

COMPARISON OF MERCURY TEST METHODS

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INTRODUCTION

Considerable controversy has evolved over the past several years related to the measurement of mercury (Hg) emissions from municipal waste combustors (MWCs). Currently, two methods are generally used in the U.S. to measure mercury emissions; EPA Methods 101A and 29. However, EPA's Multi-metals Test Method 29 has not yet been officially published. At least one state regulatory agency has officially adopted Method 29 for determining Hg emissions from for MWCs. Verein Deutscher Ingenieure (VDI) Method 3868, Section 2 is the standard method of measuring mercury in Germany.

There are differences between all three of these methods. This paper only discusses the differences between EPA 101A and VDI Method 3868, Section 2 and their potential impact on the test results. The authors are currently preparing a paper which makes a similar comparison with Method 29.

Since a considerable database has been developed in Germany using the current VDI method, it is of interest to determine if this database is suitable for U.S. applications. VDI Method 3868, Section 2 is currently under review but will probably not be modified in the future. As EPA and the various states formulate rules there is considerable pressure to adopt the European emission standards but using U.S. test methods for determining emissions. The key question is whether approximate values of $50 \mu\text{g}/\text{Nm}^3$ measured by the VDI test methods are comparable to the results from the U.S. test methods. One report has shown that there is a 22% to 35% difference in results between Methods 101A and 29 when sampling in the range of $50 \mu\text{g}/\text{dscm}$ [1].

The objective of this paper is to compare the sampling and analyzing methods used for testing mercury in flue gases by a side-by-side evaluation of U.S. and German methods as discussed in this paper.

The next step will be a full test program designed to determine any differences in mercury emission measurements. The authors are planning a field test program for the Spring of 1994 to determine if the EPA and VDI test methods are compatible.

DISCUSSION

The comparison is based on the following test methods.

(1) U.S. EPA Methods 1 through 5, and 29 in 40 CFR Part 60 Appendix A, and Method 101A in 40 CFR Part 61 Appendix B

1 Planing	5	Particulate
2 Velocity	29	Multi-metal Sampling Method
3 Gas Analysis	101A	Mercury
4 Moisture		

and

(2) VDI Methods 2066 Section 1 and Section 2 Draft (VDI 2066 Blatt 1 und Blatt 2 Entwurf), general sampling methods similar to U.S. EPA Methods 1-5.

VDI Methods 3868 Section 1 Preliminary Draft (VDI 3868 Blatt 1 Vorentwurf), multi metal sampling corresponding to EPA Method 29 and Section 2 Preliminary Draft (Blatt 2 Vorentwurf), mercury sampling and analytical [2], [3] methods similar to EPA 101A.

SAMPLING PROCESS

Requirements for the In-line Length of Duct Sampling and the Number of Grid Points

USA. The straight distance normalized by the duct diameter before and after the sampling point determines the minimum number of grid (traverse) points in the cross-section of the duct [4].

Germany. The straight distance before and after the sampling point shall be at least three times the hydraulic diameter of the ducts cross-section. If this is not possible, the straight distance before the sampling point shall be longer than the distance after the sampling point. The number of grid points depends on the cross-sectional area of the duct [5].

Comments. The EPA method is based on having eight (8) equivalent diameters of duct/stack prior to the sampling location. If eight (8) diameters are not available then as the straight run decreases the number of traverse points increase. The EPA Methods 5, 29 and 101A require sampling at each traverse point.

It is of interest to note that U.S. compliance tests are usually conducted in the stack while in Germany they are performed in an outlet duct. Grid sampling has not been conducted frequently in Germany for cost reasons, especially in relatively small ducts. Many VDI tests are conducted at a single point of average velocity in a duct.

