

## **Guidance Document for Testing and Permitting Sewage Sludge Incinerators**

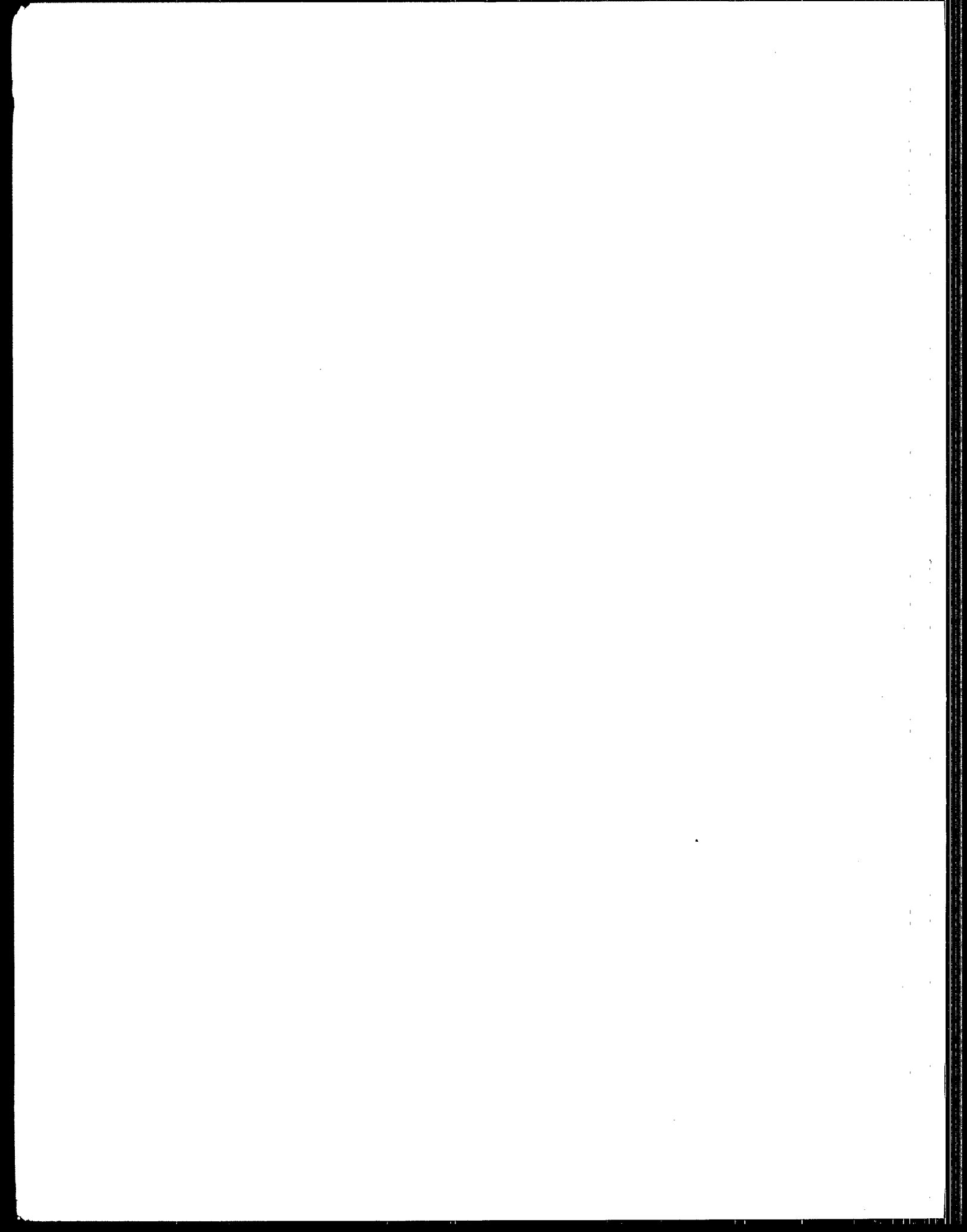
**Revised Draft Final Report**

**For U.S. Environmental Protection Agency**

**Prime Contractor  
Dynamac Corporation**

**Subcontract No. S-011-1188  
EPA Contract No. 68-03-3533  
Task No. 216  
MRI Project No. 9549-16**

**September 21, 1990**



# **MRI REPORT**

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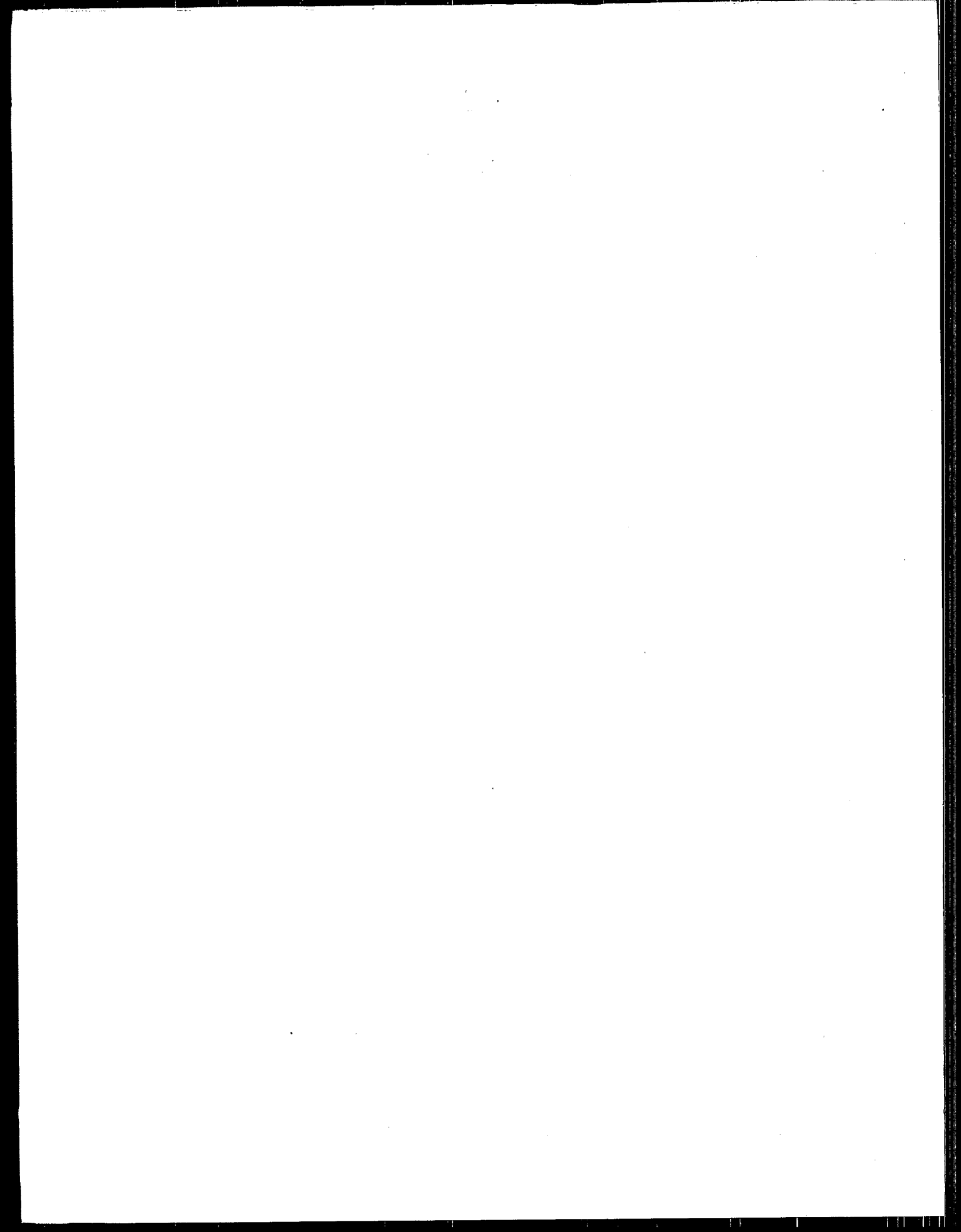
**Revised Draft Final Report**

**For U.S. Environmental Protection Agency  
Wastewater Solids Criteria Branch (WH-585)  
Criteria and Standards Division  
Office of Water Regulations and Standards  
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## PREFACE

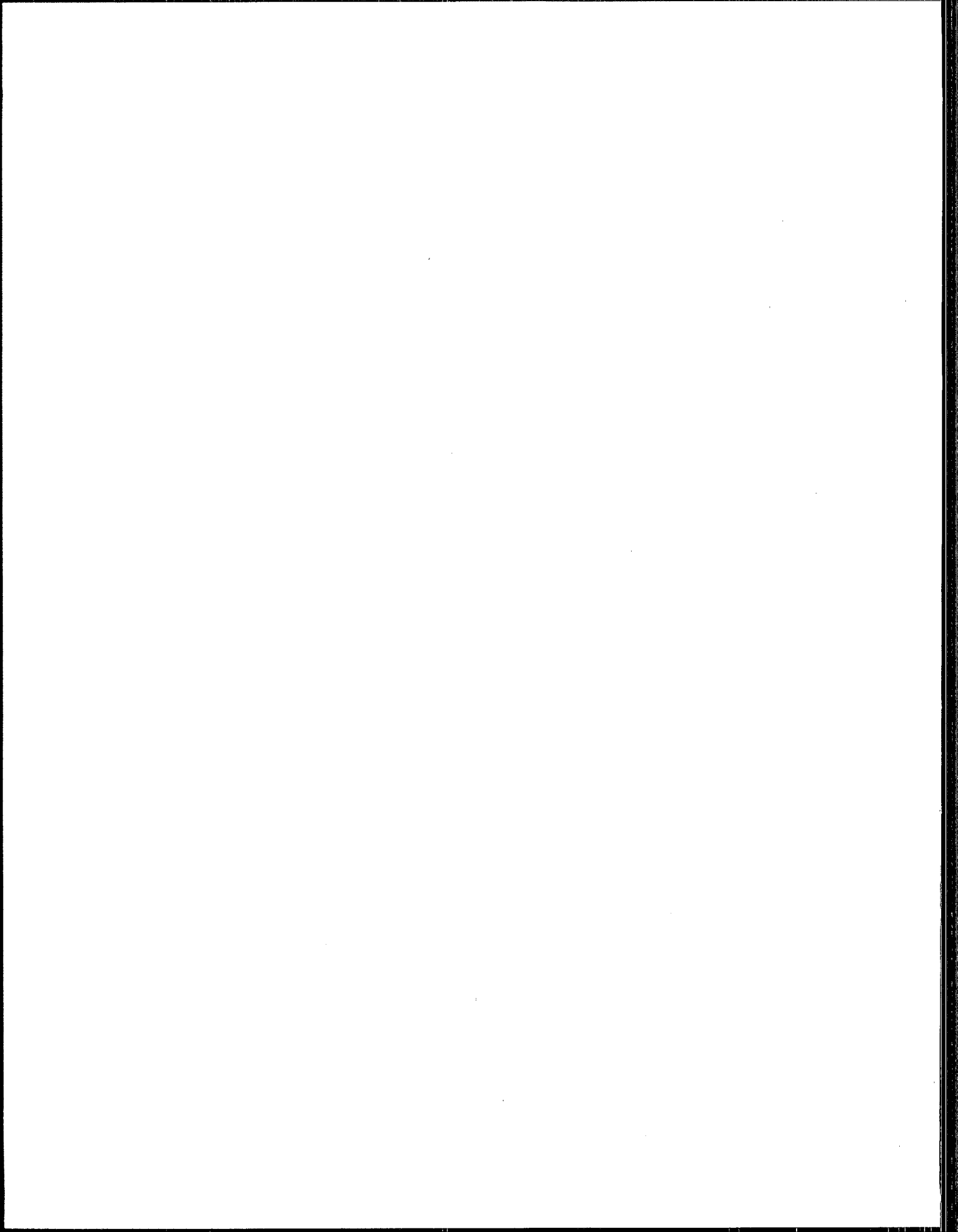
This draft document was prepared by Midwest Research Institute (MRI) for the U.S. Environmental Protection Agency (EPA) under subcontract to Dynamac Corporation on EPA Contract No. 68-03-3533. The document was developed by Bruce Boomer and Thomas Dux with assistance from Steven Schliesser and Phil Englehart. The contents of this draft have not been reviewed or approved by EPA.

Approved for:

MIDWEST RESEARCH INSTITUTE

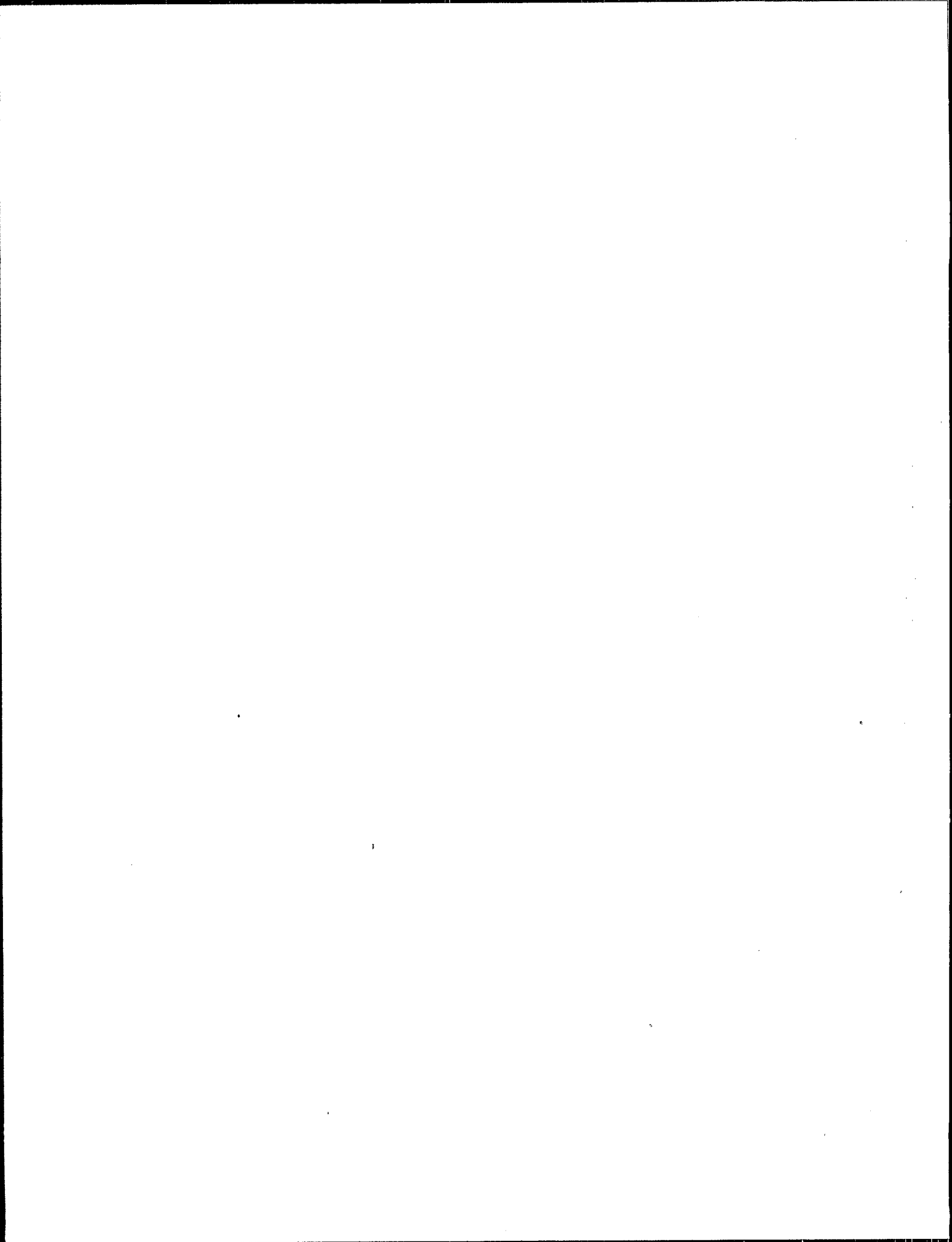
  
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September 21, 1990



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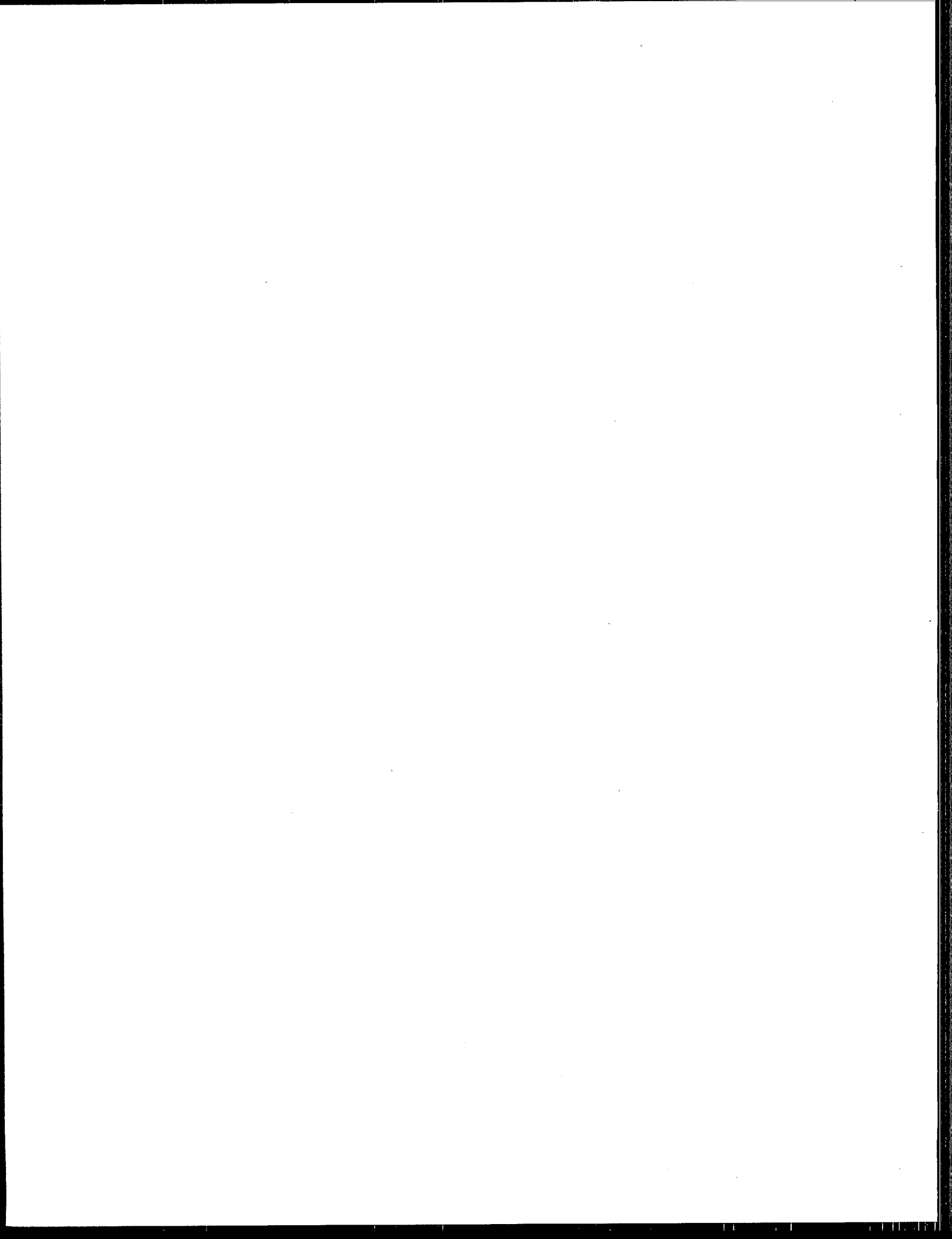
## I. INTRODUCTION

This document provides practical guidance for the testing and permitting of sewage sludge incinerators under regulations being proposed under the Clean Water Act. Designed for use by the organizations that own and operate sludge incinerators and control agency permit writers (EPA and state), the document provides guidance for testing, monitoring, and evaluating the performance of sewage sludge incinerators in conjunction with proposed rules published in the *Federal Register* on February 6, 1989.

The rules (proposed as 40 CFR 503) will establish numerical requirements for sewage sludge incinerators. A previous ruling, incorporated into 40 CFR 501, established the framework for a permitting program for sewage sludge incinerators. Although specific details in the proposed rules are subject to revision prior to final promulgation, the general approach is not expected to change. Since the Clean Water Act requires compliance within 12 months of the date the rule is promulgated (or within 24 months if the regulation requires construction of new pollution control facilities), owner/operators of sludge incineration facilities are encouraged to evaluate the impact of the proposed rules upon their facilities as soon as possible. This document provides a basis for evaluating sludge incinerators in response to the proposed rules.

This document addresses only the requirements proposed and promulgated under the Clean Water Act; these requirements may be administered through other EPA or state control Agency programs and permits. However, it is important to note that sewage sludge incinerators must comply as applicable with regulations of the Clean Air Act (CAA) and the Resource Conservation and Recovery Act (RCRA); this document does not address the requirements of these two programs.

Based upon the rules proposed on February 6, 1989, and subsequent developments, the permitting program for sewage sludge incinerators is expected to include the following major components:



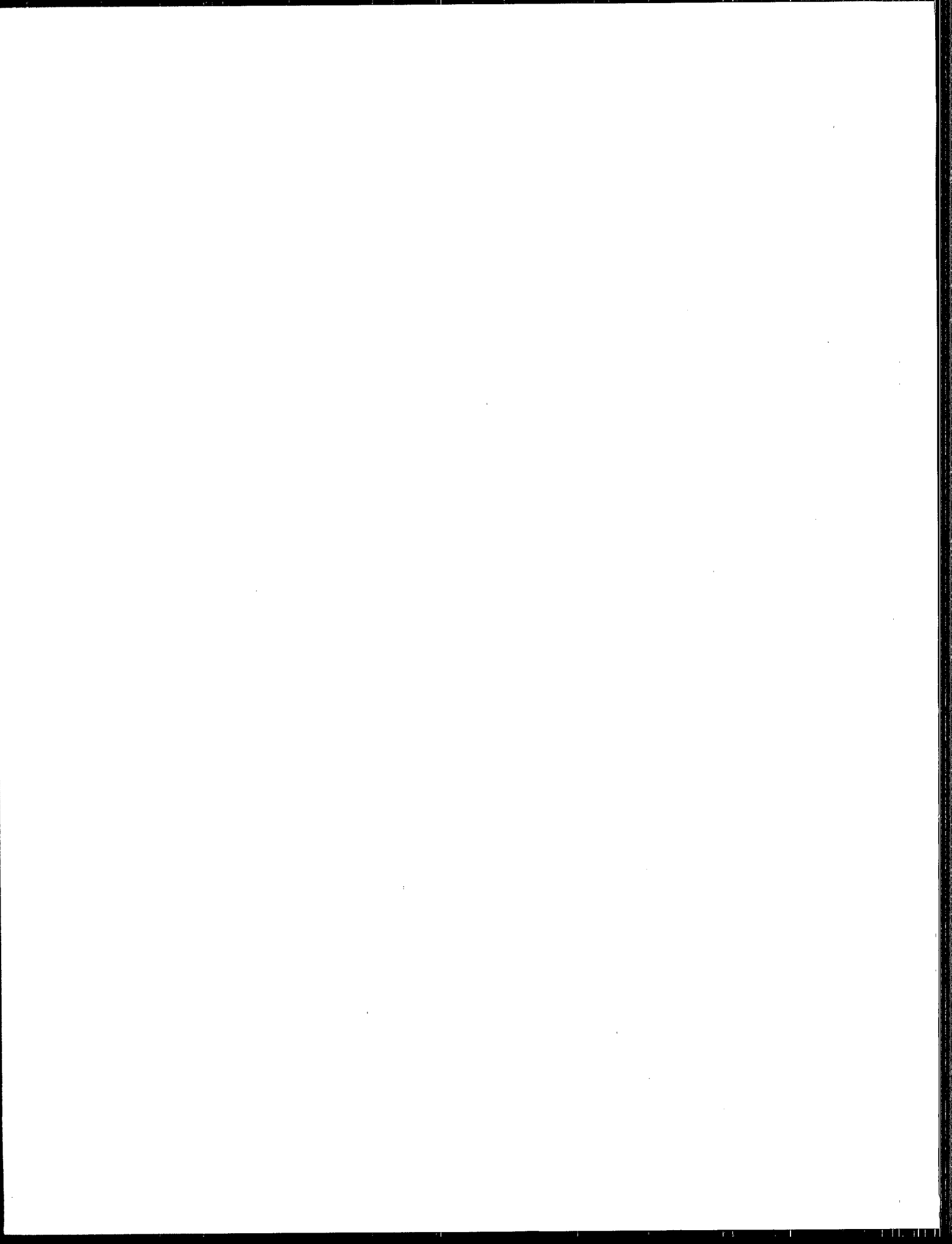
- A risk-based limitation of inputs of beryllium, mercury, lead, arsenic, cadmium, chromium, and nickel to the incinerators.
- A technology-based limitation of total hydrocarbons (THC) in incinerator emissions.
- Limitations on maximum combustion temperature, maximum oxygen content of exit gas, and selected air pollution control system parameters.
- Continuing monitoring and record keeping requirements for sludge feed and specific key operating parameters.

A series of equations are provided in the proposed rule for determining input limits for metals.

This document describes how an incinerator owner/operator can collect the appropriate data and establish an appropriate monitoring system to comply with the proposed regulations. The document also provides guidance to control Agency permit writers for reviewing test plans, reviewing the results of testing and monitoring, and establishing permit conditions. Both owner/operators and permit writers are encouraged to read this entire document to become familiar with the testing/monitoring methods available and the objectives of the permitting program. The remaining sections of the document are organized as follows:

- Chapter II--Testing and Monitoring
- Chapter III--Reviewing and Interpreting Test Results
- Chapter IV--Establishing Permit Conditions
- Chapter V--Continuing Enforcement Objectives

In an attempt to make this document as concise and functional as possible, the remaining sections are highly referenced, providing background descriptions of standard methods as appropriate and referring to readily



available EPA documents for the details associated with established procedures. For further information on the proposed rules, specific limitations, equations, and general background on sewage sludge incinerators, the reader is referred to the proposed rule and preamble (*Federal Register*, February 6, 1989) and the technical support document for sewage sludge incineration (EPA, 1989a, which is available from EPA).

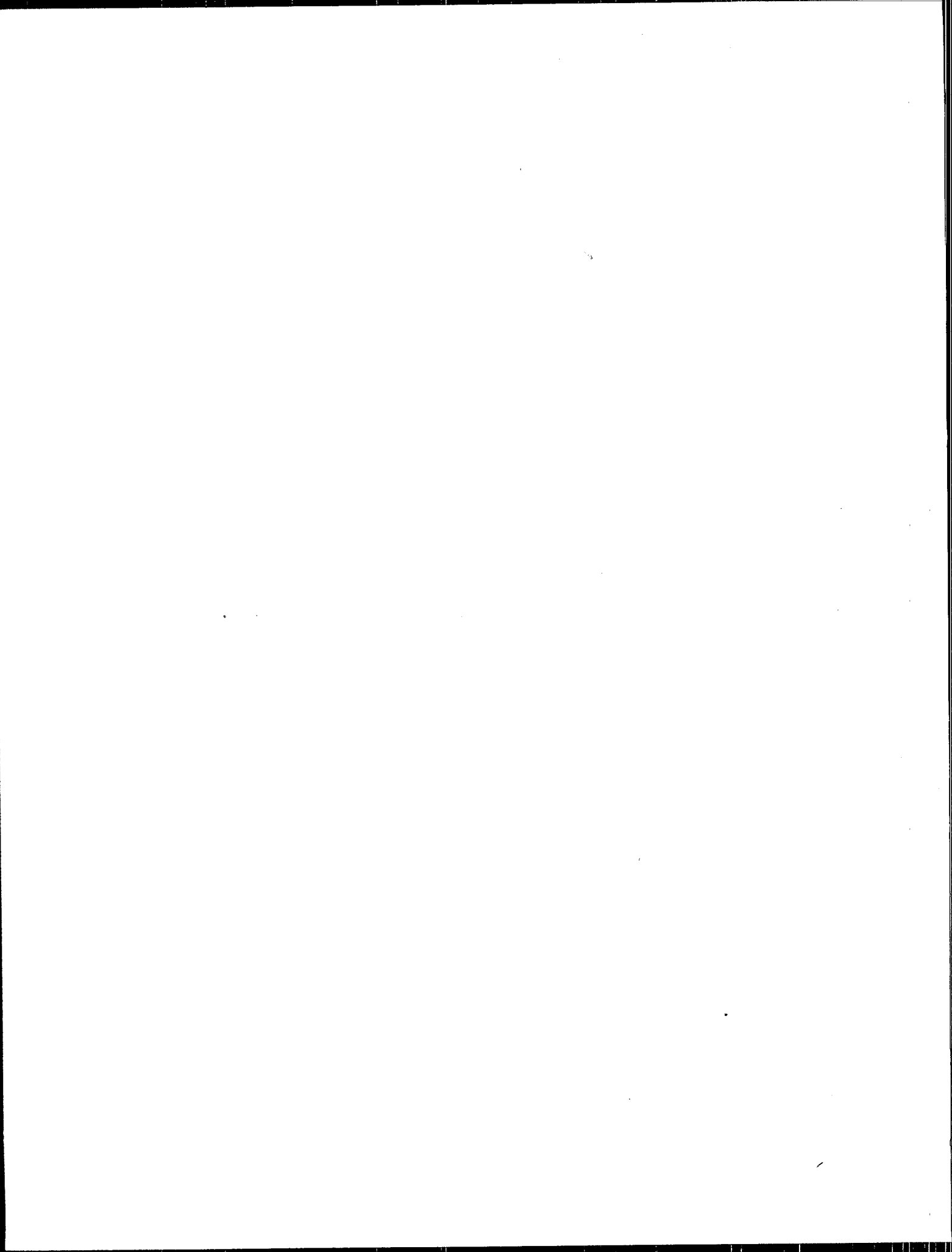
## II. TESTING AND MONITORING ACTIVITIES

The permitting program for sewage sludge incinerators is based upon limiting the toxic metal loading to the incinerator and continuously monitoring key indicators of adequate combustion and air pollution control. This requires (1) a continuing sludge characterization program to assess the input of metals and (2) instruments for continuously monitoring the operating parameters. Facilities must also measure stack emissions to develop site-specific control efficiency factors and conduct dispersion modeling to calculate a site-specific dispersion factor. These are used to calculate site-specific operating limits. This chapter describes the testing, monitoring, and modeling options available to satisfy the needs of the sludge incinerator permitting program.

### A. SAMPLING AND ANALYSIS OF SLUDGE INPUTS

Sludge inputs to incinerators must be characterized at a minimum in terms of the concentrations of toxic metals. The metals concentrations are used in a calculation to compute the allowable concentration of each metal in the feed sludge and the allowable maximum feed rate of sludge to the incinerator. These calculations are based upon the risk factors associated with each of the toxic metals. (The equations and basis for these calculations are provided in the preamble and proposed rules in the February 6, 1989, *Federal Register*).

The best sludge characterization data will result from a long-term sampling and analysis program that is designed to minimize the effect of random variation in sludge quality. Suggested methods for developing such a



program are provided in the *POTW Sludge Sampling and Analysis Guidance Document* (EPA, 1989c). This document notes the importance of addressing anticipated cyclic variation in pollution loading and treatment plant characteristics in characterizing the sludge characteristics. Additional guidance on sampling plan design can be found in Chapter 9 of SW-846 (EPA, 1986). This chapter provides guidance on designing a sampling plan to demonstrate that a particular waste (sludge) is beneath a particular regulatory limit (calculated maximum sludge concentration for metal of interest).

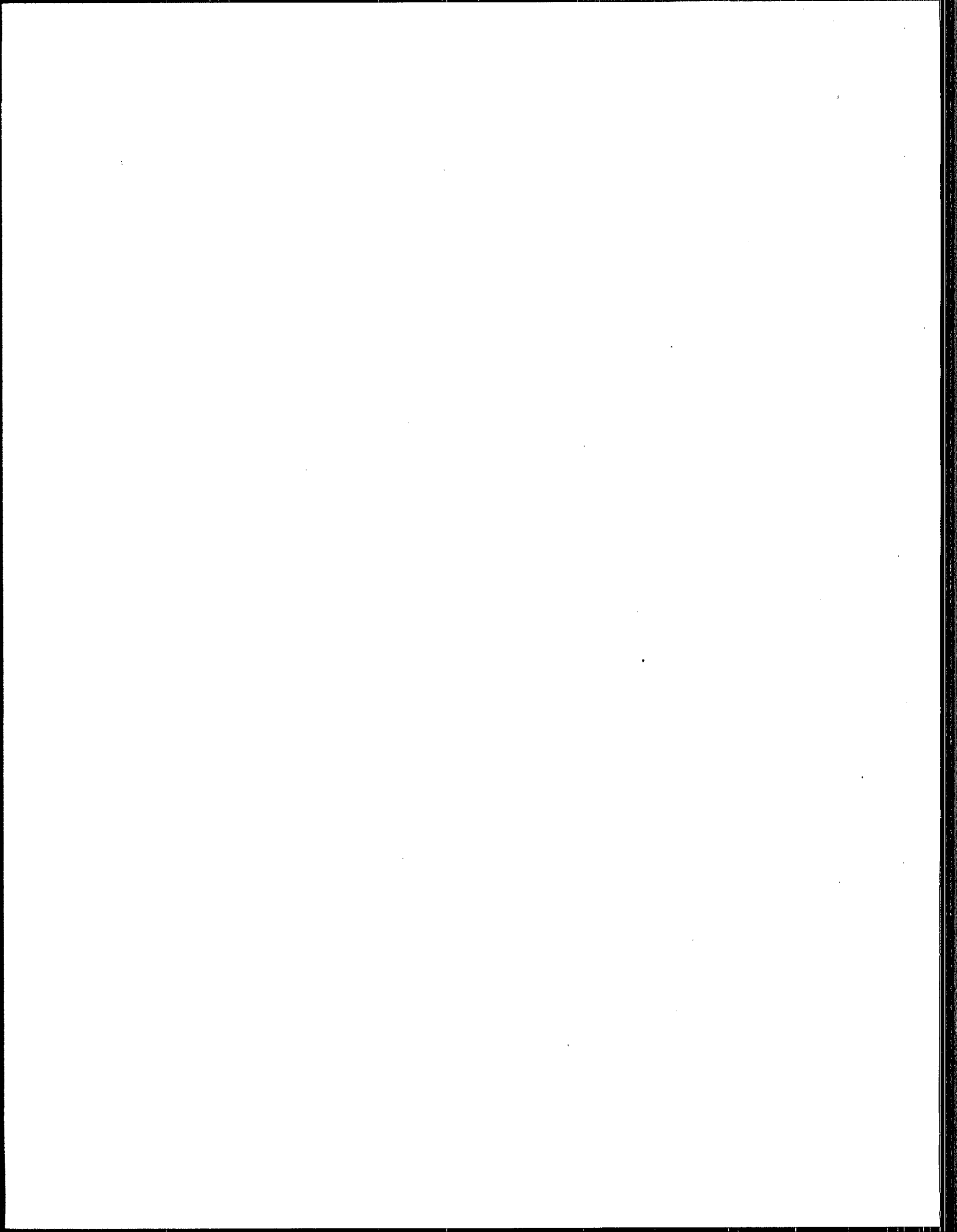
#### 1. Frequency of Sampling:

Ideally, sludge characterization data used for determining permit limits for sludge feed rates will result from a long-term sampling and analysis program or at least from a shorter term program specifically designed to collect samples that are representative of the expected range of variation. An exception will be the sampling programs designed to determine control efficiencies of toxic metals in an incineration facility. Such tests (described in Section C of this chapter) will be based upon only the characteristics of the sludge fed to the incinerator at the time of the test.

Continuing sludge characterization is required during the life of each operating permit. Required minimum frequencies (e.g., monthly, quarterly, or annually) for sampling and analysis of input sludge are based upon the design capacity of the treatment works, as described in Subpart I of the proposed rules.

#### 2. Access to Sludge Inputs and Sampling Methods:

Suggested sampling points and sampling methods are described in EPA (1989c). Each facility is required to provide access to the sewage sludge feed so that representative samples of the sewage sludge can be collected. Major considerations for sampling include the following:





- Each grab sample should be collected in a manner to be as representative per guidelines (EPA, 1989c) as possible of the total flow stream. Particular attention should be paid to obtaining samples which are representative of both liquids and solids fractions of the sludge. Metal concentrations for some sludges are higher in the solids fraction.
- Efforts must be made to minimize the possibility of contamination or any other potential chemical change to the sample during sampling and subsequent handling/storage prior to analysis.

### 3. Analytical Methods For Metals:

Measurements of the sludge for metals concentration are required. The following discussion concerning these analyses are based upon guidance in the *Hazardous Waste Incineration Measurement Guidance Manual* (EPA, 1989b), *POTW Sludge Sampling and Analysis Guidance Document* (EPA, 1989c), and *Proposed Methods for Measurements of CO, O<sub>2</sub>, THC, HCl, and Metals at Hazardous Waste Incinerators* (EPA, 1989e).

The physical properties of the waste and the calculated regulatory threshold limits (equations 1, 2, 3, and 4 of the proposed rule) should guide the choice of sample preparation and analysis methods. The method of sample preparation should be sufficiently rigorous to provide for complete digestion of the sludge, and the analytical technique must provide sufficient sensitivity to generate reliable data at the concentration levels of regulatory concern. For example, if the regulatory limit is low, determination of arsenic by inductively coupled plasma would not provide an adequate detection limit of sufficient sensitivity, and the more sensitive technique of graphite furnace atomic absorption would be appropriate.

The last two guidance documents in the previous paragraph give general background information on metals analysis. Table II-1 summarizes the specific methods given in the guidance manuals. The methods come from SW-846 (EPA, 1986) with the following specific recommendations:

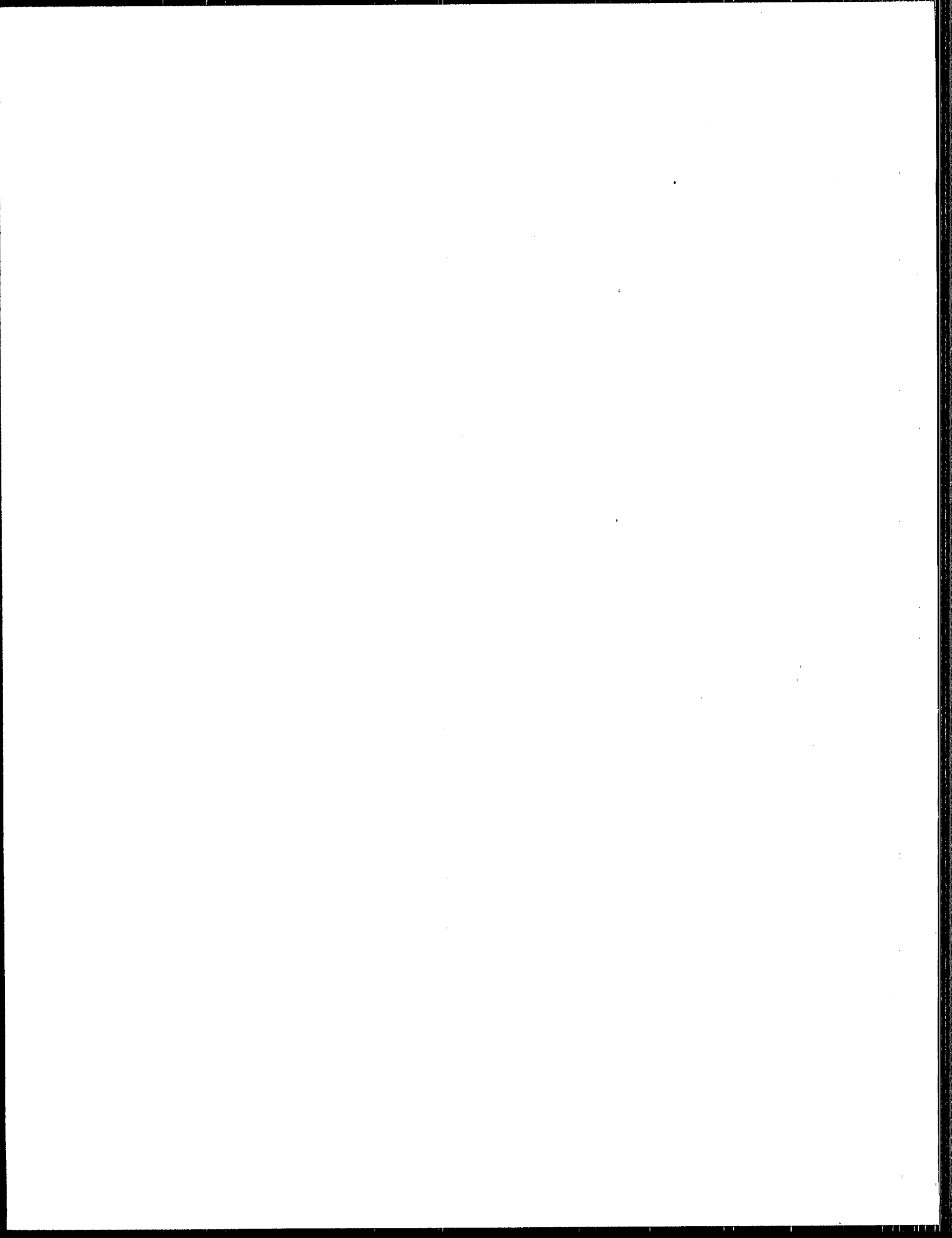


TABLE II-1

METHODS OF PREPARATION AND ANALYSIS OF  
SLUDGE SAMPLES FOR METAL ANALYTES<sup>a</sup>

<u>Analyte</u>	<u>Preparation Method</u>	<u>Analysis Method</u>	<u>Analysis Type<sup>b</sup></u>
As	3050	6010	ICP
	3050	7060	AAS-GF
	7061	7061	Hydride
Be	3050	7090	AAS-DA
	3050	6010	ICP
	3050	7091	AAS-GF
Cd	3050	7130	AAS-DA
	3050	6010	ICP
	3050	7131	AAS-GF
Cr	3050	7190	AAS-DA
	3050	6010	ICP
	3050	7191	AAS-GF
Pb	3050	7420	AAS-DA
	3050	6010	ICP
	3050	7421	AAS-GF
Hg	7471	7471	AAS-CV
Ni	3050	7520	AAS-DA
	3050	6010	ICP

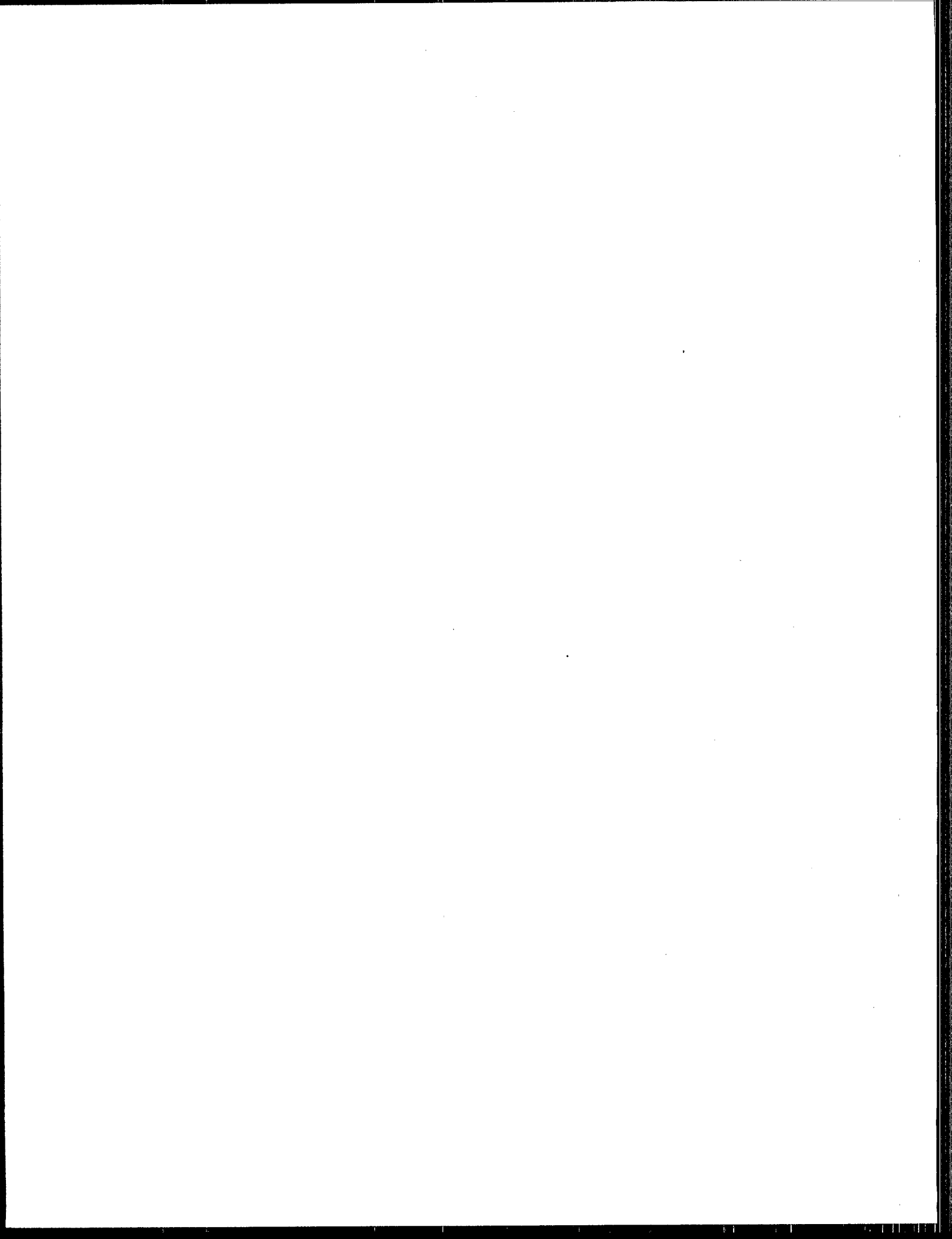
<sup>a</sup> All methods come from the *Test Methods for Evaluating Solid Waste* (SW-846 Third Edition, November 1986).

