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FOR
HALOGENS AND HALOGEN ACIDS**

Larry D. Johnson
Methods Branch, MD-44
Air Methods Research Division
National Exposure Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Presented At
EPA/A&WMA International Symposium
Measurement of Toxic and Related Air Pollutants
Research Triangle Park, NC
May 1996

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Larry D. Johnson
Methods Branch, MD-44
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ABSTRACT

EPA Methods 26 and 26A and Proposed Methods 0050 and 0051 are in widespread use for collection and quantitation of stationary source emissions of halogens and halogen acids from a variety of source types. Considerable research has been conducted in evaluation of these methods, but research information about the methods has not been published in one convenient summary and much of the technical community is unaware of its existence.

This paper provides historical and scientific background for the EPA sampling methods in use today, along with some of their strengths and limitations. The primary evaluation studies are summarized, and publication references are given. The SW-846 Methods Manual versions of the procedures are compared with the versions from CFR40 part 60. Relatively new research work is summarized, along with recent changes in the methods, and critical operating factors.

INTRODUCTION

Sampling and quantitation of stack emissions from hazardous waste combustors and from boilers and industrial furnaces co-firing hazardous waste are required as part of the Resource Conservation and Recovery Act (RCRA) permitting process. Hydrochloric acid and chlorine are currently regulated, and consideration is being given to setting requirements for the similar bromine compounds. Hydrochloric acid emissions from municipal incinerators are regulated under the Clean Air Act and chlorine, hydrochloric acid, and hydrofluoric acid are listed among the 189 Hazardous Air Pollutants in the Clean Air Act Amendments of 1990 (CAAA).

EPA's Office of Research and Development has developed and evaluated two variations of the same sampling and analysis technology for measurement of halogens and halogen acids. The version using EPA Method 5 sampling hardware and many Method 5 procedures is shown in Figure 1. The sampling follows Method 5 isokinetic procedures with full stack traverse. HCl and other halogen acids are very water soluble, and sampling is often downstream of a scrubber where water droplets may occur. Because of their likely halogen acid content, the droplets must be collected isokinetically to avoid non-representative sampling. The isokinetic version of the sampling technology shown in Figure 1 corresponds to EPA Method 26A¹ and Proposed EPA Method 0050², which will be described and discussed more fully later in this paper. A midjet impinger train packaging of the same sampling technology, which may be used when isokinetic sampling is not required, corresponds to EPA Method 26¹ and Proposed EPA Method 0051². Considerable research has been conducted in evaluation of these methods, but research information about the methods has not been published in one convenient summary and much of the technical community is unaware of its existence. A summary of the more important studies relative to these methods follows.

The earliest work with a major influence on the EPA methods was reported in 1979 by Cheney and Fortune³. They investigated collection of HCl in NaOH solutions of several concentrations followed by four different titration procedures. A mercuric nitrate titration after collection in 0.1M NaOH was

ultimately recommended. Cheney and Fortune followed their earlier work with another study reported in 1984⁴. In the second study, they investigated reaction and sorption losses of HCl during sampling. Use of disc filters made of quartz was recommended to minimize losses to the filter material, and relatively high flow rates were recommended to minimize interactions with collected alkaline particulate material.

Stern, et al. presented their work during 1983, and it appeared in print in 1984⁵. They reported development and laboratory evaluation of a sampling and analysis system for collection and speciation of halogens and halogen acids. The sampling equipment was essentially the midjet impinger version of that shown in Figure 1, but ion chromatography was chosen for the analysis because of its high selectivity, low detection limit, and multiple ion capability. Collection and quantitation of HCl (130 ppm) and Cl₂ (19 ppm) were successful in the presence of 250 ppm SO₂ and 600 ppm NO_x. It was demonstrated that dilute H₂SO₄ was a superior collection medium for the halogen acids as compared to water. When water was used, some retention of the halogen compounds resulted, presumably from disproportionation reactions. The presence of the dilute acid suppressed these types of reactions and resulted in excellent speciation. Poor recovery was obtained with HBr (10 ppm). The authors speculated that the poor performance for HBr was due to sorption or line losses. The fact that virtually all of the HBr was collected in the first impinger would be consistent with that hypothesis, and would rule out poor impinger collection as the problem.

