

## COMPARISON OF THE PERFORMANCE OF LONG-TERM AUTOMATED SAMPLING METHOD OF AMESA AND THOSE OF JIS-TYPE I AND TYPE III MANUAL SAMPLING METHODS FOR DIOXINS IN FLUE GAS

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### Abstract

This paper is aimed to compare the performance of AMESA, a long-term automated dioxin sampling method, with that of Japanese authorized method, JIS K0311 Type I sampling method. The 2005 revision of JIS K0311 for monitoring dioxins in flue gas has added a cooled probe method of Europe's EN1948 as JIS-Type III to the approved sampling methods. Comparable tests of AMESA and JIS-Type I method were performed for two municipal waste incineration facilities where AMESA units were installed and operated over the past three years. During that period a number of parallel tests were conducted to confirm that the two methods yield comparable results in dioxins concentrations. Correlation between the two methods were found to be very good. Additional new breakthrough tests in Europe confirmed that the absorption capacity of the XAD-II absorbent used in AMESA was adequate for long-term sampling of dioxins, furans and the other unintentionally formed Persistent Organic Pollutants (U-POPs) listed in the Stockholm Convention<sup>1</sup>.

### Introduction

Dioxin emissions from waste incineration facilities in Japan are regulated under the dioxin control special law<sup>2</sup>. This law requires every facility owner to conduct an emission test at least once a year according the authorized test method JIS K0311<sup>3</sup>. The JIS covers both dioxin analysis method and sampling method. The latter was revised in 2005 to increase one sampling method of Type I to three different sampling methods of Type I through Type III, which is the so called "cooled probe method" of EN1948<sup>4</sup>. AMESA is a long term automated sampling method for dioxins in flue gas and was evolved from the cooled probe method.

AMESA is usually attached to the flue gas line of an incineration facility and is set to automatically samples a gas under isokinetic conditions for 6 hours to one month.. AMESA's performance as a Continuous Emission Monitoring system (CEMs) has been certified by the UK certification agency, MCERTS since 2005 and also by the German certification agency, TUV since 1998. Good agreement of AMESA measurements with those of the cooled probe method have been reported several times<sup>5,6,7,8</sup>. Due to the fact that all standard methods are designed for short-term sampling several new breakthrough tests were done in Europe, to approve in addition to the former tests<sup>5,8,9,10</sup> the capability of AMESA to sample up to 1 month PCDDs/PCDFs and other U-POPs on

the used XAD-II cartridge.

There are more than 100 installations of AMESA over the world, of which 4 installations in two incineration facilities are in Japan. Continuous monitoring of dioxins in flue gas of waste incineration facilities are not required by law in most countries except for Belgium (since 2000). As a second area, the authority of the Lombardia region of Italy will start next year to demand the continuous dioxin monitoring of waste incinerators. In Japan, one year's monitoring service consists of 12 monthly long-term samplings followed by dioxin analyses and a short period of JIS-AMESA parallel sampling. The data used for this paper came from these JIS-AMESA parallel samplings conducted under the regular monitoring and maintenance service..

### Material and Methods

JIS-Type I device and AMESA were used for a parallel test of dioxins in flue gas once or twice a year at each of the two facilities. Both facilities were newly constructed at the time of AMESA installation. The dioxin levels at these facilities are in the order of ambient concentration level, namely pg-TEQ/m<sup>3</sup> level instead of ng-TEQ/m<sup>3</sup> level. AMESA usually collect 500 m<sup>3</sup> of flue gas over a one month period while a high volume air sampler for dioxins in ambient air usually collects 1000 m<sup>3</sup> of air over a 24 hour period. Because of the comparable sample volume, AMESA samples yields accurate analysis results for dioxins in flue gas even at the very low concentration level.

In contrast to the long term sampling of AMESA, a short term parallel test of JIS vs. AMESA collects only 4 m<sup>3</sup> to 12 m<sup>3</sup> of flue gas over a period of 4 to 10 hours. This small volume of the samples causes a higher uncertainty in determination of dioxins concentrations at laboratory analysis. JIS-Type I manual sampling method requires cares for maintaining isokinetic sampling condition and temperatures of filter paper and adsorbing XAD resin. Because of the cares required during sampling and attendance of sampling personnel at site, the manual sampling usually can not be extended over a day. Therefore, conducting 10 hours of actual sampling with the manual sampling device at site is considered to be the most one can do in conventional dioxin sampling practice.

### Results and Discussion

#### JIS vs. AMESA Comparative Tests

There were 8 pairs of parallel sampling tests, which were conducted at the two facilities over the past 3 years. Results of dioxins concentrations of JIS-Type I and AMESA methods are summarized in Table 1. As seen from the table, 3 out of the 8 parallel tests meet the tolerance level of relative percent difference (RPD) < 30%, which is set in JIS K0311 for a new method, i.e. AMESA, to be considered as comparable to Type I. However, similar to the uncertainty of 35% given in EN1948:2006-06, which is related to the limit value of 0.1 ng-TEQ/m<sup>3</sup>, it has to be considered that the tolerance level (<30%) of JIS was surely also related to the same limit value.