<sup>b</sup> AAS-DA: Atomic absorption spectrometry by direct aspiration method.

AAS-GF: Atomic absorption spectrometry by graphite furnace method.

AAS-CV: Atomic absorption spectrometry by cold vapor method.

ICP: Inductively coupled plasma atomic emission spectroscopy.

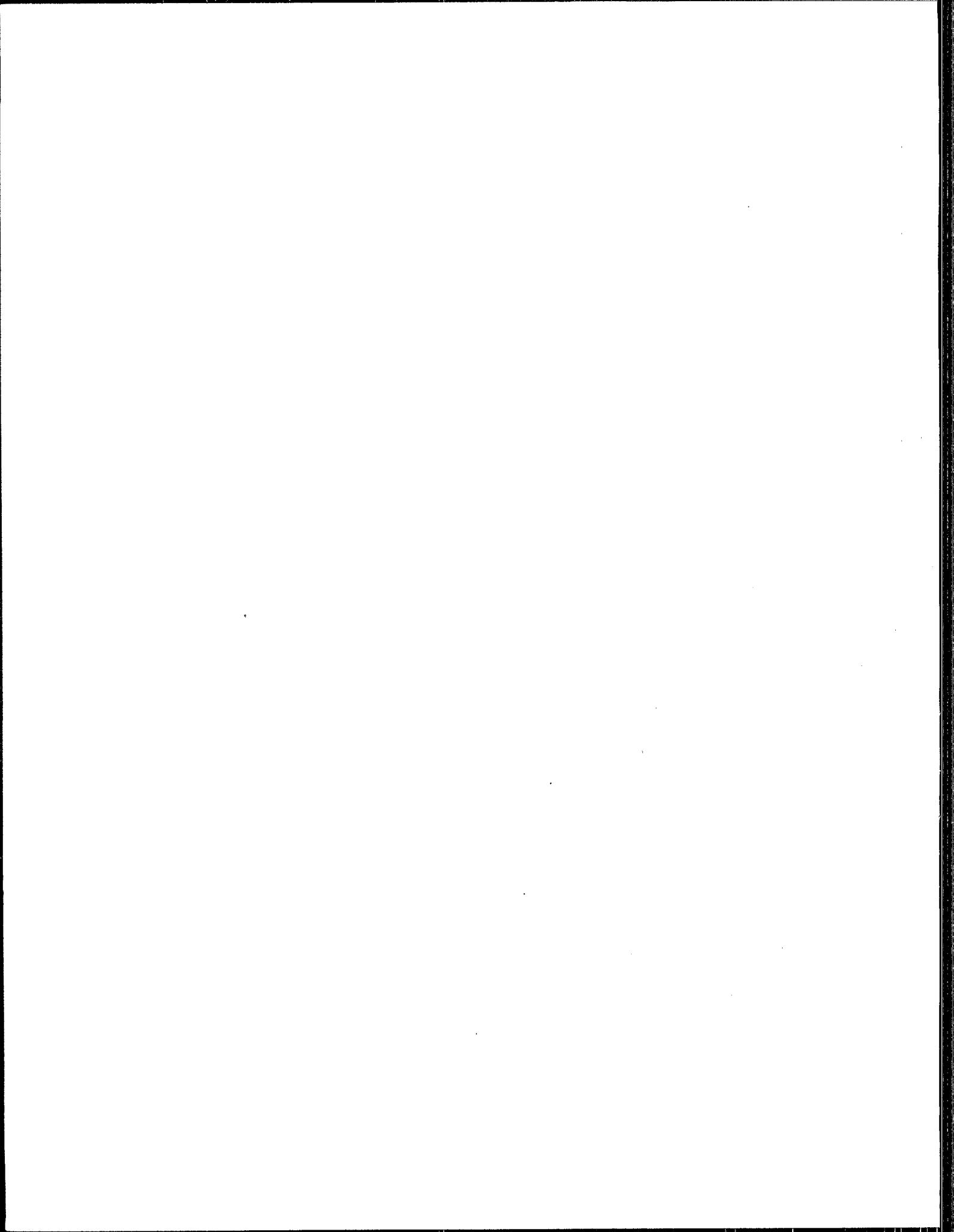


- Method 3050 for digestion. In Table II-1 the preferred method is 3050 which is applicable to sludges, sediments, and soil samples. However, if the sample is more aqueous in nature, Methods 3010 or 3020 are suggested in EPA (1989b).
- Analysis by direct aspiration atomic spectrometry or Method 6010 for inductively coupled plasma.
- Low concentration analysis by graphite furnace atomic spectrometry.
- Method 7471 for mercury cold vapor atomic absorption (CVAA).

#### 4. Quality Assurance and Quality Control (QA/QC) Procedures:

General quality assurance and control procedures are discussed in SW-846 and are covered in detail in EPA (1989c; 1990). The "POTW Sludge Sampling and Analysis Guidance Document" (EPA, 1989c) states that "sludge sampling and analysis programs for determining compliance with permit conditions should include a written QA Plan." A QA plan gives the data quality objectives of a sampling and analysis effort and details the sampling, analysis, quality control, and quality assurance procedures which will be employed to ensure that data quality is sufficient to support the regulatory decisions based upon the data. A general discussion on QA plan development can be found in EPA (1980). EPA (1990) contains specific information on development of QA plans for sampling and analysis of hazardous waste incinerators. Some general applicable topics concerning QA/QC are discussed in this section.

a. Sampling QA/QC: One primary objective in sampling for this rule is to obtain representative comparable sludge samples over a relatively long compliance period. The POTW sampling document (EPA, 1989c) and Chapters 1, 2, 3, and 9 of SW-846 are useful in designing a sampling strategy. From a QA/QC perspective, the sampling design should be formalized into a standard operating procedure (SOP). This SOP should justify the sta-



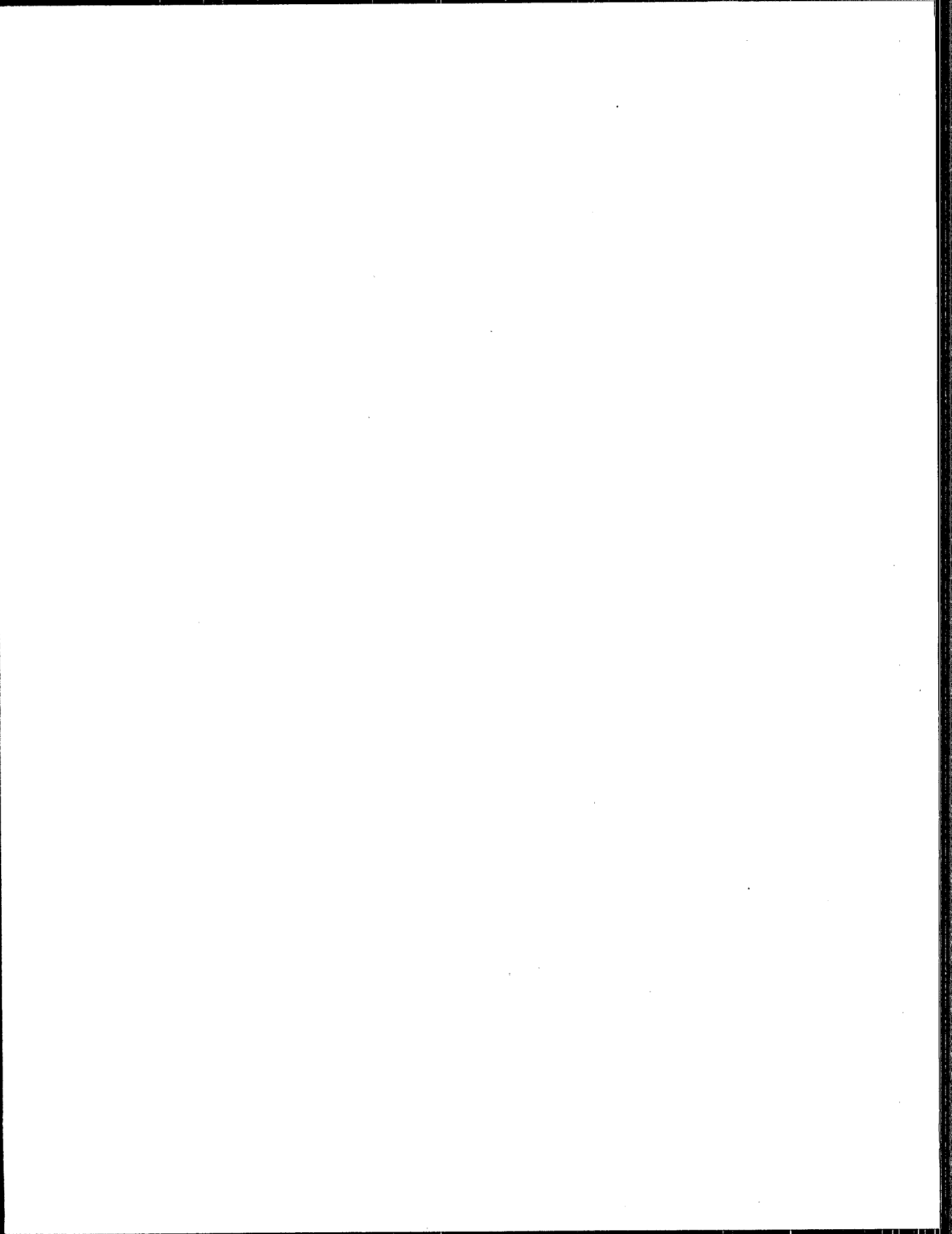
tistical design of the sampling strategy, specify the sampling frequency, give a detailed description of the sampling procedures, and delineate required sample documentation. Each time a sample is taken, the documentation of the sampling event needs to be sufficient to demonstrate compliance to the SOP.

b. Sample custody, handling, and holding times: General guidance on sample preservation, sample custody, sample storage containers, and holding times can be found in Section 2.5 of the POTW sampling document and Chapter 2 of SW-846. For sample custody considerations, all samples must be given unique identifiers which are readily traceable from the field sampling records, through the analysis records to the final reportable data.

Holding times, sample preservation methods, and sample containers must be specified for each analysis type and must follow the established guidance. Holding times are dependent upon the properties of the sample matrix and the analytes of interest. Holding times can vary from 28 days for mercury to 6 months for chromium. These preservation procedures should be delineated in the sampling SOP. There must be sufficient field and laboratory documentation to ensure that sample handling and holding time procedures were followed. All sample results should be reported with the dates of sample collection, sample preparation, and sample analysis. If the established procedures are not followed, the acceptance of analytical data must be justified in terms of the end use of the information.

As an additional check on sample handling, field blanks should be collected on a regular basis. Field blanks should consist of a water rinse (free of metal analytes) of sampling equipment before the sample has been collected. This check will assure that the observed sample concentration was higher than any possible contamination from sample handling.

c. Analysis QA/QC: The methods of analysis of the sludge for metals should be designated during the planning stage and should also be written as an SOP to be a companion document to the sampling SOP. The analysis SOP should indicate the following:

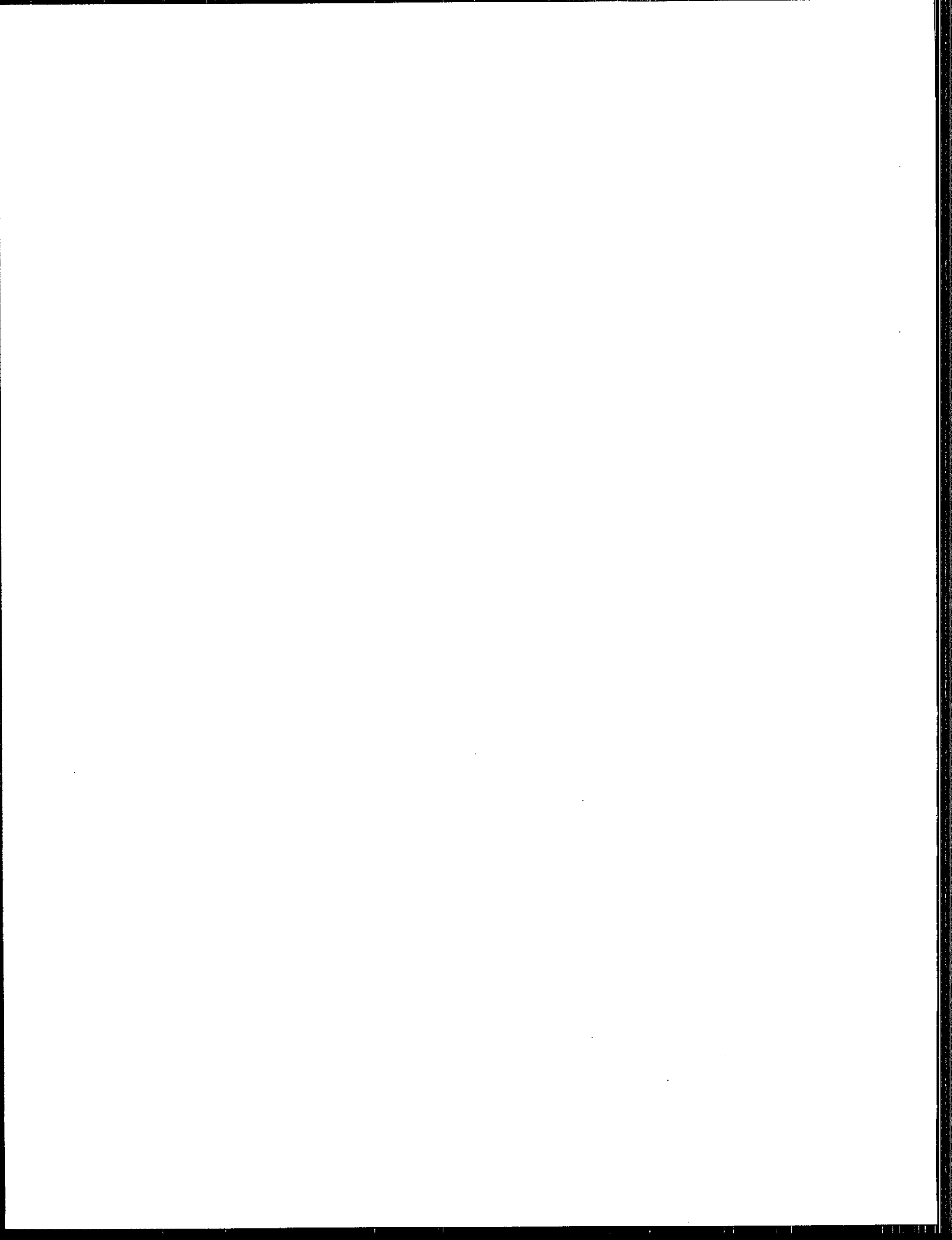




- The sampling SOP reference.
- The estimated analyte concentration of regulatory concern.
- The analytical methodology.
- The QC procedures for documenting the accuracy and precision of the analytical result.
- The reportable data and required records for complete documentation.

Each determination for metals analysis should be reported along with QA/QC information giving the precision and accuracy of the data. However, the specific analysis method and QC procedures for documenting the precision and accuracy of the determination can vary depending upon the laboratory conducting the analysis. For example, precision can be measured by analysis of the sludge sample and a sample split, while accuracy is measured by splitting the sample and fortifying the split sample. Some laboratories use a different method employing a control sample of known constant concentration, and multiple analyses of the control sample to provide the determination of both accuracy and precision. Control samples of metals in a sludge matrix can be commercially obtained.

All the analytical methods have QC procedures concerning calibration, accuracy, and precision. These should be supplemented with some additional QC. To establish the precision and accuracy of metals analyses, analysis of duplicate and analyte-fortified sludge samples is recommended. In the beginning of the monitoring program, a small study is recommended to demonstrate acceptable precision and accuracy for the analysis of the sludge samples. Three sludge samples are each split into three portions. Two portions are prepared and analyzed to provide precision data as percent range. The third portion is fortified with the analyte of interest at two times the level of regulatory concern and then prepared and analyzed like the other two split samples. Accuracy is measured as the recovery of the



fortified analyte compared to the average analyte level found in the two samples for precision analysis. This precision and accuracy determination should be done with a single sample for every 20 field samples or once per year, whichever is greater. The accuracy and precision should meet the statistical criteria of the sampling and analysis design presented in the QA plan.

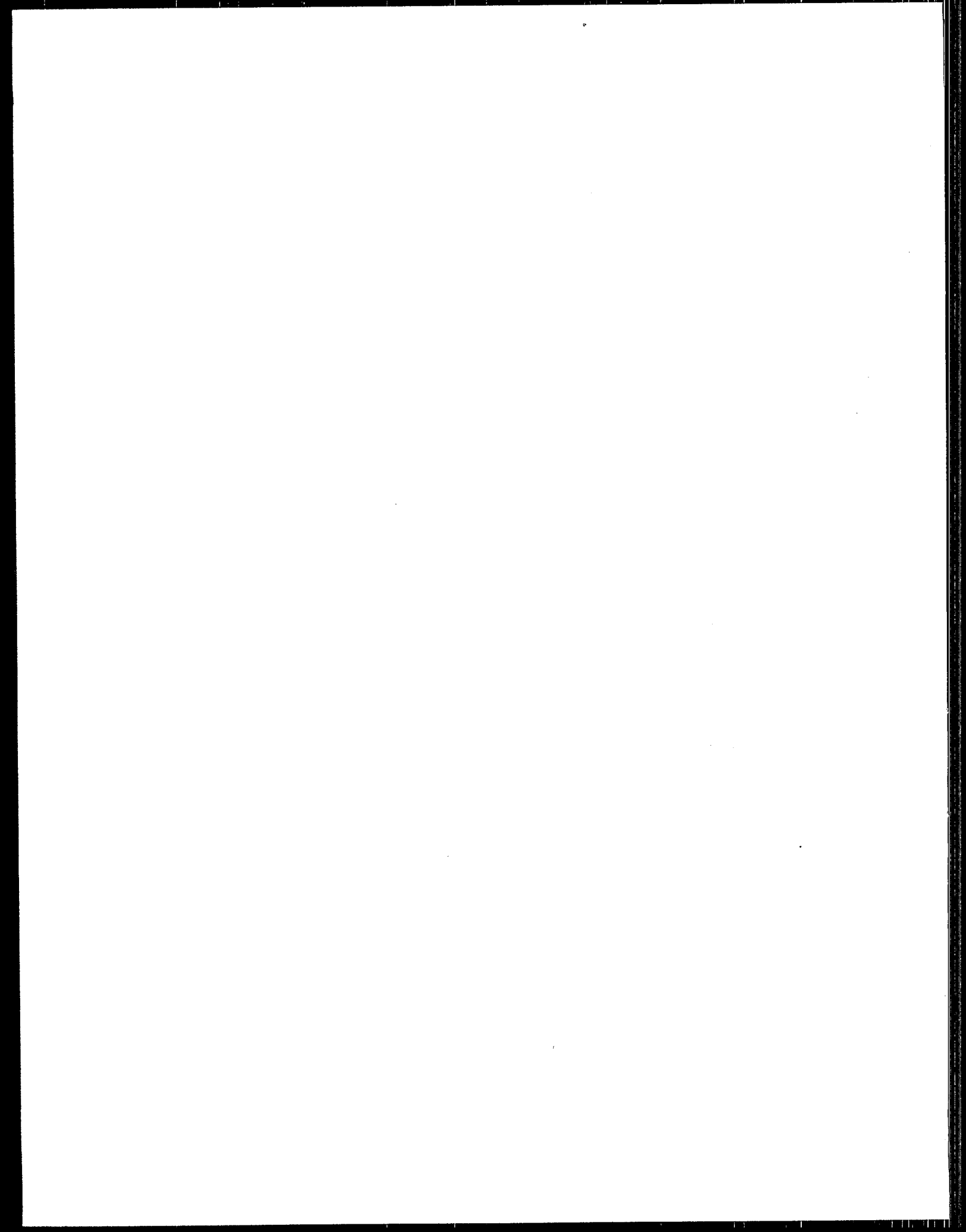
#### B. MONITORING OF KEY OPERATING PARAMETERS

Key operating parameters for sludge incinerators are monitored continuously to indicate that adequate combustion conditions are being maintained in the incinerator and to minimize toxic metals emissions. Key parameters specifically identified in the proposed rules to be monitored continuously include:

- Sludge feed rate.
- Temperature.
- Oxygen.
- Total hydrocarbons.
- Selected air pollution control device parameters.

Maximum or minimum values will be established for each of these monitored parameters. Limits are established for maximum sludge feed rate based upon formulas provided in the proposed rule. Sludge feed rate limitations are based upon the risk associated with the total sewage sludge feed rates for all sewage sludge incinerators located at each treatment facility.

Limits for maximum combustion temperature in a sewage sludge incinerator and maximum oxygen content for exit gas from incinerators will be based upon the results of performance testing. Limitations for selected



parameters for the air pollution control system will also be specified in a permit to indicate appropriate performance of the emission control devices. These limits will be based upon monitored information collected during performance tests.

The following pages briefly discuss the monitoring of each of the identified parameters.

1. Sludge Feed Rate:

Although the sludge feed rate to a sewage sludge incinerator can be monitored by a variety of flow devices, conveyor weighing systems and volumetric methods appear to be the most common methods used.

Conveyor weighing systems include belt weighers and weigh belts/augers. All conveyor weighing systems are fairly similar in operation, mainly differing because of placement locations of the weighing device. In general, the accuracy of these systems is around  $\pm 2\%$ . Sludges can be monitored with the systems, provided that wet material does not drain off the conveyor belt. Screw augers, however, may be used in such cases to replace the conventional conveyor belt. A summary of details on weight belt/auger systems is provided in Table II-2.

Volumetric methods include calibrated augers and pumps, rotary feeders, and belt conveyors. These systems are not generally available precalibrated but must be calibrated by the user for each particular feed material. The accuracy of the method depends upon steady operation at a given speed and assumes appropriate feeders are used to ensure the cavities are always filled to capacity. Most of these methods can provide some kind of tachometer signal to indicate speed, which must be related to feed rate by performing calibration tests. A summary of details about calibrated screw feeders used in sewage sludge applications is provided in Table II-2.

Each selected feed rate device must have an accuracy of at least  $\pm 5\%$  over its operating range. The device must be designed and installed to facilitate periodic recalibration of the device over its operating range (i.e., a zero adjustment and an adjustment near the maximum flow rate).



TABLE II-2

SUMMARY DETAILS ON TWO COMMON SLUDGE FEED RATE MEASUREMENT DEVICES

Weigh Belts or Augers

Operation/implementation: This is a combination belt scale and conveyor system. A prefeeding unit (typically an auger screw) feeds material onto a conveyor belt, which is mounted on a weight sensor (i.e., load cells). As the weight of material is sensed, adjustments to the screw speed are made by a microprocessor/controller, enabling a constant mass feed rate to be achieved. Similar systems are available which use an auger conveying system.

Usage: All types of solids, granules, and powders. Uses include sewage sludge and shredded metal.

Operating range: Capacity typically is 60 lb/hr to 48,000 lb/hr (based upon average density of 40 lb/ft<sup>3</sup> on a dry material basis).

Output: Typically mass flow rate and totalization.

Measurement frequency: Continuous, with signal averaged at 1-min intervals.

Calibration: Weigh system is counterbalanced and includes electronic adjustments for any on-site dampening necessary. Load cells may be calibrated by vendor.

Accuracy:  $\pm 1\%$  based upon 1-min sampling cycles.

Limitations: Due to effects of momentum, shifting weights, etc., feeds of widely varying density will affect accuracy somewhat, perhaps to  $\pm 3\%$ . Overload of weigh belt may cause poorer performance as well. May not give direct indication of weight charged to incinerator. (The material may "roll" along the conveyor, so that its velocity lags behind that of the conveyor.)

Notes: Similar operations can be installed with feed systems other than conveying belts. For example, a screw auger can be mounted upon the weight sensors, thereby making a weigh auger system.

(continued)

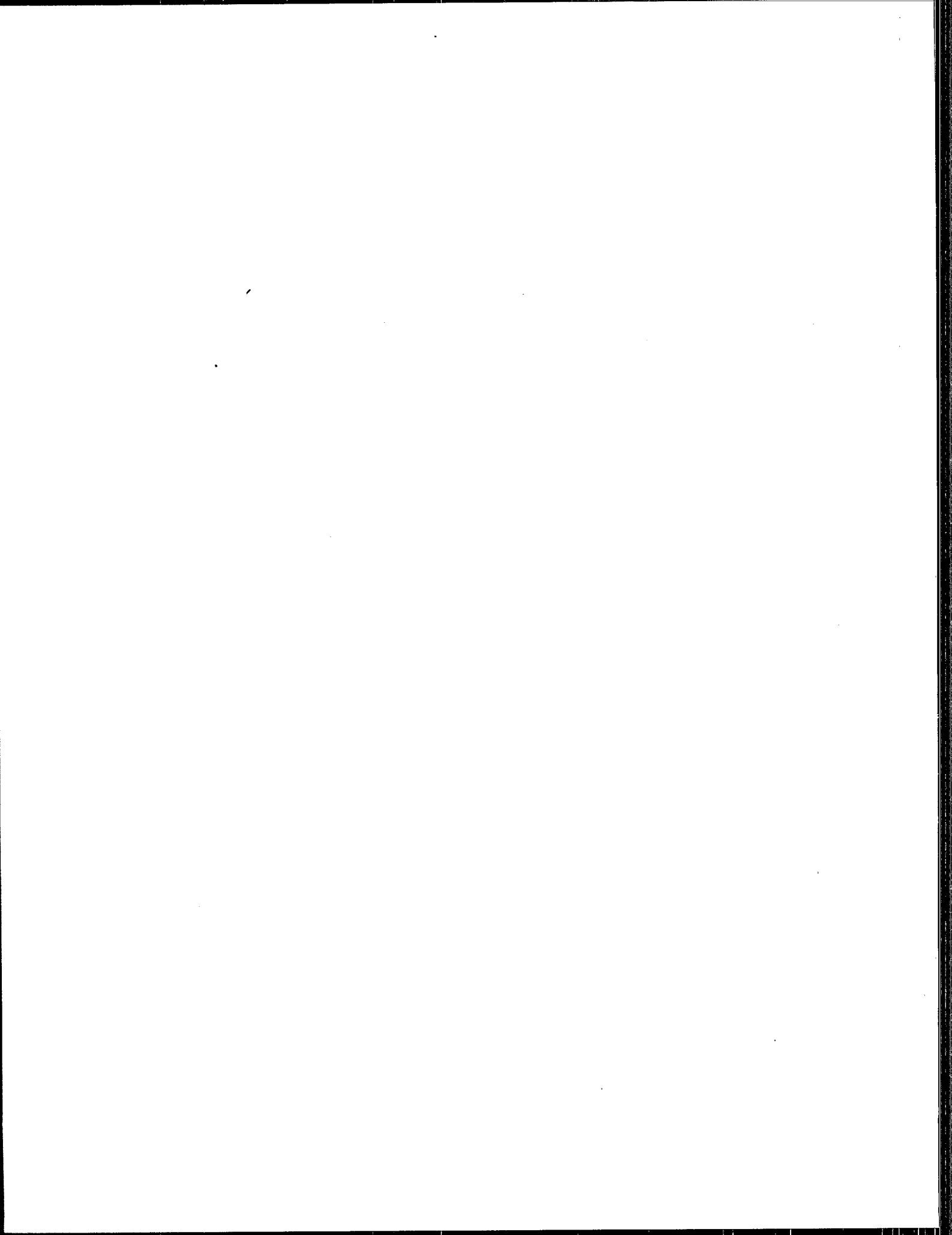




TABLE II-2 (CONCLUDED)

Calibrated Screw Feeders

Operation/implementation: A vibrating (to maintain constant flow) hopper filled with process material empties into a screw auger which has been calibrated by the vendor or user to give a volumetric feed rate. Auger speed can be varied, allowing for a broad range of volumetric feed rates, dependent upon the size of the auger screw.

Usage: Used for dry materials of fairly consistent density including powders and granules, solvent-laden filter cakes at an industrial facility, sewage sludge, and contaminated soil.

Operating ranges: 0.04 ft<sup>3</sup>/hr maximum up to 600 ft<sup>3</sup>/hr maximum depending upon size of the auger screw and rotational speed. For a dry material basis of 40 lb/ft<sup>3</sup>, this amounts to 1.5 lb/hr maximum up to 24,000 lb/hr maximum.

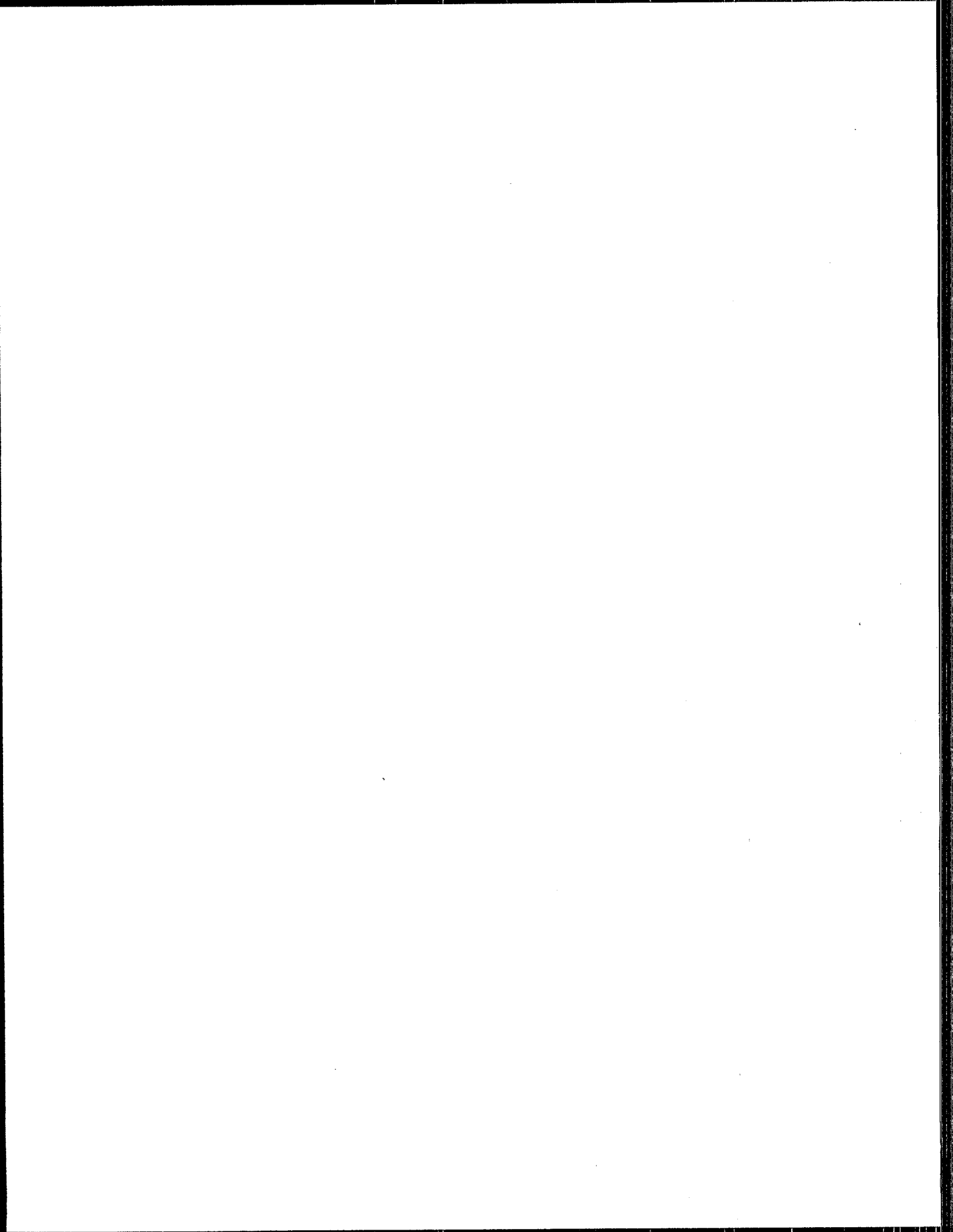
Output: Tachometer reading indicates rpm which correlates with volumetric feed rate.

Measurement frequency: Continuous.

Calibration: Tachometer of screw calibrated by rpm, which is correlated to volume of materials tested.

Accuracy:  $\pm 2\%$  of set rate.

Limitations: Due to volumetric calibration of feed system, use with materials of varying density may not provide suitable mass feed rate.

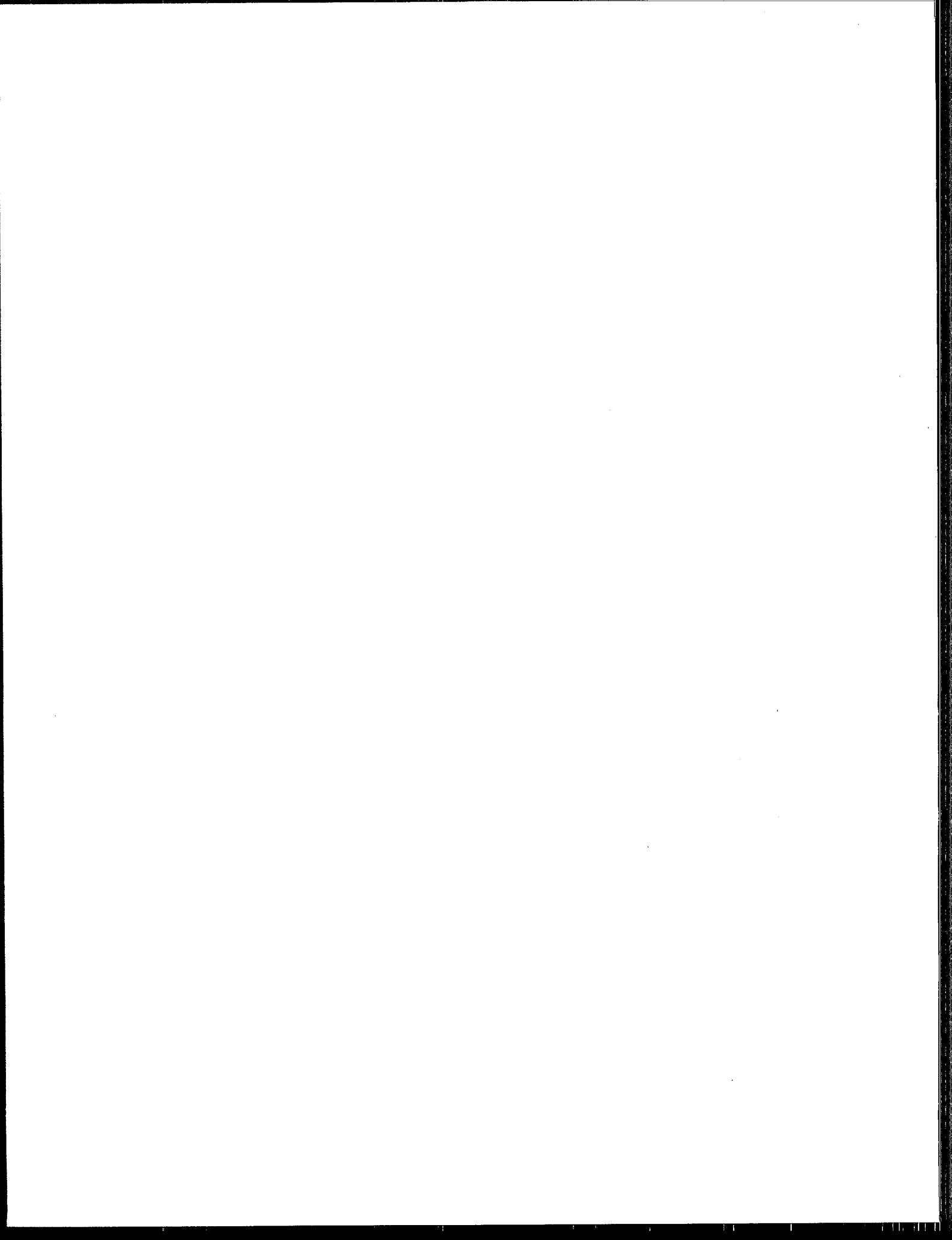


## 2. Temperature:

Temperatures within a sewage sludge incinerator are typically monitored by thermocouples located at various points within the system. Minimum required locations for thermocouples are specified in the proposed rules for multiple hearth, fluidized bed, electric, and rotary kiln incinerators. Maximum temperatures in the combustion zone (or outlet duct) are monitored to minimize the emission of toxic metals from the incinerator.

The thermocouples are always enclosed in a thermowell to protect the small thermocouple wires and the critical thermocouple "hot" junction from direct exposure to the combustion gases and entrained dust particles. Thermocouples are usually located near the exit of the combustion chamber to provide a representative temperature reading away from the flame zone, which can otherwise cause erratic temperature readings as well as damage to the thermocouple. Thermowells may extend several inches past the inner wall of the refractory into the gas stream, or may extend only to the depth of the refractory. Thermowells that extend past the refractory provide a more accurate measure of the gas temperature and respond more quickly to temperature changes; however, this type also may be subject to dust and slag buildup, which can slow response to temperature changes. Thermocouples may also be located upstream of the air pollution control system to provide a warning or control mechanism for high temperature excursions that could damage control equipment.

Thermocouples are available in a variety of types, with each type constructed of specific metals or alloys. The temperature ranges and reported accuracy vary by type. The environment the thermocouple is suited for also varies.



A summary of thermocouple types and limitations is given below.

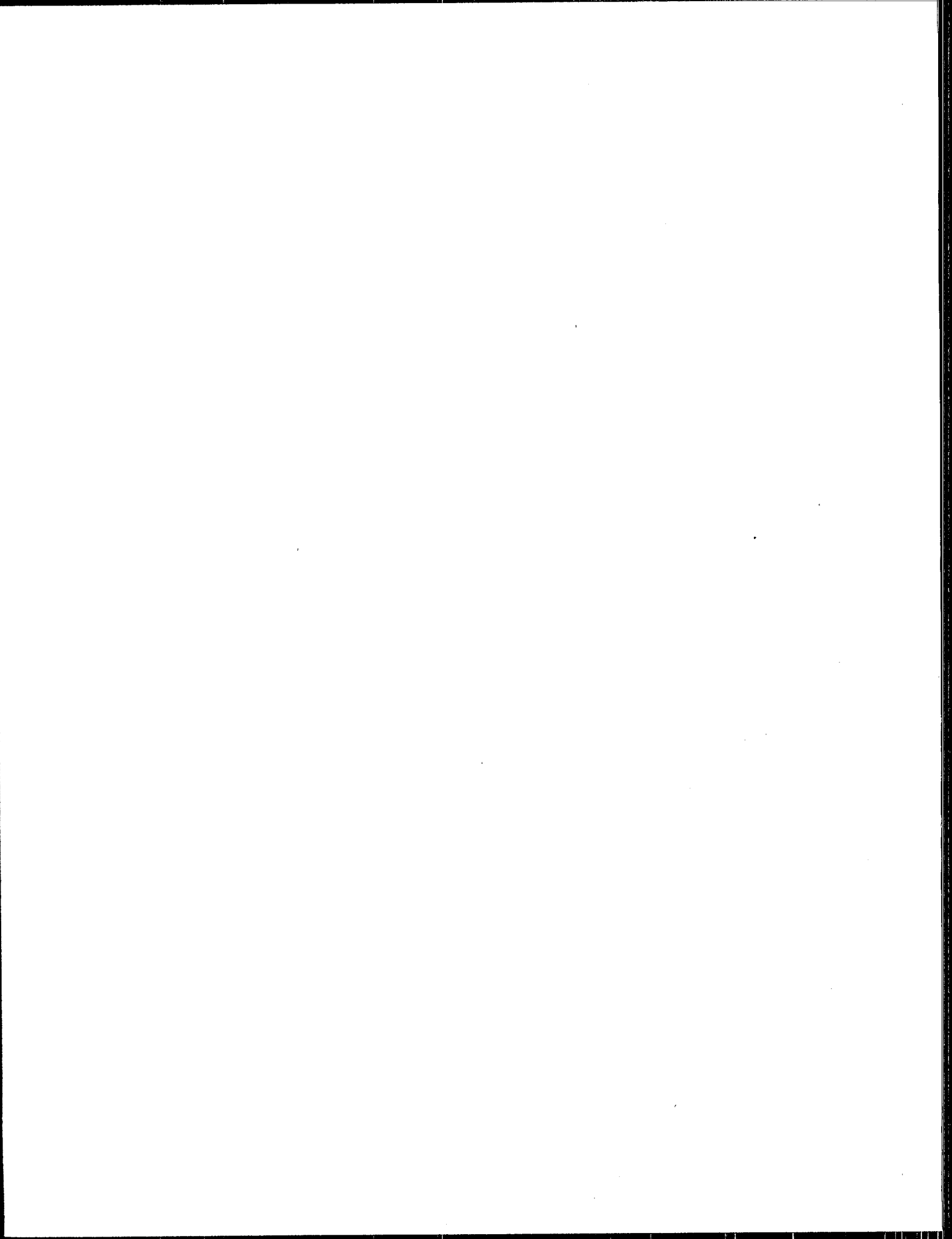
Type	Materials	Upper Temp. (°F)	Thermocouple Accuracy (±%)	Environment
J	Iron/constantan	1400	0.75	Reducing, vacuum, or inert
E	Chromel/constantan	1650	0.50	Oxidizing or inert
K	Chromel/alumel	2300	0.75	Oxidizing or inert
S	Pt 10% rhodium/pure Pt	2650	0.25	Oxidizing or inert (no metal tubes)
R	Pt 13% rhodium/pure Pt	2650	0.25	Oxidizing or inert (no metal tubes)
B	Pt 30% rhodium/pure Pt 6% rhodium	3100	0.50	Oxidizing or inert (no metal tubes)

Note: Accuracies do not consider environmental effects or location.

Source: *Complete Temperature Measurement Handbook and Encyclopedia*, Omega Engineering Inc., 1986.