The Hg outlet (i.e. stack) emissions from MWCs primarily exist as a vapor. A small amount of Hg may also be present at the outlet as a very fine particulate (generally less than 2 microns). At the inlet sampling locations (prior to the air pollution control equipment) a significant portion of the total Hg may be particulate associated, depending on the flue gas temperature. The major species of Hg from MWCs is HgCl_2 . Hg^0 only accounts for 5 to 10 percent of the emissions [6]. The mean size of HgCl_2 is about 4.5 Å and Hg^+ is about 1.5 Å which means that Hg will act as a gas and that traversing should not have a significant impact on outlet sampling results. Additionally, since in most plants the flue gases have gone through several cleaning devices and a fan, the gases should be well mixed and the impact of stratification minimized. In modern MWCs most of the particulates have also been removed from the outlet gases by highly efficient ESPs or baghouses. Therefore, most Hg emissions will be in the vapor phase and the impact on the accuracy of the test results from traversing should be reduced.

At inlet sampling locations, where poor gas distribution can exist or there is a heavy particulate loading, there should be differences in the results of the EPA methods with VDI methods without traversing. However, in these cases and in different sampling locations, VDI does recommend traversing. This could be important in the future since it appears that the U.S. standards for Hg emissions may allow compliance determination based on either percent reductions or a concentration level.

Location of the Filter/Filterhead

USA. The gas/particulate matter is sampled isokinetically through a probe and then passed through a glass filter. A Teflon-coated glass frit is used as a back-up to the filter. This coating makes clean-up of the support media easier

than the VDI method. The filter [7] (Fig. 1) is located outside the duct and held at a temperature of $120 \pm 14^\circ\text{C}$ ($248 \pm 25^\circ\text{F}$).

A cyclone can be used with Method 101A for the removal of coarse particles, but is commonly not used. For further details refer to EPA Method 101A, Figure 3-3.

Germany. The gas/particulate matter is sampled isokinetically by a probe/filter [8] head apparatus. The filter head apparatus (Fig. 2 and 3) is located directly after the probe within the stack/duct. This means the removal of particulate matter occurs at the actual flue gas temperature. The permissible maximum flue gas temperature [9] is $< 300^\circ\text{C}$ (572°F).

Comments. The location of the filter should have no impact on the concentration of total Hg when sampling the outlet emission of most modern MWCs. However the distribution of Hg between the filter and the impingers may be influenced by the sampling procedures. This is especially true at inlet locations where the flue gas temperatures are generally $> 200^\circ\text{C}$ (400°F). At the outlet locations flue gases are generally $< 150^\circ\text{C}$ (300°F), therefore, the filter temperature for the EPA and VDI methods will be similar.

Sampling Procedure

USA. With Method 101A, the flue gas sample is taken from the source and pulled through an optional filter and three one-liter impingers (containing an absorption solution) which are connected in series. With Method 29, the sample is pulled through a filter and two pairs of impingers connected in series that contain two different absorption solutions. Typical sampling times are between one and two hours with a sample volume of $0.8 - 1.7 \text{ Nm}^3$ ($28 - 60 \text{ dscft}^3$). The volume flow rate [10] is approximately 12 to 20 liters/minute.

Germany. A $1-4 \text{ m}^3/\text{h}$ sample of the flue gas is taken from the source. From this a slip stream with a gas flow volume of 1 to 3 liters/minute is sampled through at least two and commonly three $\frac{1}{4}$ liter impingers (containing an absorption solution) which are connected in series [11].

A sampling time of $\frac{1}{2}$ to 2 hours is suggested [12] and a flue gas sample volume of 0.03 to 0.36 m^3 is obtained. It is possible to sample several parallel gas flow volumes from the original slip stream.

Comments. The use of smaller impingers in Germany is correlated to the smaller gas sampling rate. The gas/solution ratio used in Germany (0.15 to 3 liters of flue gas per milliliter absorption solution) is always smaller than the U.S. ratio (5 to 7 liters of flue gas per milliliter absorption solution). This is also correlated to the less concentrated KMnO_4 solution used in Germany (see below).

