomo a Fusione SSV	G4 IT7816 e FlowTest IT 6587	21,7	21,0	0,66

Fig. 1 VELOCITY OF THE GASEOS STREAM



Parameter	WATER VAPOUR
Method:	UNI EN 14790:2006 Stationary Source Emissions - Determination Of The Water Vapour In Ducts

Repeatability:

Preliminary determination of the Water Vapour in dioxins and PCBs dioxin-like analysis (UNI EN 1948-1-3-4)

Coupled type of paired values (s)	0,326	% V/V
Repeatability limit (t=2) t x S x RADQ(2)	0,922	% V/V
Number of tests carried out (n)	15	
CV %	2,69%	
Average of valves obtained in the tests performed	12,11	% V/V
Extended uncertainty expressed as a percentage (t=2)	5,38%	

N°	Data	Industrial plant	Notes on equipment	% V/V X_1	% V/V X_2	Differenza (range) $(X_1 - X_2)$ R_i	(range)^2 $(X_1 - X_2)^2$ R_i^2	Delta % singole misure
1	1-ott-16	GEOFOR	AVL / AVC	12,32	12,76	0,44	0,19	3,50877193
2	1-ott-16	GEOFOR	AVL / AVC	13,87	13,98	0,11	0,01	0,78994614
3	1-ott-16	GEOFOR	AVL / AVC	14,62	14,76	0,14	0,02	0,953029272
4	1-feb-16	VARI	bianchi Ninci	18,9	18,2	0,70	0,49	3,773584906
5	7-mar-16	VARI	bimachi	13,60	14,50	0,90	0,81	6,40569395
6	14-mar-16	VARI	Bianchi-ninci	16,50	15,80	0,70	0,49	4,334365325
7	12-mag-16	VARI	bianchi Ninci	9,30	9,60	0,30	0,09	3,174603175
8	3-ago-16	VARI	Bianchi del' uto	8,2	8,9	0,70	0,49	8,187134503
9	9-nov-16	VARI	Ninci	16,10	15,80	0,30	0,09	1,880877743
10	10-apr-17	Fomo a Fusione SSV	AVC/AVL	9,30	9,10	0,20	0,04	2,173913043
11	10-apr-17	Fomo a Fusione SSV	AVC/AVL	9,60	9,50	0,10	0,01	1,047120419
12	10-apr-17	Fomo a Fusione SSV	AVC/AVL	9,80	9,60	0,20	0,04	2,06185567
13	10-apr-17	Fomo a Fusione SSV	AVC/AVL	10,00	9,70	0,30	0,09	3,045685279
14	10-apr-17	Fomo a Fusione SSV	AVC/AVL	9,60	9,20	0,40	0,16	4,255319149
15	10-apr-17	Fomo a Fusione SSV	AVC/AVL	10,30	9,90	0,40	0,16	3,960396604

FIG 2 - WATER VAPOUR content

Parameter	OXYGEN
Method:	UNI EN 14789:2006 Stationary Source Emissions - Determination Of Volume Concentration Of Oxygen (o[2]) - Reference Method – Paramagnetism

Repeatability:	Preliminary determination of oxygen in dioxins and PCBs dioxin-like analysis (UNI EN 1948-1-3-4) (inserire valori)		(U.d.M.)
	Coupled type of paired values (s)	0,145	% O2
	Repeatability limit (t=2) t x S x RADQ(2)	0,409	% O2
	Number of tests carried out (n)	10	
	CV %	1,10%	
	Average of valves obtained in the tests performed	13,16	% O2
	Extended uncertainty expressed as a percentage (t=2)	2,20%	

N°	Data	Industrial plant	Notes on equipment	% O2 X_1	% O2 X_2	Differenza (range) $(X_1 - X_2)$ R_i	(range)² $(X_1 - X_2)^2$ R_i^2	Delta % singole misure
1	4-ott-16	CHIMET	Cell. /Paramagnatico	14,42	14,35	0,07	0,00	0,486618005
2	5-ott-16	chimet	Cell. /Paramagnatico	12,48	12,12	0,36	0,13	2,926829268
3	10-nov-16	CIS LINEA 3 (FIRENZE/MASSA)	Parama/ Parama	12,40	12,20	0,20	0,04	1,62601626
4	10-nov-16	CIS LINEA 3	Cell. /Paramagnatico	12,70	12,50	0,20	0,04	1,587301587
5	7-mar-17	CIS LINEA 1	Cell. /Paramagnatico	11,4	11,6	0,20	0,04	1,739130435
6	5-apr-17	GIDA	Cell. /Paramagnatico	13,90	14,30	0,40	0,16	2,836879433
7	10-apr-17	Forno a Fusione SSV	AVC IT5998/AVL IT309	13,62	13,58	0,04	0,00	0,287406454
8	10-apr-17	Forno a Fusione SSV	AVC IT5998/AVL IT310	13,83	13,80	0,03	0,00	0,241271107
9	10-apr-17	Forno a Fusione SSV	AVC IT5998/AVL IT311	13,19	13,16	0,03	0,00	0,211391448
10	10-apr-17	Forno a Fusione SSV	AVC IT5998/AVL IT312	13,84	13,82	0,02	0,00	0,110350182

