LABORATORY EVALUATION OF METHOD 0050 FOR HYDROGEN CHLORIDE*

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ABSTRACT

The EPA reference method used for collecting HCl and chlorine (Cl_2) stack gas emissions is SW-846 Method 0050. In Method 0050, gaseous and particulate pollutants are withdrawn isokinetically from the stationary source and collected in a cyclone (optional), on a filter, and in absorbing solutions. Three key issues with Method 0050 are loss of HCl in the cyclone, negative bias in stationary sources containing less than 20 parts-per-million by volume (ppmv) HCl, and positive bias in stationary sources where ammonium chloride (NH_4Cl) is present. The efficiency of the post-sampling cyclone purge for drying the cyclone and liberating any condensed water and HCl was evaluated experimentally. Recovery of spiked HCl at levels at, above, and below 20 ppmv was tested in order to confirm the presence of a negative bias and to identify the source of this negative bias. The existence of a positive bias in the HCl measurement with the presence of NH_4Cl was tested by spiking an aerosol containing NH_4Cl into the sampling train to identify the source of the positive bias.

INTRODUCTION

The EPA reference method used for collecting HCl and chlorine (Cl_2) in stack gas emissions from hazardous waste incinerators, municipal waste combustors, and boilers and industrial furnaces is SW-846 Method 0050. (1) In Method 0050, gaseous and particulate pollutants are withdrawn isokinetically from the stationary source and collected in a cyclone (optional) and in absorbing solutions (Fig. 1). The cyclone is used to collect liquid droplets and particulate matter. The cyclone is usually included in the sampling train to protect the filter when high levels of moisture and high levels of particulate matter are present. However, the cyclone may be removed from the train when the source emissions do not contain liquid droplets. It is important to protect the filter from getting wet because a wet filter will create a larger pressure drop in the sampling train.

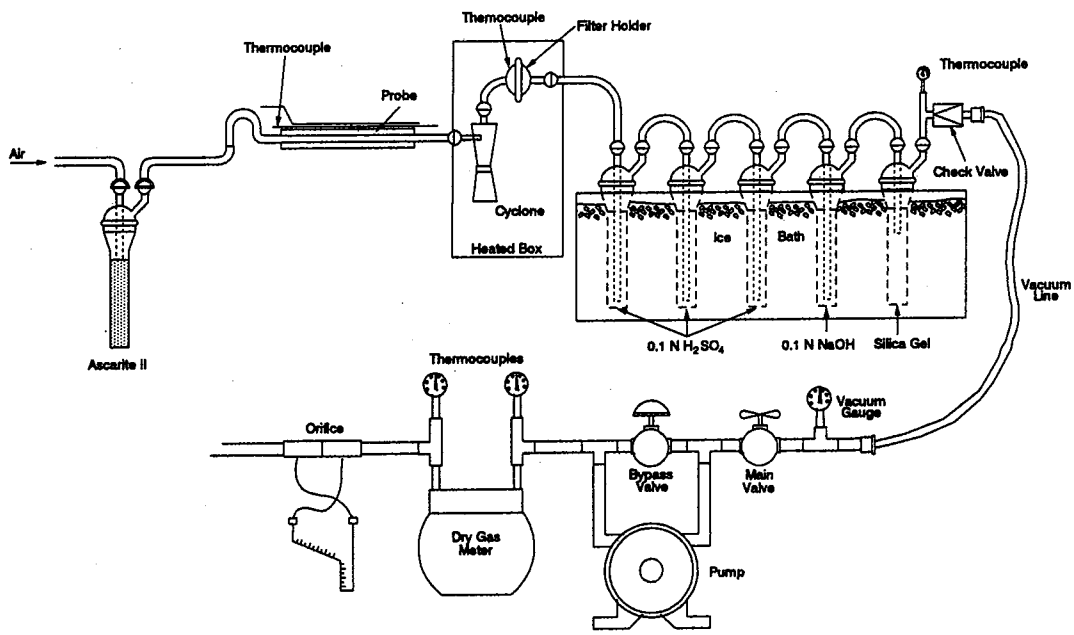

Fig. 1. HCl train used for cyclone purge studies.