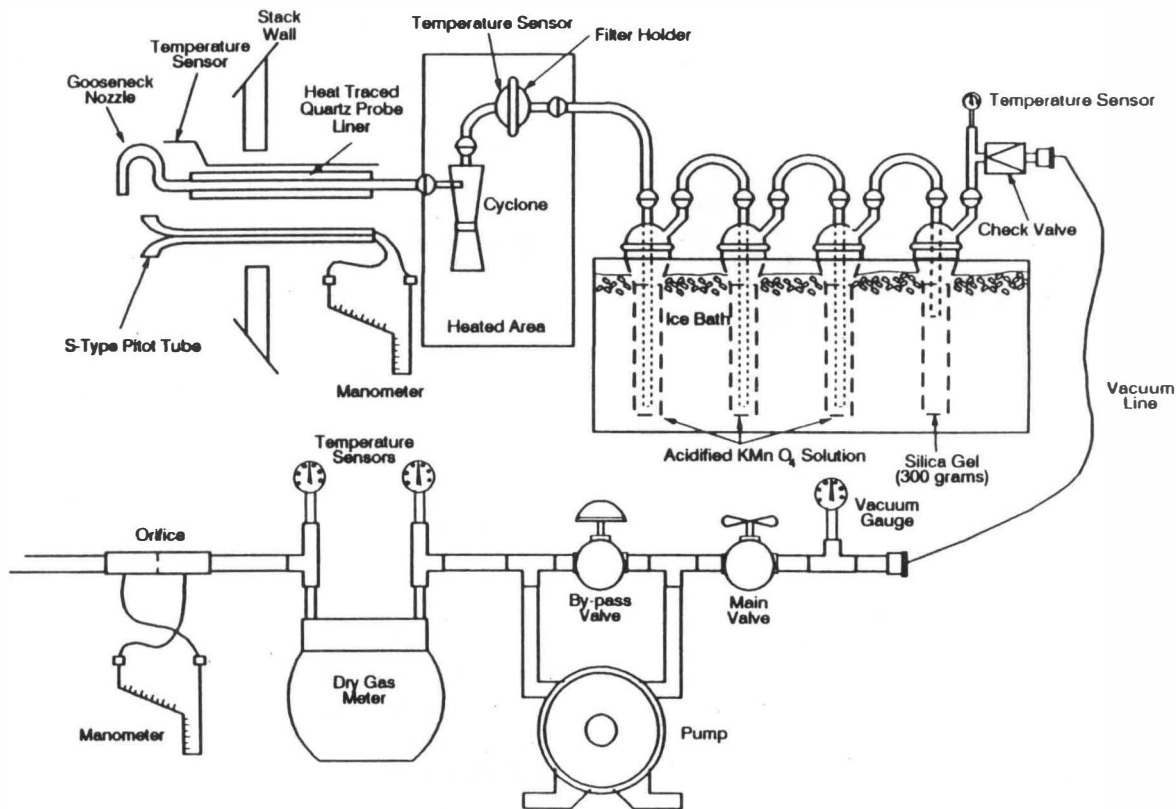
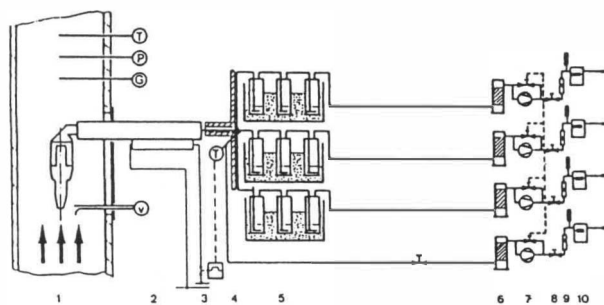


