# Selected Article

## Development of Mercury Analyzer for Stack Gas – ENDA-Hg5200 –
## 煙道排ガス中水銀濃度測定装置（ENDA-Hg5200）

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We made a design the new mercury analyzer for stack gas, amid mounting international concern over environmental from heavy metal. It was difficult for us to measure the mercury, because gaseous mercury is high reactivity with other material and susceptible to coexistence gas. Especially, existing analyzer had a problem that stability of measurement value was no good. So, we selected the materials at sample line and examined most suitable condition for measurement mercury, and made a design new dry reducing catalyst in the probe unit. And we made a design new hydrogen chloride scrubber for extend the catalyst lifetime. Analyzer uses cold vapor atomic absorption and cross-modulation method, therefore can measure high sensitivity and stability.

重金属への環境配慮の関心が高まる中，煙道排ガス中水銀濃度測定装置を開発した。ガス状水銀は様々な物質との反応性が高く，共存ガスの影響も受けやすいため測定が困難である。特に，従来は連続測定においてゼロ点の信頼性に問題があった。そこで，接ガス部の配管材料選定とその使用温度など最適条件を検討し，プローブユニット内に設置する乾式の還元触媒を開発した。またサンプルガス中共存ガスの影響を低減するために，HCL除去スクラバを開発し，還元触媒の前段に配置することにより，触媒劣化を低減し長期安定稼動を実現した。測定原理には，紫外線吸収法-流体変調方式を採用し，高感度計測が可能でかつ原理的に妨害成分の影響を低減した。それにより，指示安定性に優れた連続分析計の開発をした。

## Introduction

Among metal elements, only mercury exists as liquid at normal temperature and pressure. Thus, there were a number of industry applications for mercury in past years where mercury was used for applications such as fluorescent lamps and batteries. However, use of mercury for products such as batteries is currently prohibited due to it’s affect on the human body. In particular, it has been speculated that Minamata disease in Japan to be the origin of environmental pollution. In Minamata disease, methyl mercury within the water from rivers is consumed into the human body by food chain causing dysfunctional damage in the central nervous system of the human body. Furthermore, damage to the human body from mercury in exhaust gas from coal-fired combustion has been reported in the United States. In reaction to this report in December 2005, the Environmental Protection Agency (EPA) of the United States implemented the Clean Air Mercury Rule (CAMR), a regulation to limit the a total emission of mercury from coal-fired power stations, to attempt to reduce the mercury content in exhaust gas[1]. Internationally, various countries have in negotiations to establish a treaty regarding treatment of mercury in the United Nations Environment Programme (UNEP)[2]. This has been recognized on an international level for the necessity to monitor and control mercury as a residual-prone hazardous substance from the viewpoint of biopersistence and increase in polar region pollution caused by long-distance transport. Amid growing concern for mercury monitoring, we report our development of an analyzer that continuously measures total mercury in exhaust gas by oxidized mercury ($Hg^{2+}$) to elemental mercury (Hg).

## Properties of Mercury

Mercury exists in nature in the form of inorganic mercury compounds and organic mercury compounds.

These mercury compounds have different properties. Inorganic mercury compounds exist in the various forms of elemental mercury, monovalent and elemental mercury. Elemental mercury and oxidized mercury exist as main components of mercury in stack gas and have different properties. Elemental mercury is not soluble in water and reacts with various metals to form amalgams. Intense absorption of elemental mercury is observed in light at approximately 253.7 nm within the ultra violet range. Oxidized mercury dissolves in water. It exists in the form of mercury chloride ($HgCl_2$) and has strong toxicity.

Conversely, organic mercury compounds signify a collective term of compounds in which carbons are bonded to a mercury atom inclusive of methyl mercury ($CH_3$-$Hg^+$). Organic mercury compounds have stronger toxicity than that of inorganic mercury compounds. It was the effluent from this organic mercury that caused Minamata disease.