The publications of DeWees, et al.⁶ and Steinsberger and Margeson⁷ constitute the principal evaluation base for measurement of HCl and Cl₂ by Methods 26 and 26A and Proposed Methods 0050 and 0051. The two publications are both reports of the same body of work. Building on the work of the previous authors, both laboratory evaluation and field testing were carried out. During the early phases of the investigation, the nonisokinetic midjet impinger train received most of the attention, but the isokinetic sampler was worked into later experiments. Primary focus was on evaluation of the methodology for determination of HCl, but Cl₂ was studied as a potential interferant, and all indications were that the method was performing adequately for Cl₂ as well.

During the laboratory phase of the project, a ruggedness test was conducted to evaluate the effect of six variables on HCl results. Within the ranges tested, the method was shown to be insensitive to low reagent volume, increased first impinger pH, longer sampling times, elevated impinger temperatures, higher sampling rate, and elevated Cl₂ levels up to 50 ppm. Earlier experiments showed that only a 3.4% positive bias was caused by 197 ppm of Cl₂ in a gas stream containing 221 ppm of HCl.

The methodology was field tested using dynamic spiking of gaseous HCl standards and a test protocol similar to that later specified in Method 301, Field Validation of Emission Concentrations from Stationary Sources. Key conclusions of the field test were: 1. The precision of the method for HCl ranged from 0.24-0.49 ppm at flue gas HCl levels of 3.9 to 15.3 ppm. 2. The bias of the method was <8% for HCl cylinder gases of 9.7 and 34.3 ppm. 3. The manual method agreed within 7% with a continuous HCl monitor based on gas filter correlation infrared spectroscopy (GFC/IR). 4. Flue gas CO₂ absorption by alkaline impinger reagents was insignificant with either the midjet impinger train or the Method 5 type train. 5. The midjet impinger train and the Method 5 type train showed similar results at a flue gas HCl concentration of 21.2 ppm, but the Method 5 type train produced results with a negative bias of about 50% compared to the midjet impinger train and the continuous monitor both of which averaged 4.8 ppm.

The work of Steger et al.⁸ was prompted by concern over three potential sources of error in Proposed Method 0050 and Method 26A. They investigated possible negative bias related to purging of the optional cyclone catch, negative bias at low ppm concentrations previously reported, and potential positive bias due to the presence of NH₄Cl. Key findings were: 1. A negative bias at low HCl concentrations was confirmed. The bias was variable and seemed to correlate better with gas stream moisture content than with HCl concentration. Higher probe and filter temperatures were beneficial. 2. NH₄Cl caused a positive bias under all test conditions by penetration of the filter as a vapor and

subsequent interference in the analysis. Lower probe and filter temperatures were beneficial for this interference, but detrimental from a sorption standpoint, as described above. 3. When high moisture levels force the use of the cyclone, a post-sampling cyclone purge is essential to drive any trapped HCl into the impinger catch. However, when the volume of aqueous solution in the cyclone exceeded 25 mL, the 45 minute purge required in Method 0050/26A was not sufficient to complete the task.

Powell and Dithrich⁹ investigated the use of GFC/IR for monitoring of HCl emissions from cement kilns, in part duplicating the work of Steinsberger and Margeson⁷ and confirming the efficacy of the monitoring technology tested. Method 26 testing conducted simultaneously produced results for HCl compared to those from GFC/IR which ranged from being low by a factor of 2 to extremely low by a factor of 30. In subsequent laboratory studies HCl was spiked into Method 26 trains with and without probes and filters present. Recoveries were reasonably quantitative for the impingers-only, but were low by factors of 3 to 5 for the full train. The authors concluded that the train losses were due to condensation (sorption?) to train surfaces and to reaction of HCl with alkaline particulate material collected on the filter. Any losses which may have been due to these effects were no doubt exacerbated by the use of fiberglass filter material in direct violation of Method 26, which specifies quartz or fluorocarbon coated quartz filters.