FIG. 3 OXYGEN concentration

Parameter	CARBON DIOXIDE
Method:	**ISO 12039:2001** Stationary source emissions -- Determination of carbon monoxide, carbon dioxide and oxygen - - Performance characteristics and calibration of automated measuring systems

Repeatability:	Preliminary determination of carbon dioxide in dioxins and PCBs dioxin-like analysis (UNI EN 1948-1-3-4) (inserire valori)		(U.d.M.)
	Coupled type of paired values (s)	0,044	% V/V
	Repeatability limit (t=2) t x S x RADQ(2)	0,125	% V/V
	Number of tests carried out (n)	5	
	CV %	0,58%	
	Average of valves obtained in the tests performed	7,62	% V/V
	Extended uncertainty expressed as a percentage (t=2)	1,16%	

N°	Data	Industrial plant	Notes on equipment	% V/V X_1	% V/V X_2	Differenza (range) $(X_1 - X_2)$ R_i	(range)² $(X_1 - X_2)^2$ R_i^2	Delta % singole misure
1	11-mag-16	vari	Bianchi DI Baia	9,4	9,32	0,08	0,01	0,854700855
2	11-mag-16	vari	Bianchi DI Baia	9,26	9,25	0,01	0,00	0,108049703
3	11-mag-16	vari	Bianchi DI Baia	3,87	3,89	0,02	0,00	0,515463918
4	11-mag-16	vari	Bianchi DI Baia	5,70	5,65	0,05	0,00	0,881057269
5	3-ago-16	Colaoem	Bianchi Lazzari	9,9	10	0,10	0,01	1,005025126

Fig. 4 CARBON DIOXIDE concentration

The following data are the result of the work performed by ARPAT for the purpose of accreditation of the UNI EN 1948-1-2-3-4 method. It has been performed by five sampling teams in working in different Tuscany's provinces. Multiple measurements were carried out in parallel for each test. Figures 1, 2, 3 and 4 show the values obtained in each individual test
The uncertainty was calculated as:
Ue (%) = 2 * CV% (Eq.2)
Established values for parallel measurements were calculated as 2,8 S (Eq.3)

The results were the following:

- Velocity: the analyzed speeds ranged from 13 to 23 m/s. The extended uncertainty evaluated with a t = 2 is 4,2%, while the acceptable limit for two parallel devices is 1 m / s.
- Water Vapour: the humidity analyzed ranged from 8 to 20% v/v. The extended uncertainty evaluated with a t = 2 is 5,4%, while the acceptable limit for two parallel devices is 0.9% v/v.
- Oxygen: the oxygen values obtained ranged from 11 to 14.5% V / V. The extended uncertainty assessed with a t = 2 is 2,2%, while the acceptable limit for two parallel devices is 0.4% v/v.
- Carbon Dioxide: the carbon dioxide values obtained ranged from 3,7 to 10 % v/v. The extended uncertainty assessed with a t = 2 is 1,2%, while the acceptable limit for two parallel devices is 0.12 % v/v.

It is more appropriate to express the uncertainty in percentage form and the range of acceptability for the parallel tests in absolute form; moreover, according to VDI 4219 (2009)[7], is appropriate to consider as negligible any contribution to the uncertainty being less than 5%.

Finally, after the annual calibration it may be sufficient to perform a sampling in parallel (e.g. after 6 months) to check the performance of the equipment.

References

1. UNI EN 1948:1996 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs
2. UNI EN ISO 16911-1:2013 Stationary Source Emissions - Manual And Automatic Determination Of Velocity And Volume Flow Rate In Ducts - Part 1: Manual Reference Method.
3. UNI EN 14790:2006 Stationary Source Emissions - Determination Of The Water Vapour In Ducts.
4. UNI EN 14789:2006 Stationary Source Emissions - Determination Of Volume Concentration Of Oxygen - Reference Method – Paramagnetism.
5. ISO 12039:2001 Stationary source emissions --Determination of carbon monoxide, carbon dioxide and oxygen -- Performance characteristics and calibration of automated measuring systems.
6. ISO 5725-2:1994 Accuracy (trueness and precision) of measurement method and result
7. VDI 4219 "Determination of the uncertainty of emission measurement by use of discontinuous measurement methods" (2009).