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The filter prevents halide salts from getting into the impingers and producing a positive bias in the results.

Method 0050 is particularly well-suited for sampling at stationary sources that emit acid particulate matter and acidic vapor and that are controlled by wet scrubbers. The acid particulate matter usually consists of HX dissolved in water droplets present as an aerosol. Other particulate matter, including halide salts, is collected on the filter. Acidic (0.1N H_2SO_4) and alkaline (0.1N NaOH) absorbing solutions are used to collect HX and X_2, respectively. In the acidic absorbing solution, HX is solubilized to form halide ions, X^-. Halogen gases, which have very low solubility in the acidic absorbing solution, pass through the acidic solution to the alkaline solution, where they are hydrolyzed to form a proton (H^+), X^-, and hypohalous acid (HXO). Ion chromatography (IC) is used to perform the analysis for X^- in the absorbing solutions. The acidic and alkaline solutions are analyzed separately. Method 0050 is applicable to the determination of HCl, HBr, HF, Cl_2, and Br_2.

When emissions testing results in accumulation of liquid from aerosol droplets, a post-sampling cyclone purge is used to vaporize the liquid collected in the cyclone. If effective, this purge liberates any HCl or Cl_2 that might be dissolved in the liquid in the cyclone and leaves halide salts in the cyclone. The HCl and Cl_2 are purged out of the cyclone and transferred to the impingers for subsequent measurement. To perform the post-sampling cyclone purge, conditioned ambient air is pulled through the sampling train in the field. However, to provide an accurate measurement of HCl and Cl_2, it is critical that all of the HCl be removed from the cyclone. An ineffective post sampling cyclone purge would result in underestimating emissions; hence it is critical to understand the parameters that might lead to this.

Use of Method 0050 is currently restricted to sources emitting more than 20 ppmv because of the potential negative bias. (1) Understanding the reasons for this negative bias may lead to improvements in the method and allow its use at sources emitting less than 20 ppmv.

Method 0050 shows a positive bias in HCl emissions in the presence of ammonium chloride and therefore may not provide accurate results on sources emitting ammonium chloride. Again, an understanding of the mechanism for this bias may lead to suggested ways to eliminate the bias.

EXPERIMENTAL PROCEDURES

Method 0050 Sampling Train

The Method 0050 sampling train was assembled as shown in Fig. 1 using all-glass components. For studies of the cyclone purge, the first three impingers were charged with 100 mL of 0.1N sulfuric acid and the fourth impinger was charged with 100 mL of 0.1N sodium hydroxide. For determination of the low-level bias, the first two impingers were charged with sulfuric acid and the third and fourth impingers were charged with sodium hydroxide. For all trains, the fifth impinger was charged with 200 g of silica gel.

For studies of the cyclone purge (train configuration shown in Fig. 1), the cyclone condensate flask was spiked with a dilute HCl solution prepared by diluting 1 mL of concentrated HCl to 1 L with deionized water. An impinger filled with 250 g of Ascarite II® was attached to the probe of the sampling train so that air entering the train was pulled through the Ascarite II®. Room air, conditioned by the Ascarite II®, was pulled through the train at approximately 0.75 ft^3/min for 45 minutes. The amount of HCl solution purged from the cyclone and the weight of moisture sorbed by the Ascarite II® from the ambient air were recorded at the end of each test run. The probe and filter hot box were heated to temperature before starting the purge gas through the train. Because high levels of HCl were recovered in the probe rinse during the first five runs, the purge gas was started through the train before heating the probe and filter hot box for remaining purge runs.

The flow rate of HCl gas into the train was controlled with a Tylan® mass flow controller, and the gas flow rate was confirmed using either a bubble flow meter or a mini-Buck calibrator.