## Development of Mercury Analyzer for Stack Gas – ENDA-Hg5200 –

### Measurement Flow Diagram

A measurement flow diagram of the developed ENDA-Hg5200 stack gas mercury analyzer is shown in Figure 1 with a picture of the entire analyzer system shown in Figure 2. For example, in order to prevent loss of mercury caused by dissolution in water, oxidized mercury compounds are reduced to elemental mercury by a reducing catalyst within the probe unit at the sampling point of extraction. Subsequently, moisture within the sample gas is eliminated by the drain separator and electronic condenser. Then, the flow channel is alternatively switched into two channels within the analyzer by a solenoid valve. In one flow channel, mercury in the sample gas is removed by the mercury scrubber containing gold. In the other flow channel, sample gas is directly introduced into a cell. The cell is irradiated with a low-pressure mercury lamp that

Figure 2 Overall View of ENDA-Hg5200

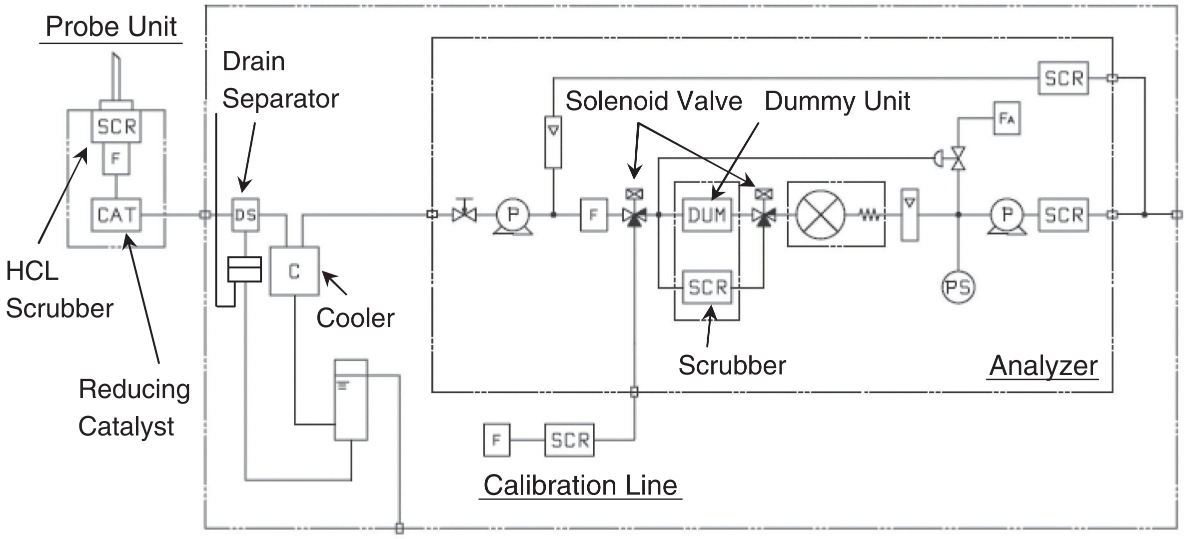

Figure 1 Measurement Flow Diagram of ENDA-Hg5200

generates an ultraviolet ray having a central wavelength of 253.7 nm. When mercury exists in the sample gas, the light of this wavelength is absorbed. A decay amount of the light is detected by the semiconductor detector (a photo diode) and is transformed to a concentration signal.

## Probe Unit

The dedicated ENDA-Hg5200 probe unit consists of a fluorocarbon polymer tube from the sampling point in the furnace to the inside of the probe unit, catalyst that reduces oxidized mercury to elemental mercury and a hydrogen chloride scrubber for removing hydrogen chloride in the sample gas.

## Reducing Catalyst

Methods for reducing oxidized mercury to elemental mercury are listed in Table 1.