Replacement thermocouples must always be the same type as the original because the receiver to which a thermocouple is connected is designed to receive the signal from a specific type of thermocouple. Thermocouples generate a small millivolt signal that increases with increasing temperature, but the amount of voltage for a given temperature is different for each type of thermocouple. It is important to realize that thermocouples operate on the basis of a junction between two different metals that generates only a small millivolt signal. Consequently, any wiring connections from the thermocouple to the receiver or any interfering electrical signals can affect the resulting temperature reading. This sensitivity necessitates the special shielding of the wire in electrical conduit.

Although thermocouples typically are very reliable, they can fail or give erroneous readings. For example, a thermocouple junction or wire may break after long exposure to high temperatures or repetitive cycling. However, a thermocouple can give erroneous readings for reasons that are not as obvious as a broken junction or wire. For example, if mechanical vibration abrades the insulation and one of the thermocouple wires comes into contact with the metal wall of the thermowell or other grounded metal surface, an



erroneous temperature reading will likely result. As noted earlier, faulty thermocouple readings may also be the result of external conditions; for example, excessive dust buildups around a thermowell can insulate it from the gas stream and result in erroneously low temperature readings. To have the ability to compare readings to identify a faulty thermocouple, dual thermocouples are often used at nearby locations in the incinerator chamber. Also, the second thermocouple enables continued monitoring of temperatures while the faulty thermocouple is being checked or replaced.

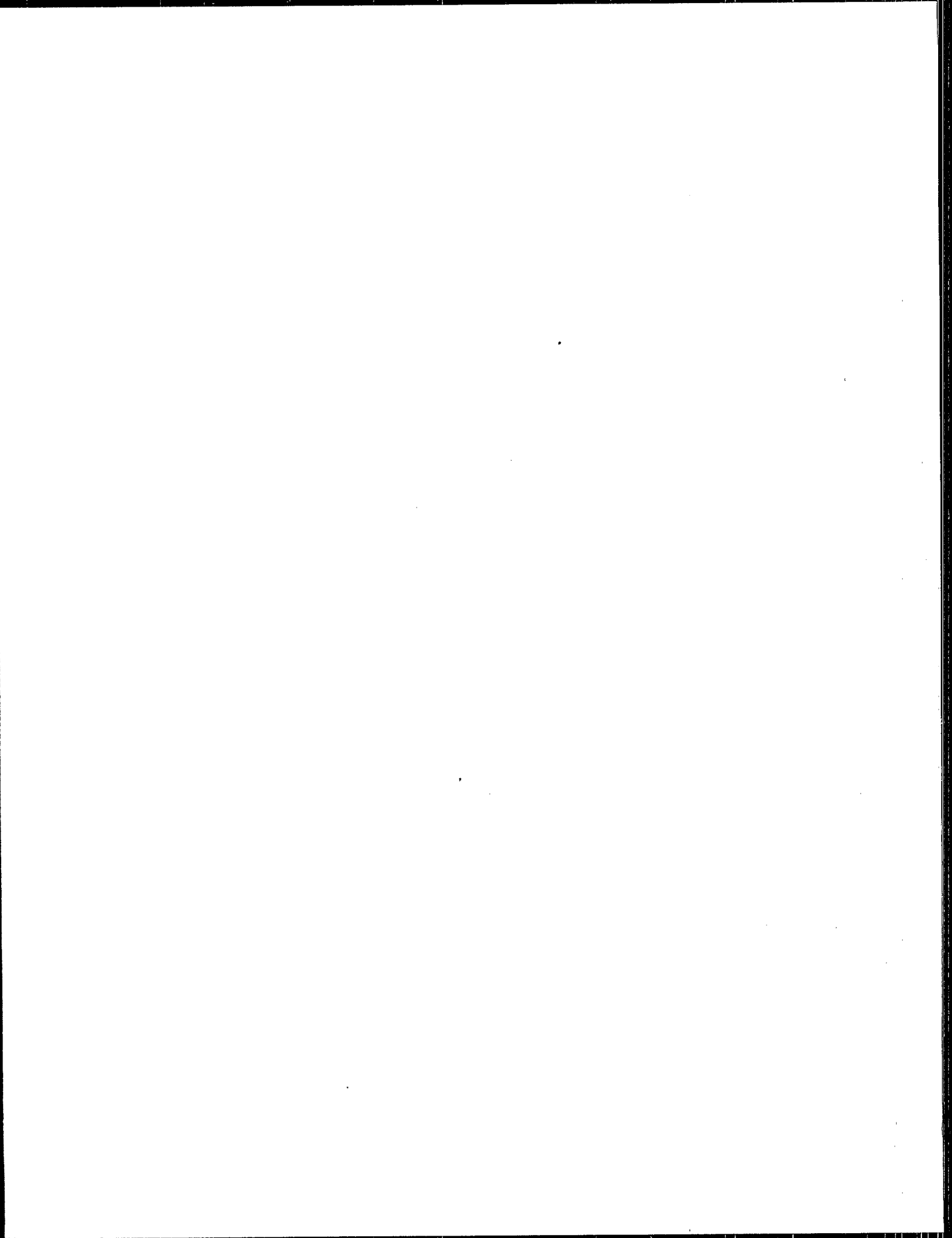
Periodic replacement of thermocouples, and checking the physical integrity of the thermowell and any outer dust buildup, is probably the best maintenance procedure. Because it is not practical to perform a high temperature calibration of the thermocouple, only periodic replacement ensures that a properly operating thermocouple is in place. The receiver should be checked periodically using calibrated equipment that produces a known millivolt signal equivalent to a specific temperature reading for a particular type of thermocouple. The generated signal can be applied to the thermocouple leads to check that the receiver's output produces the correct "temperature" reading.

### 3. Oxygen:

Oxygen in the exit gas is monitored continuously in a sewage sludge incinerator as an indirect indicator of gas velocity in the incinerator.

Oxygen monitors may be of two types: in situ or extractive. In situ merely means that the analyzer's sensor is mounted in direct contact with the gas stream. In an extractive system, the gas sample is continuously withdrawn (extracted) from the gas stream and directed to the analyzer which may be located several feet or several hundred feet away.

Extractive analyzers include a conditioning system to remove dust and moisture from the gas sample; thus, the oxygen concentration measurement is on a dry basis. In situ analyzers, on the other hand, do not include a conditioning system, and the oxygen concentration measurement is on a "wet basis." For the same gas stream, the oxygen measurement obtained with an in situ analyzer will be slightly lower than that obtained with an extractive





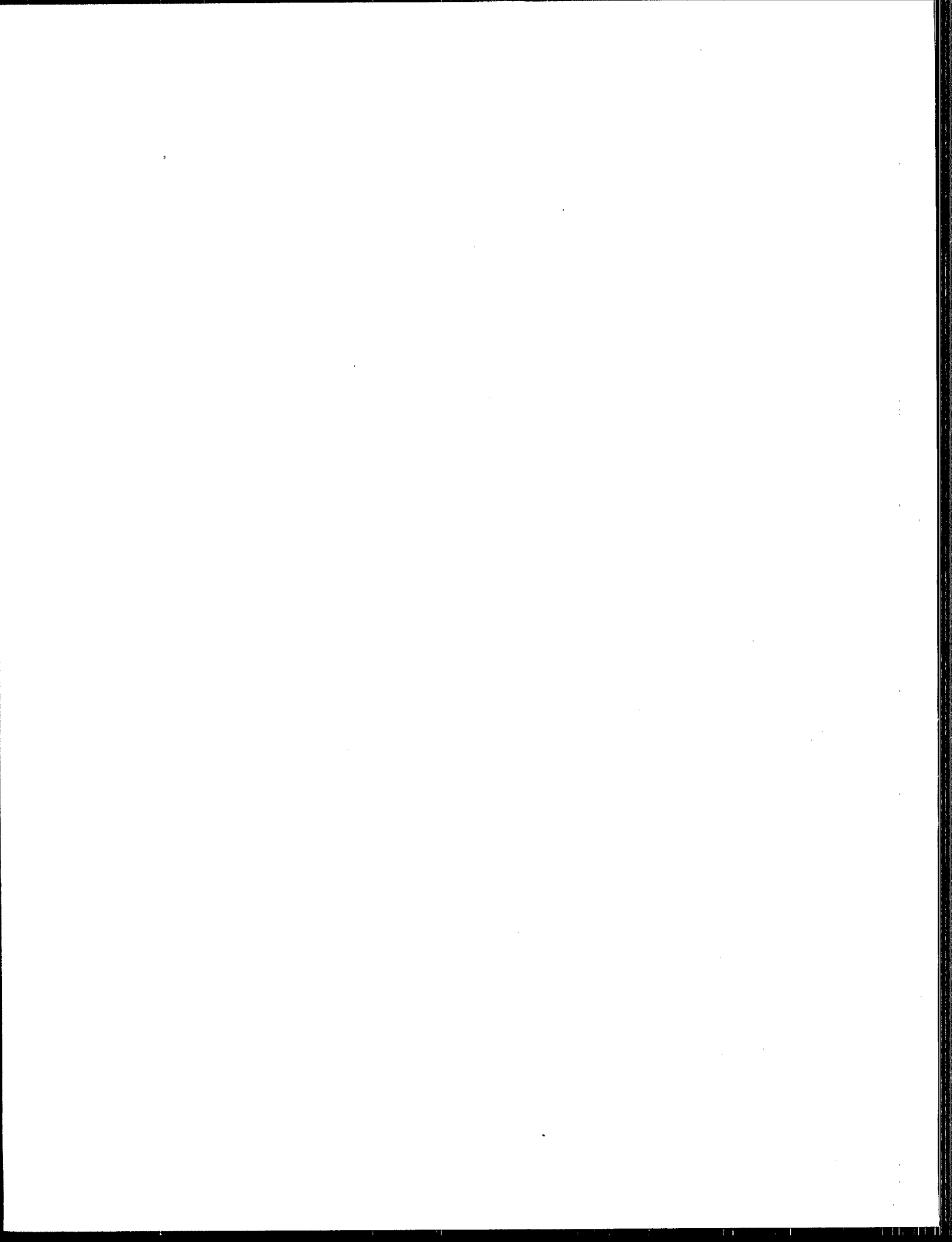
analyzer. For example, a typical combustion gas stream that contains 10% water vapor will yield a reading of 8% oxygen using an in situ analyzer and a reading of 10% oxygen using an extractive analyzer. The oxygen values for sewage sludge incinerators must be reported on a dry basis.

Oxygen analyzers are capable of good accuracy ( $\pm 1\%$  of full scale) as long as the actual gas to be sampled reaches the analyzer (no pluggage or in-leakage of air), the conditioning system (if one is present) is operating properly, and the instrument is calibrated. Electrochemical in situ monitors have rapid response time (i.e., seconds). The response times for polarographic and paramagnetic extractive analyzers are slower (several seconds to a minute). Extractive systems inherently involve longer response times, usually on the order of 1 to 2 min, depending on the sampling rate and the volume of the sampling line and conditioning system.

Problems with oxygen analyzer systems may be difficult to discern since they commonly are associated with slowly developing pluggage in the system, or small air in-leaks, etc. The extractive systems should be checked daily by the operators, and maintained and calibrated on a weekly basis by the incinerator instrument personnel.

a. In situ oxygen analyzers: In situ analyzers provide rapid response to changes in the oxygen content of the gas because the sensor is in direct contact with the gas stream. In most cases, the sensing element is enclosed in a sintered stainless steel tube, which allows the gas to permeate through the tube but prevents particles in the gas stream from entering. Most in situ oxygen analyzers are equipped with connections so that zero gas (nitrogen) or calibration gas (air) can be flushed through the permeable tube in contact with the sensing element. Flushing provides a means of zeroing and spanning the analyzer, and also creates reverse flow of gas through the permeable tube that helps to remove dust particles that eventually will clog the tube and slow the detector's response time. Even so, the tube periodically must be removed for cleaning or replaced if warranted.

Most in situ oxygen analyzers are of the electrochemical type, sometimes referred to as fuel-cell analyzers. Operation of these analyzers is

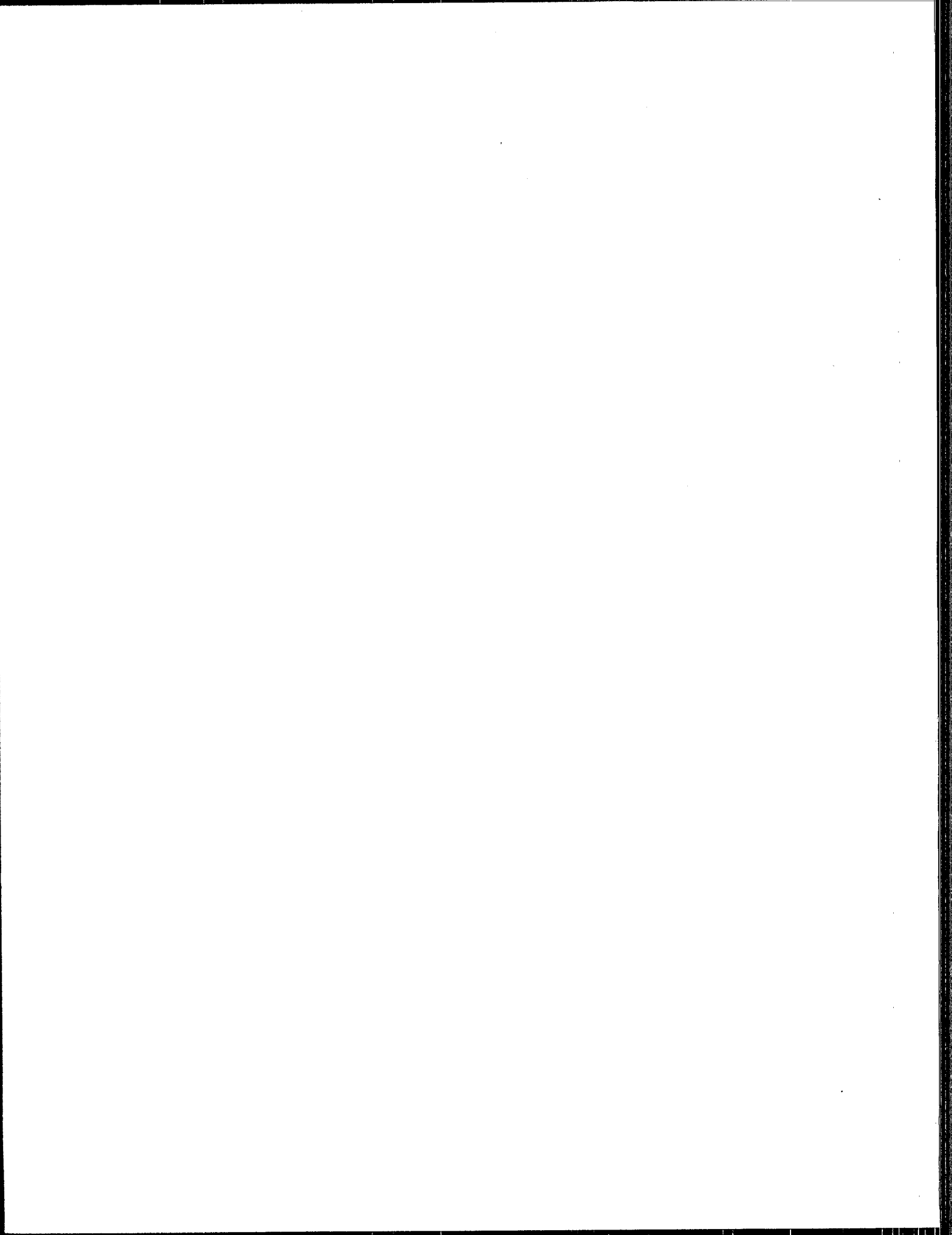


based upon an electron flow created by reaction of oxygen with a solid zirconium oxide electrolyte. Consequently, manufacturers recommend that the sensing element be replaced after several months of service.

b. Extractive oxygen analyzers: Extractive analyzers always involve a "conditioning system" for removal of water, dust, and sometimes other constituents that would interfere with operation of the analyzer. An example extractive system is illustrated in Figure II-1. The moisture knockout for removal of water vapor and the normal connections for zeroing and calibrating the analyzer are shown.

The integrity of the sample line and the conditioning system is crucial to obtaining a representative sample and accurate results. Any in-leakage of air can drastically distort the reading. The extractive system requires a pump to draw the sample gas continuously through the sample line, conditioning system, and analyzer. Most systems include a small rotameter (flowmeter) which shows that sample gas is flowing through the system. This flowmeter is always one of the first items that should be checked if any problem is suspected because loss of flow will occur if the pump fails or the system is plugged. However, even if the flow rate is correct, the measured gas concentration will not be correct if there is any problem with the leakage of air into the gas sample.

Two types of extractive oxygen analyzers, paramagnetic and polarographic analyzers, are available in addition to the electrocatalytic type described previously for in situ analyzers. Paramagnetic analyzers measure the oxygen concentration as the strength of a magnetic field in which oxygen molecules are present. Oxygen molecules are somewhat unique in displaying a permanent magnetic moment (paramagnetism), allowing oxygen concentration to be differentiated from the stack gas sample. Calibration is performed by monitoring an inert gas such as nitrogen (zero) and a gas of known oxygen concentration (span). A potential problem with this type of analyzer is its susceptibility to paramagnetic molecules other than oxygen. Nitrogen oxide and nitrogen dioxide in particular display a high degree of paramagnetism (about one-half that of oxygen), but their concentration is usually low compared to that of oxygen.



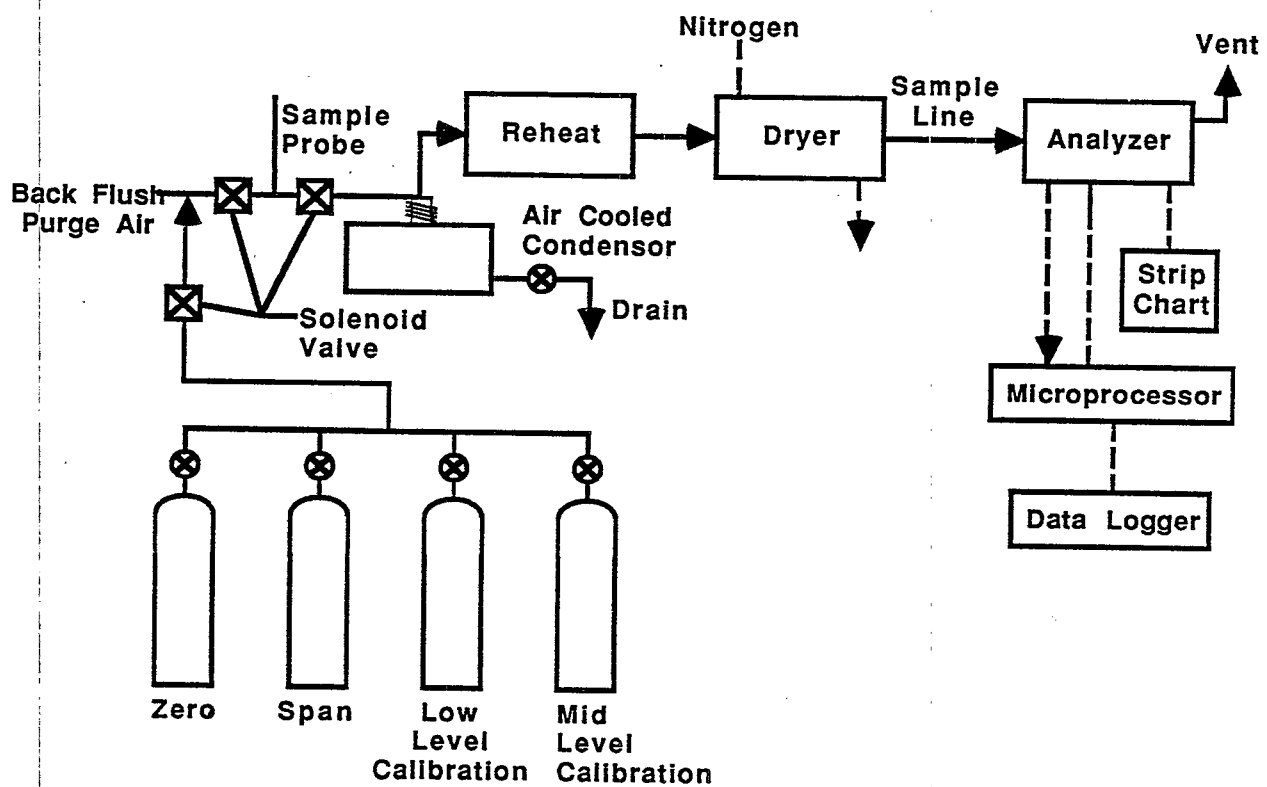
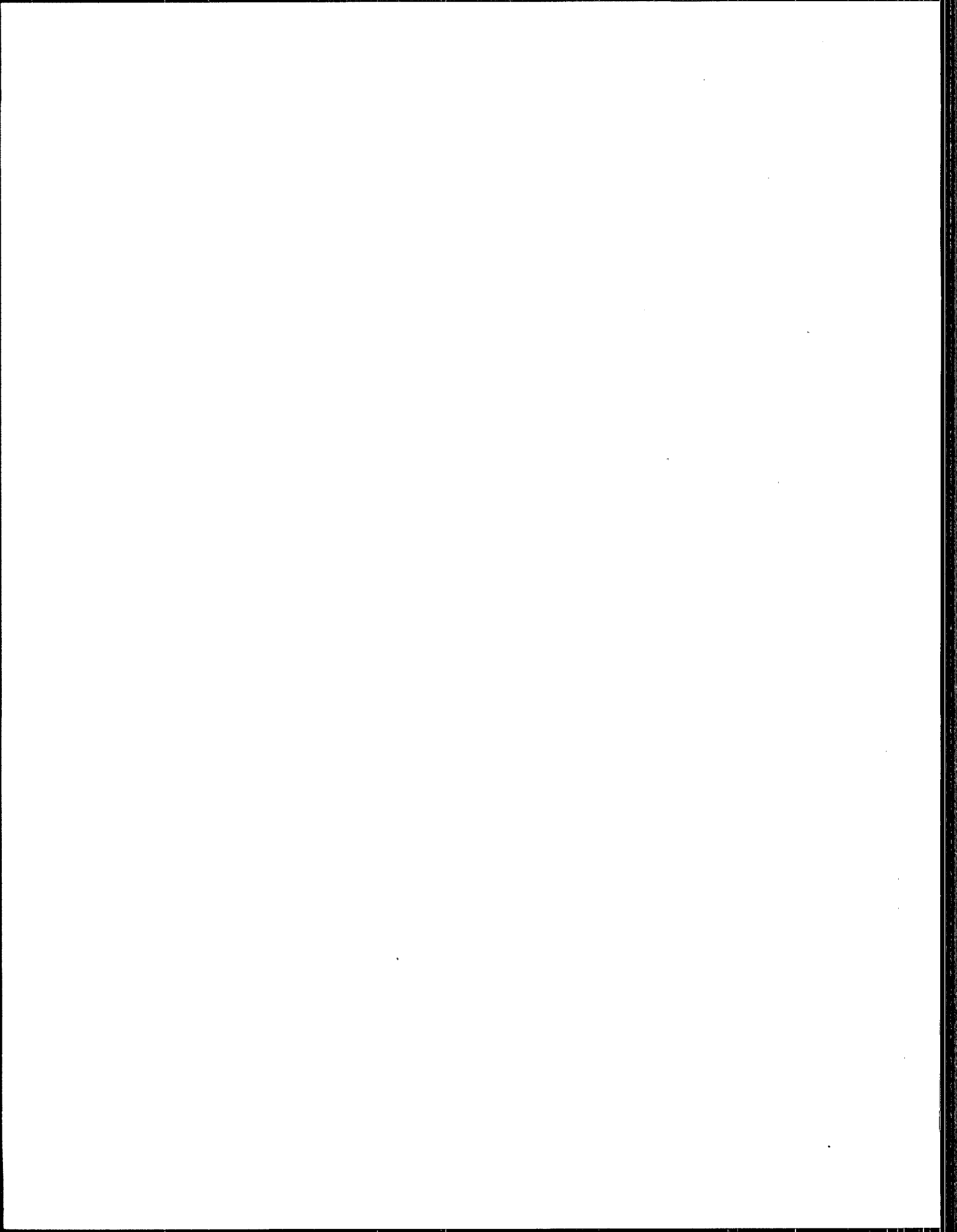


Figure II-1. Schematic of an extractive monitoring system.



Polarographic analyzers monitor oxygen concentration by allowing oxygen to pass through a selective, semipermeable membrane and react at an electrode in an oxidation-reduction reaction. Measuring the current produced by the reaction indicates the oxygen concentration. Improper conditioning of the sample gas is a potential problem with these analyzers, since moisture and particles will hinder performance of the semipermeable membrane. Calibration is performed by zeroing with an oxygen-free gas (nitrogen) and spanning with a gas of known oxygen concentration (e.g., air). Furthermore, these monitors contain a liquid electrolyte that has a limited life span and must be replaced at regular intervals.

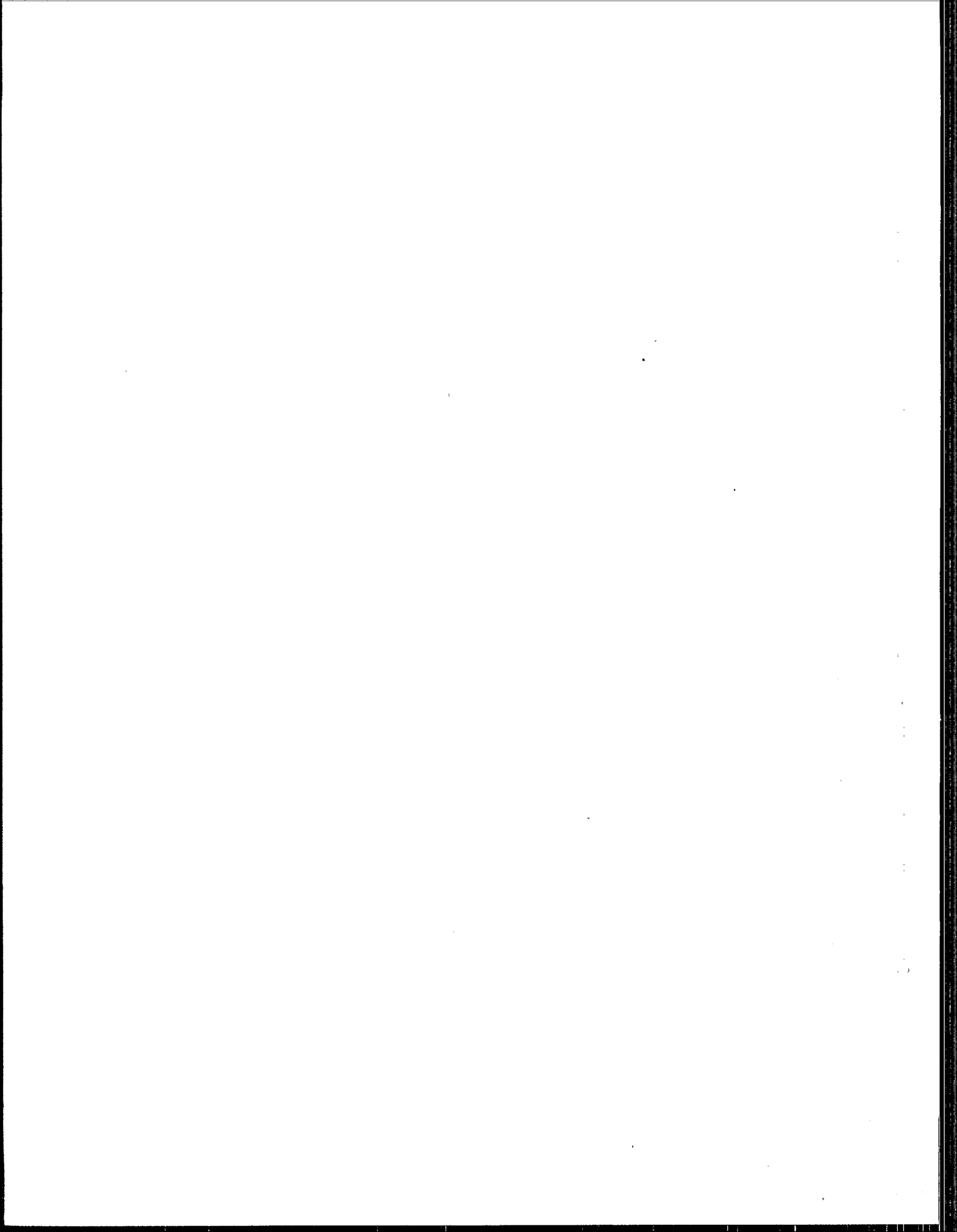
Additional background information on oxygen monitors is available in EPA (1979); additional guidance on the operation and calibration of oxygen monitors is provided in EPA (1989e).

#### 4. Total Hydrocarbon:

THC is continuously monitored in a sewage sludge incinerator as an indirect indicator of combustion efficiency for organic material in the sludge. The method measures the total hydrocarbons as a surrogate for the total gaseous organic concentration of the combustion gas stream. The concentration is expressed in terms of propane. A gas sample is extracted from the source through a heated sample line, if necessary, and a fiber filter to a flame ionization detector (FID). A standard method, Method 25A (40 CFR 60, Appendix A), is provided as Appendix B of this document. Another variation is presented in MRI (1989e) and is currently undergoing review at EPA.

The monitors equipped with FIDs essentially respond to unoxidized carbon. Monitoring efficiency remains relatively constant over a wide range of concentrations. However, water vapor may have an effect on response.

A wide variety of FID systems are commercially available for THC monitoring. A sample is usually extracted using a diaphragm pump. Prior to entering the FID, moisture may be removed by use of a condenser, and particulate may be removed by use of one or more filters. Calibration gas may be injected into the monitor immediately after the sample probe (i.e., before





filters and condensers) or immediately before the FID analyzer (i.e., after filters and condensers). A recent survey of manufacturers and facilities that use THC monitors indicated that the THC monitoring systems were operated continuously on hazardous waste incinerators with reliability (MRI, 1989).

#### 5. Air Pollution Control System:

Permits for sewage sludge incinerators will include permit limits and continuous monitoring requirements for selected parameters that indicate adequate performance of air pollution control (APC) devices. Such requirements will be developed on a case-by-case basis, depending on the APC device used and facility-specific issues.

Selected APC parameters are monitored continuously to indicate that the APC system is operated and maintained to meet all applicable requirements and to minimize toxic metal emissions. A list of performance indicator parameters for various APC technologies is presented in Table II-3 along with the common measuring devices for the respective parameters.

The performance indicator parameters include (a) APC technology-specific parameters and (b) universal APC parameters. Examples of APC technology-specific parameters include pressure drop and liquid flow for wet scrubbers, and secondary voltage and secondary current for wet electrostatic precipitators (ESPs). Because the performance of all APC devices is influenced by gas flow rate and gas temperature, these two parameters are considered to be universal APC parameters and are included for each APC technology.

#### 6. Other Parameters:

Other indicator parameters may be appropriate for continuous monitoring or permit limits for special cases or for facilities using technologies different from the types addressed in the proposed rules. Such requirements would be developed on a case-by-case basis.

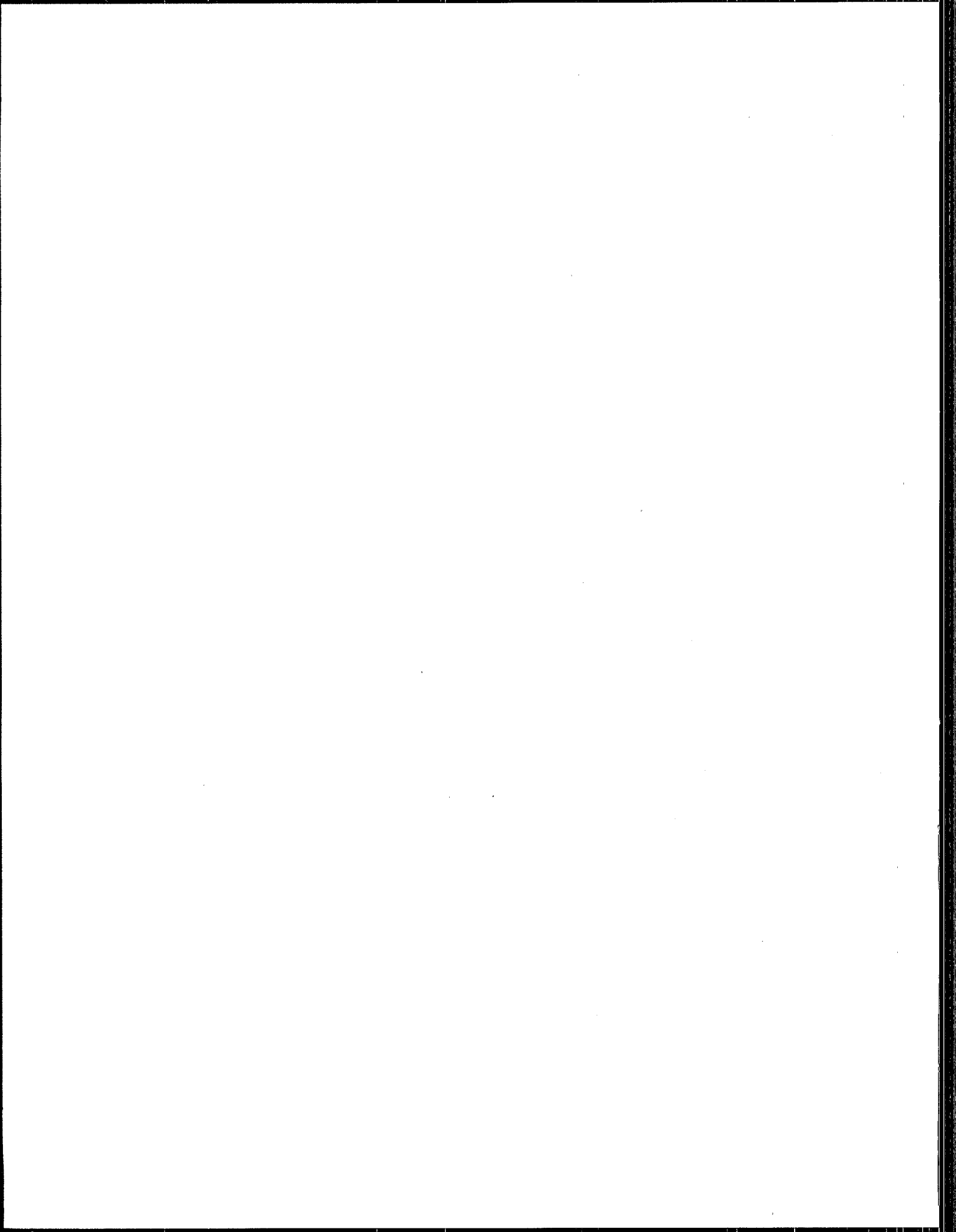


TABLE II-3  
PERFORMANCE INDICATOR PARAMETERS FOR  
AIR POLLUTION CONTROL DEVICES

<u>APC Device</u>	<u>Parameter</u>	<u>Example Measuring Devices</u>
Venturi scrubber	Pressure drop	Differential pressure ( $\Delta P$ ) gauge/transmitter
	Liquid flow rate	Orifice plate with $\Delta P$ gauge/transmitter
	Gas temperature (inlet and/or outlet)	Thermocouple/transmitter
	Gas flow rate	Annubar or induced fan (ID) parameters
Impingement scrubber	Pressure drop	$\Delta P$ gauge/transmitter
	Liquid flow rate	Orifice plate with $\Delta P$ gauge/transmitter
	Gas temperature (inlet and/or outlet)	Thermocouple/transmitter
	Gas flow rate	Annubar or ID fan parameters
Mist eliminator (types include a wet cyclone, vane demister, chevron demister, mesh pad, etc.)	Pressure drop	Differential pressure gauge/transmitter
	Liquid flow	Orifice plate with $\Delta P$ gauge/transmitter
Dry scrubber (spray dryer absorber)	Liquid/reagent flow rate to atomizer	Magnetic flowmeter
	pH of liquid/reagent to atomizer	pH meter/transmitter
	For rotary atomizer: Atomizer motor power	Wattmeter

(continued)

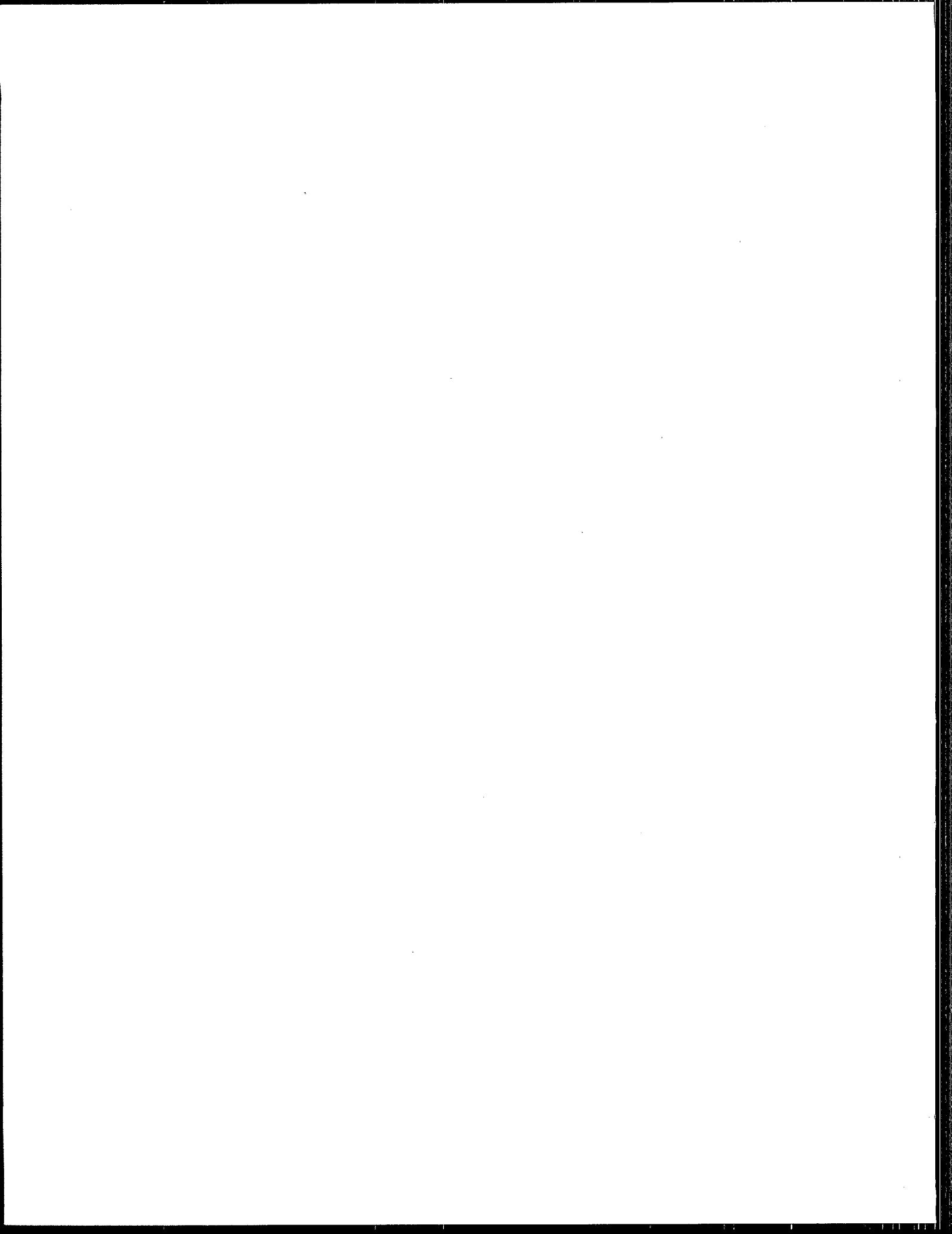
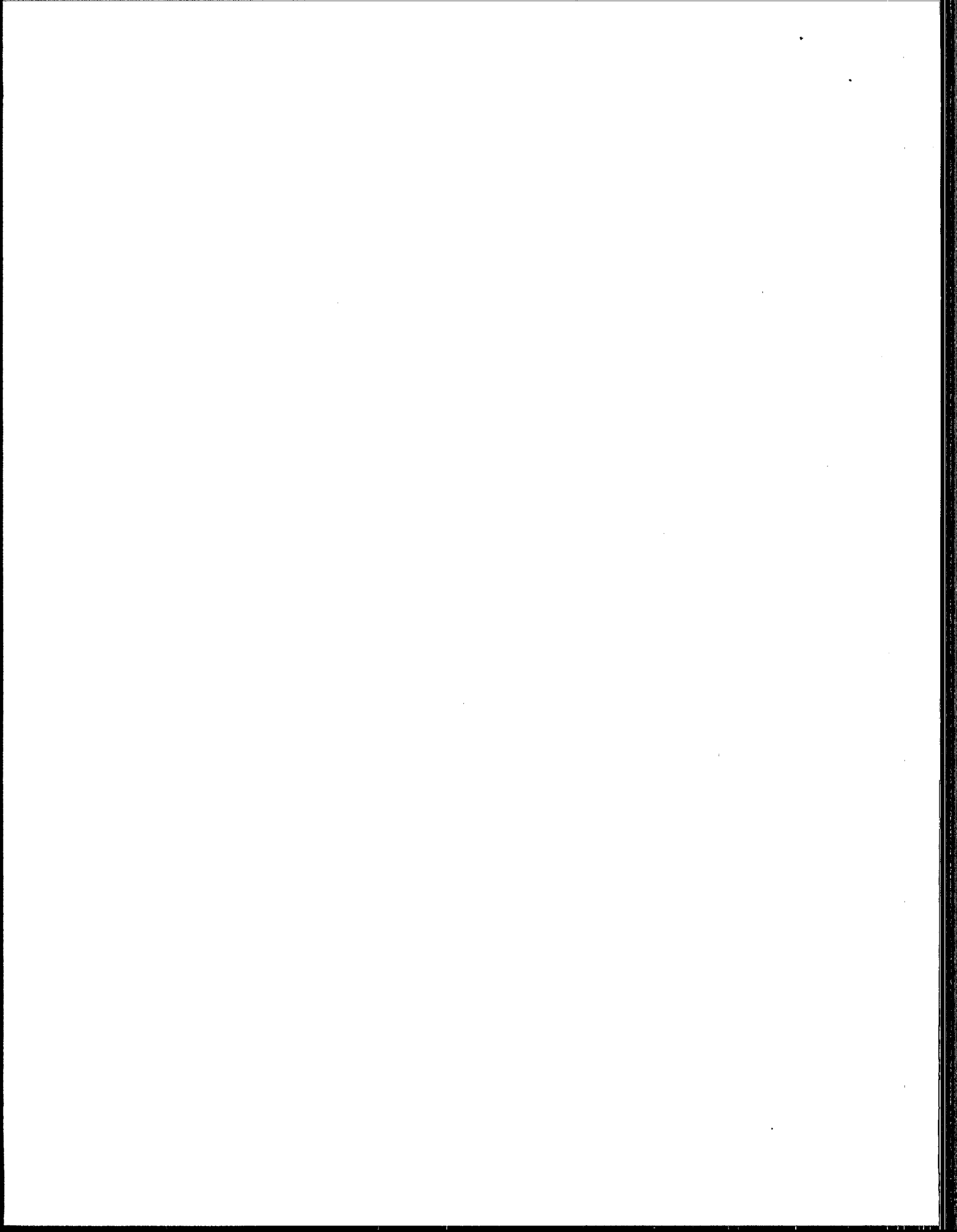


TABLE II-3 (CONCLUDED)

Fabric filter	For dual fluid flow: Compressed air pressure	Pressure gauge
	Compressed airflow rate	Orifice plate with $\Delta P$ gauge/transmitter
	Gas temperature (inlet and/or outlet)	Thermocouple/transmitter
	Pressure drop (for each compartment)	$\Delta P$ gauges/transmitters
	Broken bags	Proprietary monitors
	Opacity	Transmissometer
	Gas temperature (inlet and/or outlet)	Thermocouple(s)
Wet electrostatic precipitator (ESP)	Gas flow rate	Annubar or ID fan parameters
	Secondary voltage (for each transformer/rectifier)	Kilovolt meters/transmitter
	Secondary currents (for each transformer/rectifier)	Milliammeters/transmitter
	Liquid flow(s) (for separate liquid feeds)	Orifice plate(s) with $\Delta P$ gauge/transmitter
	Gas temperature (inlet and/or outlet)	Thermocouple(s)
	Gas flow rate	Annubar or ID fan parameters



## C. STACK GAS SAMPLING

This section describes testing activities used in determining facility-specific control efficiency values for toxic metals emissions. These efficiency values are used to calculate the maximum allowable concentration of toxic metals in the sludge feed and the maximum allowable sludge feed rate to the incinerator based upon the equations provided in the proposed rule. The test data will also be used to determine facility-specific limits for temperature, oxygen, and air pollution control conditions.