To add moisture to the train (Fig. 2), a beaker of water on a hot plate was used to generate steam. The nozzle of the sampling train was placed directly over the beaker. Room air conditioned by adding steam was pulled through the train at

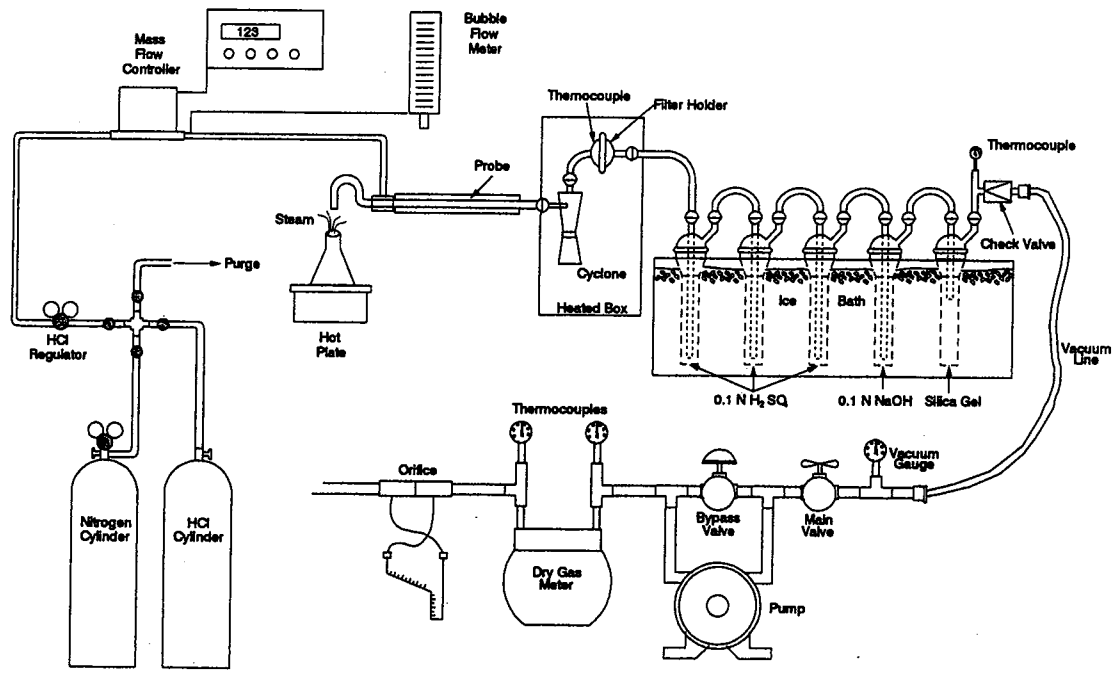

Fig. 2. HCl train used for Sub-20 ppmv studies.

approximately 0.75 ft^3/minute for two hours. For all of the runs, the probe and filter hot box were heated to nominally 121°C (250°F) or 200°C (400°F) before starting the purge gas through the train.

Aerosol Spiking System

Ammonium chloride was spiked into the train as an aerosol using a high pressure aerosol injection system (Fig. 3). The aerosol spiking system consisted of a nitrogen cylinder equipped with a high pressure regulator connected to a 1/4" stainless steel tee with a 3-foot long piece of 1/4" stainless steel tubing. One end of the tee was connected to a pressure release valve so that the spiking system could be vented after use and before disassembling. The other end of the tee was connected with 1/16" stainless steel tubing to the inlet side of a 107-mL stainless steel high pressure vessel made out of a high performance liquid chromatography column.

The outlet end of the high pressure vessel was connected to an on/off valve. The on/off valve was connected through 1/16" stainless steel tubing to a piece of capillary fused silica tubing (1 μm inner diameter). The fused silica tubing was placed inside a sheath of 1/4" Teflon® tubing and inserted into a 5/8" glass tee with screw cap ends. The middle leg of the glass tee terminated in a female socket that was placed 1/4" above an erlenmeyer flask of boiling water.

The injection system operated best at higher pressures with 1000 psig as a minimum operating pressure; however, an operating pressure of 1500 psig provided the most reliable and constant delivery rate of approximately 0.5 mL/min.