Table 1 Difference in Reduction Methods

| | | Advantage | Disadvantage |
|---|---|---|---|
| Use of Reagent | Wet-Reduction Method | Possible to measure conveniently for laboratory application. | Poor maintainability in reagent conditioning or replacement. |
| | Dry-Reduction Method | Convenient treatment of reagent. Possible to use in low temperature range. | Susceptible to influence by coexisting gas. |

In the methods to use reagents, there are wet-reduction methods in which tin (II) chloride dihydrate is dissolved into sulfuric acid. From this method, a sample of this gas flows through an L-ascorbic acid solution. In the dry-reduction method, the sample gas flows through a solid reagent having a reducing effect. The wet-reduction methods have a maintenance problem such as solution conditioning or replacement. We employ the dry-reduction method for the analyzer after investigating various methods. Counter-measures against coexisting gasses are described in the next chapter. Granulated potassium sulfite ($K_2SO_3$) is selected as the reducing catalyst. The catalyst reduces oxidized mercury to elemental mercury according to the following reaction formula.

$$HgCl_2+K_2SO_3 \quad \rightarrow \quad Hg+2KCl+SO_2+1/2O_2$$

To select optimum reduction efficiency, heating temperature was investigated. The result is shown in Figure 3. It is found that the reduction efficiency decreases below 347 °C (620 °K). Decomposition temperature of $K_2SO_3$ is approximately 497 °C (770 °K). From these results, we set the heating temperature to 377 °C (650 °K).

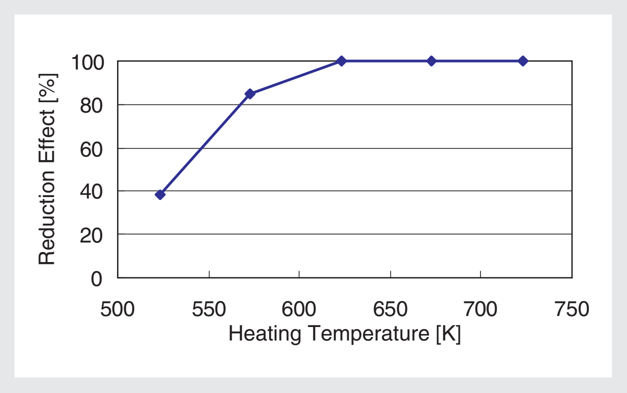

Figure 3 Change in Reduction Effect of Reducing Catalyst by Heating Temperature

## Hydrogen Chloride Scrubber

Hydrogen chloride (HCl) coexists in the stack gas of a garbage incinerator that has the following reaction on the reducing catalyst.

$$K_2SO_3+2HCl \quad \rightarrow \quad 2KCl+H_2O+SO_2$$

Thus, the surface of the catalyst is deteriorated by HCl. As a result, elemental mercury becomes difficult to reduce resulting in a lower measured value of total mercury. Consequently, the hydrogen chloride scrubber is installed upstream of the reducing catalyst to eliminate catalyst deterioration caused by HCl. In the hydrogen chloride scrubber, HCl can be removed by a neutralization reaction using a reagent whose main component is $Na_2CO_3$, which is an alkaline carbonate salt.

$$Na_2CO_3+2HCl \rightarrow 2NaCl+H_2O+CO_2$$

## Analyzer

Generally, a conventional analyzer for continuous mercury measurement is calibrated to zero in a constant period followed by samples that are constantly measured after the calibration. However, this method has a problem in which the zero point drifts. Causes of the drift include effect of interfering gasses and cell stain generated by corrosion components such as fly ash and mist. Consequently, a cross-modulation method is employed in consideration of long-term stability of the zero point. As shown in Figure 4, the low-pressure mercury lamp is

