

## 9.9 Dioxin analysis methods

### 9.9.1 Introduction

The substances called either dioxin or dioxins are the general name given to polychlorinated dibenzo-*p*-dioxins PCDDs and to polychlorinated dibenzofurans PCDFs, whereby PCDD has 75 isomers, and PCDF has 135 isomers. Because dioxins are severely toxic substances 5,000 times more poisonous than potassium cyanide, the analyst must undergo special training in its handling. Sample should be processed in a well-managed laboratory facilities, written in 9.1.7 GC/MS with a high resolution function (¥60 million to ¥100 million) and standard substances (¥10 million to ¥80 million), and waste substance processing and storage facilities are essential.

Moreover, because analysis handles values at an extremely low level of concentration, it is important to establish accurate data processing and quality control. Laboratories with just such a system are limited to special facilities in developed countries.

### 9.9.2 Sampling

#### ① Ambient air sampling <sup>1)</sup>

A collection tube (inner diameter 84 mm × length 200 mm) with two sheets of polyurethane foam fitted is attached to the latter stage of a high volume sampler filter, as described in 9.6, and suction is continued for approximately 24 hours at a rate of 700 mℓ/min.

Both the filter and polyurethane foam shall be treated by heating and washed for a minimum of 16 hours in Soxhlet to remove all of the interfering substances prior to the sampling. To assure the data accuracy, both filter and polyurethane foam from the same lot must be prepared as a travel blank.

#### ② Exhaust gas sample collection <sup>1) 2)</sup>

The particulate components are isokinetically drawn from an emission source by collection apparants of Type 2 under regulation JIS Z8808 as stated in 8.1, and the filter holder is set to a maximum of 120°C.

The gaseous components are collected in an sorbent column (XAD-2 resin) and impingers. By both methods of the Ministry of Health and Welfare and of the Environment Agency, three impingers are connected in front of the sorbent column and two are connected behind, in series, as shown in Fig. 9.9.1, and two of the ones in front are filled with water (hexane sterile water), and at the fourth impinger is filled with diethylene glycol. Never use any grease on the connecting parts. Moreover, the US EPA's method 23 A <sup>4)</sup>, uses a condenser coil in place of an impinger, which is filled with water in front of the sorbent column, thereby changing from the collection methods of semi-volatile organic substances that have been used heretofore <sup>3)</sup>.

Specimen collection sets its standard at 3 m<sup>3</sup> or more (four hours average) as a rule, following the passage of a minimum of one hour after the burning has stabilized.

The filter and absorbent should be removed all interfering components washing by Soxhlet. Further, the rolles are regulated for both the sample storage and the blank sample in detail.

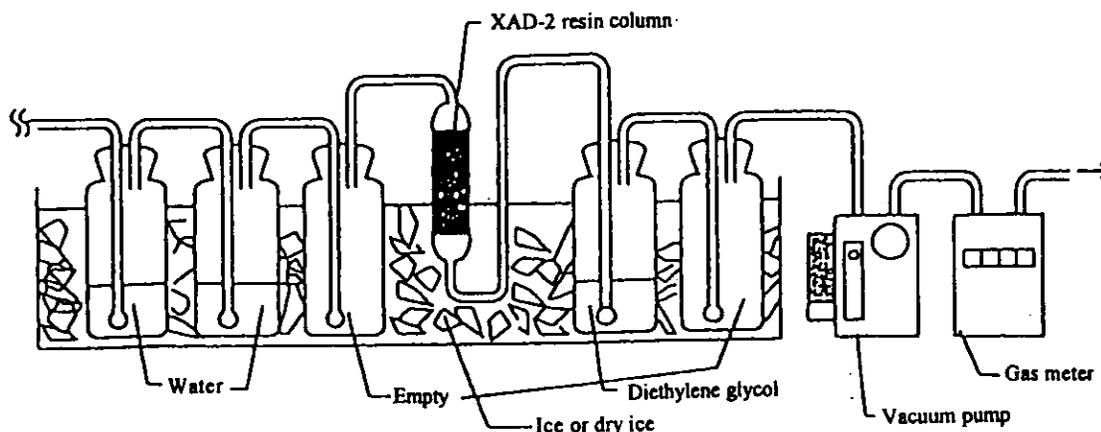


Fig.9.9.1 Configuration of exhaust gas sampling unit below the filter holder

### 9.9.3 Analytical operations

The dioxins in the collected sample are extracted individually, removed water, and concentrated, and cleaned up by means of different types of column chromatography, until it becomes colorless, the final solution is injected into high resolution GC/MS (HRGC/HRMS), and analyzed. Fig.9.9.2 gives an example of the analytical flow chart for emission samples described in the Ministry of Health and Welfare Manual <sup>2)</sup>.