Sample Train Recovery Procedures

The sampling trains were recovered in four fractions: the front half consisting of the probe and front half filter holder rinses, the filter, the acidic portion consisting of the back half filter holder rinse and the 0.1N H_2SO_4 impingers, and the basic portion consisting of the two 0.1N NaOH impingers. All of the impingers were weighed before being recovered into the appropriate tared bottles. The impingers and other train components were rinsed three times with deionized water and the rinses were added to the appropriate recovery bottles.

Ion Chromatographic Analysis

The samples were analyzed on a completely inert, metal-free Dionex DX-300 gradient chromatographic system for ion chromatography. For chloride determination, an AG4A guard column and an AS4A-SC anion separator column were used. Chloride was eluted using a buffer solution consisting of 17-mmolar sodium carbonate and 18-mmolar sodium bicarbonate. Ammonium was eluted using a buffer solution consisting of 40-mmolar HCl and 4-mmolar D,L-2,3-diaminopropionic acid monohydrochloride. Data from the Dionex 300 were processed through a Perkin-Elmer Nelson 2600 chromatography data system.

Before sample analysis, the instrument was calibrated using four standards over the range of 5.0 to 20.0 ppm for chloride and ammonium. A least squares fit applied to the data points resulted in a curve with a correlation of 0.9950 or better. Quality control samples made from separate sources of chloride and ammonium were analyzed using the established curve before and after every 20 samples. For the sample analysis to be acceptable, the quality control sample analysis had to be within ±10 percent of the target concentration. A blank and duplicate sample were analyzed for every sample set or for every 20 samples. A matrix spike and matrix spike duplicate were analyzed for every sample set or for every 20 samples. For the data analysis to be acceptable, the matrix spike and matrix spike duplicate analysis recoveries had to be within 20 percent of target. Any samples with responses above the calibration curve were diluted and reanalyzed.

POST-SAMPLING CYCLONE PURGE STUDIES

The study of the effectiveness of the post-sampling cyclone purge was performed by statically spiking 11 trains in the laboratory with aqueous solutions containing approximately 400 ppm HCl. For 7 of the 11 trains, the probe and filter were maintained at 121°C. To determine whether the effectiveness of the post-sampling cyclone purge improved with higher temperatures for the probe and filter, the probe and filter were maintained at 177°C for four of the trains.

Results of the post-sampling cyclone purge study are shown in Tables I and II. Data in Table I show that the post-sampling cyclone purge is effective for a maximum of 15 to 25 mL of liquid in the cyclone in the 45-minute purge period which Method 0050 requires. If quantitative recovery of HCl is to be obtained from the sampling train, all of the moisture collected in the cyclone, down to the last drop, must be purged into the impingers. Heating the probe and filter to 177°C improves the reproducibility and increases the effectiveness

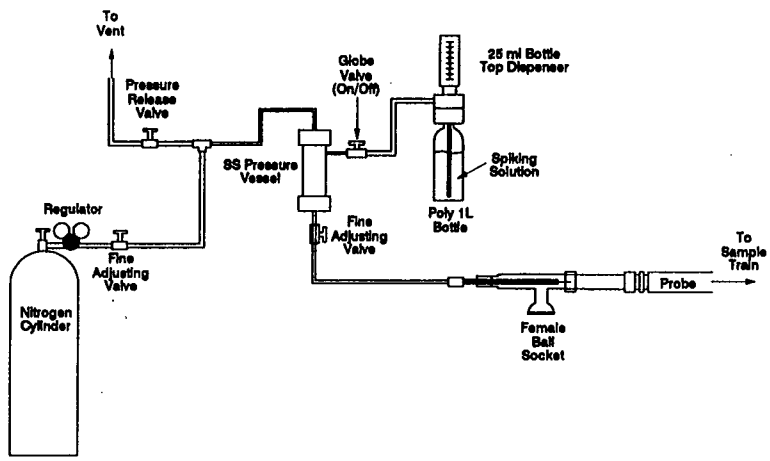

Fig. 3. Ammonium chloride spiking system.