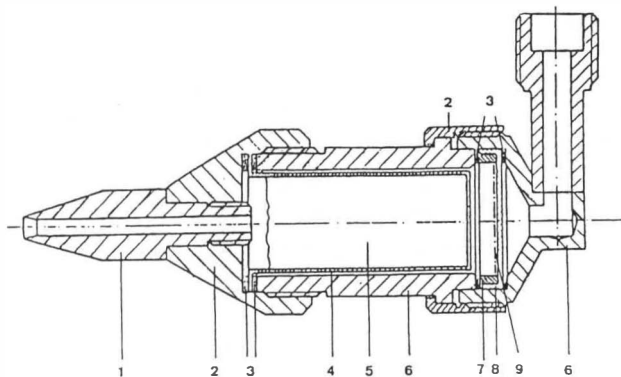
FIG. 1 EPA METHOD 101A SAMPLING TRAIN



LEGEND

- 1 PARTICLE COLLECTION SYSTEM
- 2 PROBE: CONTROLLED, HEATED
- 3 BYPASS TEMPERATURE CONTROL
- 4 ADAPTER: INSULATED AND TEMPERATURE CONTROLLED
- 5 ABSORPTION SYSTEM
- 6 CONDENSER
- 7 GAS PUMPS: CONTROLLED
- 8 VOLUME FLOW METER
- 9 VALVE
- 10 GAS FLOW COUNTER WITH THERMOMETER
- T TEMPERATURE MEASUREMENT
- P PRESSURE MEASUREMENT
- G GAS ANALYSIS
- V VELOCITY MEASUREMENT

FIG. 2 SAMPLE TRAIN FOR THE SIMULTANEOUS SAMPLING OF PARTICULATE AND GASEOUS COMPOUNDS



LEGEND

- | | | | |
|---|-----------------------|---|---------------|
| 1 | PROBEHEAD | 5 | GRATE WOOL |
| 2 | PROBEHEAD UNIT | 6 | ENCLOSURE |
| 3 | GASKET | 7 | SPRING WASHER |
| 4 | FILTER WOOL CONTAINER | 8 | FILTER HOLDER |

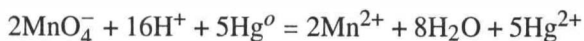
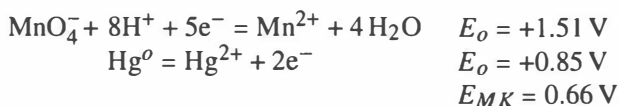
FIG. 3 VDI PARTICULATE COLLECTION SYSTEM IN TANDEM CONFIGURATION

Absorption Solution

USA. 1 × 50 ml and 2 × 100 ml of a solution made from 40 g KMnO₄ in 10% H₂SO₄ for 1 liter. For further details refer to EPA Method 101A, p. 4.

Germany. 3 × 40 ml of a solution made from 30 g KMnO₄ in 10% H₂SO₄ for 1 liter. For further details refer to VDI 3868, Section 2 Preliminary Draft, p. 4 and 11.

Comments. The acidic KMnO₄ solution oxidizes Hg⁰ to Hg²⁺ according to:



The original metallic mercury of the flue gas remains as a Hg²⁺ ion in solution after oxidation. Potassium peroxodisulfate K₂S₂O₈ (E_o = +2.01 V) offers an alternate suitable oxidation substance. With its larger normal potential than potassium permanganate, it is a stronger oxidizing agent, and also has the advantage that no undesirable manganese dioxide (MnO₂) deposit is formed.

Mercury has the potential to either attach to or be bound in manganese dioxide. If manganese dioxide is deposited in the instruments or in the impingers, it is possible that it will bind with the mercury, leading to lower than actual analytical results. However, the purple colored KMnO₄

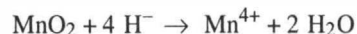
solution has a practical advantage. A fading color signals the required exchange of the absorption solution. This is especially helpful when an SO₂ rich flue gas is sampled (SO₂ is a reducing agent and is oxidized to SO₄²⁻, E_o = +0.17 V).

Apparatus Rinsing/Dissolving of Residues

USA. With Method 101A the contents of the 3 impingers are combined in a 1000 ml glass collecting flask. The apparatus is rinsed with 400 ml of the same 4% KMnO₄ solution used as the collection solution. The rinse is then added to the 1000 ml glass collecting flask. Any visible residues remaining in the impingers are dissolved with 25 ml of 8 N HCl. The HCl rinse is collected separately [13]. The filter and filter dust are stored in a separate container with 4% KMnO₄ solution [14] (Fig. 4).

Germany. The absorption system is closed and without decanting is transported to the analytical laboratory [15]. The apparatus is rinsed with a half concentrated nitric acid solution (w(HNO₃) = 31%). The nitric acid solution is stabilized with a few milliliters of absorption solution to a distinct violet color and then analyzed separately [16]. The particulate filters and the collected dust are removed and stored separately in air tight, prepared containers [17].