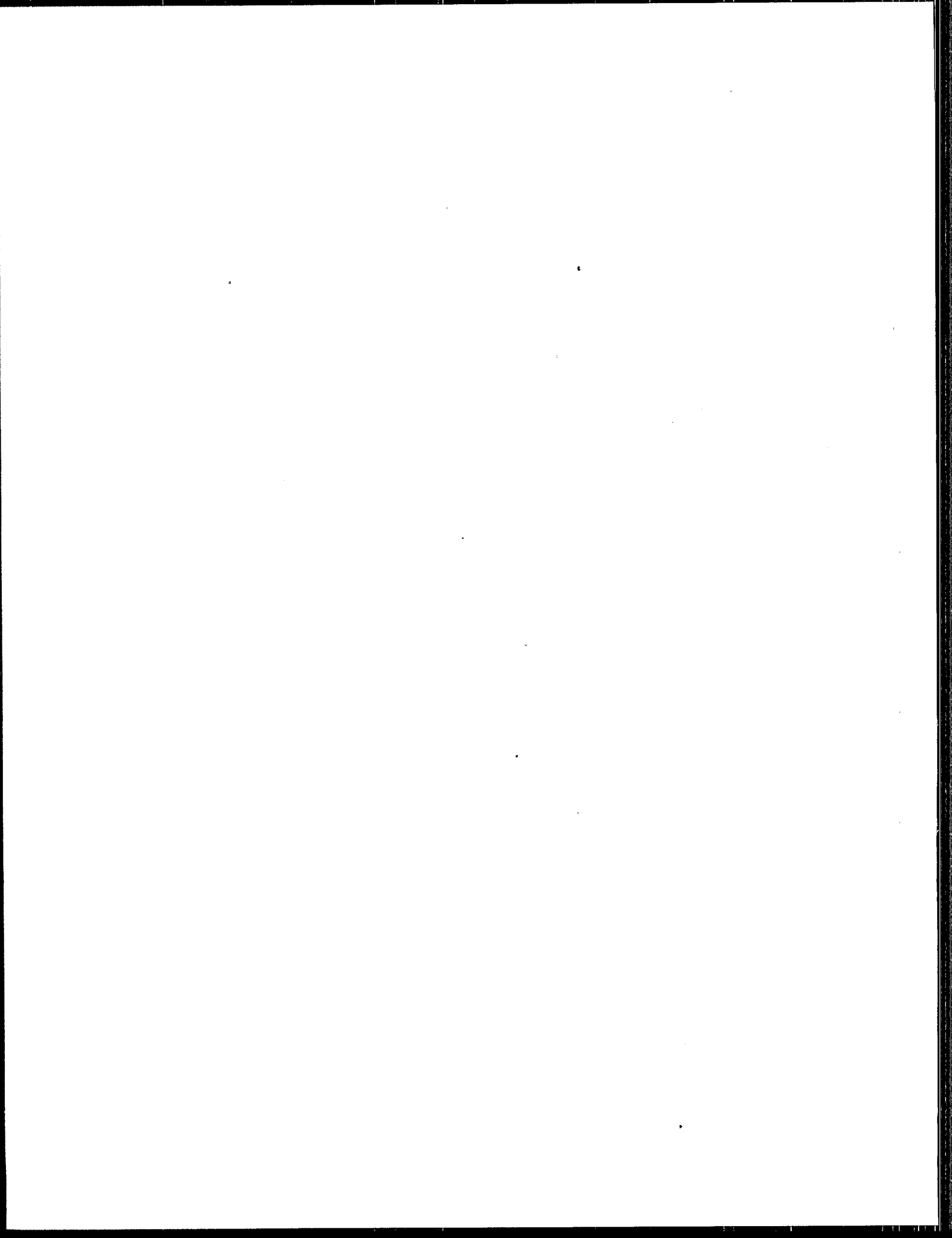
### 1. Test Design:

The stack test must be designed to gather all needed information in an acceptable manner. Major elements of the testing are:

- Sampling and analysis of sludge feed for metals.
- Sampling and analysis of stack emissions for metals.
- Monitoring and documentation of operating conditions during the test (including temperature(s), oxygen, total hydrocarbon, sludge feed rate, and air pollution control devices).

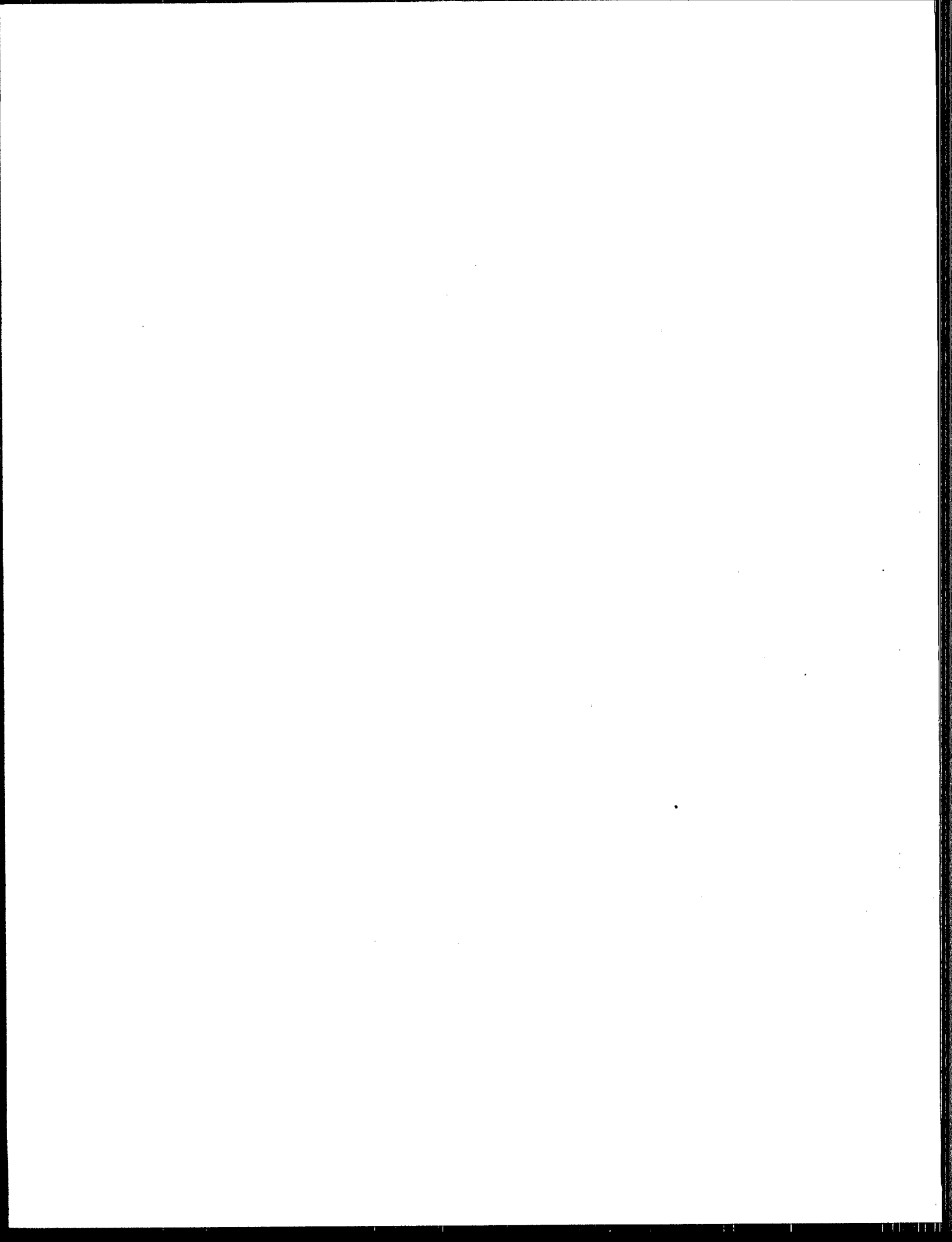
A few general guidelines are appropriate:

- The test should be conducted at worst case conditions (i.e., with the highest expected feed rate of sludge, at the highest temperature, etc.) for metals emissions in order to obtain the most flexible permit conditions. However, the system must be operated within its design specifications to demonstrate adequate performance in controlling metals emissions.





- All testing and monitoring must be conducted concurrently (or phased to account for material lag time). Sludge feed samples must be collected and analyzed to calculate an input loading rate for each investigated toxic metal for comparison with outlet emission rates.
- Three replicate test runs are requested for each specific set of operating conditions. This provides added assurance that the incinerator is operating in a consistent manner. Operating conditions should be maintained as consistently as possible for the three test runs.
- Measurements of temperature, oxygen, THC, sludge feed rate, and air pollution control indicators should be recorded continuously, or, at a minimum, every 60 sec.
- All monitoring instruments should be recalibrated immediately prior to and after the test. Documentation of calibrations should be included in the test report.
- Sludge feed samples should be collected at least every 15 min during each stack sampling test period. Individual samples can be composited into one sample analyzed per test run.
- Sampling should not begin until the incinerator has reached a steady state on sludge feed. A minimum of 60 min (or 120 min for a multiple hearth) of operation feeding sludge is recommended prior to sampling.
- Minimum stack sampling time for each run (actual sampling time not including time for port changes, etc.) should be 1 hr.
- Custody procedures should be used for handling all samples. Full chain-of-custody procedures are typically much more labor-intensive but may be used at the applicant's option.

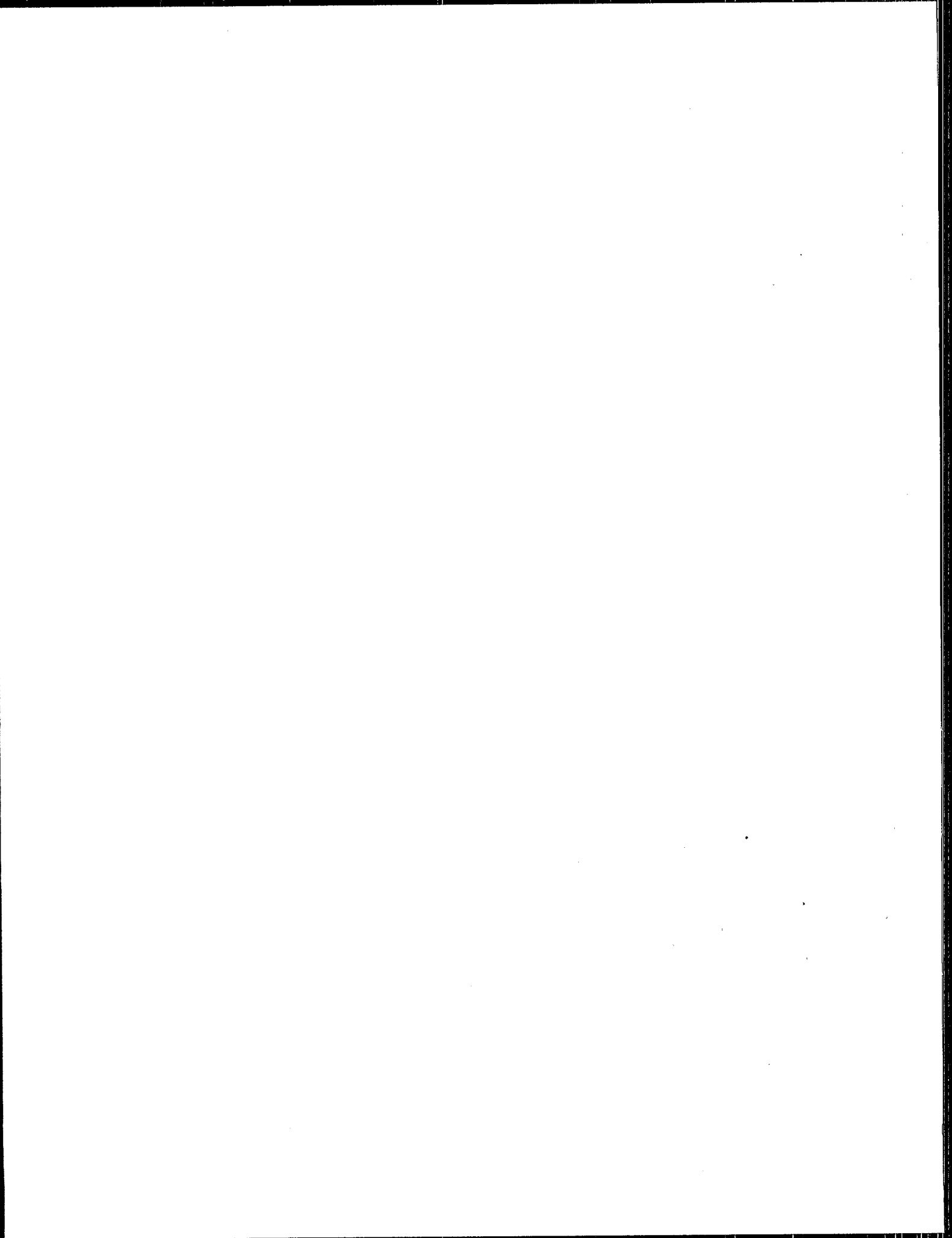


- Results should be reported in a format which includes all information and data necessary to calculate final results and verify quality assurance objectives. Results should be presented in as clear and succinct a format as possible.

## 2. Methods for Measuring Metals Emissions:

Specific EPA methods for sampling and analysis of metal emissions are Method 12 for lead, Method 101A for mercury, Methods 103 and 104 for beryllium, and Method 108 for arsenic. These methods may be applicable to sewage sludge incinerators in cases where only one metal is being investigated. However, for the past 3 years a method has been under development for sampling and analysis of multiple metal analytes, "Methodology for the Determination of Trace Metal Emissions in Exhaust Gases From Stationary Source Combustion Processes." A copy of this method is provided in Appendix A. Currently the draft method can be applied to 16 analytes. This makes the "Multiple Metals Method" highly appropriate for the sampling and analysis of the regulated metals emitted in the exit gas from a sewage sludge incinerator.

The Multiple Metals Method is a variation of U.S. EPA Method 5 (40 CFR 60, Appendix A) which was originally used to sample particulate matter emitted from power plants. In Method 5, samples are taken at several designated sampling points in the stack, which represent equal areas. At each sampling point, the velocity, temperature, and static pressure of the particulate-laden gas stream are measured. The sampling probe is placed at the first sampling point, and the sampling apparatus (commonly referred to as the sampling train) adjusted to take a sample at the conditions measured at this point. The sampling probe is then moved to the next point, and the process is repeated continuously until a sample has been taken from each designated sampling point. To achieve valid results in a particulate source test, the sample must be withdrawn at the same velocity as the flow of gas in the stack. This is commonly referred to as isokinetic sampling. Measurement of



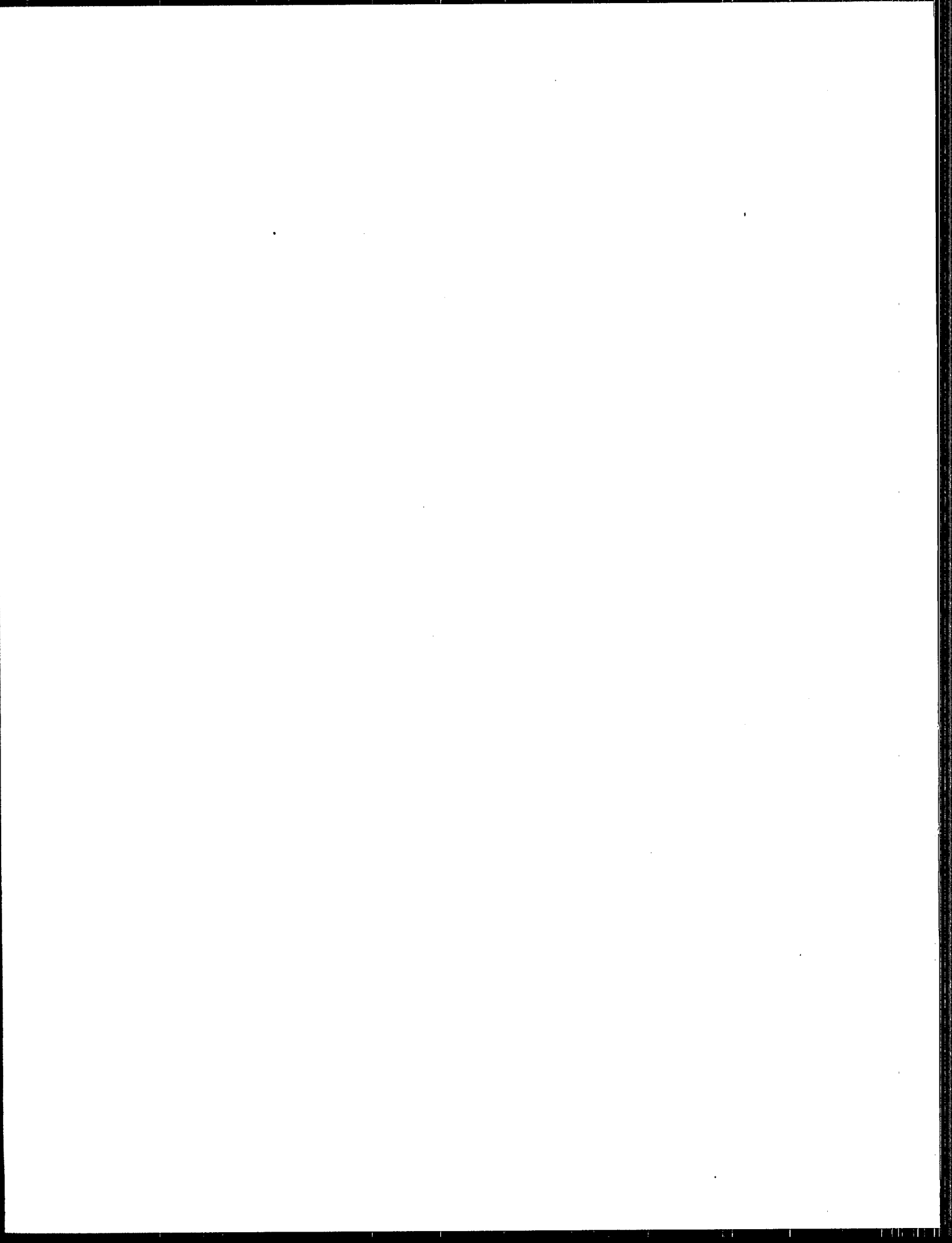
stack conditions allows adjustment of the sampling rate to meet this requirement.

As the gas stream proceeds through a Method 5 sampling train, the particulate matter is trapped on a filter, the moisture is removed, and the volume of the sample is measured. Upon completion of sampling, the collected material is recovered and sent to a laboratory for analysis.

Since the metals emitted from a sewage sludge incinerator may be in a solid form within the particulate or in a volatile form within the gas stream, a modification of the Method 5 train is necessary to collect appropriate samples for analysis of all of the regulated toxic metals simultaneously. Appendix A of this document contains the draft metals protocol *Methodology for the Determination of Trace Metal Emissions in Exhaust Gases From Stationary Source Combustion Processes*. This method describes the only system that has been proposed to collect both the volatile and nonvolatile fraction of the stack gases. This draft protocol will be incorporated into a methods document under preparation by EPA's Office of Solid Waste as background for proposed amendments to the RCRA incinerator regulations, and is also appropriate for sampling sewage sludge incinerators.

The metals train contains special solutions in the impingers to collect volatile metals. A glass probe tip is used. Full instructions on the sampling apparatus, sampling procedure, recovery of the samples, analysis, and quality assurance/quality control associated with the metals train is provided in Appendix A.

As a special note, sampling specifically for hexavalent chromium (as opposed to trivalent or total chromium) presents several problems. These problems are the stability of the sample and recovery efficiencies when separating low level samples. Both oxidizing and reducing materials may affect the stability of the samples and produce errors in the determination. At this time, EPA has a first draft of a procedure for collecting and analyzing chromium(VI) stack samples. This is included in Appendix C.



### 3. QA/QC for Metals Determinations in Stack Samples:

As noted previously, the "POTW Sludge Sampling and Analysis Guidance" (EPA, 1989c) recommends a QA plan for sludge sampling and analysis. The EPA also recommends a QA plan for demonstration tests at hazardous waste incinerators (EPA, 1990). Any demonstration test involving stack sampling is a complex and expensive experiment; a QA plan is recommended to ensure that the field sampling and laboratory analysis will provide data of sufficient quality for regulatory decision making. Guidance on preparing a QA plan for a demonstration test can be found in EPA (1990).

a. Method design: One of the biggest difficulties in metals determinations in stack samples is lack of a clear target concentration. The draft method requires specific adaptations of the procedures in order to obtain various detection limits. Using the equations in the proposed rule, the critical removal efficiency can be calculated given the known sludge metal input. This critical removal efficiency and the sludge metal input can then be used to calculate the stack gas concentration and resulting sample concentration for analysis. To assure reliable quantitation of the analyte in the stack gas, the sample concentration at the critical level should be at least five to ten times higher than the detection limit specified for the method.

b. Determination of precision and accuracy: The analysis for metals in stack gas should be accompanied by determination of the precision and accuracy of the measurement system. Various procedures are discussed in EPA (1990). Precision and accuracy are determined using the QA/QC procedures in the associated methods, plus additional analysis of two sets of metal sampling train components fortified at the critical concentration level and prepared and analyzed along with the stack gas sampling train components. Accuracy is measured as percent recovery of fortified analyte, and precision is measured as the percent range of the found analyte in each of the two sets of sampling train components.

c. Data reporting: Data reported for stack gas samples should be calculated according to the methods. In addition, data reported for the removal efficiency should be uncorrected for any background levels found





in blanks. If significant levels are found in blanks, stack gas data should be corrected only if sufficient statistical justification is given. Any removal efficiency reported from blank-corrected data should also be reported uncorrected for comparison.

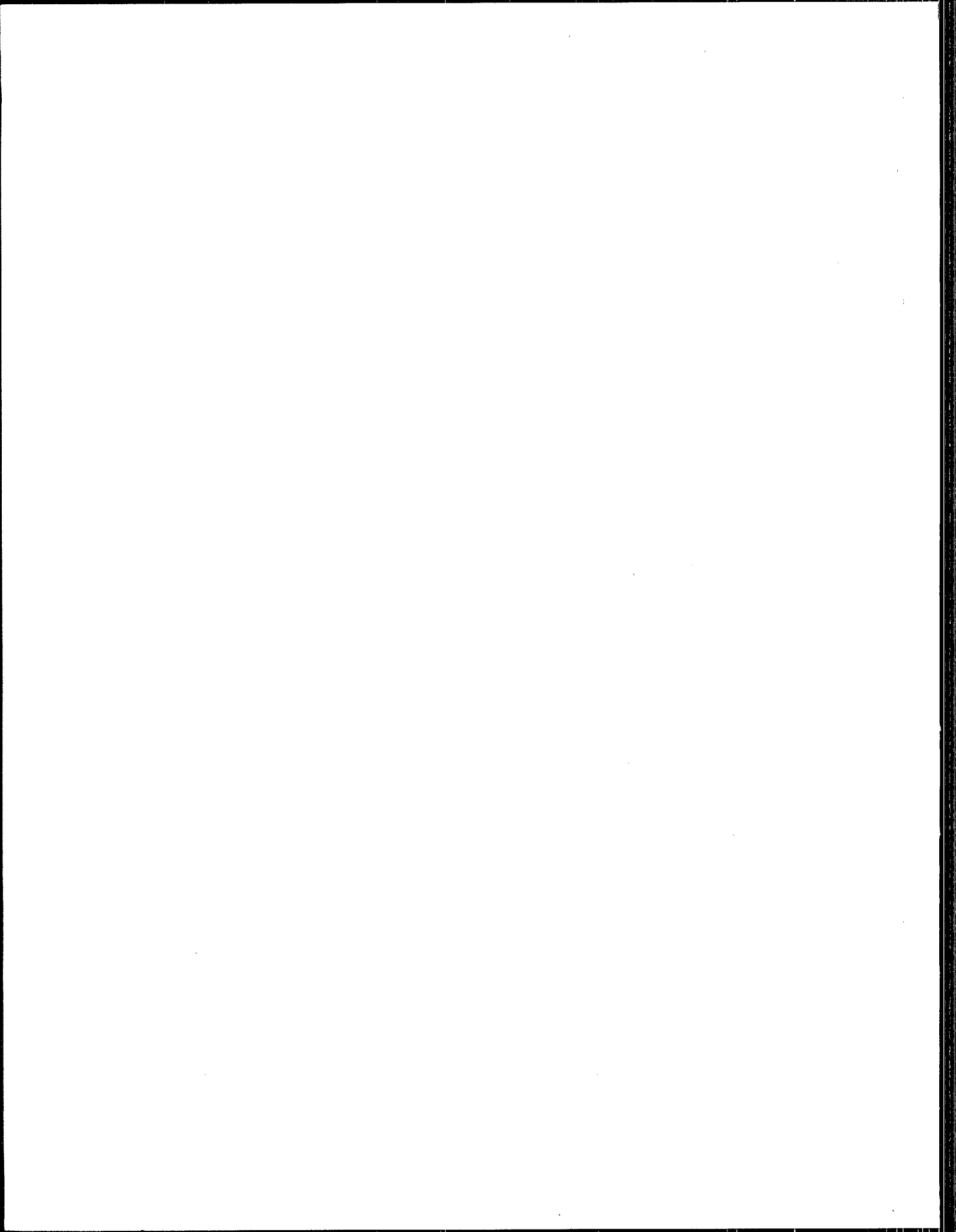
#### D. DISPERSION MODELING

In broad terms, an atmospheric dispersion model provides a relatively inexpensive means of predicting the impact that mass emissions from a given source have on ambient air concentrations experienced at locations surrounding the source. Dispersion models have a long history of application to criteria pollutant [e.g., particulate, sulfur oxides ( $\text{SO}_2$ )] air quality problems. For criteria pollutant analyses, the U.S. EPA has developed a set of approved models and has a well established set of procedures to address issues such as:

- selection of an appropriate model given site location relative to surrounding topography and land use;
- meteorological data requirements; and
- source data requirements

Although there are no directly comparable procedures that are specific to modeling metals emissions from sewage sludge incinerators, a set of modeling recommendations has been prepared for a similar source--hazardous waste incinerators. These recommendations borrow extensively from the criteria pollutant modeling procedures.

As an initial step in performing a dispersion analysis for a sewage sludge incinerator, it is recommended that the applicant become familiar with the information contained in the documents given below.

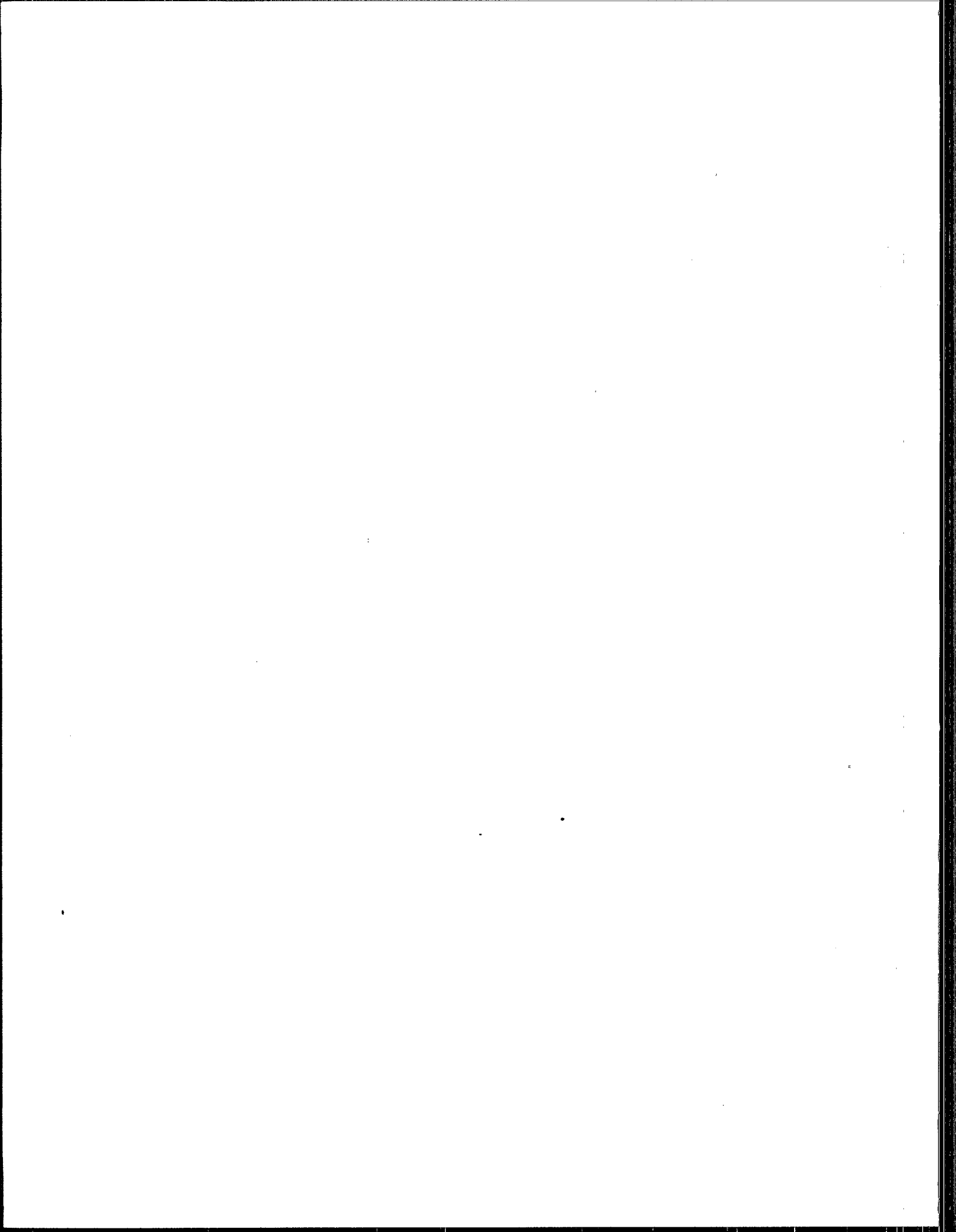


- Guideline on Air Quality Models (Revised), 1986, EPA-450/2-78-027R from the U.S. EPA Office of Air Quality Planning and Standards. This document is available from the National Technical Information Service (NTIS) as PB86-245248 and is the criteria pollutant modeling guidance cited above.
- Workbook of Atmospheric Dispersion Estimates, 1970, by D. B. Turner. This document is available from NTIS as PB191482. This document provides a very readable introduction to the fundamentals of Gaussian dispersion models.

The actual dispersion model programs (i.e., the computer source code or executable versions) can be obtained from at least two sources. For example, one can purchase a specific model from a commercial software vendor. There are many model vendors and one can obtain names and telephone numbers for several vendors by looking at the advertisements given in the Professional Services Directory of any recent issue of the Journal of the Air and Waste Management Association. Alternatively, one can obtain the most recent version of a model by accessing the U.S. EPA's computerized bulletin board system (BBS) maintained by the Support Center for Regulatory Air Models (SCRAM). For information regarding the SCRAM BBS one should write to the following address:

Support Center for Regulatory Air Models  
 SRAB (MD 14)  
 U.S. Environmental Protection Agency  
 Research Triangle Park, NC 27711

In many instances the Industrial Source Complex Long Term model (ISCLT) will be the appropriate model for estimating the impact of emissions from sewage sludge incinerators. This model is used very extensively in regulatory applications. It is generally considered to be applicable unless the topography in the area immediately surrounding the facility (0.5 km) consists of locations where the elevation exceeds the physical height of the incinerator stack. In this case it probably would be necessary to use what



are commonly referred to as complex terrain models. These models include COMPLEXI and LONGZ. Note that atmospheric dispersion in complex terrain is an ongoing research area and that there are still many questions involved in applying and interpreting the results obtained by use of the COMPLEXI and LONGZ models.

### III. REVIEWING AND INTERPRETING TEST RESULTS

This chapter serves two primary purposes. First, it provides descriptive advice to control agency permit writers who are reviewing and interpreting test results from sewage sludge sampling and analysis, data from process monitoring instrumentation, and the results from stack sampling and analysis of emissions from sewage sludge incinerators. Secondly, this chapter summarizes typical reporting requirements for the testing of sewage sludge incinerators and, thus, provides guidance to owner/operators in providing a complete test report to the control agency.

In general, the owner/operator must provide in a report to the control agency adequate information (see Table III-1) to develop a permit in response to the requirements of the proposed rules for sewage sludge incinerators. Minimum information includes a description of the incinerator facility, operating conditions, and monitoring instrumentation; the results of sludge sampling and analysis; full stack test results including documentation of sludge sampling and analysis; data from the monitoring of key process instruments; and complete documentation of stack sampling and analysis results/activities. A modeling report will be submitted to document the dispersion factor to be used for each site.

The findings of the stack testing should be presented in a concise and complete summary format, at the beginning of the test report. Test results, QC results, and analysis system performance should be thoroughly discussed and documented in the subsequent pages of the report. Sufficient detail is needed in the report to allow an agency reviewer to trace the calculations for all results from the summary presentation back to the raw data. Results also are compared to the original test methods to verify that all

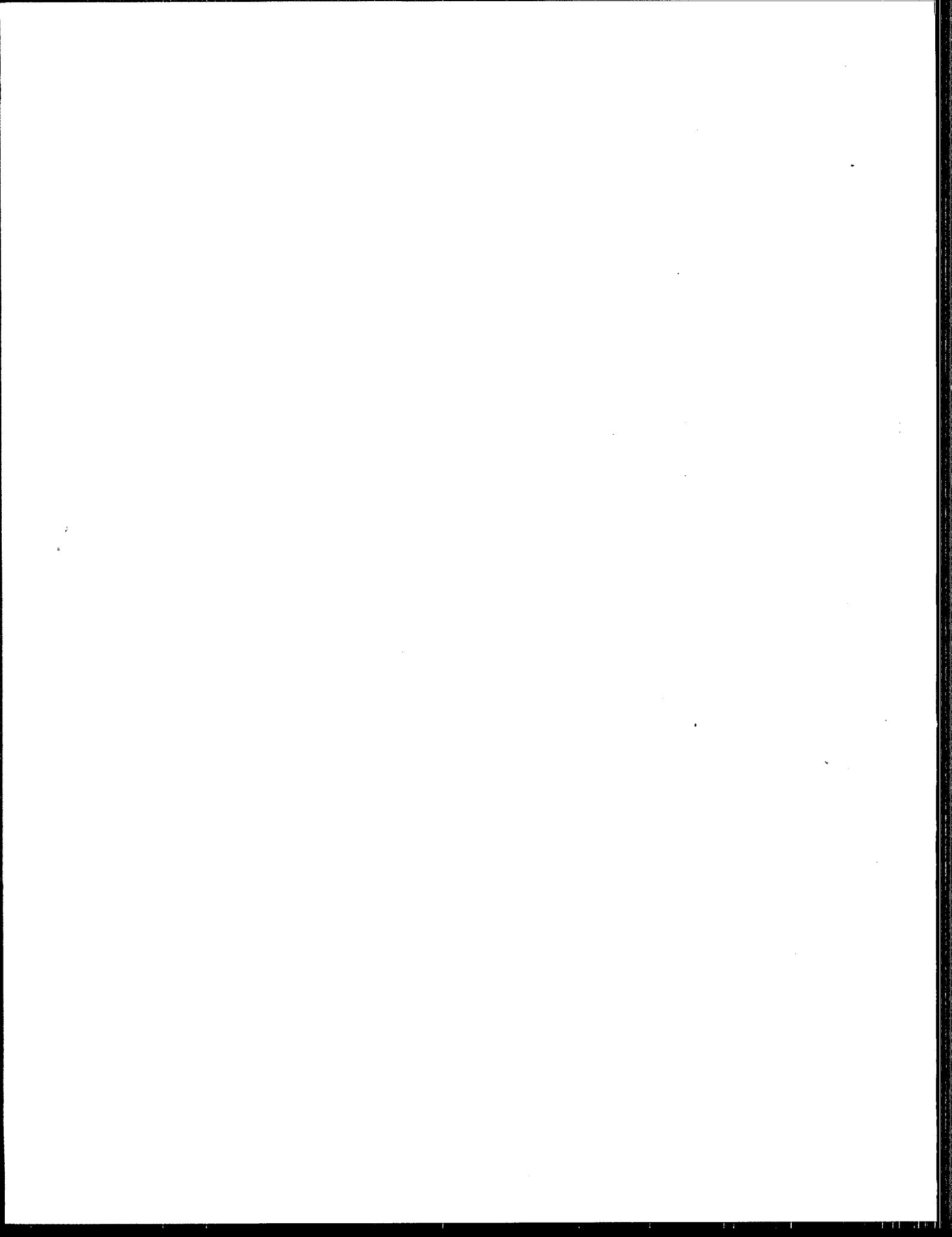
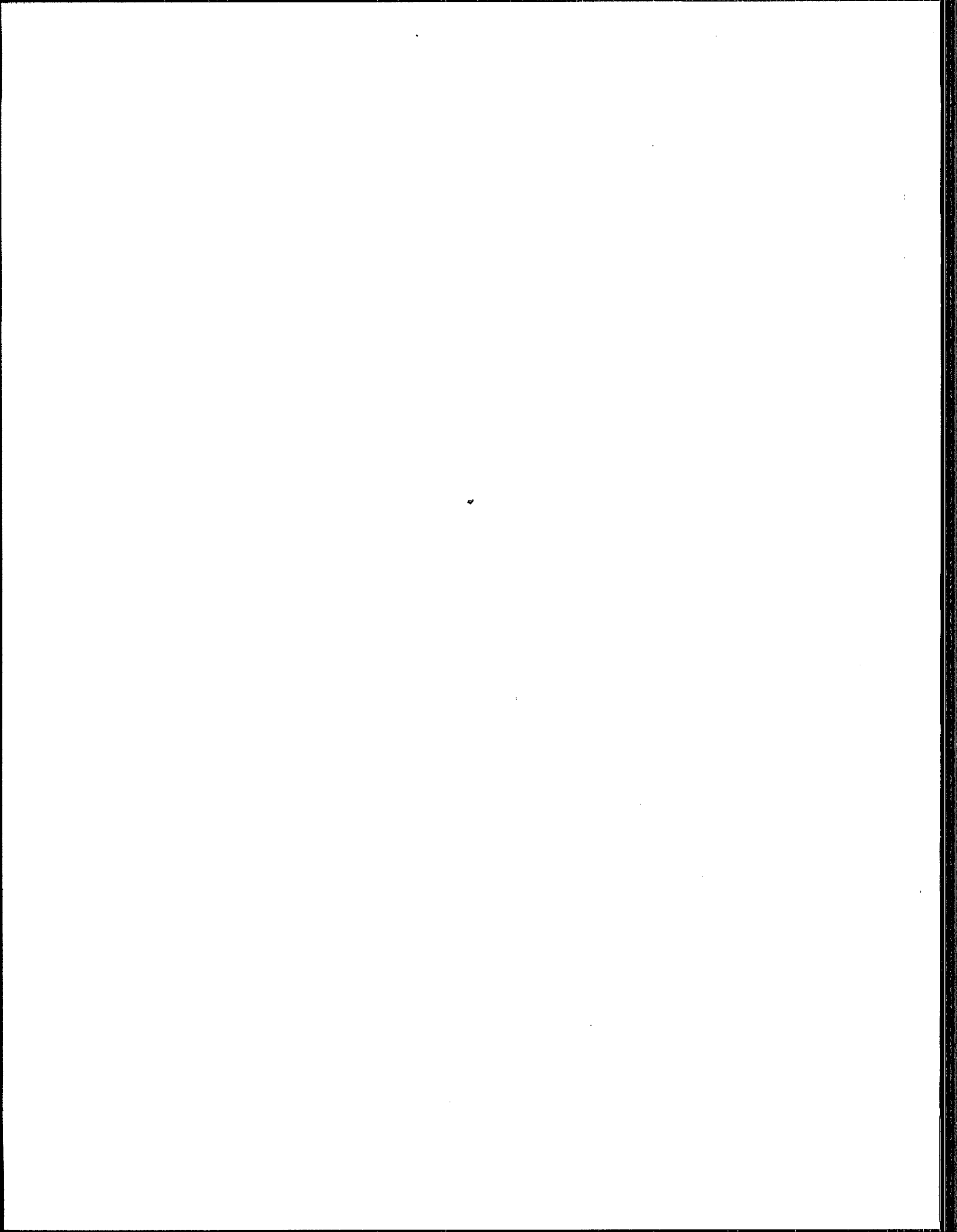


TABLE III-1

SUMMARY OF MINIMUM DATA REQUIREMENTS FOR A SEWAGE SLUDGE  
INCINERATOR PERMIT APPLICATION

- Type of incinerator
- Type of air pollution control
- Sludge characteristics
  - \* Concentration of Be, Hg, Pb, As, Cd, Cr, and Ni
- Details of adequate continuous process monitoring instrumentation (including appropriate calibration and maintenance programs) for the following:
  - \* Sludge feed rate
  - \* Temperature(s) (in specified locations)
  - \* Oxygen in exit gas
  - \* Total hydrocarbon in exit gas
  - \* Air pollution control device indicator(s)
- Results of stack testing program (see Table III-4)
- Values for:
  - \* Sludge feed rate (annual average, dry basis, daily rate)
  - \* Stack parameters such as stack height exit diameter, exit temperature, exit velocity, etc.
  - \* Dispersion factor including the EPA approval of dispersion modeling report
- Details of program to meet requirements for record keeping, reporting, and sludge monitoring





phases of the sampling, monitoring, and analysis activities were carried out in accordance with the methods. Requirements are discussed in more detail in the following sections.

#### A. SEWAGE SLUDGE SAMPLING AND ANALYSIS RESULTS

A report of the results of the sewage sludge sampling and analysis is essentially a summary of the test results and documentation of the various sampling and analysis activities and requirements as discussed in Chapter II and in the references (EPA, 1989c; 1986). A summary of critical issues for sewage sludge sampling and analysis is listed in Table III-2; the failure to document an adequate response to any of the issues on the list may justify issuance of deficiency comments or potentially the rejection of the results by the control agency as incomplete.

Minimum required sludge data will be based ideally on long-term test data. In addition, data must be provided for the sludge samples collected during the stack tests; these data will be correlated with stack emissions data to calculate facility-specific control efficiency values for regulated toxic metals.

Minimum required test results for sewage sludge characterization will include data for beryllium, mercury, lead, arsenic, cadmium, chromium, and nickel.

#### B. PROCESS MONITORING RESULTS

The control agency permit writer will evaluate the adequacy of process monitoring instrumentation based upon specific requirements in the proposed rules and the various design capabilities and practical limitations of each instrument, as discussed in Chapter II. Table III-3 summarizes the critical issues for the monitoring of the key operating parameters.