TABLE I
Amount of Hydrochloric Acid Solution Purged from the Cyclone and Recovered in the Impinger Train During Initial Purge Experiments

Run Number	HCl Solution In Cyclone (g) Initial	HCl Solution In Cyclone (g) Final	HCl Solution Removed from Cyclone (g)	Probe and Filter Temperature (°C)	HCl Recovered in Impinger Train[a] (%)
A-1[b]	97.7	44.0	53.7	121	NA
A-2[b]	48.0	22.2	25.8	121	NA
A-3	23.2	1.5	21.7	121	7.82
A-4	19.2	0.8	18.4	121	8.56
A-5	25.2	0.0	25.6	177	54.5

NA = Not Analyzed
[a]Total of three acid impingers.
[b]Samples were not analyzed because significant quantities of spike solution remained in the cyclone.

TABLE II
Comparison of the Amount of Hydrochloric Acid Solution Purged from the Cyclone and Recovered in the Impinger Train at Different Probe and Filter Temperatures

Run Number	HCl Solution In Cyclone Initial (mL)	HCl Solution Removed From Cyclone	Probe and Filter Temperature (°C)	HCl Recovered in Impinger Train[a] (%)
A-6	15.0	10.8	121	10.6
A-7	15.0	14.2	121	24.6
A-8	15.0	15.0	121	78.3
A-9	15.0	16.0	177	92.8
A-10	15.0	15.1	177	92.5
A-11	15.0	15.3	177	100

[a]Total of three acid impingers.

of the cyclone purge procedure. At this temperature, all 15 mL of the HCl solution added to the cyclone was consistently removed within the 45-minute purge period and over 90 percent of the spiked HCl was recovered in the impinger train. If the volume of water collected in the cyclone during the sampling period is greater than 25 mL, the 45-minute purge period, even at probe and filter temperatures of 177°C, will not be adequate for complete purging of the cyclone, and the cyclone cannot be purged in the field.

STUDIES OF THE NEGATIVE BIAS AT CONCENTRATIONS BELOW 20 PPMV

To evaluate the existence and extent of negative bias, twelve trains were dynamically spiked in the laboratory with three levels of HCl ranging from 5 to 25 ppmv. Three of the 12 trains were spiked at 25 ppmv to confirm the accuracy of the Method 0050 train above 20 ppmv and to demonstrate that the spiking, sampling, and analytical systems were functioning properly. To demonstrate the bias of the method for sampling HCl concentrations below 20 ppmv and to determine whether the bias varied with concentration, triplicate trains were spiked at 12 and 5 ppmv with the probe and filter heated to 121°C. Triplicate trains were also spiked with HCl at approximately 4 ppmv, with moisture at approximately 16 percent with the probe and filter heated to 200°C to determine the effect of probe and filter temperature on the negative bias.

Results of these experiments are shown in Table III. With the probe and filter operated at 121°C, HCl recoveries ranged from 70.7 percent to 83.2 percent with a train spike of 5 ppmv. These low recoveries confirmed the previously observed negative bias below 20 ppmv. When probe and filter rinses were included in the calculation of recovery, HCl recoveries ranged from 88 percent to 100 percent when the trains were spiked at 5 ppmv. These results suggest loss of HCl in the probe. However, when the trains were spiked at 12 ppmv, recoveries were greater than 100 percent, indicating that a negative bias is not consistent at all concentrations. Figure 4 shows the negative bias at low HCl concentrations correlates strongly with increased moisture content of the gas stream, rather than HCl concentration.

When the probe and filter of the Method 0050 sampling train were operated at 200°C, the bias ranged from -0.35 to +0.48 mg HCl and the recovery of spiked HCl ranged from 98 to 103 percent. These data indicate that the observed negative bias when sampling concentrations below 20 ppmv can be eliminated by operating the train at 200°C.