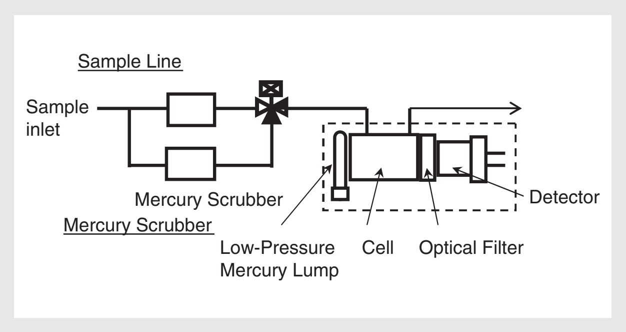

Figure 4 Chart of Principle of Analyzing Part

used as a light source and photo-diode used as a detector. A cold vapor atomic absorption method is employed as the principle of measurement. A component consisting of diatom earth that is impregnated with gold (hereinafter referred to as a "mercury scrubber") is used in the reference line to remove mercury by the amalgam reaction of gold with mercury. To select the mercury scrubber, we investigated the effects of formulation ratios of gold and diatom earth, heating temperature, various components and flow rates. The results for each test combination are described in the next chapter. We installed similar mercury scrubbers at the outlet of measured gases to evaluate with careful consideration to the environment.

## Selection of Mercury Scrubber

### Formulation Ratio of Gold and Diatom Earth

With respect to the formulation ratio of gold and diatom earth, compositions containing gold (weight ratio) of 15%, 30%, 35% and 45% are prepared. An optimum formulation ratio was investigated for breakthrough time. In the preparation method for the compositions made of gold and diatom earth, gold chloride ($AuCl_3 \cdot 2H_2O$) and diatom earth were immersed into pure water. The mixture was heated to evaporate chlorine and water to allow the gold to be deposited onto the diatom earth. In the breakthrough experiment, vaporized elemental mercury containing gas with different concentrations were introduced into the mercury scrubber prepared as described above. The indicated values were then measured by the analyzer installed in the subsequent stage. The breakthrough time is defined as a time when the indicated value of the analyzer exceeds 0.005 mg/m$^3$. The test result is shown in Figure 5.

From this result, the composition having the formulation ratio of 30% illustrated the longest breakthrough time. We considered that this result was obtained due to the surface area of the gold deposited onto the diatom earth.

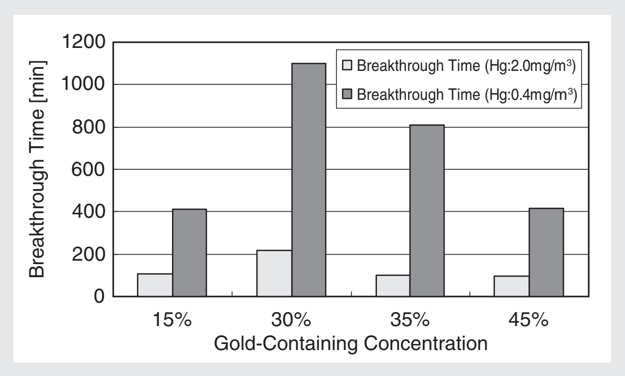

Figure 5 Results of Breakthrough Tests Based on Difference in Gold Content

### Heating Temperature of Mercury Scrubber

We evaluated the effect of heating temperature of the mercury scrubber in order to investigate the optimized condition of the amalgam reaction of gold with mercury. The test method is the same as the method described above. The mercury scrubber having the formulation ratio of 15% was heated at 50 °C (323 °K), 80 °C (353 °K) and 150 °C (423 °K), respectively, was measured for breakthrough time. The results are shown in Figure 6.

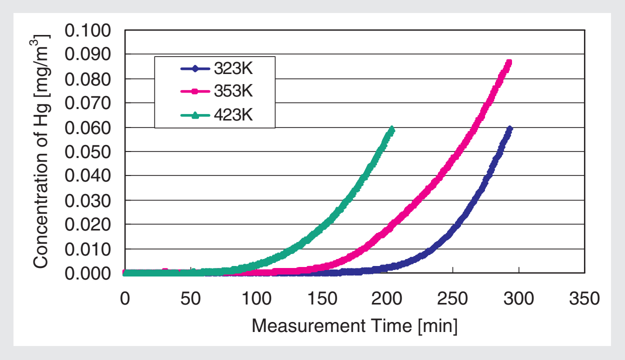

Figure 6 Results of Heating Temperature Tests for Mercury Scrubber

Based on the results, longer breakthrough time of the mercury scrubber was obtained at lower heating temperatures. We consider that the result relates to a reaction rate in that the reaction becomes slower when the temperature becomes higher. In consideration of these results and influence to ambient temperature, we determined that heating at 50 °C (323 °K) was the optimum condition.