		JIS Type I	AMESA	Abs.Diffr.	RPD %	RPD <30 %	AbsD <0,3*TDL	RPD % rel. to 0,1	RPD< 35% acc.EN1948
Facility A	Run 1	0,0005	0,00021	0,00029	82	No	Yes	0,29	Yes
	Run 2	0,00086	0,0015	0,00064	54	No	Yes	0,64	Yes
	Run 3	0,00059	0,00054	0,00005	9	Yes	Yes	0,05	Yes
	Run 4	0,00021	0,00027	0,00006	25	Yes	Yes	0,06	Yes
Facility B	Run 1	0,000015	0,000033	0,000018	75	No	Yes	0,018	Yes
	Run 2	0,0026	0,0039	0,0013	40	No	Yes	1,3	Yes
	Run 3	0,000017	0,000018	0,000001	6	Yes	Yes	0,001	Yes
	Run 4	0,000076	0,00016	0,000084	71	No	Yes	0,084	Yes

Table 1. Results of JIS-Type I vs. AMESA parallel tests conducted at the two facilities.

Note: RPD=Relative Percent Difference, TDL=Target Determination Limit (0.01 ng-TEQ/m<sup>3</sup>)

The emission standard for waste incineration facilities built after December 1999 is 0.1 ng-TEQ/m<sup>3</sup>. Target determination limit (TDL) for dioxin analysis is usually set to be one tenth of the applicable emission standard. Therefore, the analytical uncertainty of the tolerance at this TDL is 0.3 \* 0.01 = 0.003 ng-TEQ/m<sup>3</sup>. All absolute differences of the parallel tests are found to be less than the analytical uncertainty.

Regression of the parallel test data is shown in Figure 1. AMESA exhibited an excellent correlation with JIS Type I with R<sup>2</sup> = 0.97. This high correlation is a surprisingly good, considering the low concentration level and the small sampling volume encountered in the parallel tests. These results are in good agreement with the earlier

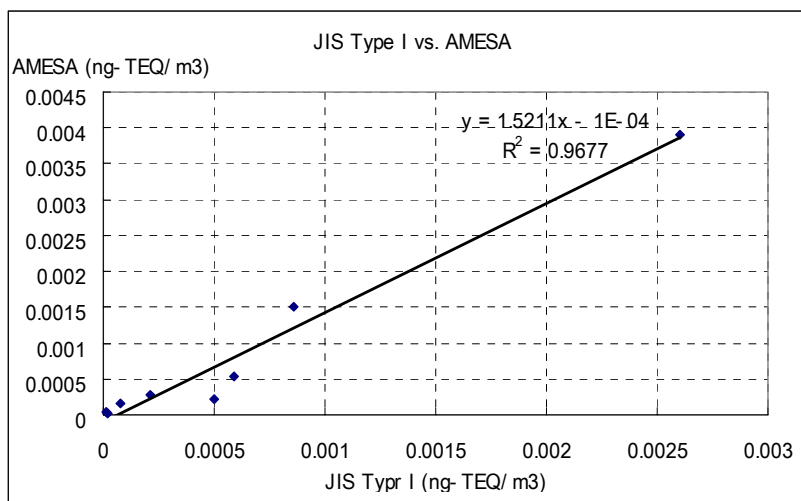


Figure 1. Correlation between JIS-Type I and AMESA measurements published results of several comparison tests<sup>5,6,7,8</sup>.

**Breakthrough Tests**

Because the manual methods specified in JIS K0311, EN 1948 or US EPA method 23A are all designed for short term dioxin sampling, it has to be proved for AMESA that the adsorption capacity of the used XAD-II cartridge

be sufficient for a 4 weeks sampling<sup>5,8,9,10</sup>. These results could be confirmed in new tests done in incineration facilities in Belgium, Italy and Sweden for all dioxins, furans (see table 2) and U-POPs.

	1 <sup>st</sup> cartridge (pg TEQ/m <sup>3</sup> )	2 <sup>nd</sup> cartridge (pg-TEQ/m <sup>3</sup> )
Facility 1	1,8	< 0,01
Facility 2	0,37	< 0,01

Table 2 Breakthrough results after 4 weeks sampling

### Conclusion

AMESA is designed to measure a long term average concentration by maintaining the isokinetic sampling conditions. To make a long-term flue gas sampling possible, AMESA is fully automated for gas sampling. This is in contrast to JIS-Type I where gas sampling depends on human observations for maintaining isokinetic conditions and temperature controls for filter and XAD-II absorbent.

In this study, AMESA was used for a short term sampling to make the parallel tests possible. If the two facilities where AMESA units were installed had a higher dioxins concentration level near the emission standard, the parallel tests would yield better results in both RPD and correlation than those of the present study. Due to the non-portable nature of AMESA device, RPD results of the study will not be improved easily in the future. Furthermore, AMESA was proved to fulfil the requirements according acceptable losses given by the different standard methods with the confirmations of the previous and new breakthrough tests. Therefore, together with the good correlation between JIS Type I and AMESA and the small absolute differences between them, AMESA can be considered to be fully comparable to Type I and Type III.

### References

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