Comments. A possible build-up of manganese dioxide in the apparatus is dissolved with acid, for example HCl or HNO₃:



Nitric acid oxidizes mercury as well (E_o for NO/NO₃⁻ = +0.96 V). In the U.S. method this is insured by rinsing with a HCl and KMnO₄ solution.

ANALYSIS OF MERCURY

The Treatment of Particle Bound Mercury

USA. For Method 101A the filter and dust are put in a beaker with a concentrated nitric acid solution, then covered with a watch glass and held at 70°C. After filtration the filtrate from the impinger absorption solution is added [18].

Germany. The dust loaded glass wool or filter is extracted with half concentrated nitric acid solution in a reflux unit maintained at 127°C (400 K). The oxidation potential of the acid is the reason why mercury stays in the ionic form in solution although water already evaporates. An aliquot fraction of the separated solution is analyzed with a cold vapor atomic absorption spectroscopy (CVAAS) technique [19].

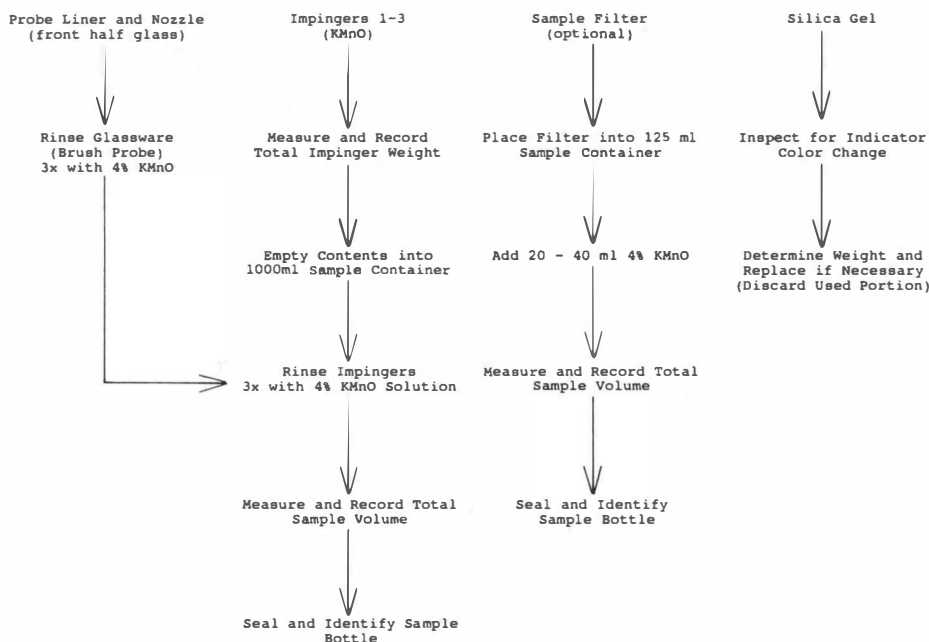


FIG. 4 METHOD 101A SAMPLE RECOVERY SCHEME

Treatment of Mercury in the Absorption Solution

USA. The absorption solution for Method 101A is filtered, combined with the filtrate from the filter extraction, cleaned and analyzed with the CVAAS. The separated manganese dioxide is treated with 8 N HCl and then analyzed as well [20].

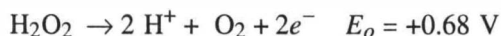
Germany. The absorption solution in the impingers is not filtered, but analyzed directly [21] (see the comments below).

Reduction of the Unused KMnO_4 and Nitric Acid in the Absorption Solution to the Point of Color Loss (Shortly Before the Actual Analysis)

USA. The reducing agent is hydroxylamine sulfate $[\text{NH}_3(\text{OH})]_2\text{SO}_4$ or hydroxylamine hydrochloride $[\text{NH}_3(\text{OH})]\text{Cl}$ in a NaCl solution [22]. Thus the actual reducing agent is hydroxylamine NH_2OH .