PRINCIPLES OF OPERATION

EPA Air Test Method 26 and Method 26A are essentially the same as Proposed Method 0051 and Proposed Method 0050, respectively. Methods 26 and 26A have been extended to deal with other halogens and halogen acids in addition to chlorine and chloride, but the principles of operation are still the same.

The following description is worded in terms of sampling and analysis of HCl and Cl₂ with Proposed Method 0050, but it also applies to the other three methods and the other halogens and halogen acids. Method 0050 contains all of the elements necessary to cope with the usual multiphase mixture extracted from incinerator stacks. A heated glass or quartz probe and probe nozzle assembly is followed by a heated filter and a series of liquid filled impingers, which perform the dual role of cooler/condenser and sample collection medium. The usual gas moving and measuring hardware follows.

It is a straightforward matter to collect HCl in either acidic, neutral, or basic solution, and to analyze for the resultant chloride ion with any one of dozens of determinative analysis techniques. The situation becomes more complex when the distinction must be made between HCl and chlorine and when the stack emissions contain chloride salts which might interfere with the analysis. One of the best ways to trap chlorine is by the use of dilute sodium hydroxide, but this produces a chloride ion as well as a hypochlorite ion. This confuses interpretation of the results if HCl and chlorine are both sampled.

In Proposed Method 0050, the chloride salts are removed from the sample stream by the filter, while both HCl and chlorine pass through. Some glass fiber filters have sorbed unacceptable quantities of HCl, probably due to alkaline impurities on or in the glass surface. The filter specified for Proposed Method 0050 is a fluorocarbon polymer coated quartz material. Reports of inconsistent operating behavior of the coated filter have led to approval of quartz filters as an alternative. Uniform and adequate heating of the probe and the filter is essential when collecting HCl. Any trace of moisture condensation will result in removal of HCl from the gas stream, and a resulting low bias in the final data. This problem becomes even more serious at HCl concentrations in the low ppm range. Even dry probe and filter surfaces may sorb HCl if their temperature is too low. The filter support must be fluorocarbon polymer rather than fritted glass, since the latter can remove significant amounts of HCl.

If sufficient water is present in the sample stream to wet the filter, it will be necessary to include the optional cyclone for droplet removal. Inclusion of the cyclone complicates the sample recovery process later, so it should not be added unless necessary. Wetting of the filter is unacceptable, since it allows salt migration through the filter and possible contamination of the HCl collection elements.

Once HCl and chlorine pass through the filter, the HCl is collected in the dilute sulfuric acid solution and the chlorine is collected in the dilute sodium hydroxide. The dilute acid prevents capture of chlorine in the earlier impingers and thus provides for a cleaner separation of the two substances of interest.

After shipment to the laboratory, the dilute acid from the first three impingers (assuming the optional impinger is used) is combined and analyzed for chloride ion by ion chromatography using Method 9056¹⁰ or Proposed Method 9057². The BIF Methods Manual specifies analysis of samples from Method 0050 by means of Proposed Method 9057. That method has been proposed as part of the Third Update to the SW-846 Manual², but may be discontinued and replaced by Method 9056. Method 9057 was developed for chloride analysis only, while Method 9056 is effective for all of the common halide ions, including chloride. The two methods contain very similar ion chromatography procedures, and should yield the same result for chloride ion. The determinative analytical method included in Methods 26 and 26A is equivalent if not identical to Method 9056.

Method 9056 offers a far better combination of sensitivity and specificity than any other chloride method. The chloride from the first three impingers is reported as HCl, using the appropriate equation from Method 0050. The combined contents of the fourth and fifth impingers is analyzed by Method 9056 and reported as chlorine using the proper equation from Method 0050. The assumption is made that the chlorine disproportionates in the basic solution to form one chloride ion and one hypochlorite ion. Reports have been received that reducing agents in the stack gas, perhaps sulfur dioxide, have collected in the dilute hydroxide along with the chlorine and have ultimately caused reduction of a portion of the hypochlorite to chloride. If that reduction occurs, the disproportionation stoichiometry no longer applies, and the calculated result for chlorine is too high, perhaps as much as double the true concentration. Since no way has been discovered to predict or determine the extent of this problem in a given sample acquisition, a modification to the methodology was needed.