TABLE III
Results of the Negative Bias Experiments

Run Number	Date	Filter/Probe Temperature (°C)	Concentration HCl Spiked (ppmv)	Percent Moisture	HCl (Total mg)		Bias[a]	Recovery[b] (%)
					Spiked	Measured		
B-4	3-9-93	121	26.2	8.74	107	95.6	-11	89.3
B-5	3-11-93	121	25.1	4.35	103	106	+3	103
B-6	3-11-93	121	25.2	3.43	103	112	+10	110
B-7	3-16-93	121	12.3	2.04	49.8	51.8	+2.0	104
B-8	3-16-93	121	12.3	2.70	49.8	49.7	-0.1	99.8
B-9	3-16-93	121	12.3	1.42	49.8	47.0	-2.8	94.3
B-10	3-17-93	121	5.16	9.26	21.0	17.5	-3.5	83.2
B-11	3-17-93	121	5.16	6.93	21.0	15.4	-5.6	73.3
B-12	3-17-93	121	5.16	7.41	21.0	14.8	-6.2	70.7
C-12	9-20-93	205	4.36	15.6	18.1	18.6	+0.5	103
C-13	9.22-93	176[c]	4.21	15.4	17.6	17.3	-0.3	98.0
C-14	9-22-93	210	3.93	17.2	16.5	16.8	+0.3	102

[a]Bias = Measured-Spiked.
[b]Recovery (%) = Measured/Spiked x 100.
[c]The filter and probe were heated to 122C for the first 35 minutes and then the temperature was increased to 206°C.

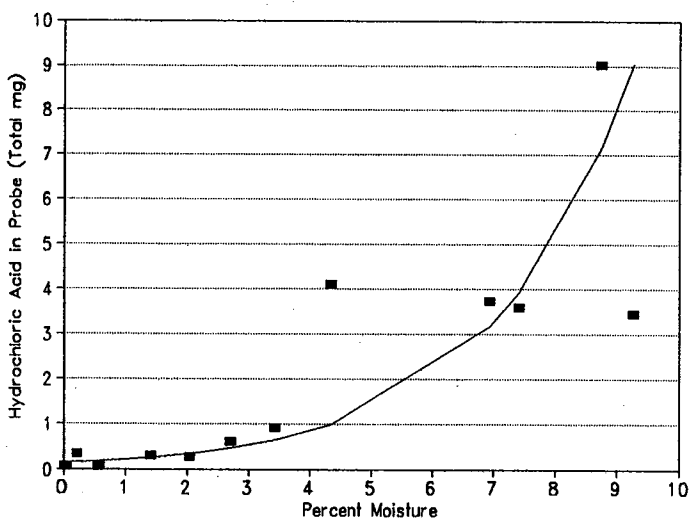

Fig. 4. Plot of HCl retained in the probe versus moisture spiked into the train.

STUDIES OF THE POSITIVE BIAS IN THE PRESENCE OF AMMONIUM CHLORIDE

To study the effect of the presence of ammonium chloride, fifteen trains were dynamically spiked with ammonium chloride at two temperatures and at two levels of moisture. Of the 15 trains, 11 were spiked with ammonium chloride at 121°C. Four of the 11 trains were spiked at low levels of moisture (no steam added during sampling). One of the four trains was spiked with a methanol solution of ammonium chloride. The other 7 trains were spiked with ammonium chloride at high levels of moisture (steam added during sampling). Three of these seven trains were also spiked with HCl to see if there were synergistic effects between HCl and ammonium chloride. Three trains were spiked with NH_4Cl at 205°C.

Table IV shows the bias measured for HCl for all of the trains. Table V summarizes the bias measured for HCl for each condition tested. Under all test conditions, the presence of ammonium chloride introduced a positive bias into the HCl measurement. This positive bias resulted from penetration of the filter by NH_4Cl and subsequent dissociation of the NH_4Cl in the 0.1N H_2SO_4 solution. A statistically-significant positive bias in the HCl measurement was observed even when the amount of NH_4Cl spiked was as low as 2.44 ppmv. The positive bias in the HCl measurement increased when the temperatures of the probe and filter increased. The positive bias in the HCl measurement appeared to be independent of the type of filter used in the Method 0050 sampling train. In the presence of both HCl and NH_4Cl, a synergistic effect appears to occur, increasing the positive bias in the HCl measurement.