As noted in Table III-1, monitored data for sludge feed rate must be submitted in a permit application to provide the minimum data requirements for determining permit conditions. In addition, the stack test report must



TABLE III-2

CRITICAL ISSUES FOR SEWAGE SLUDGE SAMPLING AND ANALYSIS

- Justification for sampling and analysis strategy
- Sampling frequency/number of samples
- Sampling method and location
- Collection of equal volumes for each subsample making up composite
- Duration and timing of sampling (timing is especially important during a stack sampling effort)
- Preparation of containers and equipment
- Field compositing methods
- Sample storage, preservation, holding time, and shipping
- Sample custody
- Sample preparation methods
- Analysis parameters and methods
- Preparation and analysis of standards
- Analytical instrument operation/calibration curves
- Blanks (sampling/analysis)
- Determination of accuracy and precision
- Detection limits
- Calculation of results
- Discussion of the fulfillment and attainment of quality assurance and quality control objectives
- Discussion of any sampling and analysis difficulties

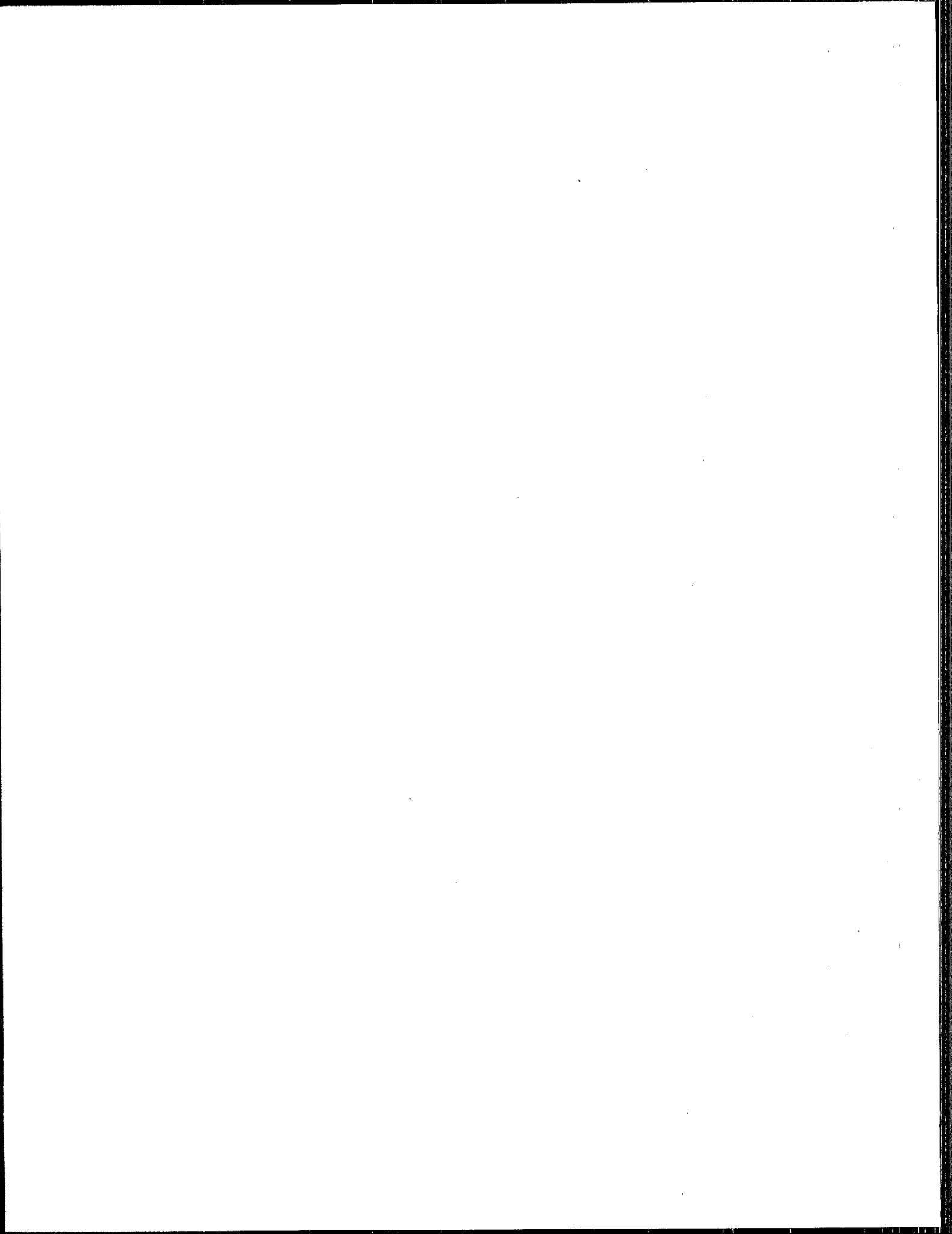
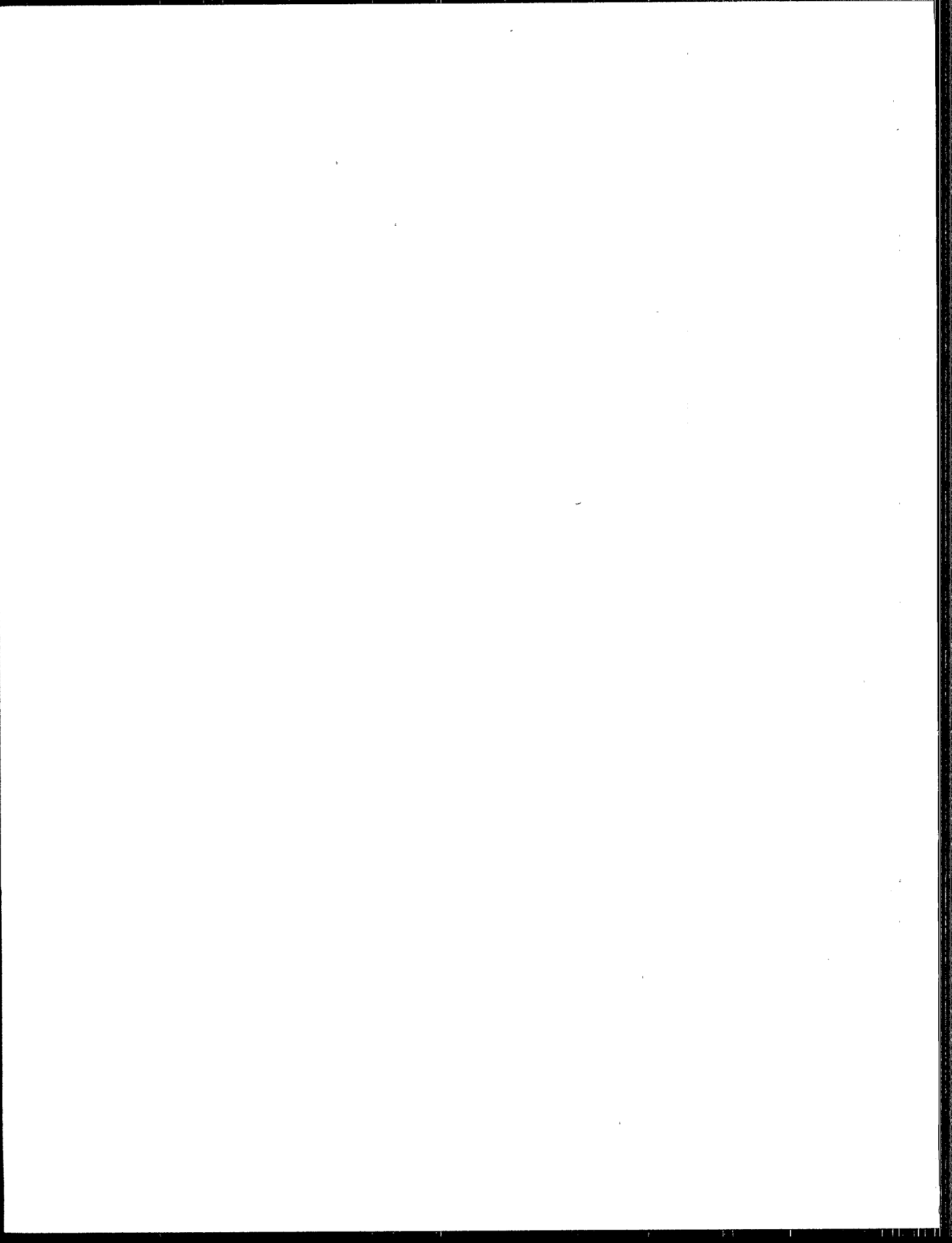


TABLE III-3

CRITICAL ISSUES FOR MONITORED INDICATORS OF SEWAGE SLUDGE  
INCINERATOR PERFORMANCE

- Monitoring of appropriate parameters
- Location and number of sensors
- Methods of monitoring
- Instrument calibration
  - \* Method
  - \* Frequency
  - \* Documentation
  - \* Calibration prior to stack sampling
- Frequency of data readouts/records
- Correction of data (e.g., dry basis, oxygen correction) as required
- Other maintenance issues (availability of spare parts, etc.)
- Discussion of the fulfillment and attainment of quality assurance and quality control objectives



include documentation of the monitored parameters during each stack sampling run. Data to be reported and documented in the test report should include:

- A summary table of each parameter indicating average, minimum, and maximum values for each test run.
- Printouts from a data logger or strip chart of the raw data collected.
- Documentation of instrument calibrations made prior to the first test (or prior to each test run if applicable).
- Documentation of calculations and factors used to adjust raw data to final data (i.e., dry basis, oxygen correction for THC, etc.).

#### C. RESULTS OF STACK SAMPLING AND ANALYSIS

The results of stack sampling and analysis are reported in a summary table; detailed in a descriptive report of findings, methods/activities, and problems; and fully documented via field sheets, raw data, etc., to allow a thorough review of the requirements of the sampling and analysis methods. A summary list of critical issues for testing metals emissions from sewage sludge incinerators is provided in Table III-4; the failure to document an adequate response to any of the issues on the list may justify the issuance of Table III-3 deficiency comments or potentially the rejection of the results by the control agency as incomplete.

#### IV. APPROACH TO ESTABLISHING PERMIT LIMITS

This chapter describes how a permit writer will develop specific permit limits for a sewage sludge incinerator based on the required information submitted by the applicant. This decision process can also be used by a permit applicant to preview possible permit conditions.

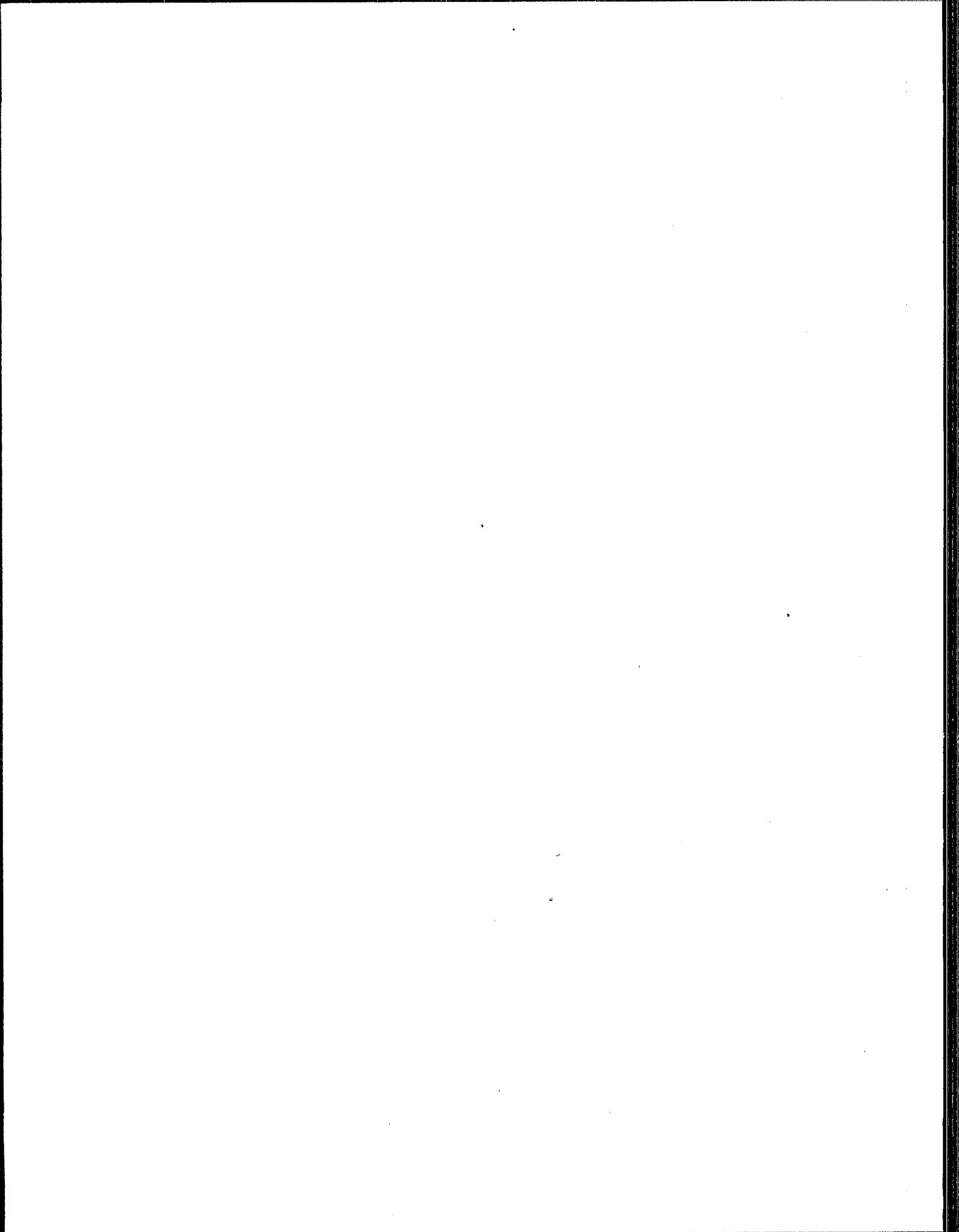




TABLE III-4

CRITICAL ISSUES FOR TESTING METALS EMISSIONS FROM  
SEWAGE SLUDGE INCINERATORS

- Identification of sampling objectives and methods
- Location of sampling ports
- Traverse points
- Absence of cyclonic flow verified
- Equipment calibration
- Stack gas velocity/flow rate calculation
- Gas analysis/calculation
- Field data sheets
- Isokinetic calculations
- Proper temperatures maintained
- Sampling rate/volume/time
- Mandatory leak checks performed with acceptable results
- Number of replicate runs per test condition
- Sample recovery documentation
- Handling/distribution of samples for analysis
- Filter weight/moisture determination
- Sample storage, preservation, shipping, and holding time
- Sample custody
- Sample preparation methods
- Analysis methods
- Preparation and analysis of standards
- Analytical instrument operation/calibration curves
- Blanks (sampling/analysis)
- Determination of accuracy and precision
- Calculation of results (based upon input sludge characteristics)
- Discussion of the fulfillment and attainment of quality assurance and quality control objectives



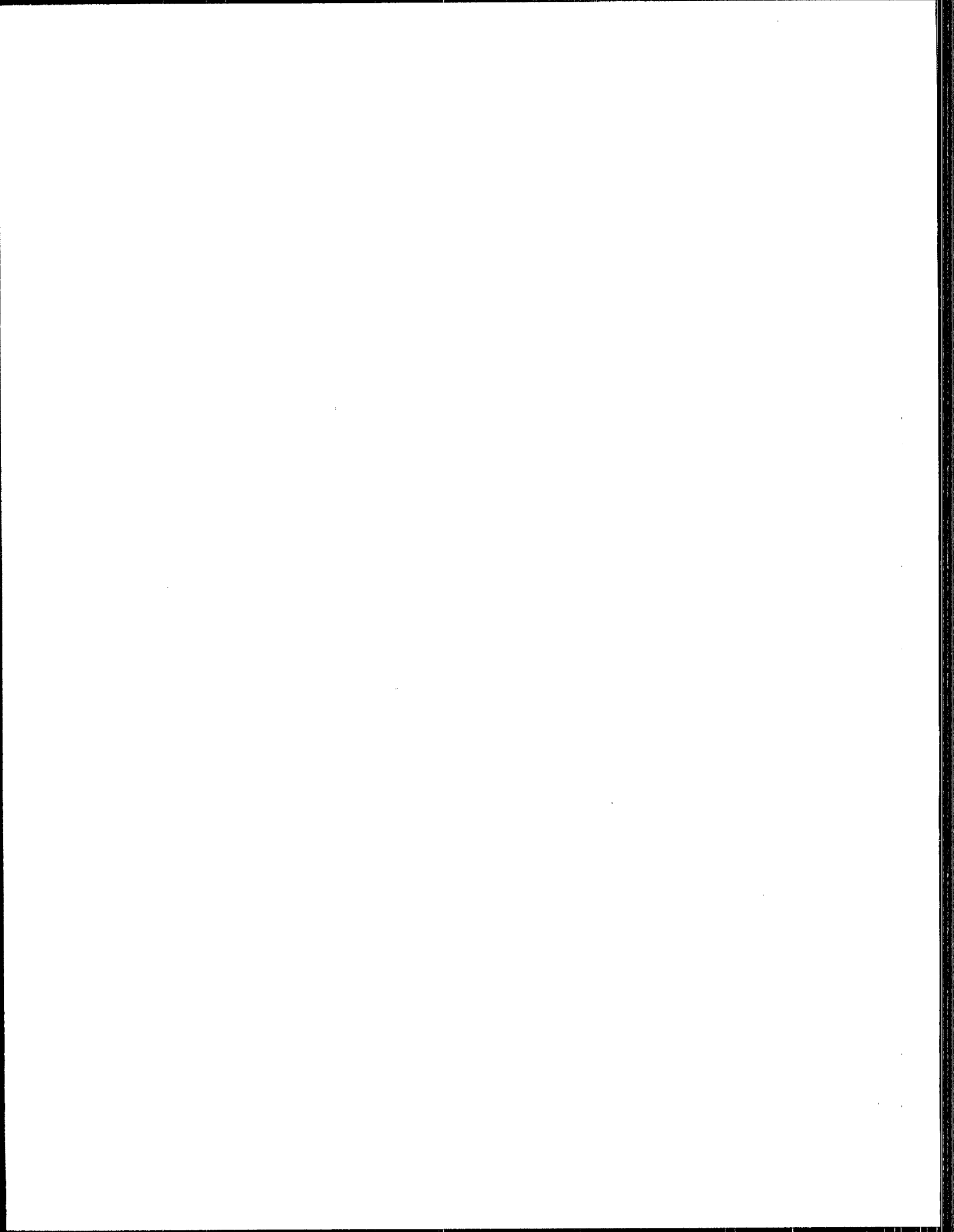
Many of the numerical permit limits are calculated using formulas provided in the proposed rules (*Federal Register*, February 6, 1989). The specific formulas and factors are not repeated here since they are subject to revision prior to promulgation. However, the following pages discuss how a permit writer will use the calculations and submitted information to develop specific permit conditions. Individual parameters are addressed in the following sections. The use of assumed factors will allow an applicant to estimate possible permit limitations.

#### A. SLUDGE FEED RATE

A major objective of the sewage sludge incinerator permitting program is a risk-based limitation of inputs of beryllium, mercury, lead, arsenic, cadmium, chromium, and nickel to each incinerator. Limitations of metal inputs result in limitations of potential metal emissions to the atmosphere.

The specific limits for each metal are based upon formulas contained in the proposed rule that involve such factors as control efficiency and dispersion. Two major variables in each formula are the concentration of the regulated metal in the sewage sludge and the input rate of sludge to the incinerator.

Sludge feed rate will serve as the continuously monitored parameter; a maximum value specified in the permit will serve as a limit to the input of the most critical metal, i.e., the metal that requires the lowest sludge feed rate in the risk-based calculations described in the proposed rule. In determining permit conditions, the concentration of each metal will be assumed to be a constant, based upon the average of accumulated sludge analysis data for that metal. (Ideally, long-term information will be available for these evaluations.) Allowable sludge feed rates are calculated for each metal using the formulas; the lowest value is selected as an operating limit. A continuing sludge analysis effort, required by the regulations, serves as a long-term check of the validity of the average concentration values used to determine maximum sludge feed rate.



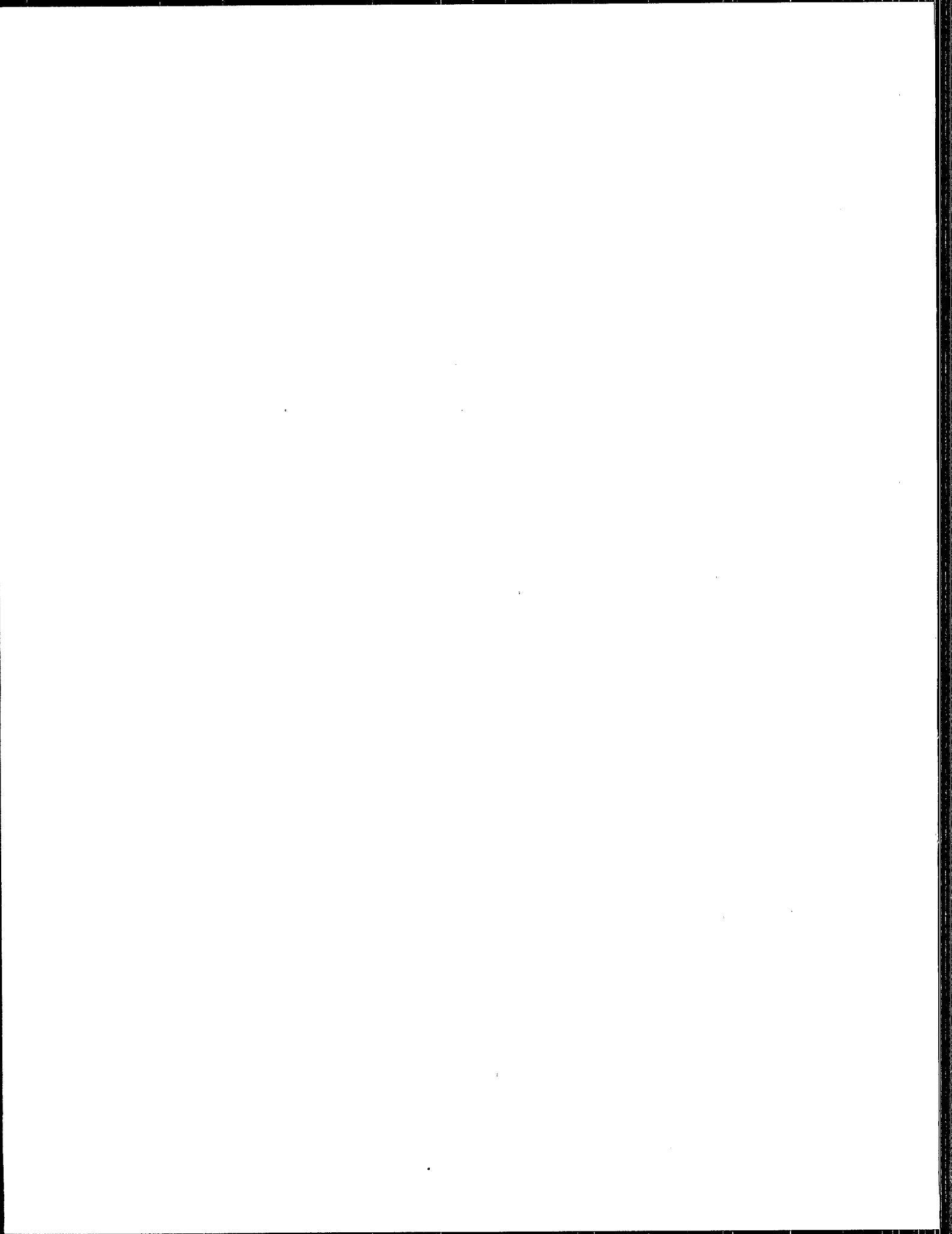
The individual steps of determining the maximum allowable sludge feed rate are as follows:

1. Gather the input information needed to use the formulas provided in the proposed rules. Inputs include:
  - Average concentration of each regulated metal in the sewage sludge (based upon long-term data collection)
  - Site-specific factors for dispersion and control efficiency obtained from site-specific studies/emission tests

Note that the calculations involve the combined feed of all incinerators within the property line of the treatment works.

2. Solve the formulas for sewage sludge feed rate for each regulated metal.
3. Select the lowest calculated sewage sludge feed rate (i.e. for the metal that requires the lowest feed rate in the formulas), convert this value from dry basis to wet basis (based on historic moisture data) and compare with the design (or manufacturers recommended) maximum sludge feed rate of each incinerator.
4. Select the smaller value (i.e. the lowest calculated rate or design maximum) as the permitted maximum feed rate. The rate should be expressed on a wet basis in the permit if monitored by the facility on a wet basis. If the facility has more than one incinerator, allocate allowable feed rates to individual units so that the total feed rate (to all of the incinerators) does not exceed the sludge feed limit for the entire site.

A limited example set of calculations involving two metals is provided in Appendix D of this document.



The permit will correlate the maximum allowable sewage sludge feed rate with average concentration values for each regulated toxic metal. Each facility is required to conduct a continuing characterization of sewage sludge in the proposed rules; if the results of this characterization indicate a trend in averaged sludge data requiring a 10% or greater decrease in the maximum allowable sludge feed rate, the permit limit must be modified. Likewise, a facility can request a permit modification if data trends indicate a basis for increasing the allowable sludge rate by 10% or greater.

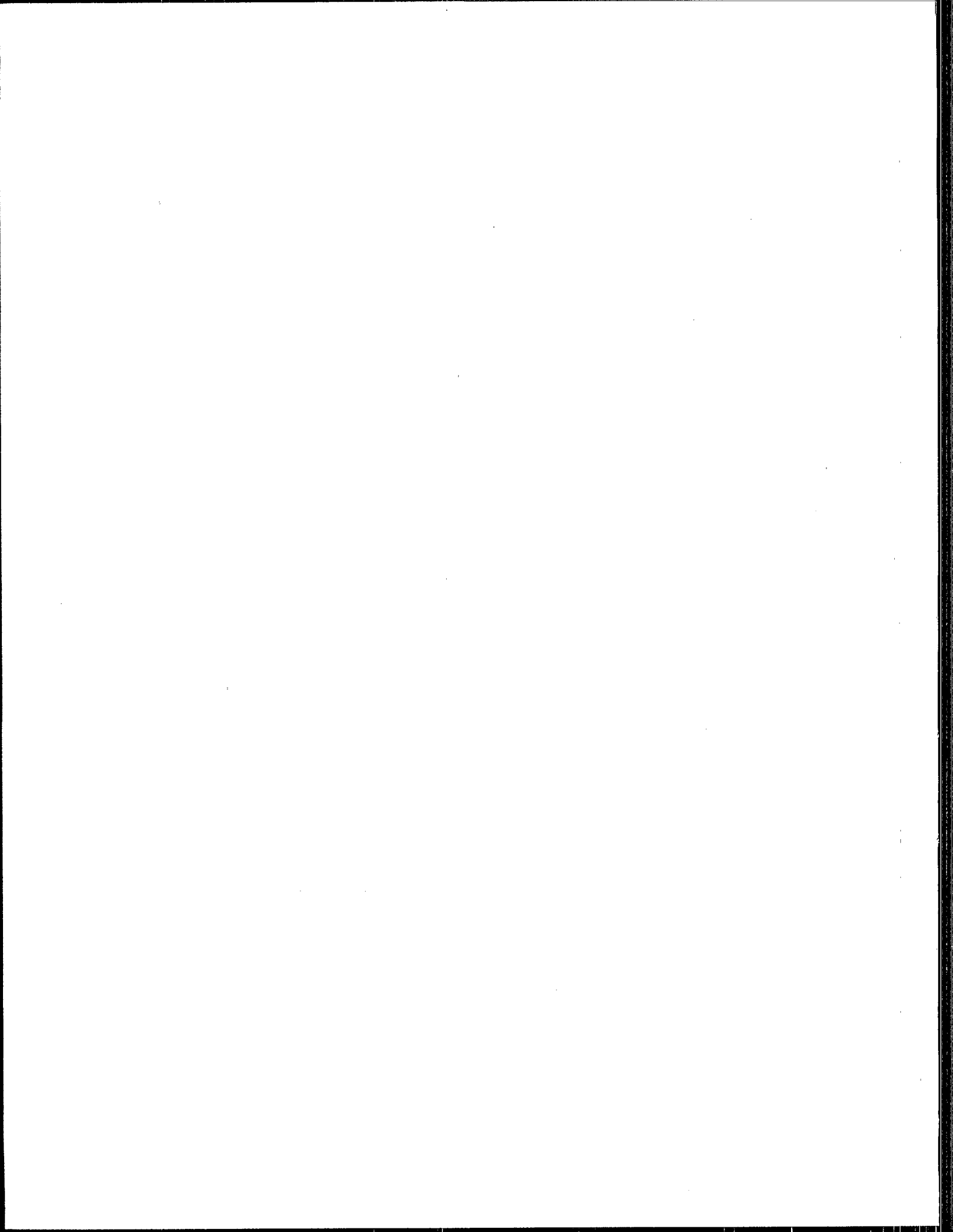
An incinerator owner/operator, as a result of completing the above exercise with preliminary or estimated information, may identify a need to modify or replace air pollution control equipment in order to maximize the allowable sludge feed rate limit.

#### B. TEMPERATURE, OXYGEN, AND TOTAL HYDROCARBONS (THC)

Limits for maximum temperature and maximum oxygen are based on the conditions documented during the tests. The maximum temperature limit should be no more than 100°F higher than the average temperature demonstrated during the tests. Likewise, the oxygen limit should be no more than 1% O<sub>2</sub> higher than the average demonstrated during the test. Oxygen limits are expressed on a dry basis. A technology-based limit for THC will be included in the promulgated regulation.

#### C. AIR POLLUTION CONTROL LIMITS

The selection and monitoring of selected indicators of air pollution control was addressed in Chapter II. Permit limits for the indicators selected by the permit writer should reflect design operating conditions (i.e., within design minimum/maximum ranges recommended by the manufacturer of the control device) and the operating conditions documented during stack testing. Permit limits for the indicator parameters should not be more than 20% above/below the average value demonstrated during the tests (e.g., a minimum scrubber pressure drop of 16 in if the test average was 20 in or a maximum flow rate of 120 gpm if the test average was 100 gpm.)





#### D. DEVIATIONS FROM LIMITS

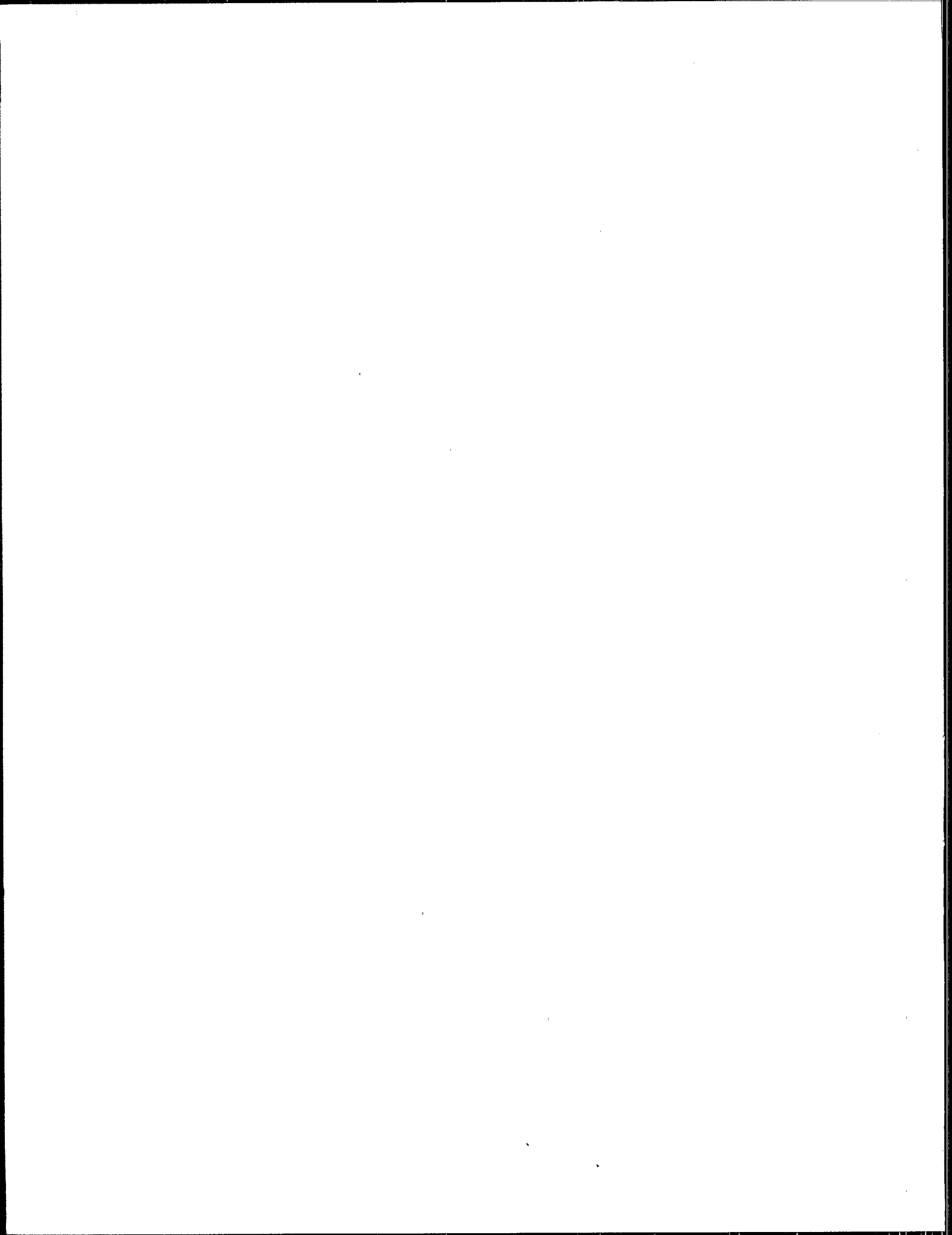
Permit writers should identify general requirements related to deviations from limits in each sewage sludge incinerator permit. Brief excursions above/below the maximum/minimum limits for continuously limited parameters are allowed if they do not cause the limit to be exceeded for more than 60 min. A report must be submitted to the control agency whenever permit limits are exceeded more than 60 min.

#### E. CALIBRATION AND MAINTENANCE OF MONITORING INSTRUMENTATION

The permit should include requirements for the calibration and maintenance of instrumentation used to continuously monitor permit-limited parameters. Required calibration methods and the minimum frequency of calibration should be clearly identified in each permit. The method should be as specific as possible. Recommended minimum frequencies of calibration are daily for oxygen monitors, daily or weekly for THC monitors, and every 6 months for sludge feed rate and air pollution control indicators.

Permits should also identify the key steps of a preventative maintenance program for the THC and oxygen monitors. The preventive maintenance program typically is based on manufacturers' recommendations and includes such items as:

1. Checking the integrity of probe and sample line and backflushing as necessary.
2. Checking and maintaining the sample conditioning system, e.g., cleaning or replacing filters.
3. Cleaning optical lens (in situ monitors).
4. Checking operation of recorders and data loggers (e.g., replacing pens, ink, charts, etc.).



The preventive maintenance program should be established by the facility and should identify daily, weekly, monthly, and annual maintenance activities. The permit should require a maintenance log to document adherence to the maintenance program.

#### F. RECORD KEEPING

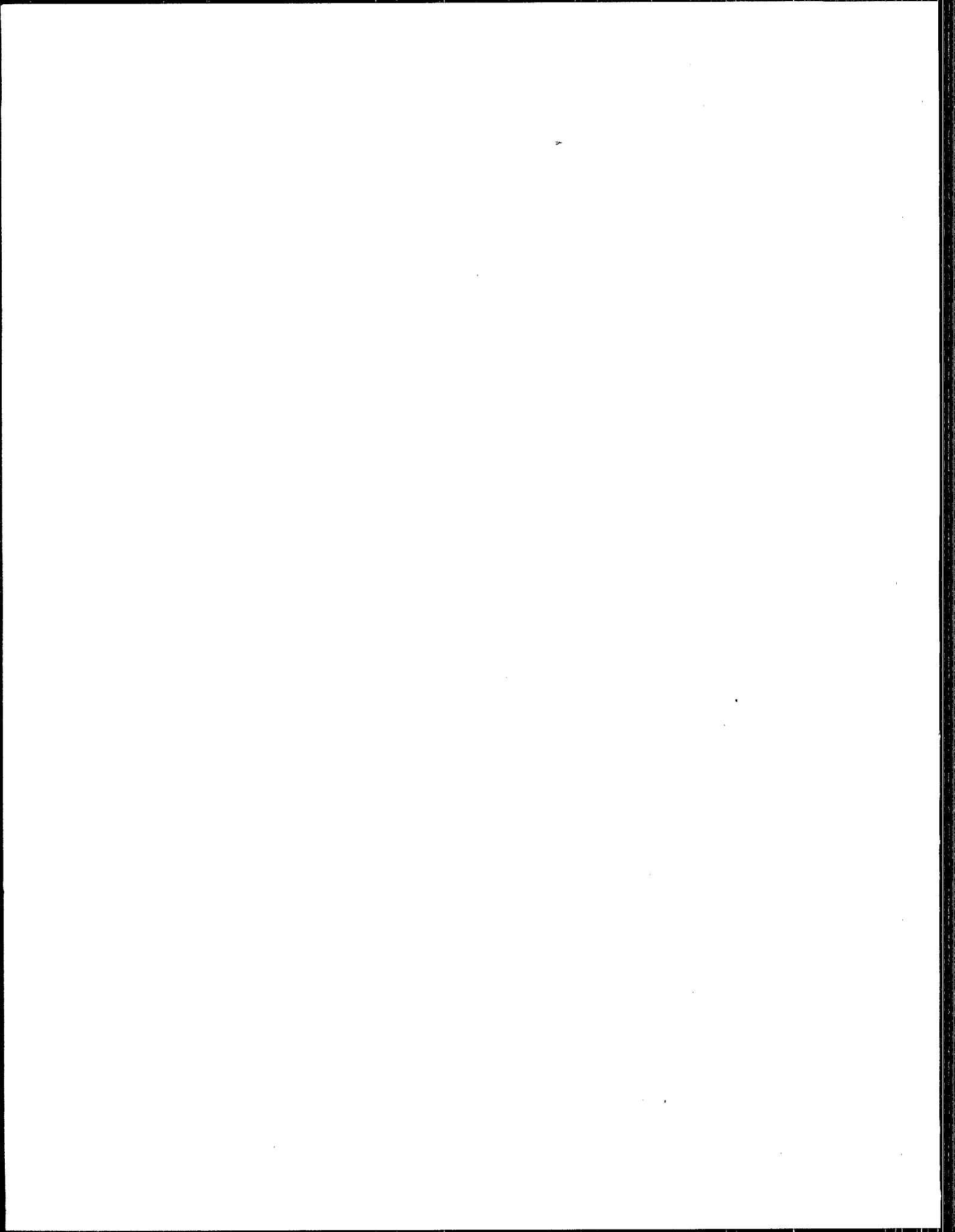
Sewage sludge incineration facilities are required to maintain detailed records to document compliance with regulations and permit conditions. These records are important for compliance inspections conducted by EPA and state agency staff. The required records can be reviewed by inspectors to demonstrate recent and past operations at the facility. Permit writers should be very specific in each permit in defining the following:

- Which records must be maintained?
- What is the content and format of the records?
- What is the frequency of inputs to each type of records (continuous, weekly, etc.)?
- How are the records stored for ease of access?

In general, documentation to be maintained by the facility includes:

- Records associated with continuously monitored operating parameters (e.g., strip charts, computerized logs, operator logs).
- Records associated with sludge characterization and the calculation of allowable sludge feed rates.
- Calibration and maintenance logs.

The content and format of each record should be defined in the permit in sufficient detail to ensure that all needed information will be



available to inspectors. Records of calibrations should document date, calibration method, initial reading, and final reading. The permit should clearly identify the minimum frequency of inputs to records (i.e. continuous strip charts or data logging every 60 seconds). Specific requirements for strip charts may include minimum chart speed and minimum labeling of date and time (e.g., daily manual labeling by the operator).

All records should be stored for ease of access for inspections (i.e., in one central location).

#### V. CONTINUING ENFORCEMENT OBJECTIVES

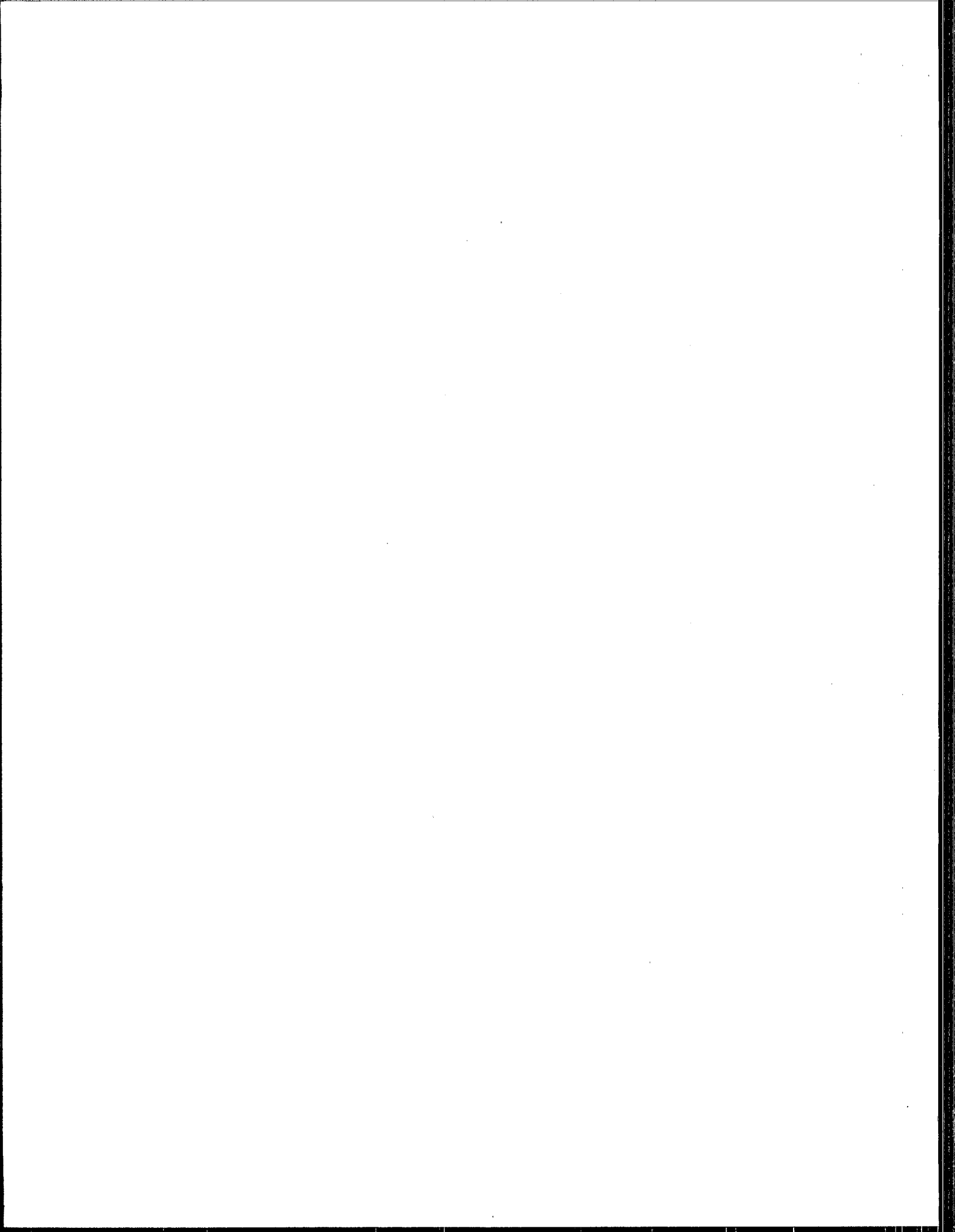
After a permit is issued for a sewage sludge incinerator, the control agency will evaluate the facility's continuing compliance with the applicable regulations and permit conditions by reviewing submitted reports and conducting inspections.

The basis for enforcement includes:

- Records of sewage sludge characterization.
- Records/observations of continuously monitored operating conditions.
- Records/observation of monitoring instrumentation function.

The control agency will review submitted reports and on-site records of continuing sewage sludge sampling and analysis to evaluate any variations in metals concentrations that would impact the risk-based calculation of the maximum allowable sludge feed rate.