A simple remedy has been incorporated into methods 26 and 26A, but not yet into Proposed Methods 0050 and 0051. The remedy, which performed well in an unpublished laboratory study, is to add a small amount of sodium thiosulfate to the dilute caustic solution in order to consistently drive the chlorine reduction product all the way to chloride ion. The equation for calculation of chlorine concentration in the stack gas is changed to reflect the fact that one chlorine molecule in the stack sample is represented by two chloride ions in the impinger catch rather than one. One can speculate on the likelihood of chlorine and a reducing agent such as sulfur dioxide coexisting in the stack in the first place, but the remedy also protects against gradual reduction of the hypochlorite during sample shipping and storage. Addition of thiosulfate is expected to be incorporated into Proposed Methods 0050 and 0051 during the promulgation process.

CRITICAL OPERATING ELEMENTS

It is imperative that all elements ahead of the filter be adequately heated in order to prevent moisture condensation or direct sorption of halogens and halogen acids. The acids are particularly prone to losses because of their high water solubility. Possible contamination by halide salts prevents rinsing of front half equipment surfaces to recover deposited material. Steger, et al. recommend running the train at 200 °C to eliminate the negative bias due to sorption and condensation. Even running the train at 200 °C will not always be sufficient to keep the filter dry if unusually large amounts of water are present. In such cases the optional cyclone must be employed. It is important that the filter not become wet enough to allow migration of soluble halide salts through the filter as solutions. Penetration of the filter in this manner could cause contamination of the impinger catch and subsequent positive bias in the halogen acid results.

Filter material must be either the designated fluorocarbon coated quartz or plain quartz. Cheney demonstrated that fiberglass filters sorb unacceptable quantities of HCl, and that fiberglass "plugs" are

even worse. Sieve style filters, as opposed to mat configurations do not adequately filter fine particulate. Filter support material should also be inert, preferably fluorocarbon. Glass frits apparently do not always cause problems, but are best avoided.

Continued maintenance of a high pH in the back impingers is a must for adequate collection of the halogens. This is only a problem in sampling high acidity emissions. Steinsberger and Margeson⁷ showed that scrubbing of CO₂ from combustion gas into 0.1M NaOH is so inefficient that it does not seriously decrease the pH. The higher concentration NaOH necessary to compensate for higher quantities of acids in some sources may scrub CO₂ more efficiently. Data on CO₂ scrubbing as a function of base concentration, has not been located to date, but will be generated if not found in the near future. It is considered necessary for a proper understanding of the limitations of the halogen sampling technology as well as the methods for hexavalent chromium and HCN, all of which depend upon collection into basic solution. The use of pH indicators in the impingers is currently under investigation as part of a project to develop a sampling method for HCN. Results will be directly transferable to the halogen/halogen acid methods. In the meantime it is prudent to check the pH occasionally during sampling, using pH paper or other means, especially if stack acidity is high.

Careful handling with special concern for minimization of contamination is made even more important with this methodology than usual, because the analytical finish alone cannot discriminate between halide ion from halogen/halogen acid and that from ionic salts.

LIMITATIONS AND AREAS OF CONCERN

All methods have limitations and areas of concern. The halogen/halogen acid methods work well within the ranges of concentrations and variables studied, as well as in numerous cases of field application. The following discussion should not be construed as critical of the methodology, the evaluation studies performed in the past, or the quality of the data taken to date with the methods. Many questions have been answered, but there are still aspects and applications of the methods which could profit from further research.

Filter Penetration

Any substance which is capable of penetrating the filter and forming chloride ion in the impinger is a possible source of HCl interference for Methods 0050, 0051, 26 and 26A. Fortunately, there are not many substances that have that capability. Phosgene could certainly interfere, but if a combustor is emitting phosgene at high enough concentrations to seriously bias the HCl results, high HCl results is probably the least of the operator's problems. There has been considerable discussion whether ammonium chloride is volatile enough to penetrate the filter as a vapor and to cause a positive bias. It now appears that it may be possible under certain conditions. If ammonium chloride is thought to be causing significant bias in HCl results, an alternative technique, such as an infrared spectrophotometry based monitor, should be considered. Hypochlorous acid, if present in the stack might be volatile enough to penetrate the filter, or might decompose on the hot filter to form chlorine. If hypochlorous acid passed the filter as a vapor, it would be captured by either the acidic impinger solutions or the basic ones, but the distribution between these collector elements is currently unknown.