CONCLUSIONS

The higher probe and filter temperatures tested increase the efficiency of collection of HCl. However, at higher train temperatures, the magnitude of the positive bias due to the presence of ammonium chloride increases. The presence of ammonium chloride at the source must be recognized and data qualified for positive bias. When the use of the cyclone is required because of the presence of moisture droplets, a post-sampling cyclone purge must be conducted to successfully eliminate all remaining moisture from the cyclone to eliminate negative bias in HCl measurements. However, if the volume of water/HCl in the cyclone is greater than 25 mL, the 45-minute purge required in Method 0050 will not be sufficient for a complete purge.

TABLE IV
Summary of Spiked Train Experiments Sampling at 0.76 CFM for Two Hours

Run Number	Date	Filter/Probe Temperature (°C)	Amount/Concentration NH_4Cl Spiked	Percent Moisture	HCl (Total mg)		Bias[a]
					Spiked	Measured	
C-1	9-7-93	124	29.5 ppmv (180 mg)	15.5	0	24.3	+24.3
C-2[b]	9-7-93	126	2.44 ppmv (15.0 mg)	16.2	0	1.38	+1.38
C-3	9-8-93	128	34.2 ppmv (210 mg)	18.9	0	8.36	+8.36
C-4	9-10-93	121	31.8 ppmv (195 mg)	22.0	0	8.26	+8.26
C-5	9-10-93	194	29.1 ppmv (180 mg)	21.4	0	112	+112
C-6	9-10-93	207	29.1 ppmv (180 mg)	22.4	0	115	+115
C-6W	9-13-93	210	29.4 ppmv (180 mg)	21.8	0	115	+115
D-7	9-13-93	125	29.1 ppmv (180 mg)	4.18	0	39.3	+39.3
D-8[c]	9-14-93	123	29.1 ppmv (180 mg)	4.48	0	27.3	+27.3
C-9	9-16-93	123	29.1 ppmv (180 mg)	17.9	91.0	143	+52.0
C-10	9-16-93	124	30.1 ppmv (186 mg)	18.7	90.4	154	+63.6
C-11	9-17-93	121	29.1 ppmv (180 mg)	19.2	89.6	159	+69.4
D-15	9-23-93	123	24.4 ppmv (150 mg)	4.04	0	19.5	+19.5
D-16	9-23-93	121	29.1 ppmv (150 mg)	4.03	0	19.4	+19.4
M-17[d]	9-23-93	122	41.2 ppmv (255 mg)	4.63	0	37.7	+37.7

[a]Bias = Measured-Spiked.
[b]Capillary spiking nozzle plugged during run.
[c]Teflon® filter used instead of quartz.
[d]NH_4Cl in methanol solution used instead of aqueous NH_4Cl solution.

TABLE V
Summary of Measured HCl Bias for Each Test Condition

Test Condition					Measured HCl Bias (total mg)		
Filter/Probe Temperature	Added Moisture	HCl Spiked	NH_4Cl Solvent	Filter Type	Average	Standard Deviation	Relative Standard Deviation (%)
Low	High	No	Water	Quartz	+13.6	9.23	67.7
High	High	No	Water	Quartz	+114	1.73	1.52
Low	Low	No	Water	Quartz	+26.1	11.5	44.0
Low	High	Yes	Water	Quartz	+61.7	8.86	14.4
Low	Low	No	Water	Teflon®	+27.3	a	
Low	Low	No	Methanol	Quartz	+37.7	a	

[a]Result of one determination only.

REFERENCES

1. Test Methods for Evaluating Solid Waste -- Physical/Chemical Methods. SW-846, Third Edition, September, 1986. Washington, D.C.