### Influence on Interference of Other Components

Sulfur dioxide ($SO_2$) is one of the coexisting gases in exhaust gas that has ultraviolet absorption at approximately 253.7 nm which is the absorption wavelength of mercury. This absorption in itself causes influence of interference. The analyzer, which employs the cross-modulation method as its principle, is considered to have no influence of interference. However, for the purpose of verification, indication was confirmed by flowing $SO_2$ into the analyzer. As a result, a relation between heating temperature of the mercury scrubber was observed to have an influence in the indication. It is found that the absorption amount of $SO_2$ to the mercury scrubber cannot be negligible. Therefore, we implemented the following counter measures. In the case of, exhaust gas from coal combustion, $SO_2$ concentrations are higher and mercury concentrations are low. Thus, the heating set point of the mercury scrubber is set at a higher temperature. Conversely, in the case of exhaust gas from a garbage incineration, $SO_2$ concentrations are lower and mercury concentrations are higher. Thus heating set point of the mercury scrubber is set at a lower temperature.

## Investigation of Flow Rate

In order to obtain longer lifetime of the mercury scrubber, a decreased flow rate into the cell was investigated. First, the length of the cell to which sample and reference gases were introduced was set to the shortest length from the viewpoint of measuring concentration range and other factors. Similarly, a pipe from the solenoid valve for a cross-flow to the cell was set at a shorter length with the gas flush volume including the cell set to minimum. The result was a relation between the gas flow rate and sensitivity. More specifically, the measured value of mercury in this volume is shown in Figure 7. The sensitivity is almost equal when the flow rate is 200 mL/min or more. Hence, the flow rate in the cell was set to 200 mL/min. A flow rate of a sample collection part from the sampling point to a pump outlet port is set to 600 mL/min in consideration of response from the sampling point. We confirmed that this response satisfied the specification of response time in practice.

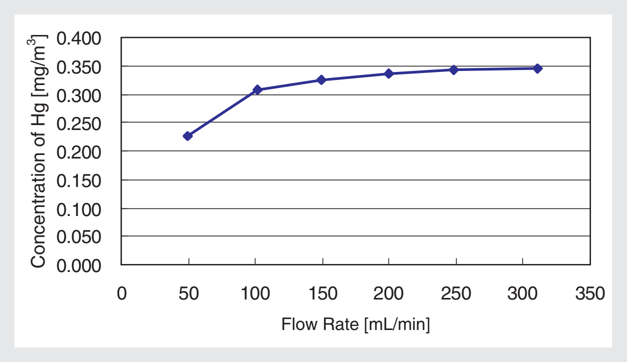

Figure 7 Relation of Sensitivity to Flow Rate

## Implementation Test at Waste Incinerator Factory

In order to evaluate all functions of the analyzer, an implementation test was performed at a fully operational waste incinerator factory. The test was performed at two locations where conditions of exhaust gases were different from each other.

### Measured Result at Inlet of Stack

The waste disposal factory where the test was performed had a structure in which each exhaust gas was exhausted from the outlet of ash fusion furnaces is converged at the inlet of a stack where it was observed that mercury concentrations had a tendency to fluctuate. A probe was installed adjacent to the existing probe? (manufactured by other company) for comparison. The developed analyzer was installed away from the existing analyzer by approximately 3 m and exhaust gas was measured. The result is shown in Figure 8. As illustrated in the graph, the developed analyzer had comparable correlation with the existing analyzer with a correlation coefficient of 0.9846.