The analysis is performed for all isomers of dioxins including the chlorine isotope <sup>37</sup>Cl, from tetrachlorides (T<sub>4</sub>CDD, T<sub>4</sub>CDF) to octochlorides (O<sub>8</sub>CDD, O<sub>8</sub>CDF), by means of the SIM (Selected Ion Monitor) method.

In order to identify and determine the dioxins by internal standard method, 17 types of C<sub>12</sub>-PCDD and PCDF are prepared as standard materials. As internal standard substances, 16 to 19 types of <sup>13</sup>C<sub>12</sub>-PCDD and PCDF, and <sup>37</sup>Cl-PCDD are used. Different isomers are used to add the internal standard for each sampling spike, cleanup spike, and syringe spike.

The cleanup spike uses a total of 10 types of PCDD and PCDF as an internal standard made by <sup>13</sup>C<sub>12</sub> for each chlorinate, which are added into the sample before the cleanup (however, in the US EPA method, as OCDFs are not added to avoid the interference, a total of nine spikes are used). These purpose are to make possible the ultra trace analysis by an isotope dilution method, and to check if the cleanup has carried out definitely through the recovery rate. Moreover, the US EPA method, prescribes that the internal standard is added immediately before the extraction operation and check the total recovery rate through the extraction and the cleanup operation.

The syringe spike is added immediately before the injection of sample into the GC/MS, in order to avoid the effect of the sensitivity change of the analyzer. The total concentration is formed from the relative concentration and the syringe spike responses.

In order to guarantee that the sample contamination is small, a sampling spike is added into the absorbent used, and its recovery rate is obtained. Further, all experimental procedures in the laboratory are conducted as same as actual samples. The total operation blank is analyzed, and the blank values are confirmed below the detection limit.