One potential penetration mechanism which is sometimes perceived to be a problem, is not problematic at all. An intact and well installed filter of the type specified will not pass significant quantities of solid halide salts such as NaCl, CaCl₂, and KCl. Filtration efficiency actually increases for finer particulate matter, after reaching a minimum at about 0.3 micrometers^{11,12}. The presence of undue amounts of ions such as sodium, potassium, or calcium in the impingers is probably due to contamination during handling, a broken filter, or operation with a wet filter. Attempts to correct the halogen acid results by subtracting amounts from the total in proportion to cation concentrations found in the impinger catch are ultimately unsound and likely to overcorrect. Except in highly artificial laboratory situations, it

is not possible to determine in what form the ionic material entered the impinger and whether it should be subtracted or not. For example, NH_4^+ may have entered as NH_4Cl , but may equally have passed the filter as NH_3 . Sodium or potassium contamination may have been in the form of nitrates, sulfates, or dozens of other salts.

Reactions Between Halides and Halogens

Two unpublished contractor reports to EPA raise interesting questions concerning potential reactions between halogen acids and halogens during sampling^{13,14}. ETS, Inc. raised preliminary questions and EER Corp. demonstrated that reactions between halides and halogen could affect the ultimate speciation of the sample catch. It is not clear, however, whether such a reactive combination would ever be sampled in a real stack, or whether the "realignment of species" would have occurred prior to sampling. It would seem more likely that a reactive mix of this nature would be found in an internal process stream than in flue gas.

Validation Status

As previously discussed, the methodology has been well tested for collection of HCl up to 500 ppm and as low as a few ppm. The method probably works well at higher concentrations, although the speciation split may suffer in the presence of high Cl_2 levels. Laboratory data for Cl_2 collection is acceptable, but that part of the method has not been field tested with dynamic spiking. EER showed generally good results for HF in a laboratory study. HBr results have been disappointing, perhaps due to reactions during the spiking experiments.

Alkaline Particulate

The possibility of low results due to reaction of HCl with alkaline particulate material collected on the filter was of great concern to Steinsberger and Margeson⁷ and has recently resurfaced in the work of Powell and Dithrich⁹. The magnitude of this effect has not been conclusively demonstrated, and is likely variable with particulate composition. Steinsberger and Margeson⁷ recommended an optional version of Method 26 with a probe nozzle directed counter to stack flow, in order to reject as much of the reactive particulate as possible. This arrangement would not be acceptable when isokinetic sampling is required. Another option would be to employ a GFC/IR monitor, although most monitoring systems are not capable of isokinetic sampling. Monitors all employ particulate filters which could encounter the same scrubbing effects as those found in manual methods. Frequent cleaning of the filter by "blow-back" could help to minimize the problem.

Thiosulfate Interference

A unpublished report to EPA showed that thiosulfate was the best of several reducing agents tested for addition to the alkaline impinger catch before analysis¹⁵. Since the thiosulfate treatment has been added to Methods 26 and 26A, reports have been received that the thiosulfate can cause interference in the analysis if present in excess. A good discussion of suggested procedures for the adjustment of the concentration of the reducing agent is included in a recent newsletter¹⁶.

SUMMARY

These methods require care! Given careful operation, they have been shown to work well for HCl and chlorine in sampling "normal" stack emissions such as those from incinerators and power plants. More complicated and more reactive gas mixtures may cause problems which will require research to overcome. Efficacy of the methods for other halogens and halogen acids has not been as well evaluated, and the limited data available show mixed results. Good precision and accuracy become difficult to achieve with these methods at concentrations below approximately 5 ppm. Performance data at

concentrations above 500 ppm HCl are uncommon.