Germany. The reducing agent [23] is a hydroxylamine sulfate solution $[\text{NH}_3(\text{OH})]_2\text{SO}_4$ (see above) or hydrogen peroxide (H_2O_2). In Germany commonly hydroxylamine sulfate is used as the reducing agent.

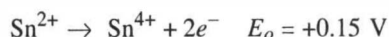


Comments. The absorption solutions contain considerable amounts of KMnO_4 and HNO_3 . The goal of this color loss/reduction process is to pinpoint the start of the mercury removal for the analysis minimizing the use of SnCl_2 or NaBH_4 (see below).

Germany. Through this reaction the manganese dioxide in the impingers which was not separated is also being dissolved, thus reduced to Mn^{2+} . The E^o for $\text{Mn}^{2+}/\text{MnO}_2$ is the equal to +1.24 V. The actual reducing agent, sodium borohydride NaBH_4 , brings the rest of the manganese dioxide into the solution during the analysis.

Method of Analysis

USA. The cold vapor atomic absorption spectroscopy (CVAAS) with the reducing agent tin (II) chloride SnCl_2 in a HCl solution is used in EPA Method 101A (Fig. 5).



Germany. The CVAAS with the reducing agent sodium borohydride NaBH_4 (3% solution, $E_o = -1.24 \text{ V}$) is used. The amalgam [24] process as a proven stronger system may also be used.

Comments. Sodium borohydride NaBH_4 is the stronger reducing agent (this is an advantage if solid MnO_2 still exists) and in its quicker reaction with the acidic sample

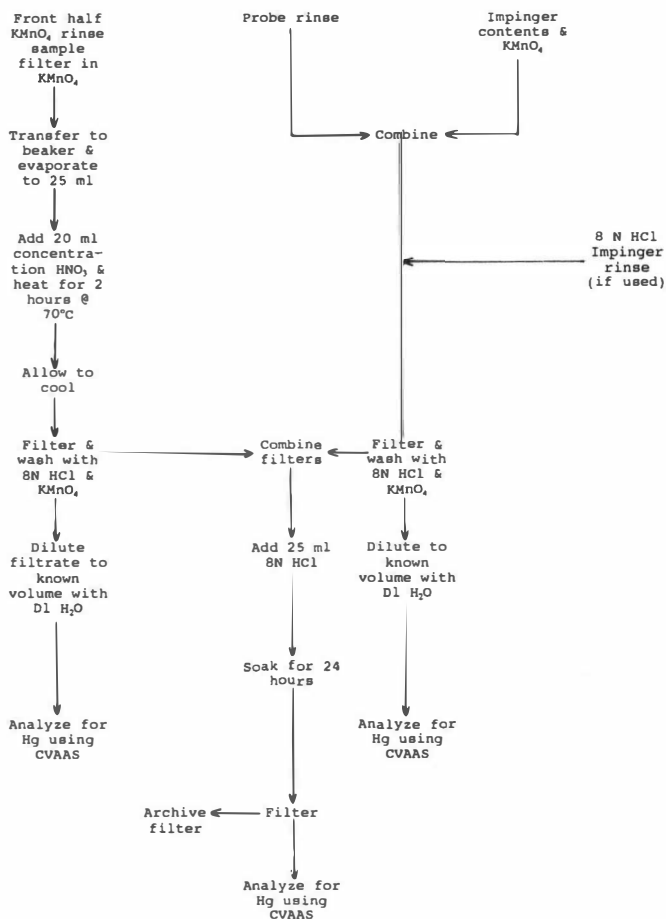


FIG. 5 METHOD 101A SAMPLE PREPARATION AND ANALYSIS SCHEME

solution produces a large amount of hydrogen H_2 . It immediately helps strip the mercury, which has been reduced to a metal, out of the solution to a large extent. When tin (II) chloride $SnCl_2$ is used, extra gas must be blown through the solution to strip out the mercury. Both reducing agents are completely suitable for this analysis.