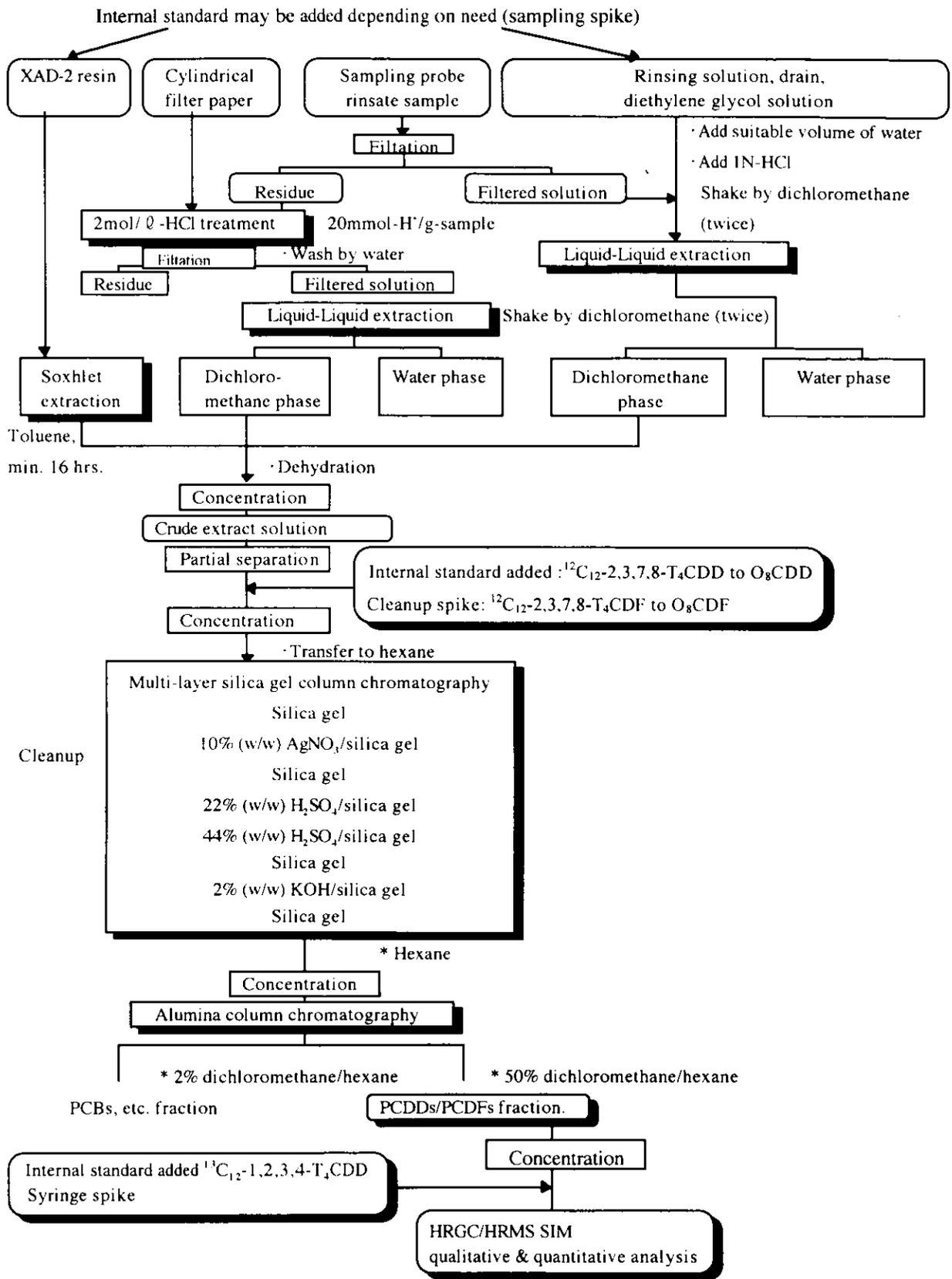


Fig.9.9.2 Analytical Scheme of Exhaust Gas Sample

#### 9.9.4 Indication of concentration

The measuring concentration is indicated for all homologues of the tetrachlorides and octochlorides as shown in Table 9.9.1. The concentrations of 2,3,7,8 position substitution isomers and the total of other isomers are indicated, together with the grand total concentrations of all other isomers.

Further, with regard to 17 isomers of extremely potent toxicity, the TEQ (Toxic Equivalents) are determined through multiplying the concentration by the TEF (Toxicity Equivalency Factor), and then totalized them. These results are expressed as pg-TEQ/m<sup>3</sup> in the ambient air, and ng-TEQ/m<sup>3</sup><sub>N</sub> (dry gas volume) for exhaust gasses.

Table 9.9.1 Indication of Dioxins

	PCDDs		PCDFs	
	homologue	Isomer	homologue	Isomer
4-chlorinated substituents	T <sub>1</sub> CDDs	2, 3, 7, 8 - Other	T <sub>1</sub> CDFs	2, 3, 7, 8 - Other
5-chlorinated substituents	P <sub>5</sub> CDDs	1, 2, 3, 7, 8 - Other	P <sub>5</sub> CDFs	1, 2, 3, 7, 8 - 2, 3, 4, 7, 8 - Other
6-chlorinated substituents	H <sub>6</sub> CDDs	1, 2, 3, 4, 7, 8 - 1, 2, 3, 6, 7, 8 - 1, 2, 3, 7, 8, 9 - Other	H <sub>6</sub> CDFs	1, 2, 3, 4, 7, 8 - 1, 2, 3, 6, 7, 8 - 1, 2, 3, 7, 8, 9 - 2, 3, 4, 6, 7, 8 - Other
7-chlorinated substituents	H <sub>7</sub> CDDs	1, 2, 3, 4, 6, 7, 8 - Other	H <sub>7</sub> CDFs	1, 2, 3, 4, 6, 7, 8 - 1, 2, 3, 4, 7, 8, 9 -Other
8-chlorinated substituents	O <sub>8</sub> CDD	1, 2, 3, 4, 6, 7, 8, 9 -	O <sub>8</sub> CDF	1, 2, 3, 4, 6, 7, 8, 9 -
Σ (4-chlorinated~8-chlorinated)	PCDDs	—	PCDFs	—