Inspectors will observe instrument readouts and review records of monitored parameters to determine compliance with operating permit limits and reporting requirements. Observations of the function of monitoring instruments and the review of calibration and maintenance records serve as a check



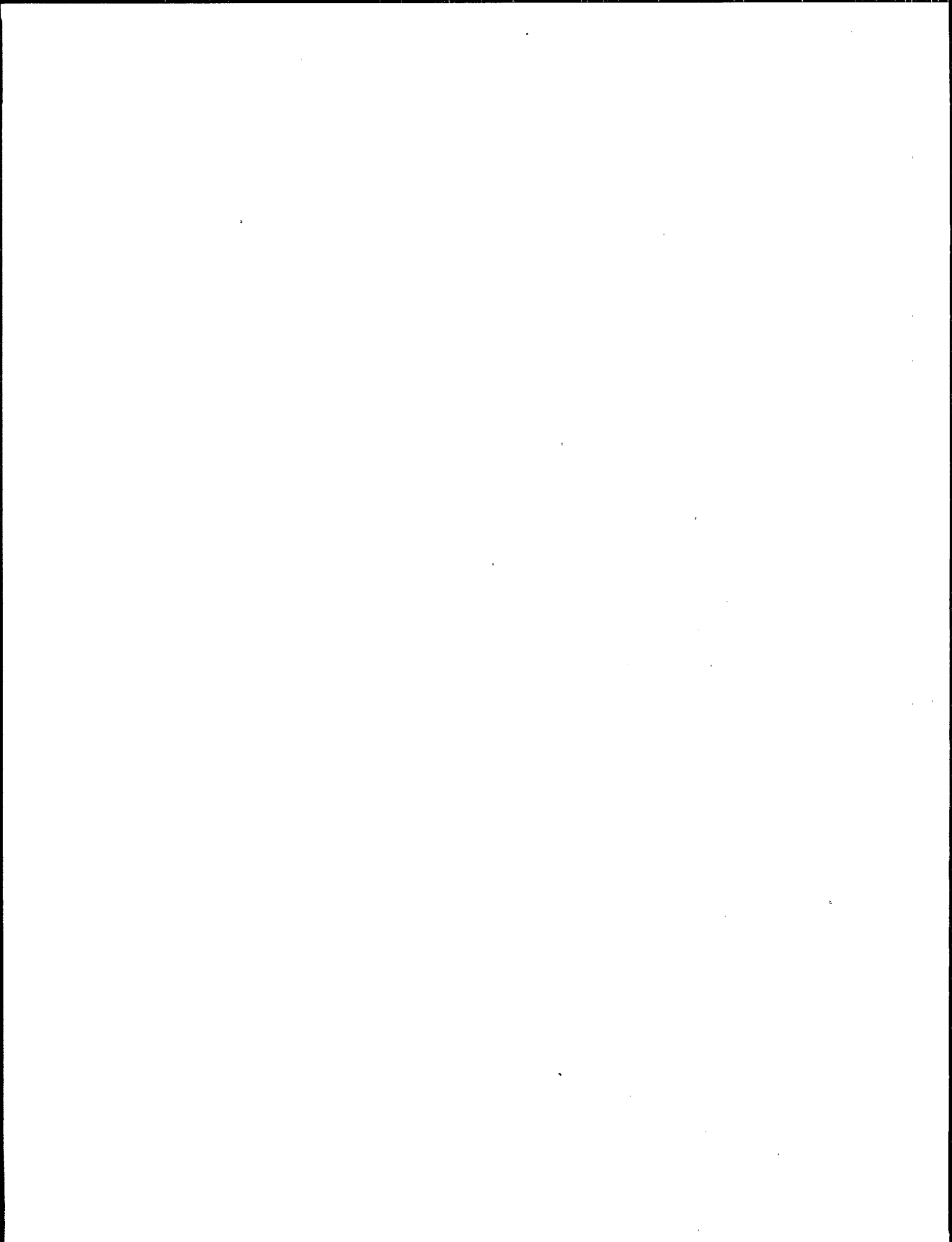
of the completeness and validity of readings and response to specific permit requirements.

## VI. REFERENCES

### A. PRIMARY REFERENCES

The following references were used to develop this document:

- U.S. Environmental Protection Agency. 1979. Continuous air pollution source monitoring systems handbook. EPA 625/6-79-005. June 1979.
- U.S. Environmental Protection Agency. 1980. Interim guidelines and specifications for quality assurance project plans, EPA/QAM-005/80, Office of Research and Development.
- U.S. Environmental Protection Agency. 1986. Test methods for evaluating solid wastes. SW-846, Office of Solid Waste and Emergency Response, Washington, DC. 3rd Edition. September 1986.
- U.S. Environmental Protection Agency. 1989a. Technical support document - incineration of sewage sludge. EPA Office of Water Regulations and Standards, Washington, DC, February 1989.
- U.S. Environmental Protection Agency. 1989b. Hazardous waste incineration measurement guidance manual. Prepared for the U.S. Environmental Protection Agency, Office of Solid Wastes, Washington, DC. EPA 625/6-89-021. June 1989.
- U.S. Environmental Protection Agency. 1989c. POTW sludge sampling and analysis guidance document. Environmental Protection Agency, Washington, DC, Office of Water Programs. August 1989.

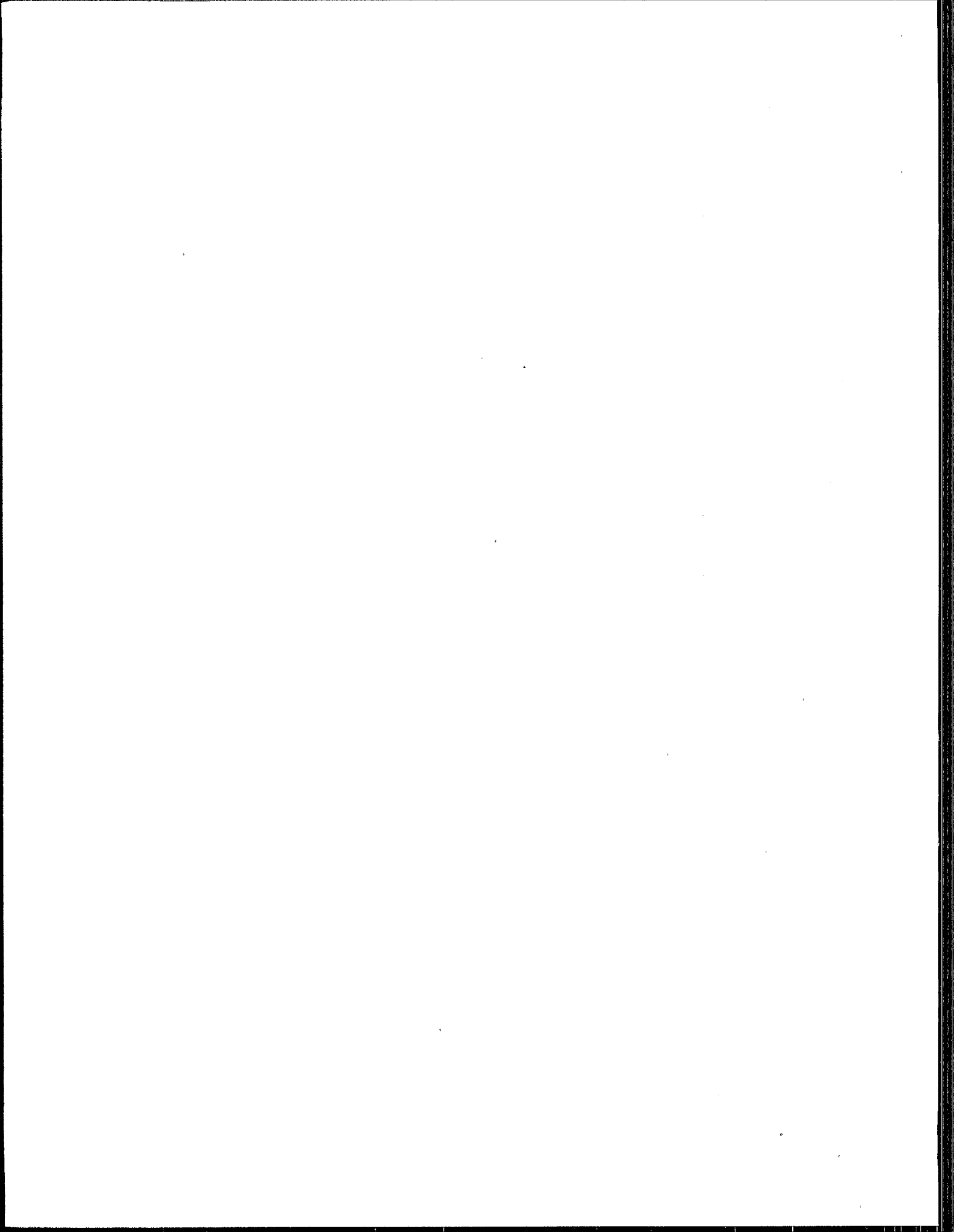




- U.S. Environmental Protection Agency. 1989d. Operation and maintenance of hospital medical waste incinerators. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA-450/3-89-002. March 1989.
- U.S. Environmental Protection Agency. 1989e. Proposed methods for measurements of CO, O<sub>2</sub>, THC, HCl, and metals. Prepared for the U.S. Environmental Protection Agency, Office of Solid Wastes, Washington, DC. Environmental Protection Agency, Office of Solid Waste. November 1989.
- U.S. Environmental Protection Agency. 1990. Handbook on quality assurance/quality control procedures for hazardous waste incineration. Prepared for the U.S. Environmental Protection Agency, Cincinnati, OH. EPA-625/6-89/023, January 1990.
- Federal Register. 1989. Standards for the disposal of sewage sludge, proposed rule. U.S. Environmental Protection Agency, Washington, DC. February 6, 1989.
- Midwest Research Institute. 1986. Methods for continuous rate monitoring of nonliquid hazardous wastes to incinerations. Prepared for the U.S. Environmental Protection Agency, Region IV, Atlanta, GA. EPA Contract No. 68-01-7038, Work Assignment R04-01-73. October 1986.
- Midwest Research Institute. 1989. THC monitor survey. Prepared for the U.S. Environmental Protection Agency, Office of Solid Wastes, Washington, DC. Draft Final Report. June 1989.

#### B. SECONDARY REFERENCES

The following references may provide additional detailed information on air pollution control devices and incineration:

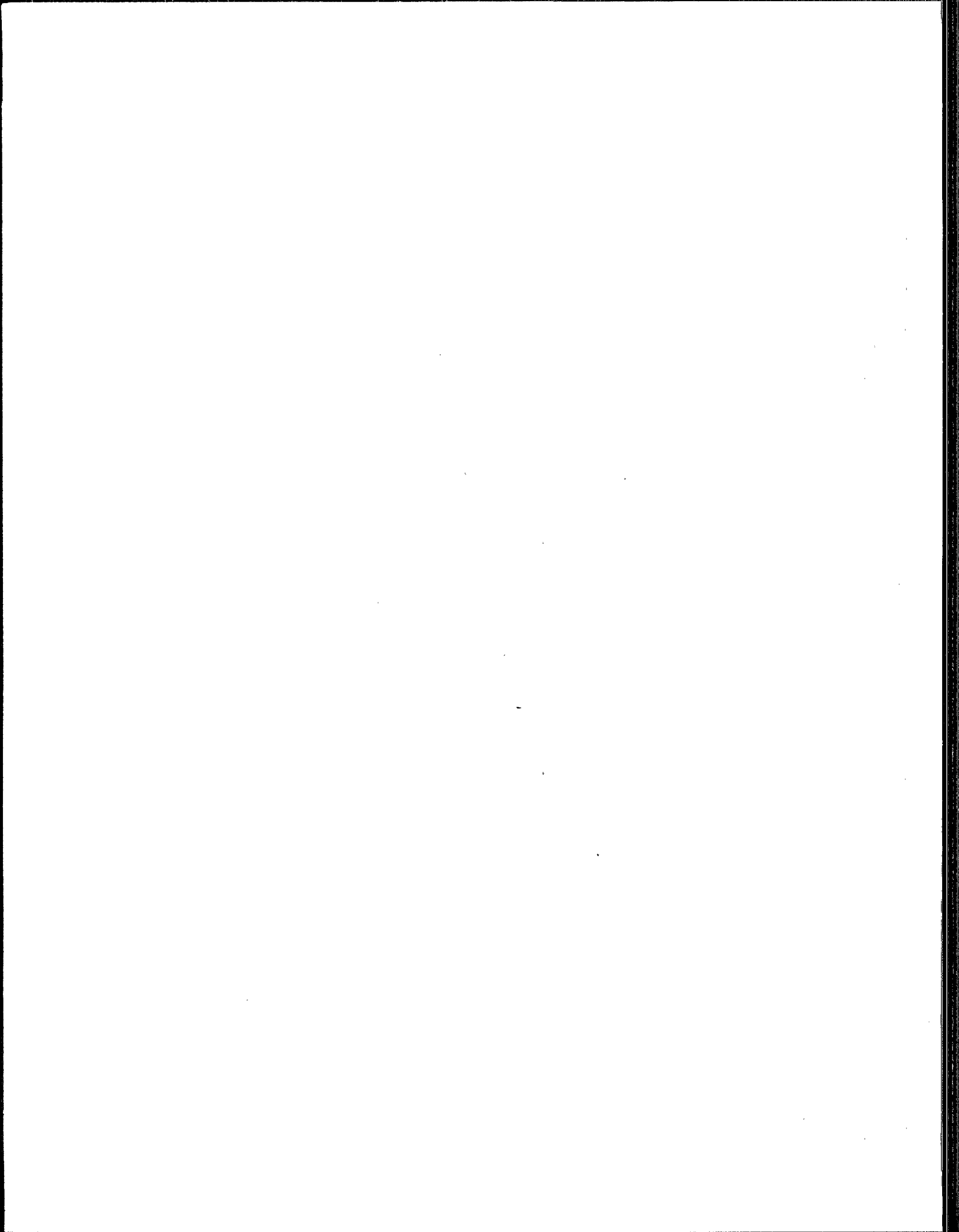


## Air Pollution Control Devices

- U.S. Environmental Protection Agency. 1981. Inspection manual for evaluation of electrostatic precipitator performance. EPA-340/1-79-007. March 1981.
- U.S. Environmental Protection Agency. 1983. Wet scrubber inspection and evaluation manual. EPA-340/1-83-022. September 1983.
- U.S. Environmental Protection Agency. 1984. Fabric filter inspection and evaluation manual. EPA-340/1-84-002. February 1984.
- U.S. Environmental Protection Agency. 1985. Operation and maintenance manual for electrostatic precipitators. EPA/625/1-85-017. September 1985.
- U.S. Environmental Protection Agency. 1985. Flue gas desulfurization inspection and performance evaluation. EPA/625/1-85-019. October 1985.
- U.S. Environmental Protection Agency. 1987. Municipal waste combustion study - flue gas cleaning technology. EPA/530-SW-87-021d. June 1987.
- U.S. Environmental Protection Agency. 1989. Hospital waste incinerator field inspection and source evaluation manual. EPA-340/1-89-001. February 1989.

## Incineration

- U.S. Environmental Protection Agency. 1989. Guidance on setting permit conditions and reporting trial burn results. EPA/625/6-89/019. January 1989.
- Water Pollution Control Federation. 1988. Incineration manual of practice OM-11. Alexandria, VA.

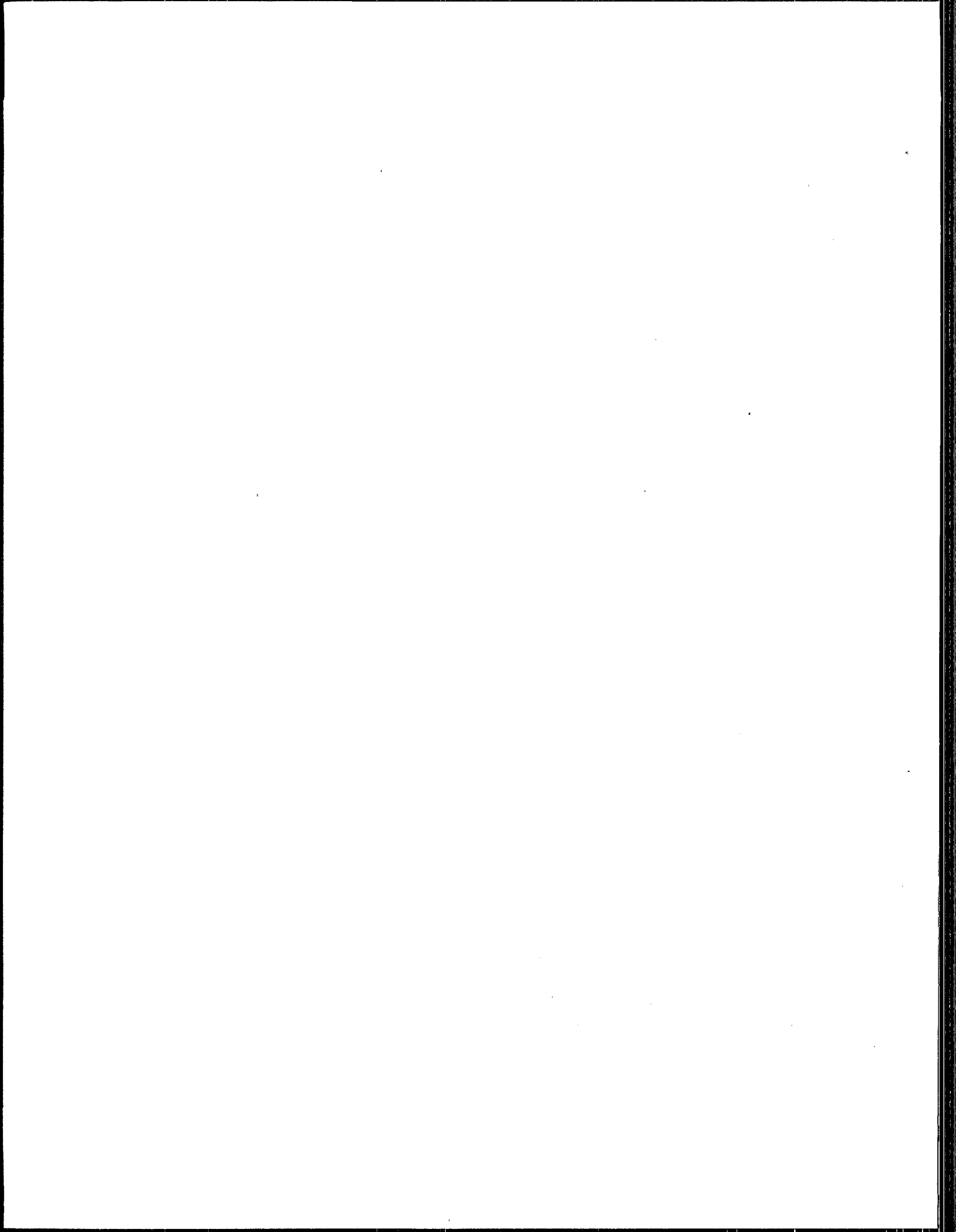


## APPENDIX A

### DRAFT MULTIPLE METALS SAMPLING TRAIN PROCEDURE<sup>a</sup>

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<sup>a</sup>This method is a preliminary draft that has not been formally released by EPA.



DRAFT 8/28/89

## METHODOLOGY FOR THE DETERMINATION OF METALS EMISSIONS IN EXHAUST GASES FROM HAZARDOUS WASTE INCINERATION AND SIMILAR COMBUSTION PROCESSES

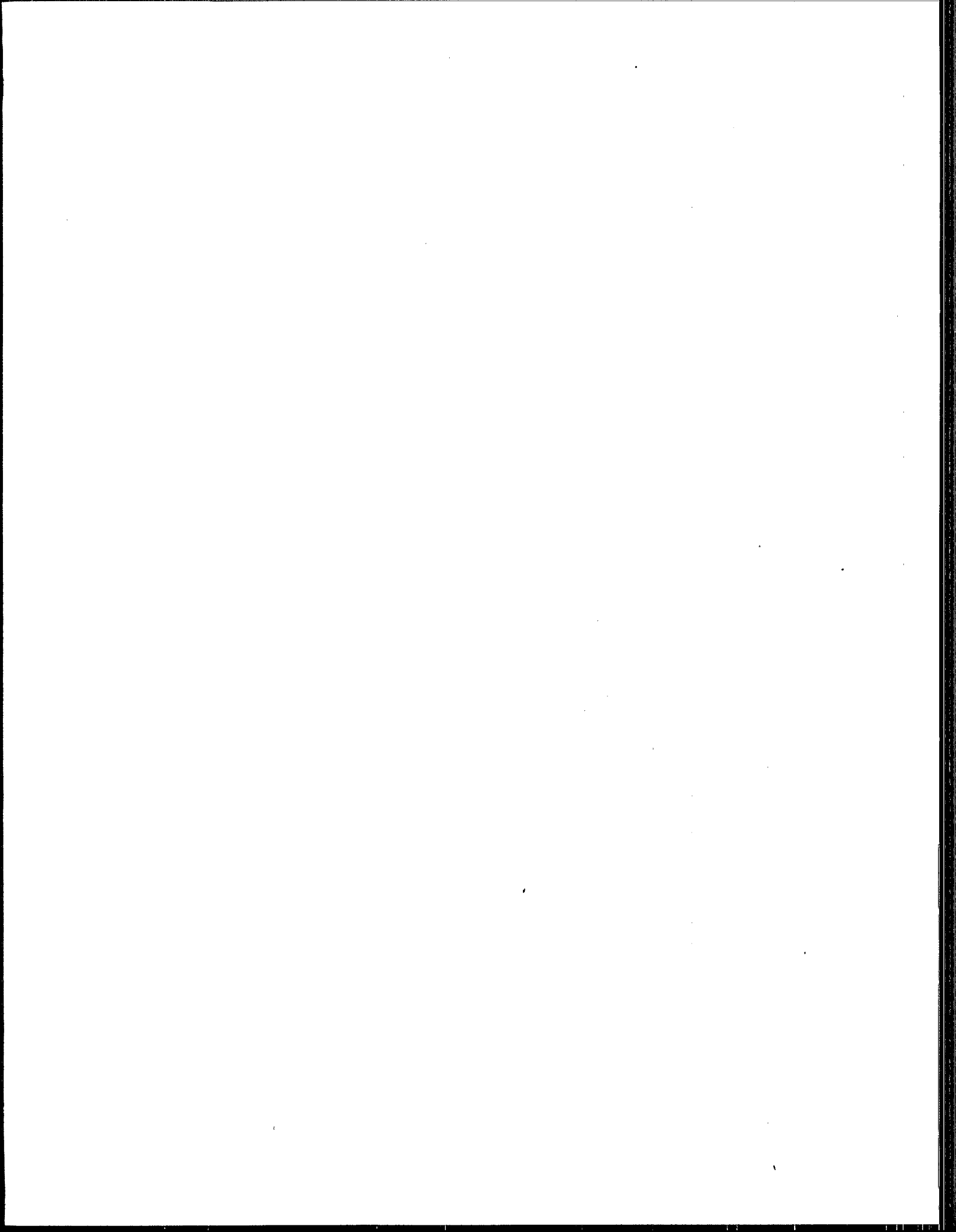
### 1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) emissions from hazardous waste incinerators and similar combustion processes. This method may also be used for the determination of particulate emissions following the additional procedures described. Modifications to the sample recovery and analysis procedures described in this protocol for the purpose of determining particulate emissions may potentially impact the front half mercury determination.\*

1.2 Principle. The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing a solution of dilute nitric acid in hydrogen peroxide in two impingers, and acidic potassium permanganate solution in two (or one) impingers. Sampling train components are recovered and digested in separate front and back half fractions. Materials collected in the sampling train are digested with acid solutions to dissolve inorganics and to remove organic constituents that may create analytical interferences. Acid digestion is performed using conventional Parr<sup>®</sup> Bomb or microwave digestion techniques. The nitric acid and hydrogen peroxide impinger solution, the acidic potassium permanganate impinger solution, and the probe rinse and digested filter solutions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS). Except for the permanganate solution, the remainder of the sampling

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\*Field tests to date have shown that of the total amount of mercury measured by the method, only 0 to <2% was measured in the front half. Therefore, it is tentatively concluded, based on the above data, that particulate emissions may be measured by this train, without significantly altering the mercury results.



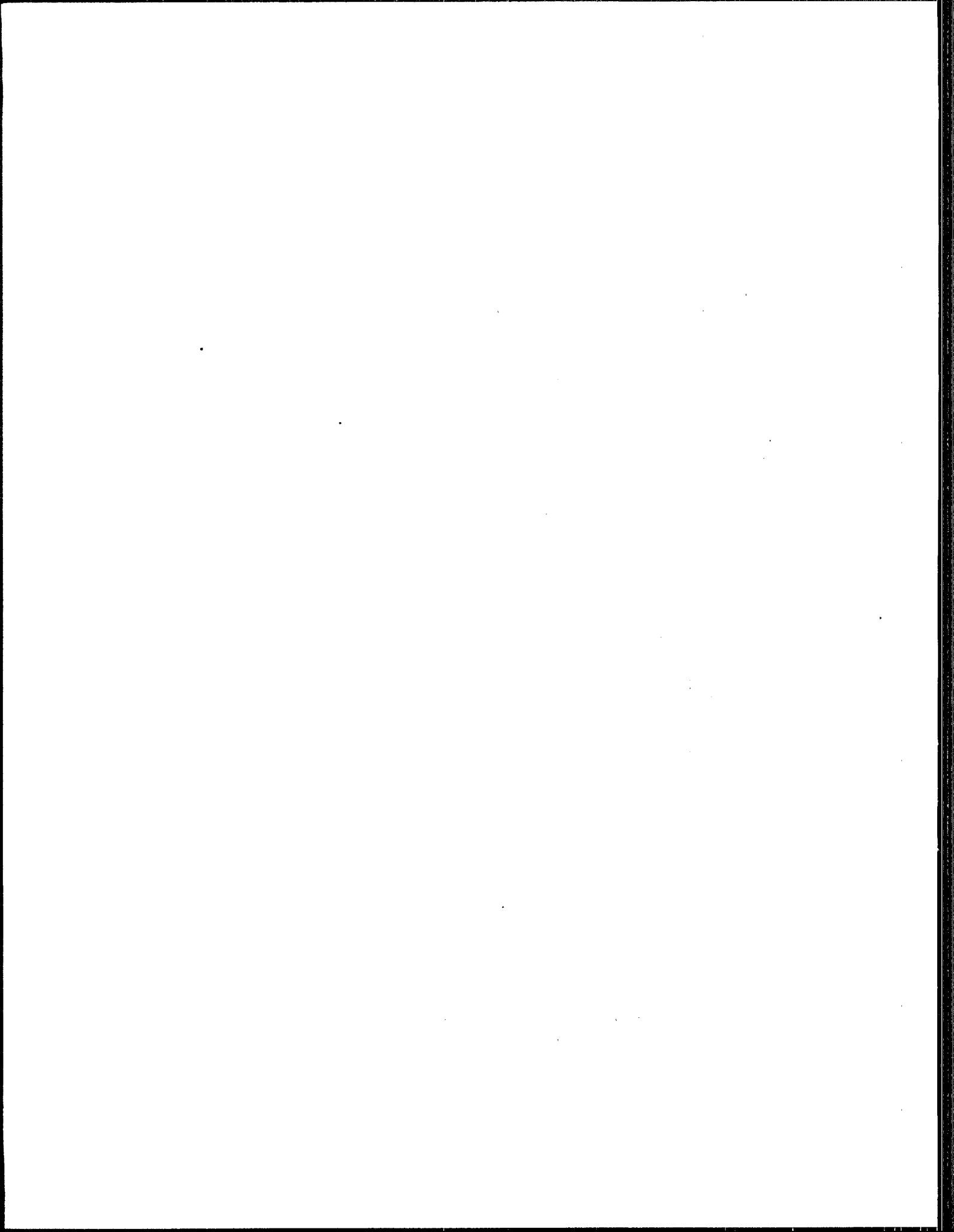


train catches are analyzed for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, lead, selenium, and thallium, if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analyses of all metals if the resulting in-stack method detection limits meet the goal of the testing program. For convenience, aliquots of each digested sample fraction can be combined proportionally for a single analytical determination. The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals including actual sample matrix effects checks.

## 2. Range, Sensitivity, Precision, and Interferences

2.1 Range. For the analyses described in this methodology and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter (ug/ml) range in the analytical finish solution can be analyzed using this technique. Samples containing greater than approximately 50 ug/ml of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 ug/ml of cadmium should be diluted to that level before analysis.

2.2 Analytical Sensitivity. ICAP analytical detection limits for the sample solutions (based on SW-846, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Ti (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml. The use of GFAAS can give added sensitivity compared to the use of direct aspiration AAS for the



following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

Using (1) the procedures described in this method, (2) the analytical detection limits described in the previous paragraph, (3) a volume of 300 ml for the front half and 150 ml for the back half samples, and (4) a stack gas sample volume of 1.25 m<sup>3</sup>, the corresponding in-stack method detection limits are presented in Table A-1 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where: A = analytical detection limit, ug/ml.

B = volume of sample prior to aliquot for analysis, ml.

C = stack sample volume, dscm (dsm<sup>3</sup>).

D = in-stack detection limit, ug/m<sup>3</sup>.

Values in Table A-1 are calculated for the front and back half and/or the total train.

To ensure optimum sensitivity in obtaining the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition should be used to establish the quality of the data.

Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table A-1 for a specific test by using one or more of the following options:

- o A normal 1-hour sampling run collects a stack gas sampling volume of about 1.25 m<sup>3</sup>. If the sampling time is increased and 5 m<sup>3</sup> are collected, the in-stack method detection limits would be one fourth of the values shown in Table A-1 (this means that with this change, the method is four times more sensitive than normal).
- o The in-stack detection limits assume that all of the sample is digested (with exception of the aliquot for mercury) and the final liquid volumes for analysis are 300 ml for the front half and 150 ml for the

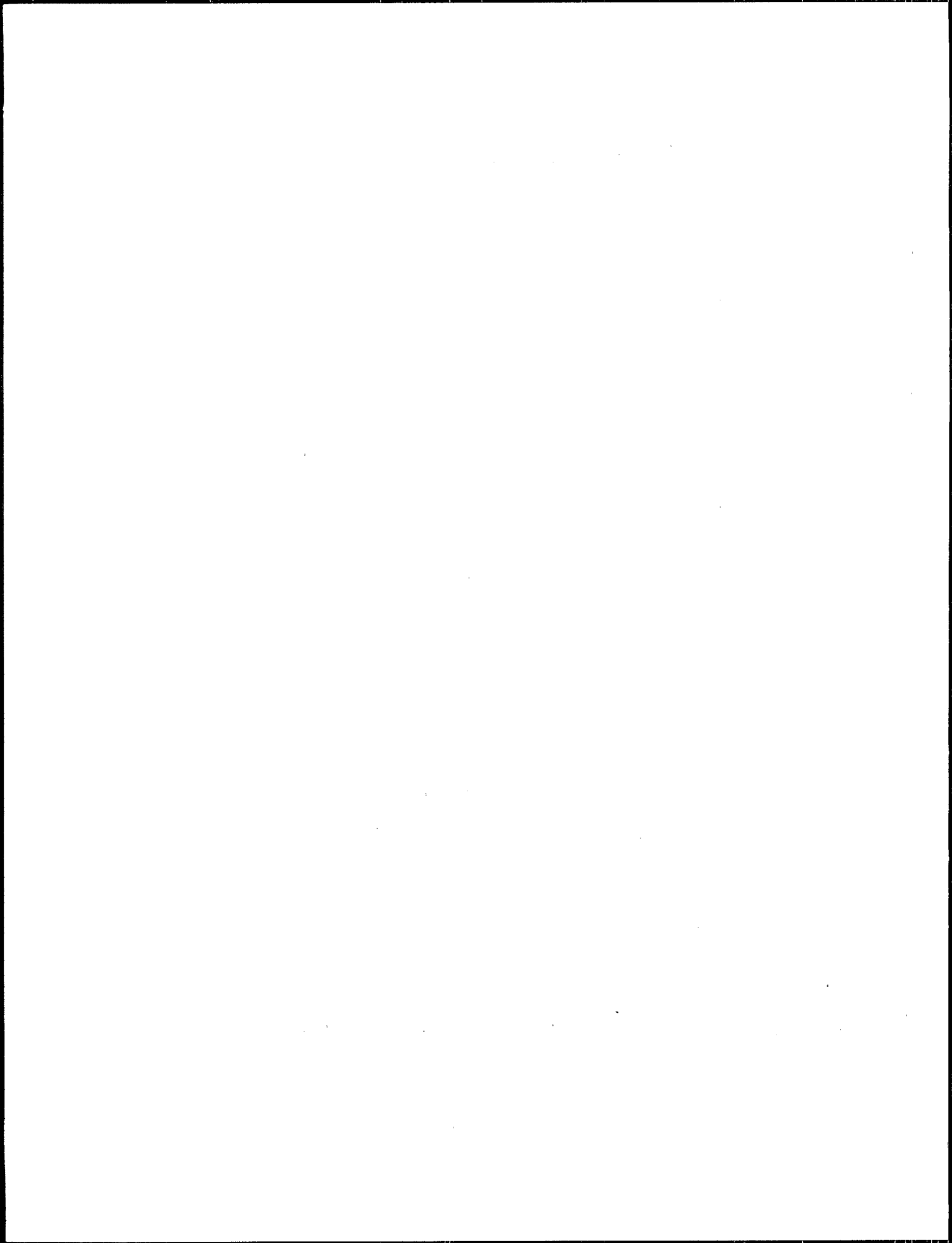


TABLE A-1. IN-STACK METHOD DETECTION LIMITS ( $\mu\text{g}/\text{m}^3$ )  
FOR TRAIN FRACTIONS USING ICAP AND AAS

Metal	Front Half Fraction 1 Probe and Filter	Back Half <sub>1</sub> Fraction 2 Impingers 1-3	Back Half <sub>2</sub> Fraction 3 Impingers 4-5	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.05**	0.03**	0.03**	0.11**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

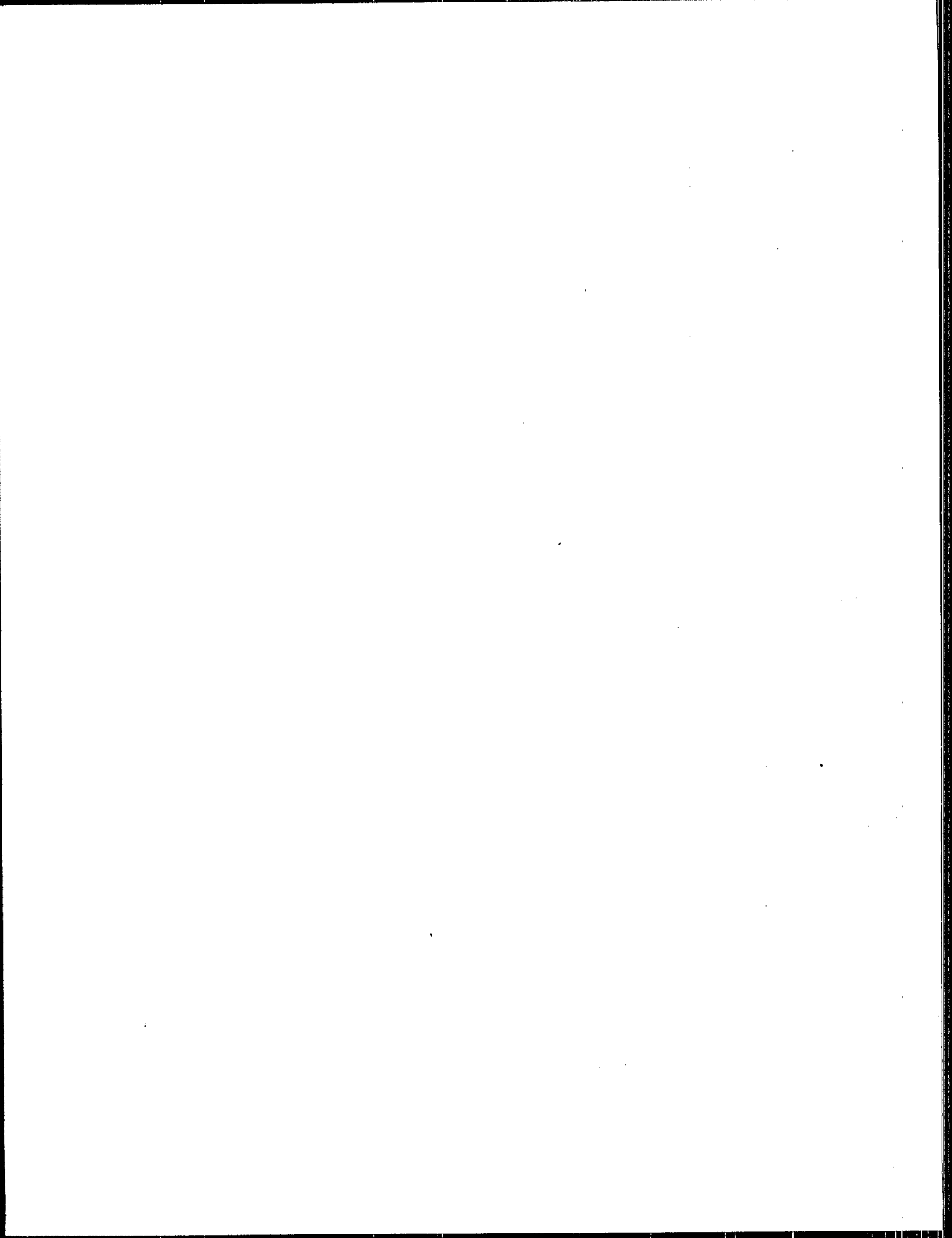
( ) \* Detection limit when analyzed by GFAAS.

\*\* Detection limit when analyzed by CVAAS.

Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

back half sample. If the front half volume is reduced from 300 ml to 30 ml, the front half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back half volume is reduced from 150 ml to 25 ml, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal sample volume. A volume less than 25 ml may not allow resolubilization of the residue and may increase interference by other compounds.

o When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).



- o Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase limits. The front half and back half<sub>1</sub> samples (Fractions 1 and 2) can be combined prior to analysis. The resultant liquid volume (excluding Fraction 3, which must be analyzed separately) is recorded. Combining the sample as described does not allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of Fraction 3 must be considered.
- o The above discussion assumes no blank correction. Blank corrections are discussed later in this method.

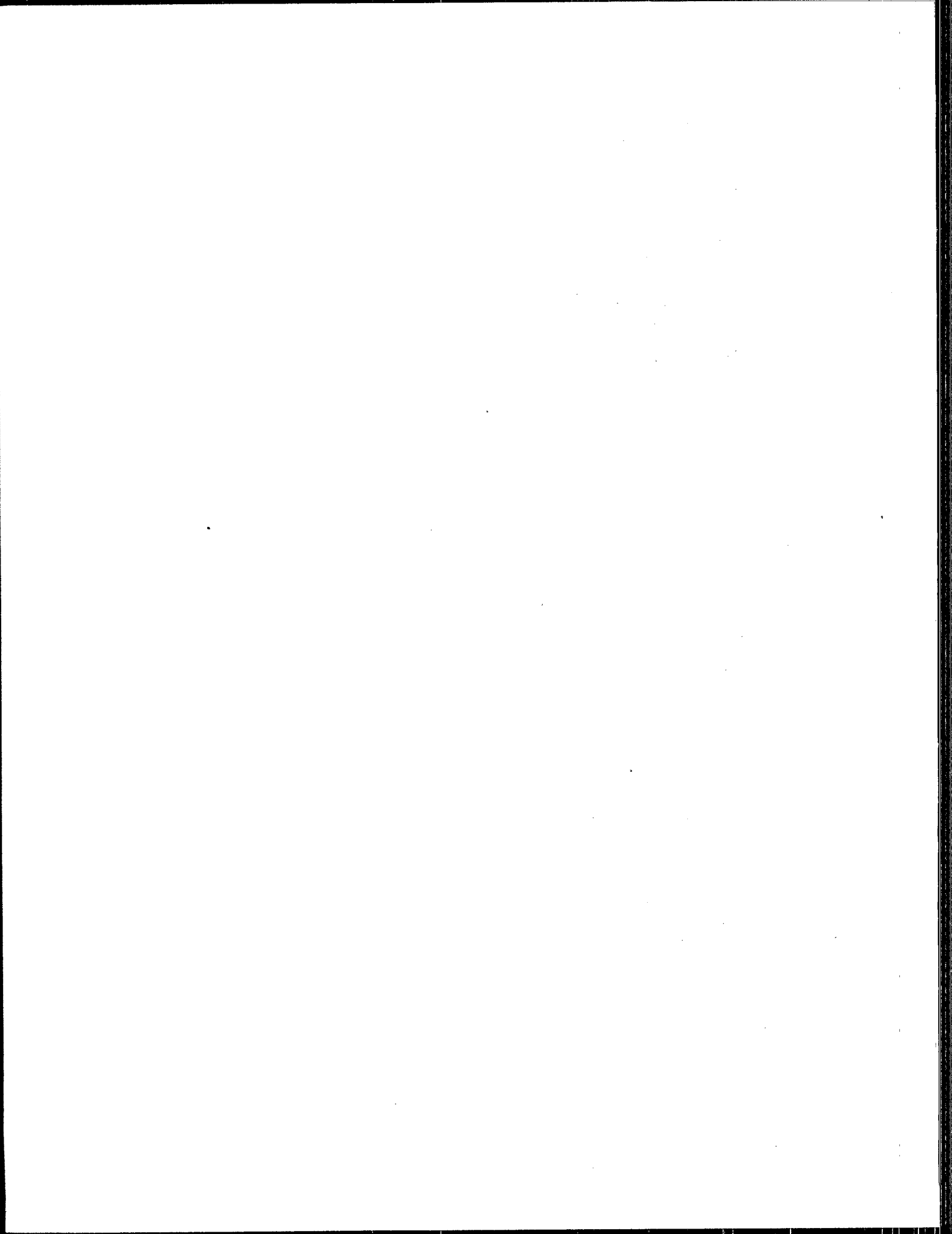
2.3 Precision. The precisions (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese and silver were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

2.4 Interferences. Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICAP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Refer to EPA Method 6010 (SW-846) for details on potential interferences for this method. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

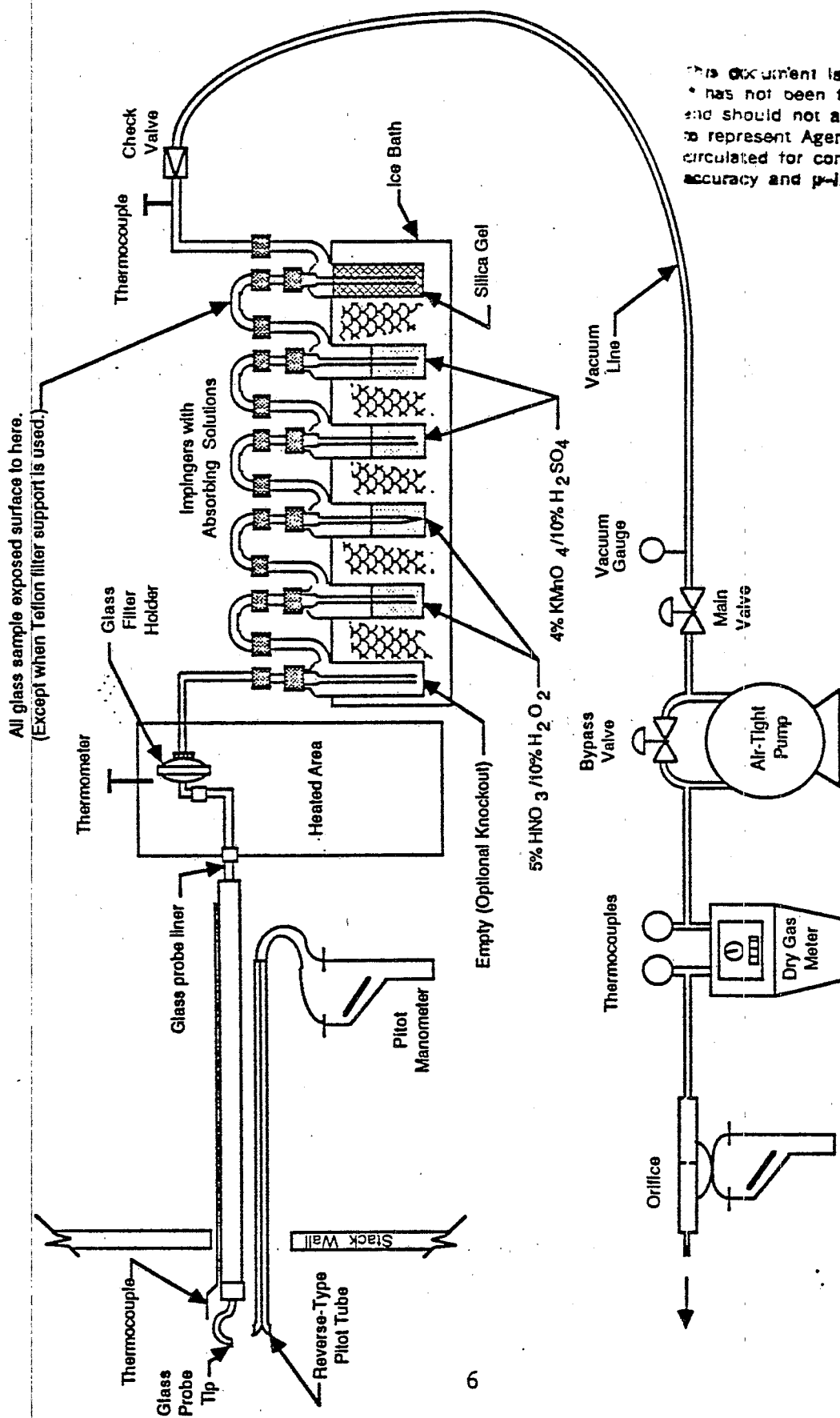
### 3. Apparatus

3.1 Sampling Train. A schematic of the sampling train is shown in Figure A-1. It is similar to the Method 5 train. The sampling train consists of the following components.