### Measurement Test at Outlet of Filter Dust Collector

Treatment of exhaust gas at the outlet of a dust filter collector at this factory is controlled with a bag filter and wet-treatment. As a result, the gas concentrations of hydrogen chloride and mercury are approximately 300-400 ppm and 0.000 mg/m$^3$, respectively.

Thus, we focused on evaluating a hydrogen chloride scrubber and the stability of the zero point. As a result, the removal capacity of hydrogen chloride was not reduced during the three months of continuous measurement. The measured values indicated a range of 0.000 to 0.002 mg/m$^3$. It was confirmed that stability was maintained at lower levels of mercury concentrations.

## Stability of Indication

Zero-point drift is unavoidable in conventional analyzers due to contamination in the cell tube caused by corrosive components such as fly ash and mist in the exhaust gas. When the zero-point drift occurs, data is lost over several time periods because the analyzer must be is calibrated to

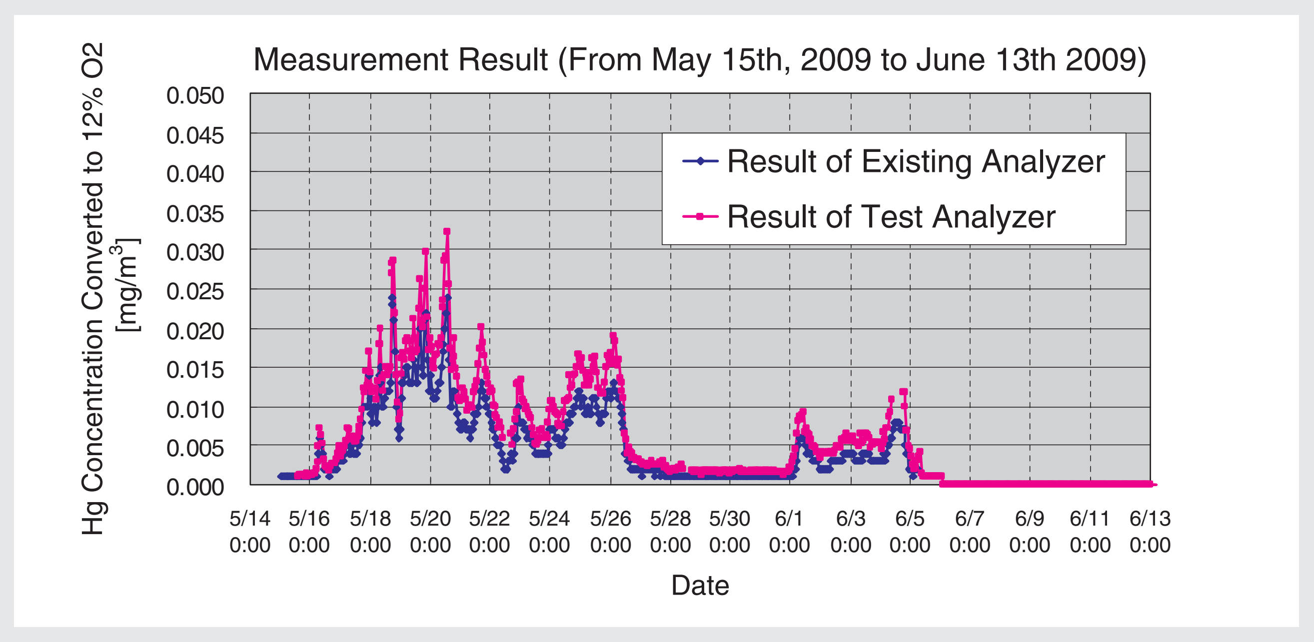

Figure 8 Test Result at Inlet Port of Stack [Representative Chart]

zero on a much more frequent basis.

In this test, a long-term continuous test was performed using the exhaust gas from this waste disposal factory. Zero Gas (nitrogen gas) and Span Gas (mercury-containing gas) with known concentrations are used to confirm the stability of the developed analyzer from start of measurement to termination of measurement. Here, the concentration of Span Gas is set to approximately the same concentration as the sample gas. The results are shown in Table 2. The results show that less than 1.0% of F.S. range was obtained in the cases of both Zero Gas and Span Gas. Therefore, the developed analyzer has excellent stability. Consequently, it was found that the analyzer can be calibrated to zero in a calibration cycle approximately once a month thereby minimizing the amount of lost data during continuous online measurements.