Silver interferes with the analysis in both reducing agents due to the possible formation of amalgam in the solution. Arsenic, bismuth and copper may also interfere in a small amount when $NaBH_4$ is used for the same reason. Selenium and iodide create a large interference when tin (II) chloride is used. This is not evident with the use of $NaBH_4$ until large concentrations are present (see Table 1).

With the few known chemical interferences both reducing agents compliment each other almost ideally.

For practical reasons the sodium borohydride $NaBH_4$ is often chosen for the mercury analysis over the tin (II) chloride $SnCl_2$. With the use of $NaBH_4$ the same apparatus (which is usually available) can be used for the hydride technique. The use of both reducing agents in the same system is not recommended due to a possible build-up of precipitating amalgam of Sn and Hg and thus possible

TABLE 1 THRESHOLD CONCENTRATIONS OF ELEMENTS WHICH CREATE A SIGNIFICANT INTERFERENCE IN THE COLD VAPOR CVAAS TECHNIQUE FOR THE ANALYSIS OF MERCURY [25]

Element	Threshold Concentration (Mass Fraction) for the Reduction	
	With	
	$SnCl_2$ Solution [g]	$NaBH_4$ Solution [g]
Sb	≥ 1	≥ 2.5
Ag	≥ 0.005	≥ 0.005
Cu, As, Bi	> 10	≥ 0.25
Se	≥ 0.0005	≥ 0.5
I	≥ 0.003	> 1

plugging of the system. Therefore, a separate reaction section or operational system must be used for the tin (II) chloride. From an economic standpoint this is a luxury.

Possible Applications/Detection Limits

USA. The standard deviation [26] for Method 101A is considered to be $4.8 \mu g/ml$ absorption solution in the concentration range of $50-130 \mu g/m^3$. The detection limit is not stated but is believed to be between 1 and $10 \mu g/dscm$. The detection limits for Hg were determined during the test program EPA sponsored at the Camden County Resource Recovery Facility in New Jersey. This program, based on a one hour sample time and a sample volume of 30 dscf, showed the detection limit in the flue gas was $0.05 \mu g/dscm$ and the analytical detection limit was $0.0002 \mu g/ml$ [27].

Germany. The method is applicable for the determination for mercury concentrations in flue gases $> 5 \mu g/m^3$. The relative detection [28] limit is $3 \mu g/m^3$ using a 80 ml absorption solution with a sample volume of $0.06 m^3$ in the concentration range of $< 50 \mu g/m^3$.

To measure mercury concentrations below $3 \mu g/m^3$, German institutes use impingers and absorption volumes similar to 101A with an extended sample volume up to $1 m^3$ and using the CVAAS in combination with the amalgam process. The detection limit in the flue gas is then around $0.05 \mu g/m^3$.

CONCLUSIONS

Both methods are chemically similar and should theoretically produce comparable results. Far more significant than the outlined differences is the knowledge and experience of the personnel regarding the particular sensitivity of mercury sample and analysis. Systematic errors can occur in all parts of the procedure, especially during the sampling process, the treatment of the absorption solution, and the desorption of the particle bound mercury. Thus there

must be great care in performing sampling and analysis to obtain reproducible results.

The differences between the test methods have been illustrated in this paper. However, the only way to determine the quantitative differences between methods is to conduct a field test program using the methods side-by-side and employing EPA Method 301 to validate or prove their equivalency.

The authors hope to conduct a field test program in the Spring of 1994 to determine the equivalency between the German and U.S. test methods. The proposed program matrix is to perform side-by-side testing at three separate sampling sites at the MWC ROTEB Plant in Rotterdam, Holland. This Plant has an ESP, a scrubber system, and a Steinmüller Activated Char Reactor (ACR) to control mercury emissions. By simultaneously sampling before the scrubber, before the ACR, and after the ACR, we will be able to obtain emission rates at three different mercury concentrations. This data will give us the ability to determine equivalency over a wide range of mercury rates.

With VDI Method 3868 under review and recent changes made by EPA to the analytical procedures in Method 101A and the likely adoption of unpublished Method 29 for compliance determination, we are on the verge of losing our references for future designs for control technologies. The purpose of this paper and our proposed test program is to determine the comparability of the test methods and preserve the existing design database.

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