NOTICE

The information in this document has been wholly funded by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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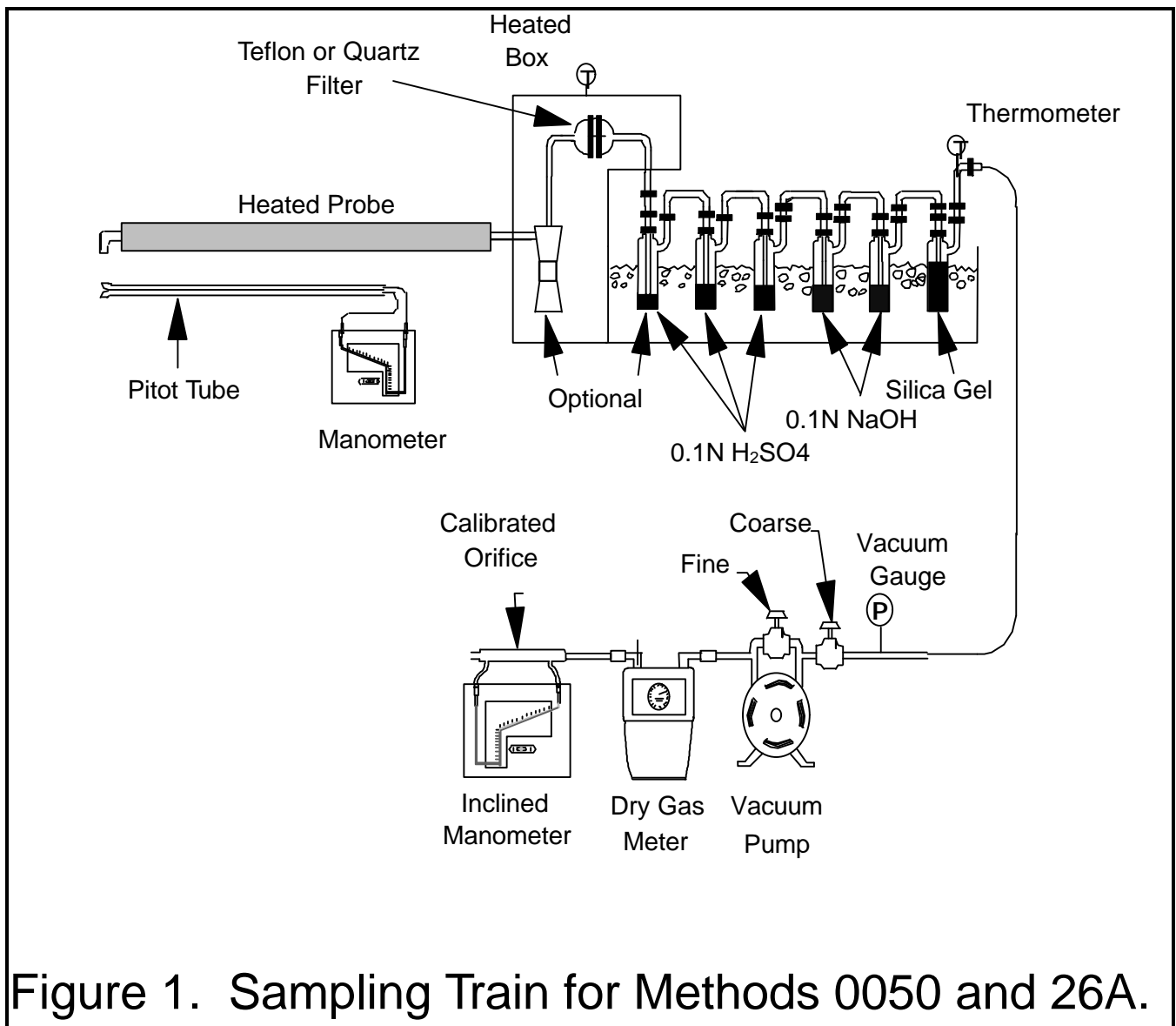


Figure 1. Sampling Train for Methods 0050 and 26A.