Table 2 Measurement results of Zero Gas and Span Gas

| Elapsed days | Zero [mg/m$^3$] | Span [mg/m$^3$] | Span Width [mg/m$^3$] | Influenced Value [%F.S.] |
|---|---|---|---|---|
| Reference Day | 0.000 | 0.070 | 0.070 | --- |
| After 9 Days | 0.000 | 0.070 | 0.070 | 0.0 |
| After 23 Days | 0.000 | 0.067 | 0.067 | -0.6 |
| After 29 Days | 0.000 | 0.069 | 0.069 | -0.2 |
| After 37 Days | 0.000 | 0.070 | 0.070 | 0.0 |
| After 43 Days | 0.000 | 0.072 | 0.072 | 0.4 |

(Note) %F.S. indicates the percentage of full scale which is an influenced value that is calculated on the basis of a measurement range of 0.500 mg/m$^3$ set as full scale (100%).

## Application to Measure Exhaust Gas from Coal Combustion

Various heavy metals and sulfur compounds exist in the flue gas matrix of exhaust gas from a coal combustion process. There is a problem in which a loss of mercury occurs that results in lower measured values primarily due to deposition of these compounds in the sampling path. In an effort to resolve this problem, we designed a unit equipped with a function to wash the sample gas (a pretreatment unit) in the previous step of the analyzer (Figure 9).

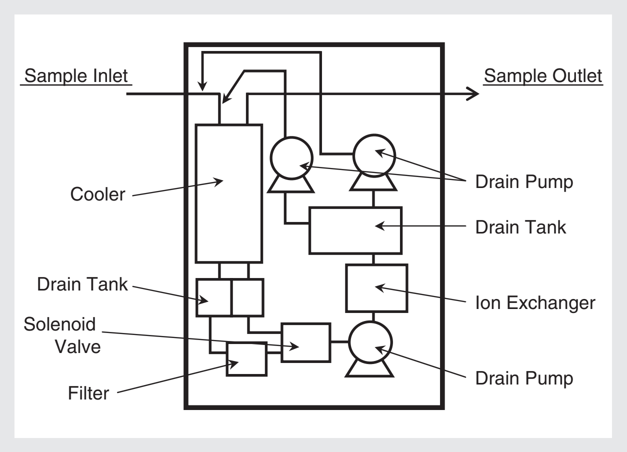

Figure 9 Pretreatment Unit for Exhaust Gas from Coal Combustion

The pretreatment unit has a function for removing and washing other metal components that coexist in the sample gas while quenching at the same time. The pretreatment method can prevent reactivity with metal compounds thereby reducing the loss of mercury that is being measured. In addition, since the analyzer provides a cleaning fluid recycle mechanism, maintenance of the analyzer is reduced.

## Conclusion

Based on the measurement results at the waste disposal factory described above, there was a good correlation with the existing analyzer. The initial objective was achieved by utilizing a practical application test of high-sensitivity measurements of mercury and the stability of the zero point. Based on the analyzer's favorable performance results on continuous measurement of low concentrations of mercury in stack gas, it can be added to a series of stack gas analyzer products. For continuous measurement of total mercury, interference components can be reduced by using the analyzer's cross-modulation and a combination of the hydrogen chloride scrubber & reducing catalyst methods.

Depending on the type of exhaust gas, the sampling unit can be configured accordingly to adequately measure samples of exhaust gas in various applications.

## References

[1] USEPA Clean Air Mercury Rule (http://www.epa.gov/CAMR/index.htm.)
[2] UNEP Mercury Programme. (http://www.chem.unep.ch/mercury/)
[3] JIS K 0222-1997: "Methods for Determination of Mercury in Stack Gas"

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