3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2. Glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or

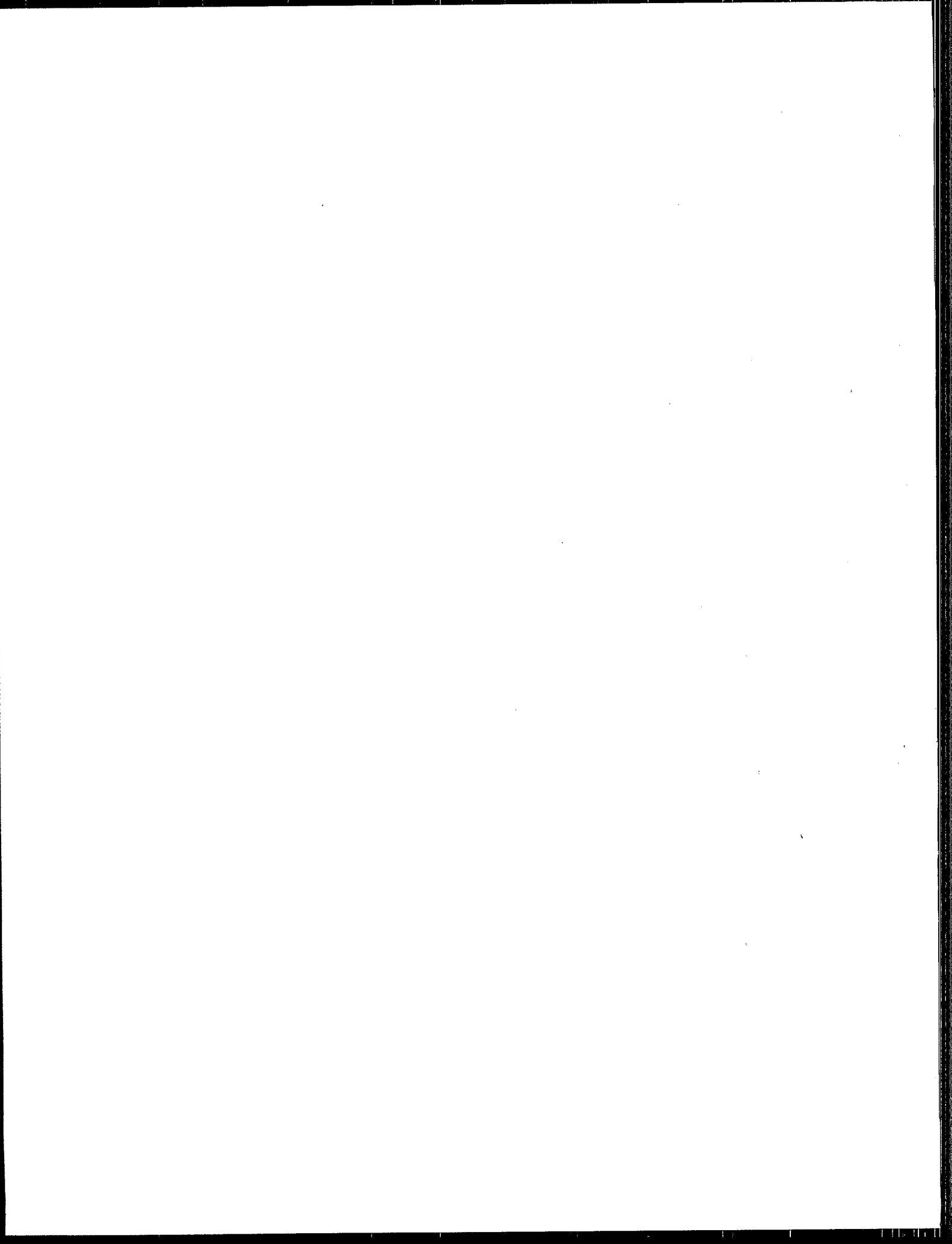






This document is a preliminary draft.  
It has not been formally released by EPA  
and should not at this stage be construed  
to represent Agency policy. It is being  
circulated for comment on its technical  
accuracy and policy implications.

Figure A-1. Schematic of multiple metals sampling train.



interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction of the stack sample test results can be made because of the effect on the results by the probe tip.

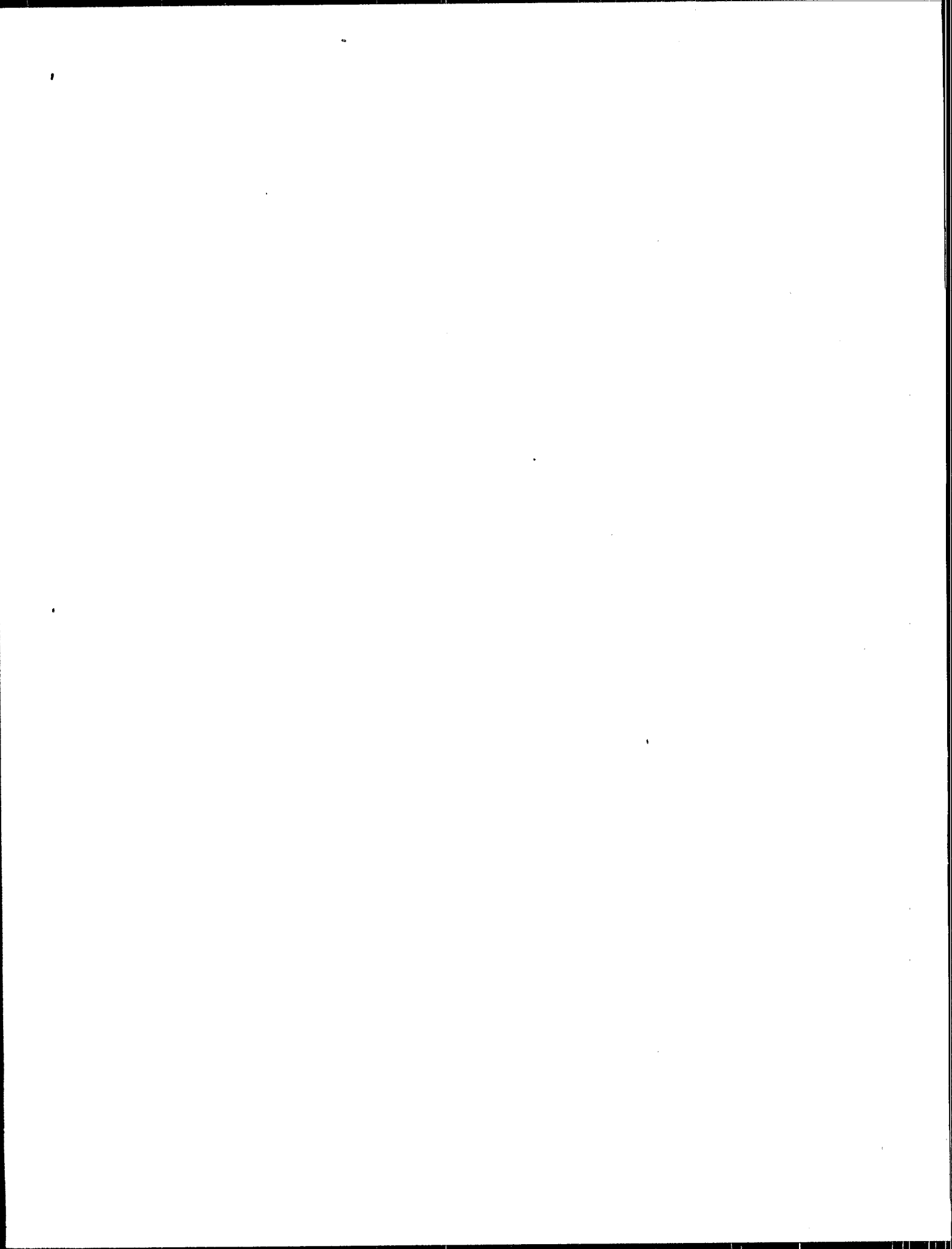
3.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 2.1 and 2.2, respectively.

3.1.3 Filter Holder. Glass, same as Method 5, Section 2.1.5, except that a Teflon filter support must be used to replace the glass frit.

3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.

3.1.5 Condenser. The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The condensing system should consist of four to six impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a water knockout trap for use during test conditions which require such a trap. The impingers to be used in the metals train are now described. When the first impinger is used as a water knockout, it shall be appropriately-sized for an expected large moisture catch and constructed generally as described for the first impinger in Method 5, Paragraph 2.1.7. The second impinger (or the first  $\text{HNO}_3/\text{H}_2\text{O}_2$  impinger) shall also be as described for the first impinger in Method 5. The third impinger (or the impinger used as the second  $\text{HNO}_3/\text{H}_2\text{O}_2$  impinger) shall be the same as the Greenburg Smith impinger with the standard tip described as the second impinger in Method 5, Paragraph 2.1.7. All other impingers used in the metals train are the same as the second impinger (the first  $\text{HNO}_3/\text{H}_2\text{O}_2$  impinger) previously described in this paragraph. In summary, the first impinger should be empty, the second and third shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 4.2.1), the fourth (and fifth, if required) shall contain a known quantity of acidic potassium permanganate solution (Section 4.2.2), and the last impinger shall contain a known quantity of silica gel or equivalent desiccant. A thermometer capable of measuring to within  $1^\circ\text{C}$  ( $2^\circ\text{F}$ ) shall be placed at the outlet of the last impinger. When the water knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers are removed.

3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.



3.1.7 Teflon Tape. For capping openings and sealing connections on the sampling train.

3.2 Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

3.2.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes. For quantitative recovery of materials collected in the front half of the sampling train. Description of acceptable all-Teflon component brushes to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

3.2.2 Sample Storage Containers. Glass bottles with Teflon-lined caps, 1000- and 500-ml, shall be used for  $\text{KMnO}_4$ -containing samples and blanks. Polyethylene bottles may be used for other sample types.

3.2.3 Graduated Cylinder. Glass or equivalent.

3.2.4 Funnel. Glass or equivalent.

3.2.5 Labels. For identification of samples.

3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

3.3 Sample Preparation and Analysis. For the analysis, the following equipment is needed:

3.3.1 Volumetric Flasks, 100 ml, 250 ml, and 1000 ml. For preparation of standards and sample dilution.

3.3.2 Graduated Cylinders. For preparation of reagents.

3.3.3 Parr<sup>R</sup> Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent).

3.3.4 Beakers and Watchglasses. 250 ml beakers for sample digestion with watchglasses to cover the tops.

3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

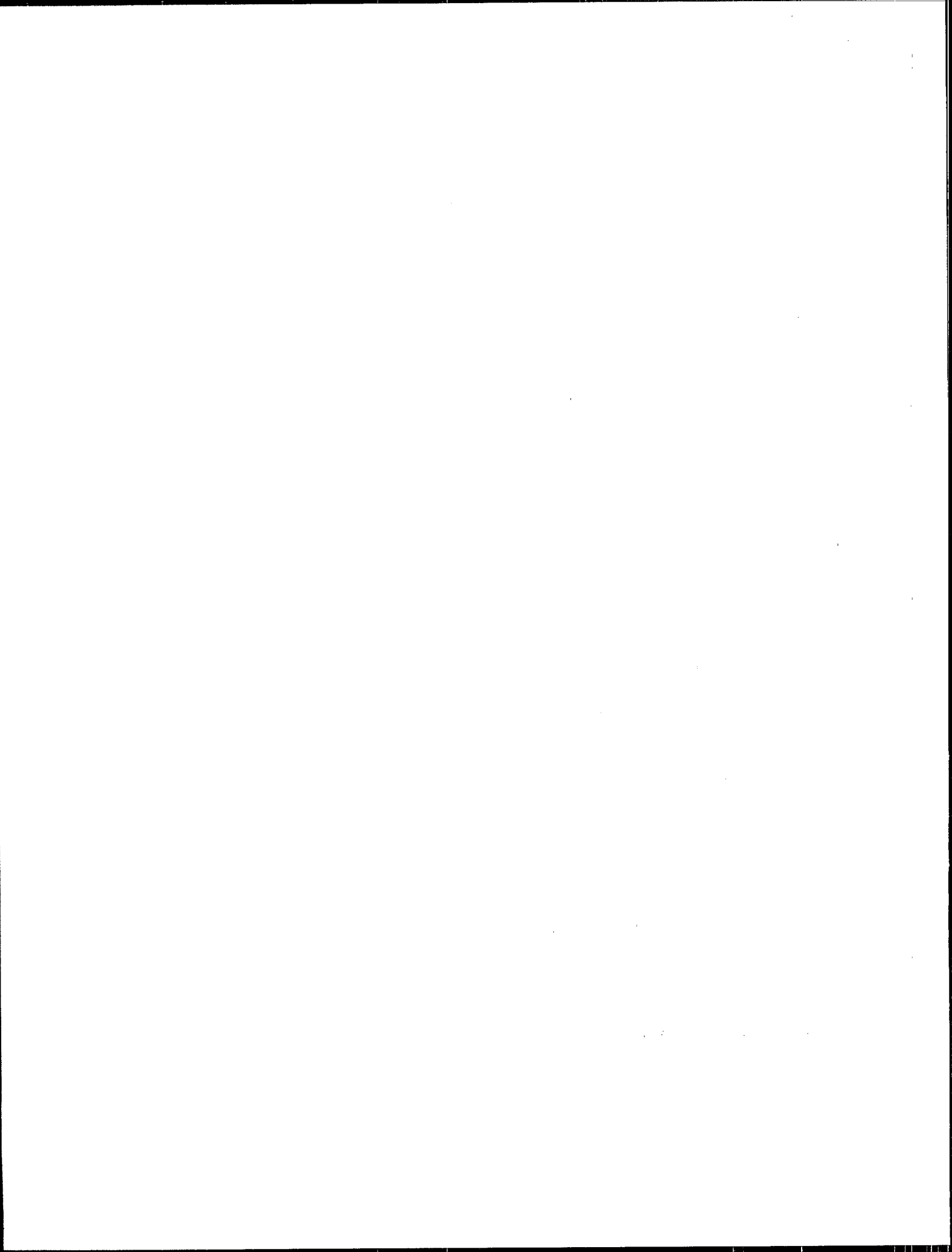
3.3.6 Filter Funnels. For holding filter paper.

3.3.7 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.

3.3.8 Disposable Pasteur Pipets and Bulbs.

3.3.9 Volumetric Pipets.

3.3.10 Analytical Balance. Accurate to within 0.1 mg.



3.3.11 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures.

3.3.12 Hot Plates.

3.3.13 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.3.13.1 Graphite Furnace Attachment. With antimony, arsenic, cadmium, lead, selenium, thallium, and hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as EPA Methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium).

3.3.13.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. Same as EPA Method 7470.

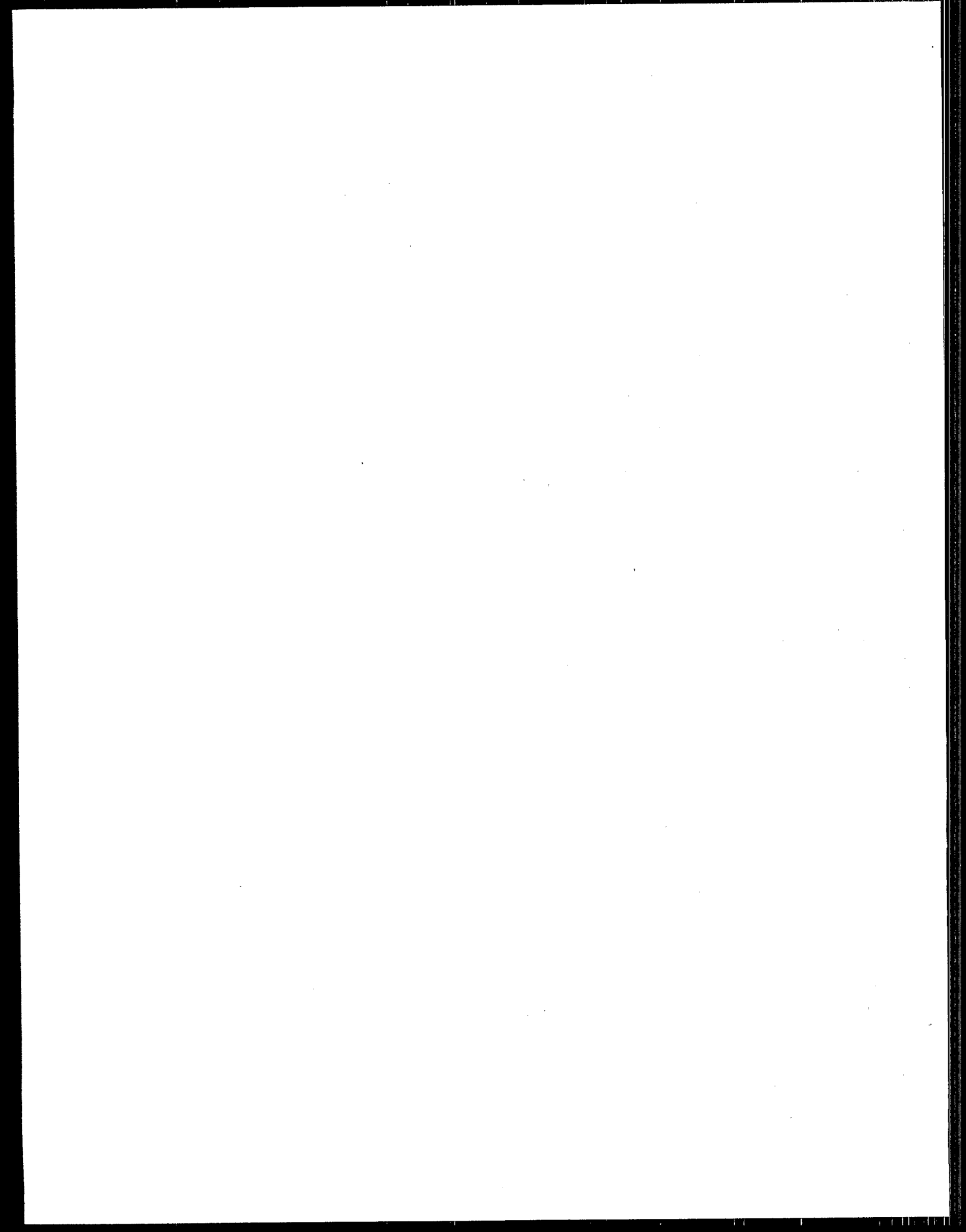
3.3.14 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010.

#### 4. Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

4.1 Sampling. The reagents used in sampling are as follows:

4.1.1 Filters. The filters shall contain less than 1.3 ug/in.<sup>2</sup> of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber filters without organic binders shall be used. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D2986-71 (incorporated by reference). For particulate determination in sources containing SO<sub>2</sub> or SO<sub>3</sub>, the filter material must be of a type that is unreactive to SO<sub>2</sub> or SO<sub>3</sub>, as described in EPA Method 5. Quartz fiber filters meeting these requirements are recommended.





4.1.2 Water. To conform to ASTM Specification D1193.77, Type II (incorporated by reference). Analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

4.1.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.1.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.1.5 Hydrogen Peroxide, 30 Percent (V/V).

4.1.6 Potassium Permanganate.

4.1.7 Sulfuric Acid. Concentrated.

4.1.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.

4.2 Pretest Preparation for Sampling Reagents.

4.2.1 Nitric Acid ( $\text{HNO}_3$ )/Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ) Absorbing Solution, 5 Percent  $\text{HNO}_3$ /10 Percent  $\text{H}_2\text{O}_2$ . Add 50 ml of concentrated  $\text{HNO}_3$  and 333 ml of 30 percent  $\text{H}_2\text{O}_2$  to a 1000-ml volumetric flask or graduated cylinder containing approximately 500 ml of water. Dilute to volume with water. The reagent shall contain less than 2 ng/ml of each target metal.

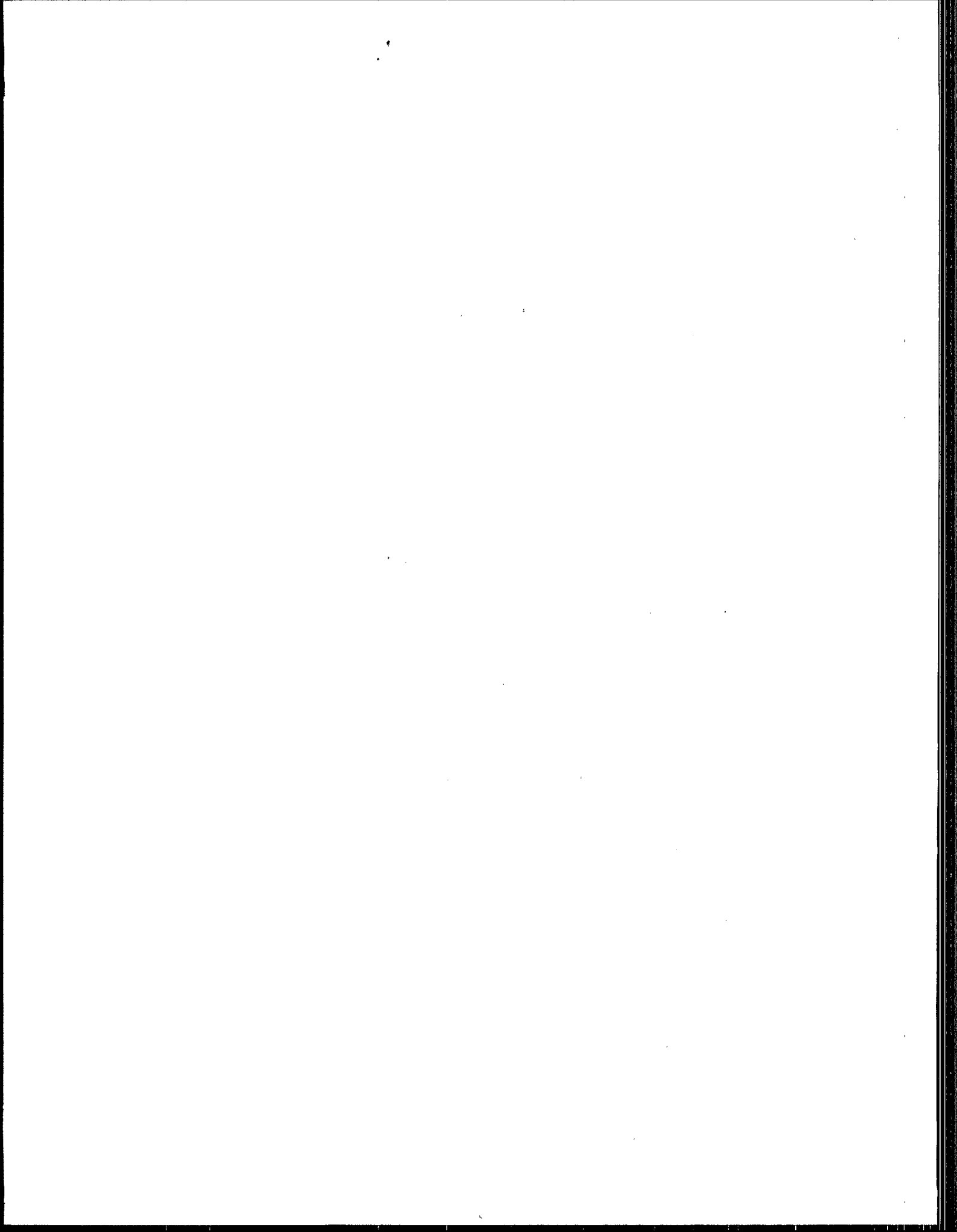
4.2.2 Acidic Potassium Permanganate ( $\text{KMnO}_4$ ) Absorbing Solution, 4 Percent  $\text{KMnO}_4$  (W/V). Prepare fresh daily. Dissolve 40 g of  $\text{KMnO}_4$  in sufficient 10 percent  $\text{H}_2\text{SO}_4$  to make 1 liter. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles should not be fully filled and should be vented both to relieve excess pressure and prevent explosion due to pressure buildup. Venting is highly recommended, but should not allow contamination of the sample; a No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.2.3 Nitric Acid, 0.1 N. Add 6.3 ml of concentrated  $\text{HNO}_3$  (70 percent) to a graduated cylinder containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

4.2.4 Hydrochloric Acid ( $\text{HCl}$ ), 8 N. Add 690 ml of concentrated  $\text{HCl}$  to a graduated cylinder containing 250 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of Hg.

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#### 4.3 Glassware Cleaning Reagents.

4.3.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.

4.3.2 Water. To conform to ASTM Specifications D1193-77, Type II.

4.3.3 Nitric Acid, 10 Percent (V/V). Add 500 ml of concentrated  $\text{HNO}_3$  to a graduated cylinder containing approximately 4000 ml of water. Dilute to 5000 ml with water.

#### 4.4 Sample Digestion and Analysis Reagents.

4.4.1 Hydrochloric Acid, Concentrated.

4.4.2 Hydrofluoric Acid, Concentrated.

4.4.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.

4.4.4 Nitric Acid, 10 Percent (V/V). Add 100 ml of concentrated  $\text{HNO}_3$  to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.4.5 Nitric Acid, 5 Percent (V/V). Add 50 ml of concentrated  $\text{HNO}_3$  to 800 ml of water. Dilute to 1000 ml with water. Reagent shall contain less than 2 ng/ml of each target metal.

4.4.6 Water. To conform to ASTM Specifications D1193-77, Type II.

4.4.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See EPA Method 7470 For preparation.

4.4.8 Stannous Chloride.

4.4.9 Potassium Permanganate, 5 Percent (W/V).

4.4.10 Sulfuric Acid, Concentrated.

4.4.11 Nitric Acid, 50 Percent (V/V).

4.4.12 Potassium Persulfate, 5 Percent (W/V).

4.4.13 Nickel Nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

4.4.14 Lanthanum Oxide,  $\text{La}_2\text{O}_3$ .

4.4.15 AAS Grade Hg Standard, 1000 ug/ml.

4.4.16 AAS Grade Pb Standard, 1000 ug/ml.

4.4.17 AAS Grade As Standard, 1000 ug/ml.

4.4.18 AAS Grade Cd Standard, 1000 ug/ml.

4.4.19 AAS Grade Cr Standard, 1000 ug/ml.

4.4.20 AAS Grade Sb Standard, 1000 ug/ml.

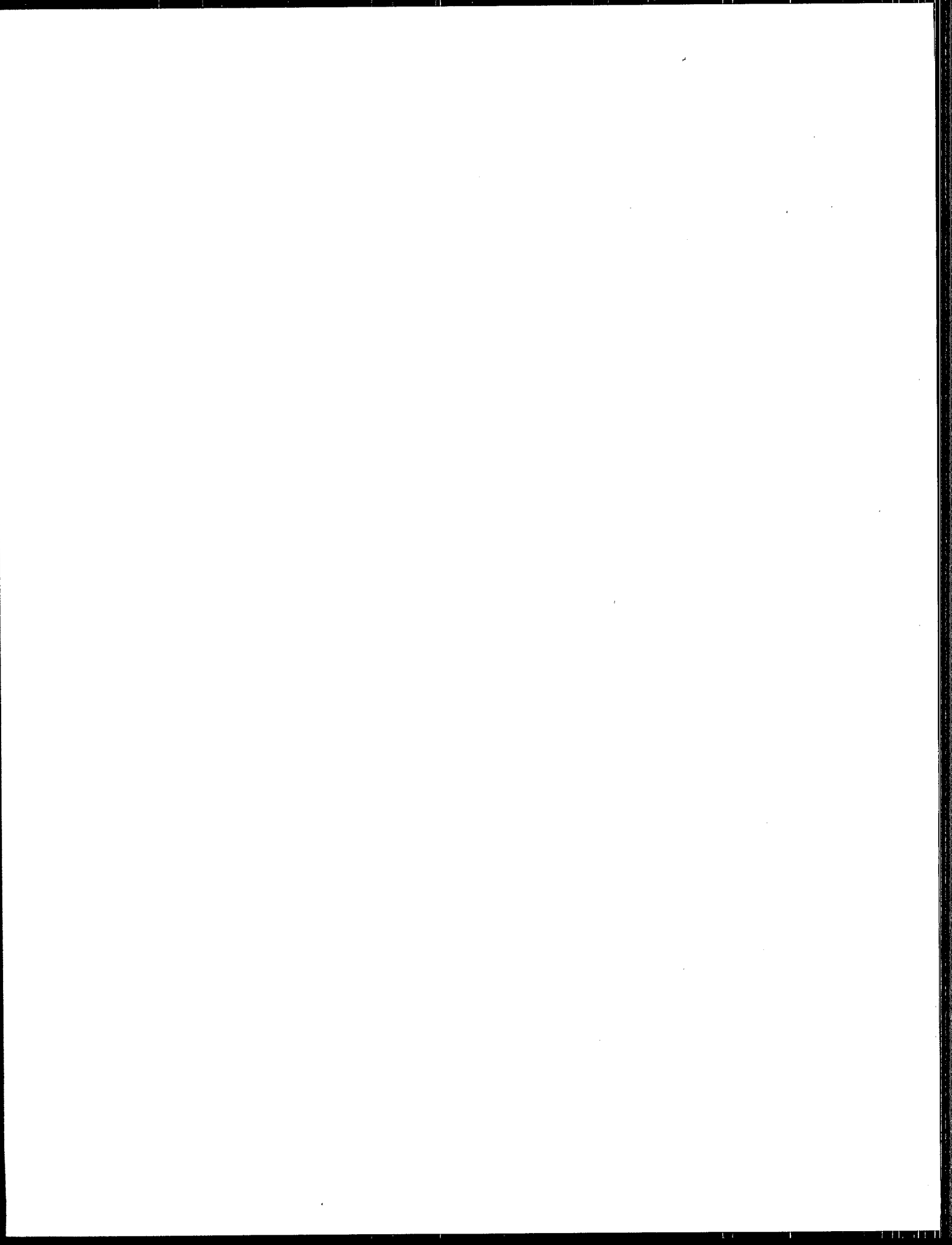
4.4.21 AAS Grade Ba Standard, 1000 ug/ml.

4.4.22 AAS Grade Be Standard, 1000 ug/ml.

4.4.23 AAS Grade Cu Standard, 1000 ug/ml.

4.4.24 AAS Grade Mn Standard, 1000 ug/ml.

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- 4.4.25 AAS Grade Ni Standard, 1000 ug/ml.
- 4.4.26 AAS Grade P Standard, 1000 ug/ml.
- 4.4.27 AAS Grade Se Standard, 1000 ug/ml.
- 4.4.28 AAS Grade Ag Standard, 1000 ug/ml.
- 4.4.29 AAS Grade Tl Standard, 1000 ug/ml.
- 4.4.30 AAS Grade Zn Standard, 1000 ug/ml.
- 4.4.31 AAS Grade Al Standard, 1000 ug/ml.
- 4.4.32 AAS Grade Fe Standard, 1000 ug/ml.

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4.4.33 The metals standards may also be made from solid chemicals as described in EPA Method 200.7. EPA Method 7470 or Standard Methods for the Analysis of Water and Wastewater. 15th Edition, Method 303F should be referred to for additional information on mercury standards.

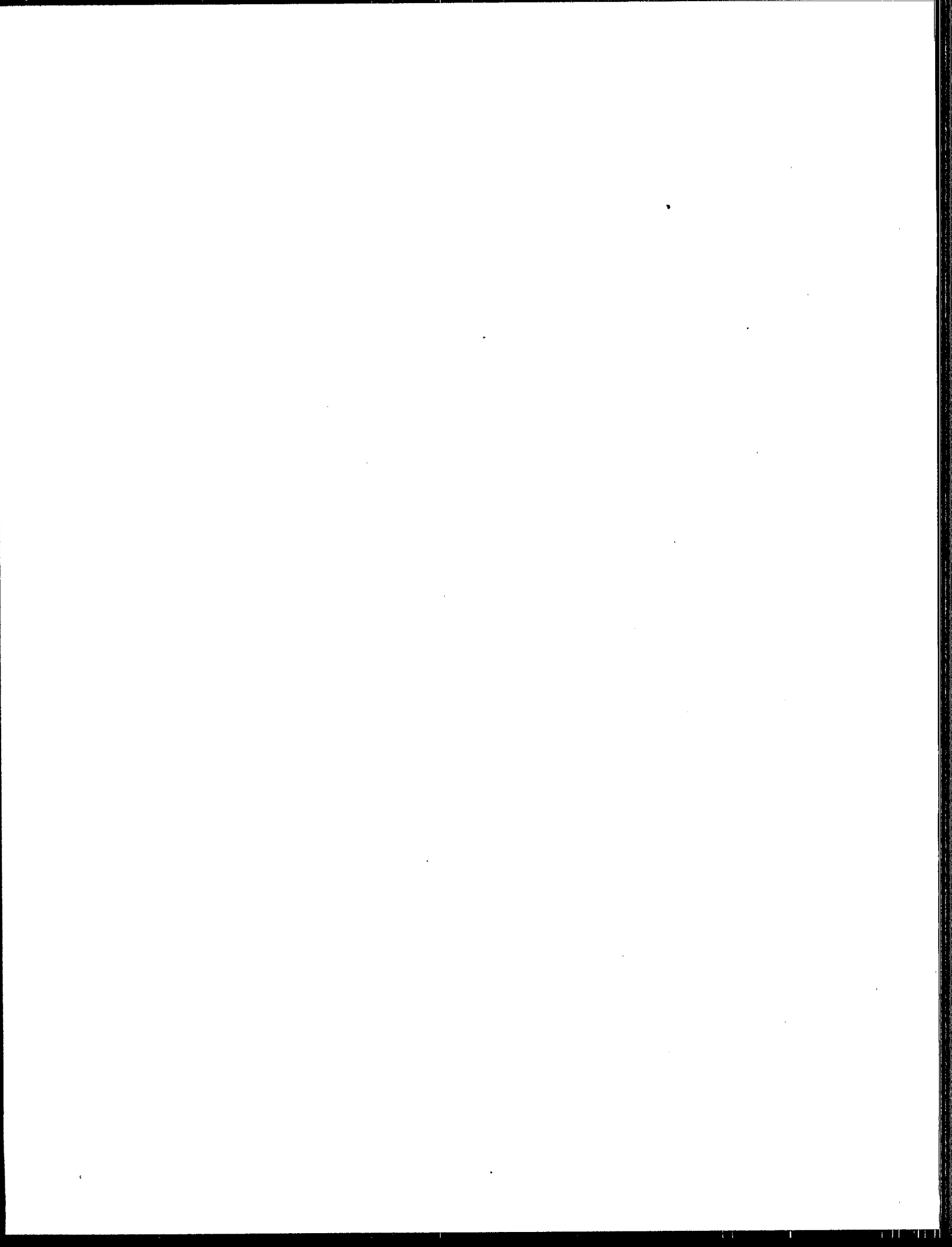
4.4.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10 ug/ml intermediate mercury standard by adding 5 ml of 1000 ug/ml mercury stock solution to a 500 ml volumetric flask; dilute to 500 ml by first adding 20 ml of 15 percent  $\text{HNO}_3$  and then adding water. Prepare a working mercury standard solution fresh daily: add 5 ml of the 10 ug/ml intermediate standard to a 250 ml volumetric flask and dilute to 250 ml with 5 ml of 4 percent  $\text{KMnO}_4$ , 5 ml of 15 percent  $\text{HNO}_3$ , and then water. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution. Quality control samples should be prepared by making a separate 10 ug/ml standard and diluting until in the range of the calibration.

4.4.35 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

#### MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 ug/ml solutions with 5 percent nitric acid. A minimum of one standard and a blank can be used to form each calibration curve. However, a



separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve should be prepared. Suggested standard levels are 50 ug/ml for Al, 25 ug/ml for Cr and Pb, 15 ug/ml for Fe, and 10 ug/ml for the remaining elements. Standards containing less than 1 ug/ml of metal should be prepared daily. Standards containing greater than 1 ug/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.4.36 Graphite Furnace AAS Standards for Antimony, Arsenic, Cadmium, Lead, Selenium, and Thallium. Prepare a 10 ug/ml standard by adding 1 ml of 1000 ug/ml standard to a 100 ml volumetric flask. Dilute to 100 ml with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched; e.g., if the samples contain 6 percent nitric acid and 4 percent hydrofluoric acid, the standards should also be made up with 6 percent nitric acid and 4 percent hydrofluoric acid. Prepare a 100 ng/ml standard by adding 1 ml of the 10 ug/ml standard to a 100 ml volumetric flask and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by dilution of the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10 ug/ml standard and diluting until it is in the range of the samples. Standards containing less than 1 ug/ml of metal should be prepared daily. Standards containing greater than 1 ug/ml of metal should be stable for a minimum of 1 to 2 weeks.

#### 4.4.37 Matrix Modifiers.

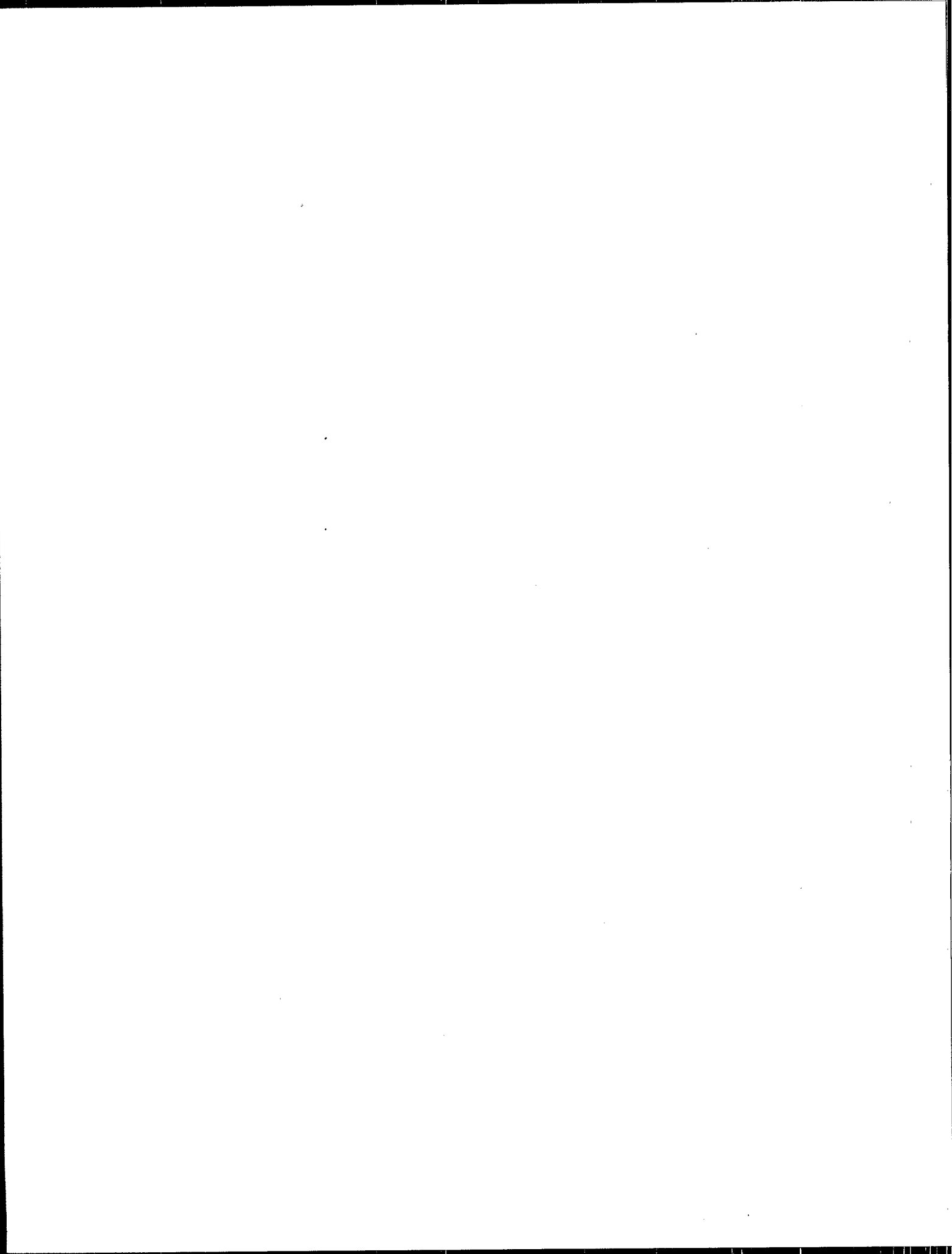
4.4.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in approximately 50 ml of water in a 100 ml volumetric flask. Dilute to 100 ml with water.

4.4.37.2 Nickel Nitrate, One-tenth Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for As.

4.4.37.3 Lanthanum. Dissolve 0.5864 g of  $\text{La}_2\text{O}_3$  in 10 ml of concentrated  $\text{HNO}_3$  and dilute to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for Pb.

## 5. Procedure

5.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers should be trained and experienced with the test procedures.





5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled, prior to sampling.

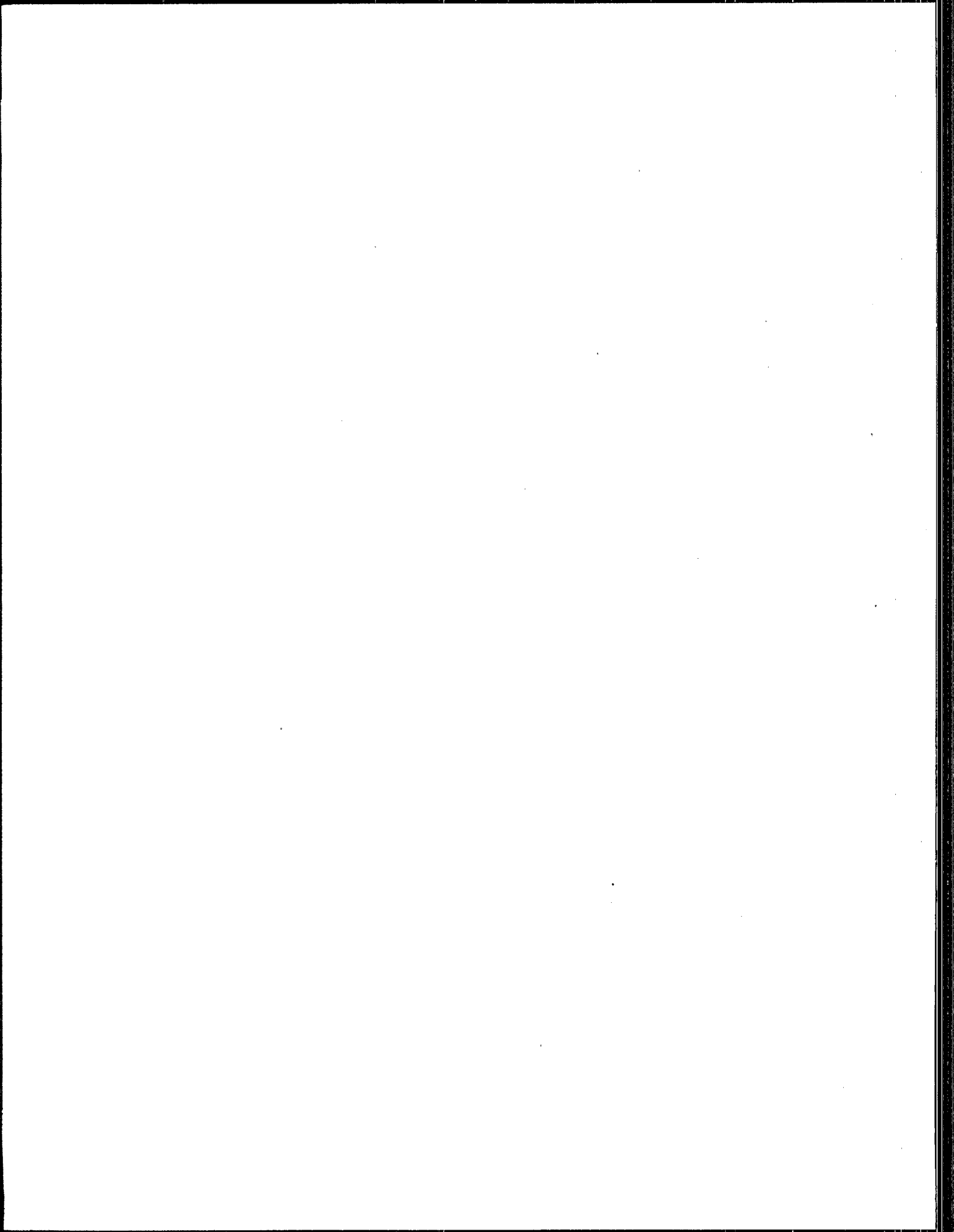
5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

5.1.3 Preparation of Sampling Train. Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the nitric acid/hydrogen peroxide solution (Section 4.2.1) in the two  $\text{HNO}_3/\text{H}_2\text{O}_2$  impingers (normally the second and third impingers), place 100 ml of the acidic potassium permanganate solution (Section 4.2.2) in the fourth and fifth impinger, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

Several options are available to the tester based on the sampling conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers is calculated or determined to be less than 150 ml. The tester shall include two impingers containing the acidic potassium permanganate solution for the first test run, unless past testing experience at the same or similar sources has shown that only one is necessary. The last permanganate impinger may be discarded if both permanganate impingers have retained their original deep purple permanganate color. A maximum of 200 ml in each permanganate impinger (and a maximum of three permanganate impingers) may be used, if necessary, to maintain the desired color in the last permanganate impinger.

Retain for reagent blanks, 100 ml of the nitric acid/hydrogen peroxide solution and 100 ml of the acidic potassium permanganate solution. These solutions should be labeled and treated as described in Section 7. Set up the sampling train as shown in Figure A-1. If necessary to ensure leak-free sampling train connections, Teflon tape should be used instead of silicone grease to prevent contamination.

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Precaution: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

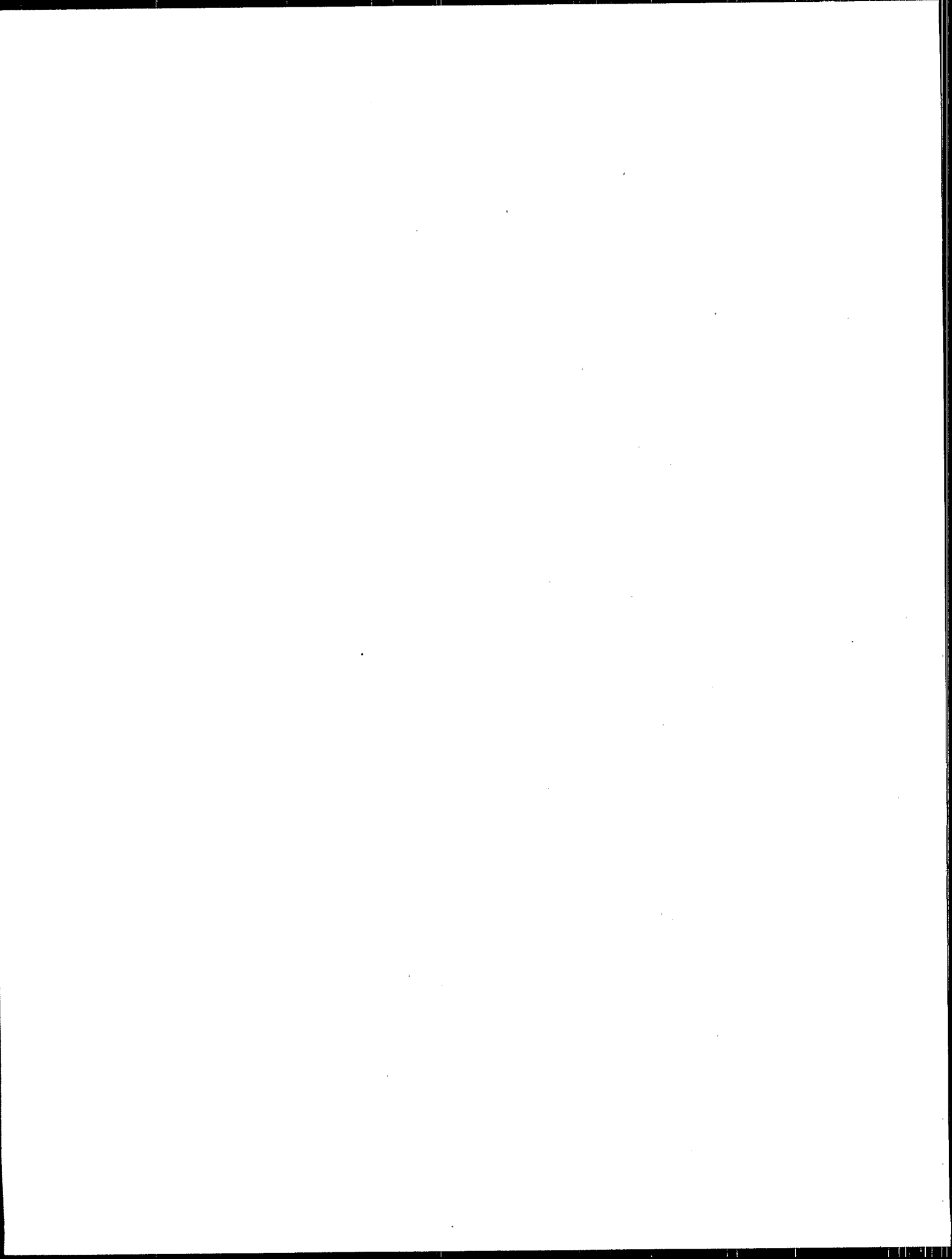
5.2 Sample Recovery. Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period.

The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a vacuum to form in the filter holder, thus causing the undesired result of drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination



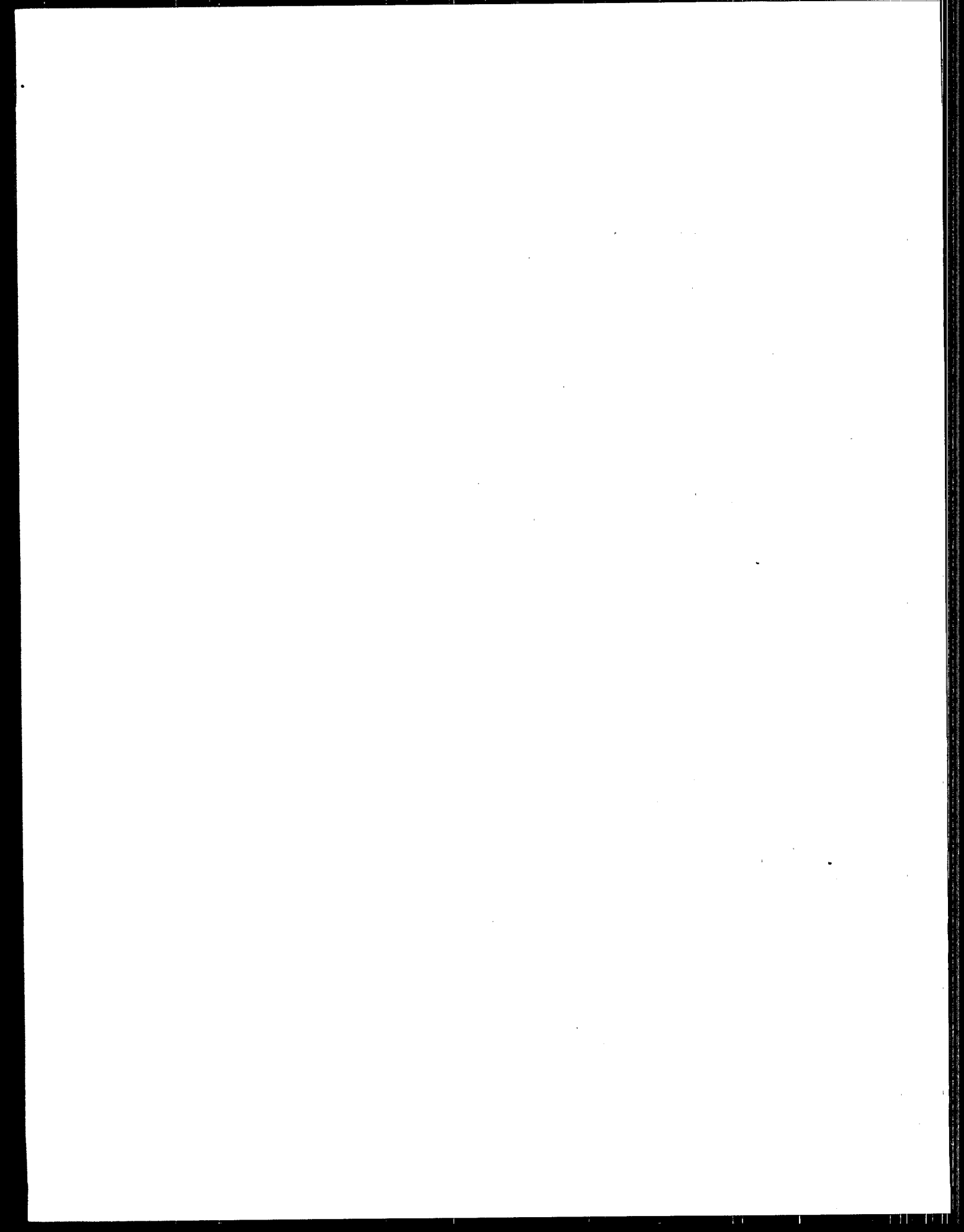
or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. The sample is recovered and treated as follows (see schematic in Figure A-2). Assure that all items necessary for recovery of the sample do not contaminate it.

5.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water should be used to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

5.2.2 Container No. 2 (Acetone Rinse). Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 100 ml of acetone and placing the wash in a glass container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nonmetallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

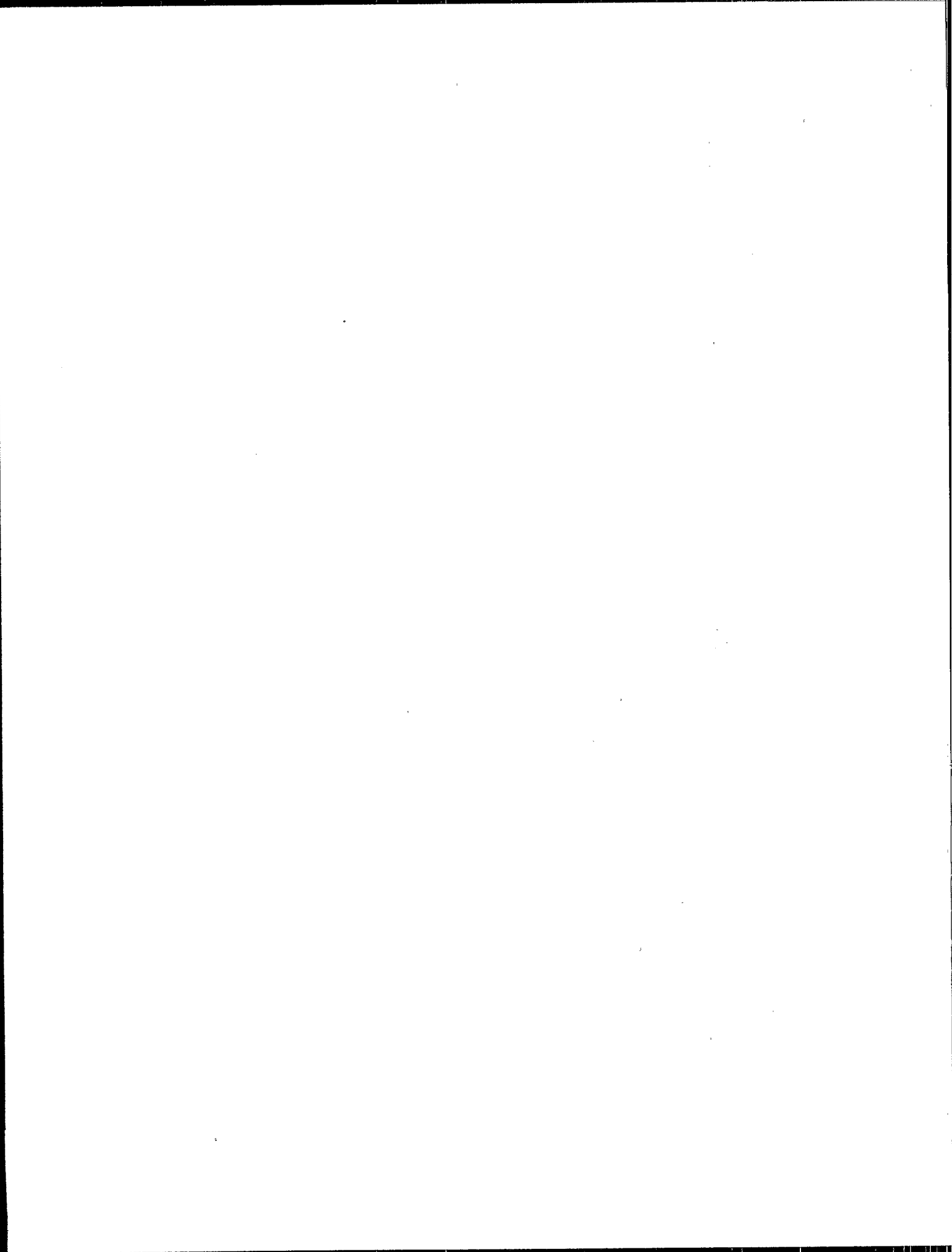
Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a nonmetallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample



[illegible]

**Figure A-2. Sample recovery scheme.**





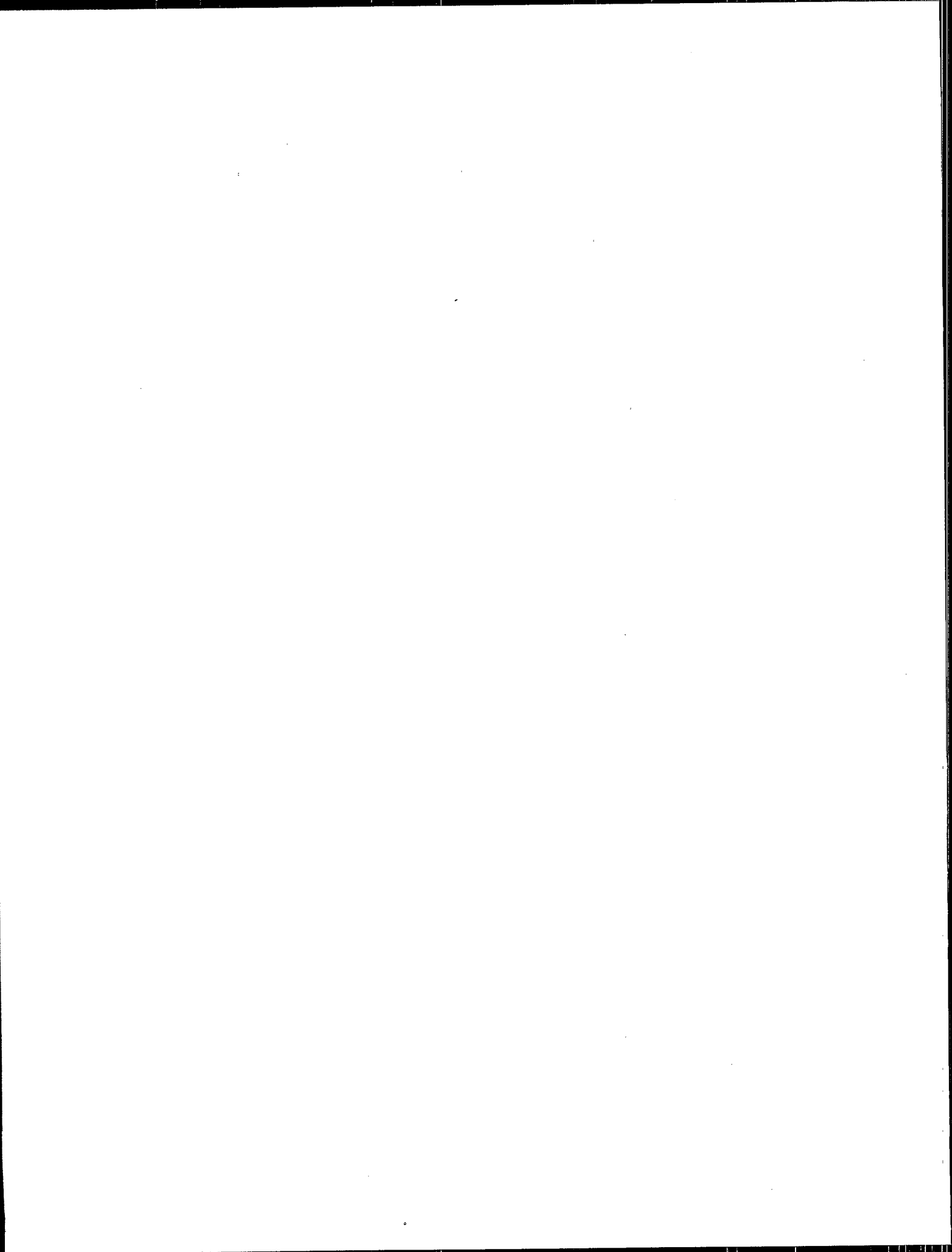
container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Clean the inside of the front half of the filter holder by rubbing the surfaces with a nonmetallic nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

5.2.3 Container No. 3 (Probe Rinse). Rinse the probe liner, probe nozzle, and front half of the filter holder thoroughly with 100 ml of 0.1 N nitric acid and place the wash into a sample storage container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water followed by acetone and discard these rinses.

5.2.4 Container No. 4 (Impingers 1 through 3, Contents and Rinses). Due to the large quantity of liquid involved, the tester may place the impinger solutions in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 ml using a graduated cylinder. Record the volume of liquid present. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N nitric acid as

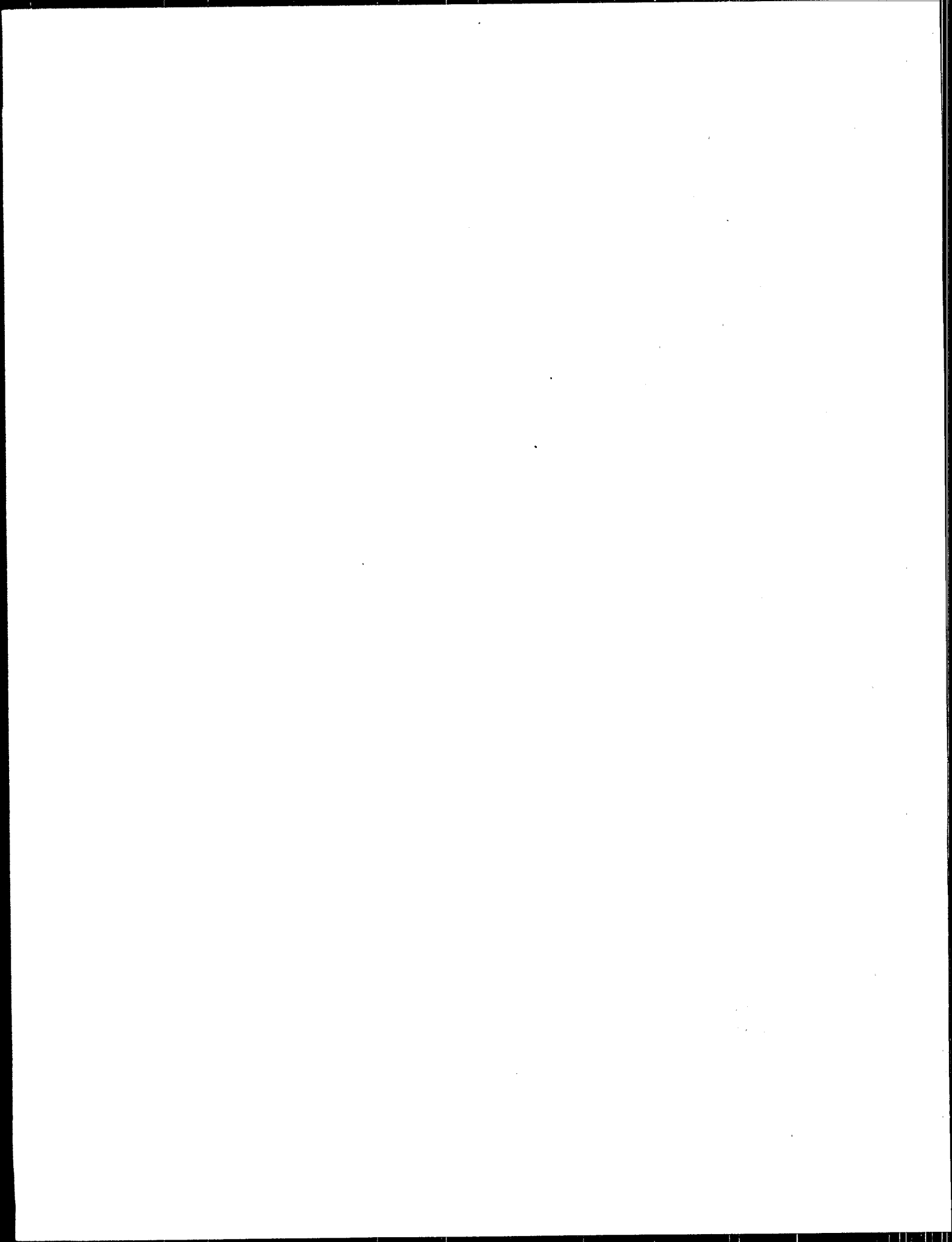


described in Method 12, Section 5.2.4. Note: The use of exactly 100 ml of 0.1 N nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Calculate the 0.1 N nitric acid rinse volume by difference. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

5.2.5 Container No. 5 (Acidified Potassium Permanganate Solution and Rinses, Impingers No. 4 & 5). Pour all the liquid from the permanganate impingers (fourth and fifth, if two permanganate impingers are used) into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Using 100 ml total of the acidified potassium permanganate solution, rinse the permanganate impinger(s) and connecting glass pieces a minimum of three times. Combine the rinses with the permanganate impinger solution. Finally, rinse the permanganate impinger(s) and connecting glassware with 50 ml of 8 N HCl to remove any residue. Note: The use of exactly 100 ml and 50 ml for the two rinses is necessary for the subsequent blank correction procedures. Place the combined rinses and impinger contents in a labeled glass storage bottle. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.2.2 and properly seal the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles should not be filled full and should be vented to relieve excess pressure. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.

5.2.6 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations.



Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

5.2.7 Container No. 7 (Acetone Blank). Once during each field test, place 100 ml of the acetone used in the sample recovery process into a labeled container for use in the front half field reagent blank. Seal the container.

5.2.8 Container No. 8 (0.1 N Nitric Acid Blank). Once during each field test, place 200 ml of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use in the front half and back half field reagent blanks. Seal the container.

5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Blank). Once during each field test, place 200 ml of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back half field reagent blank. Seal the container.

5.2.10 Container No. 10 (Acidified Potassium Permanganate Blank). Once during each field test, place 300 ml of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back half field reagent blank for mercury analysis. Seal the container.

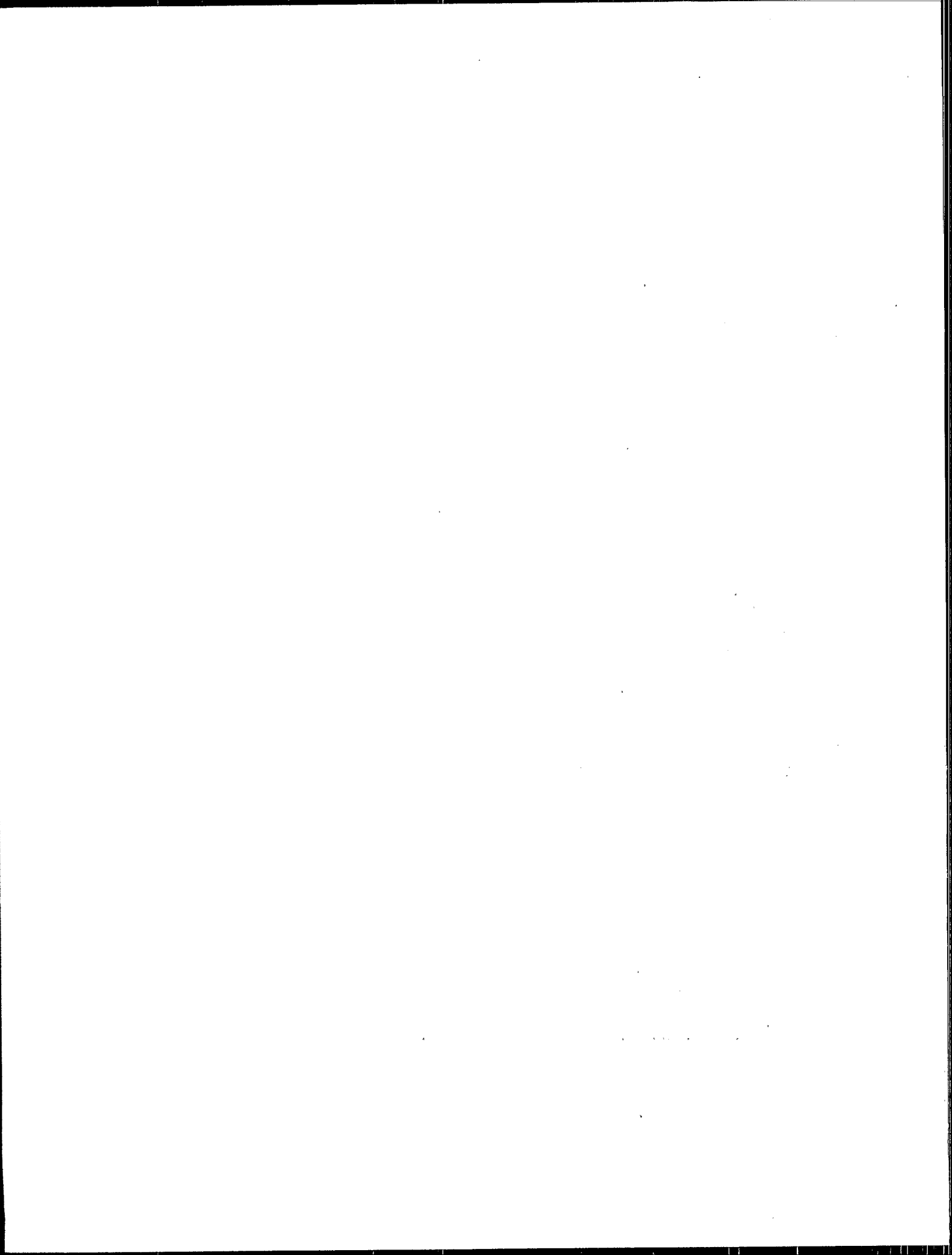
Note: This container should be vented, as described in Section 5.2.4, to relieve excess pressure.

5.2.11 Container No. 11 (8 N HCl Blank). Once during each field test, place 50 ml of the 8 N hydrochloric acid used to rinse the acidified potassium permanganate impingers into a labeled container for use in the back half reagent blank for mercury.

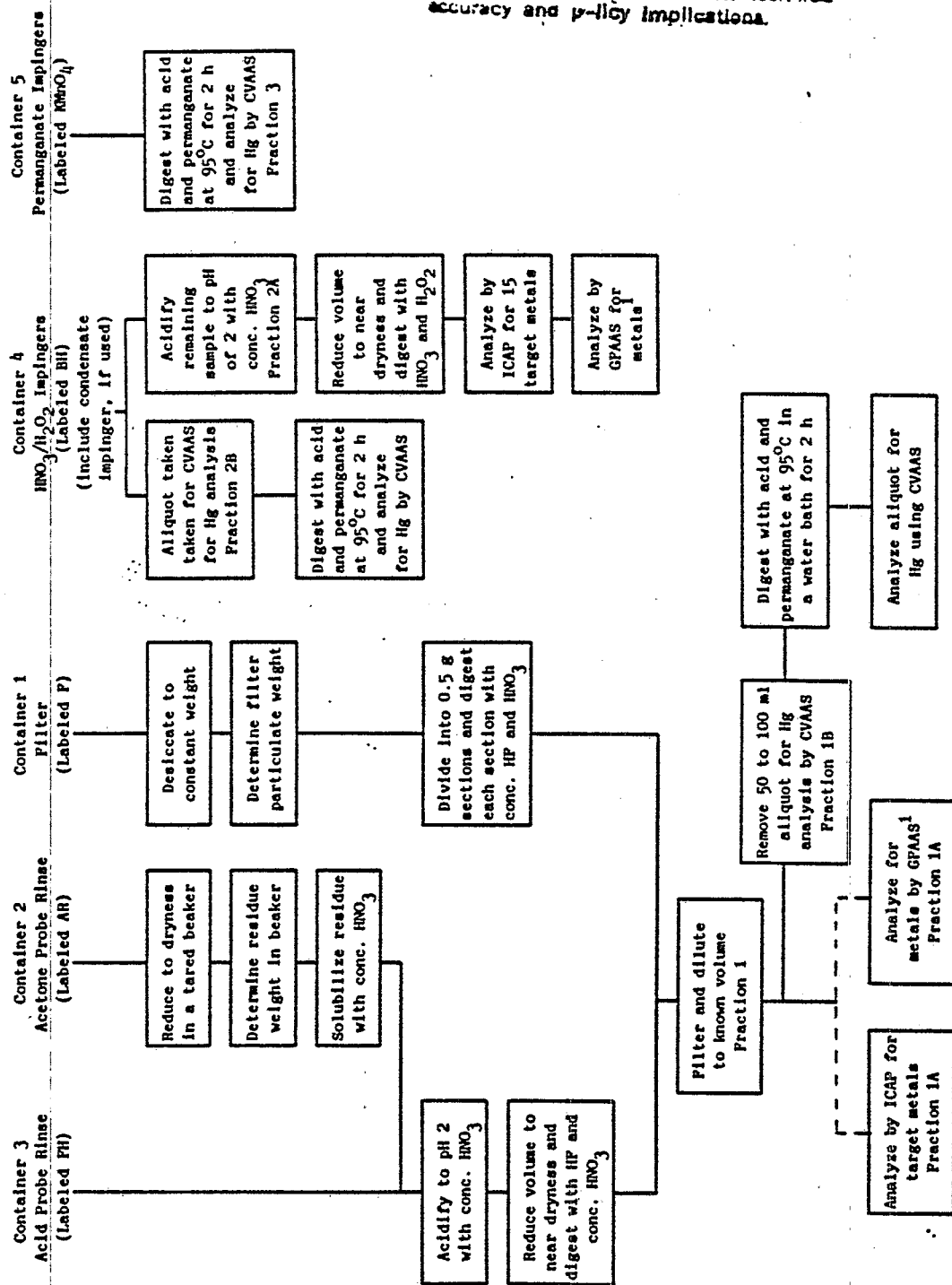
5.2.12 Container No. 12 (Filter Blank). Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. This will be used in the front half field reagent blank.

5.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure A-3.

5.3.1 Container No. 1 (Filter). If particulate emissions are being determined, then desiccate the filter and filter catch without heat and weigh to

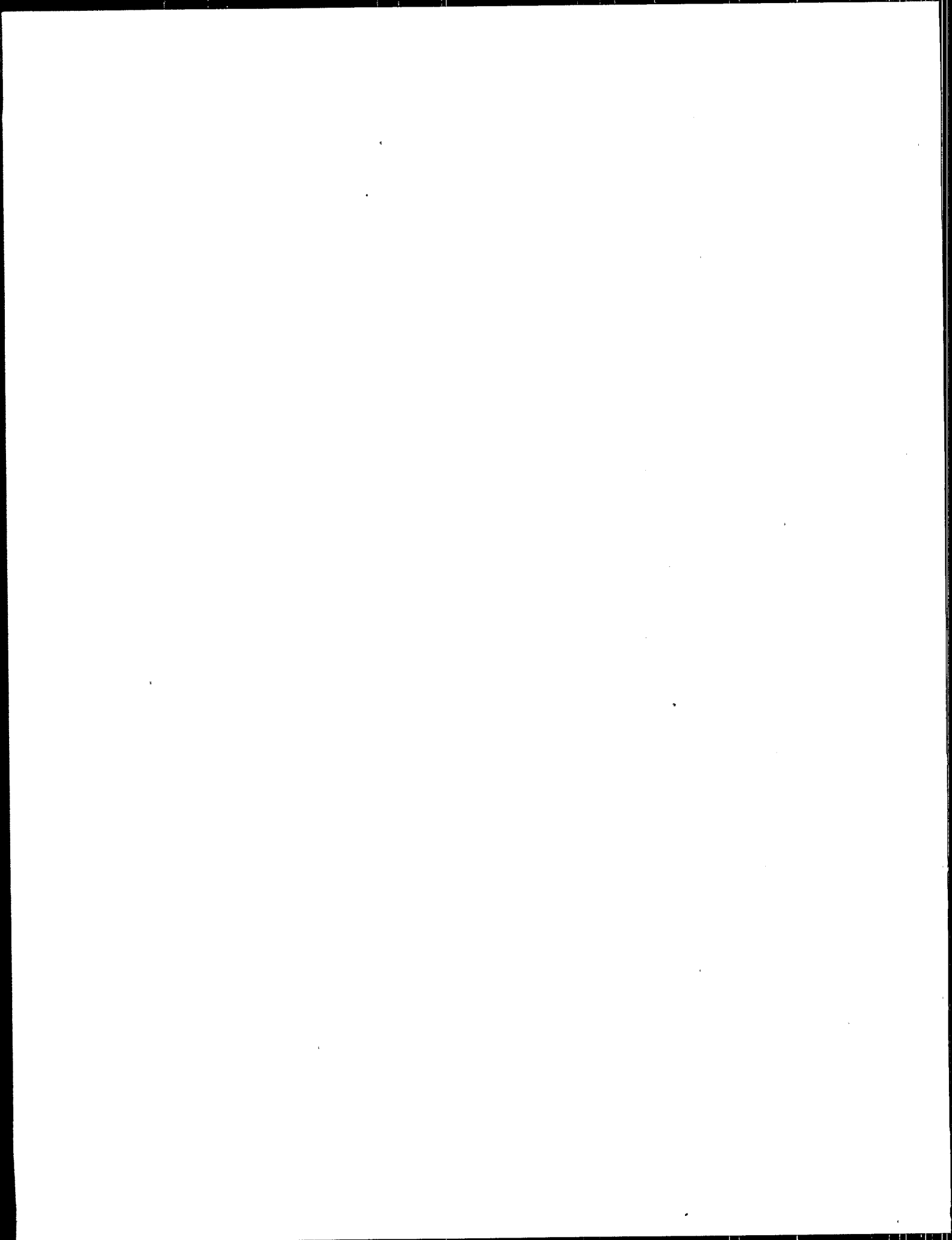


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<sup>1</sup>Analysis by AAS for metals found at less than 2 ug/ml in digestate solution, if desired. Or analyze for each metal by AAS, if desired.

Figure A-3. Sample preparation and analysis scheme.



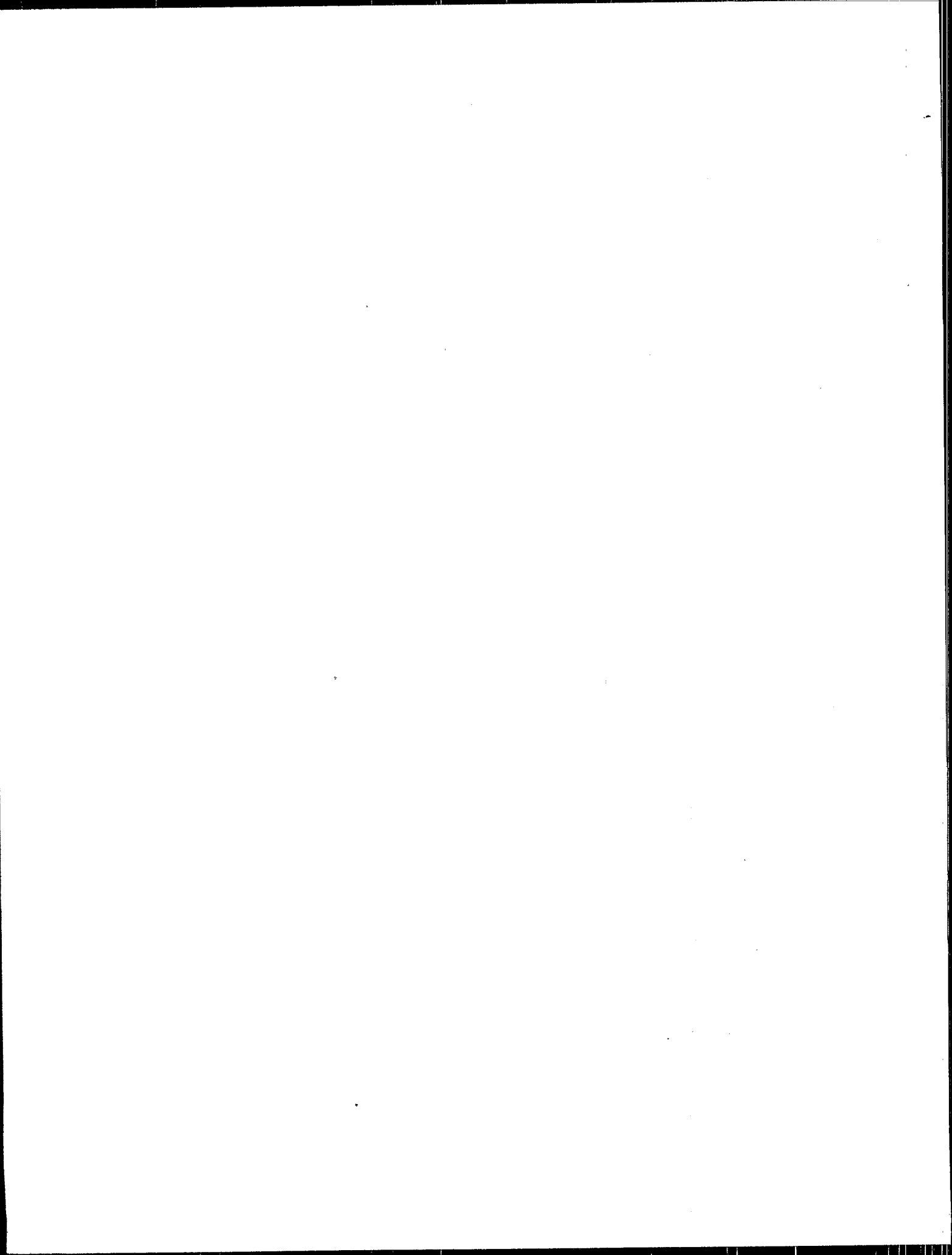


a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr<sup>R</sup> Bombs. Add 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2 minutes at 600 Watts. For conventional heating, heat the Parr Bombs at 140°C (285°F) for 6 hours. Then cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 5.3.3, below.

- Notes:
1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.
  2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to  $\pm 1$  ml or gravimetrically to  $\pm 0.5$  g. Transfer the contents to an acid-cleaned tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Resolubilize the residue with concentrated nitric acid and combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the following Section 5.3.3.

5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified with concentrated nitric acid to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 50 ml by heating on a hot plate at a temperature

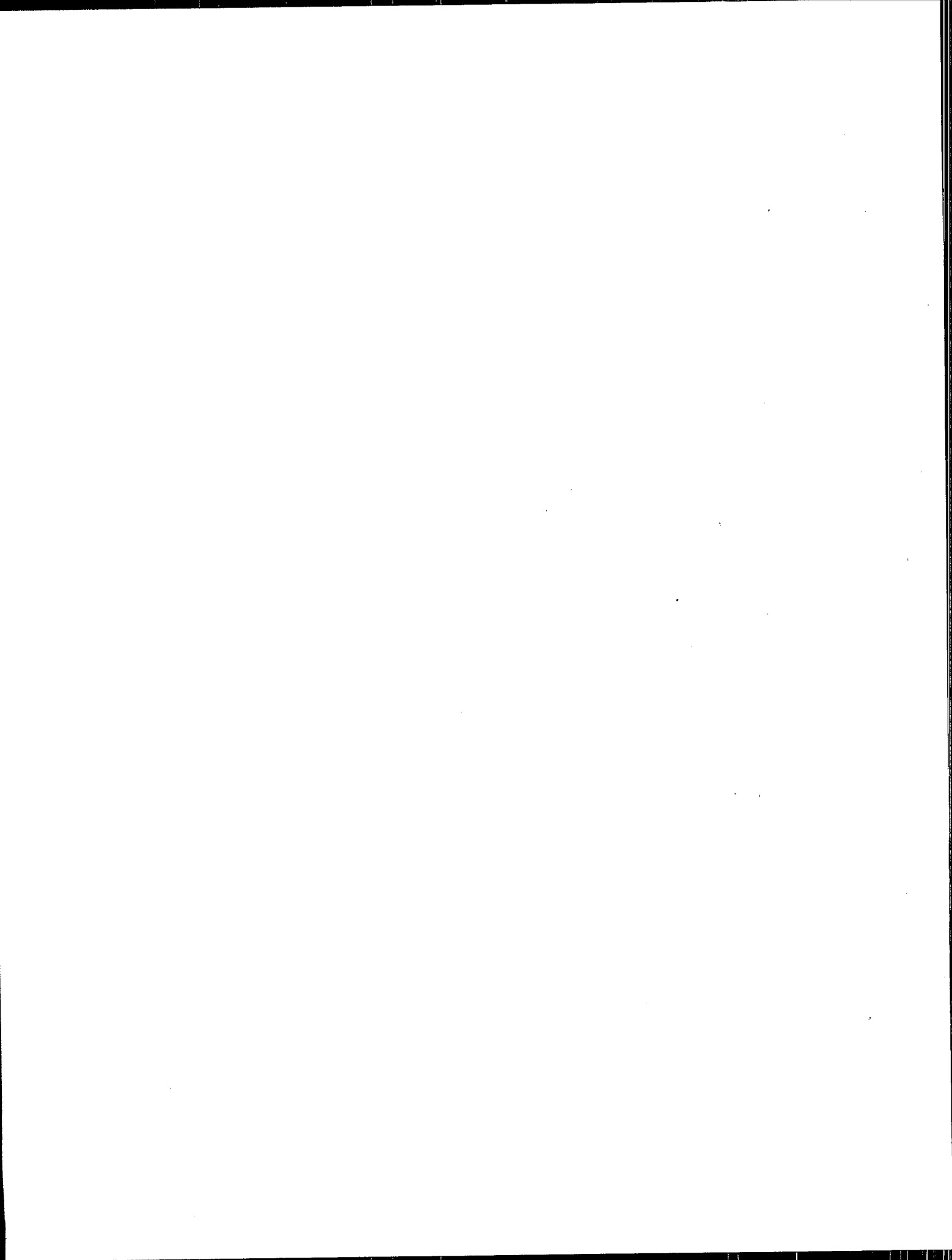


just below boiling. Inspect the sample for visible particulate matter, and depending on the results of the inspection, perform one of the following. If no particulate matter is observed, combine the sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. If particulate matter is observed, digest the sample in microwave vessels or Parr<sup>R</sup> Bombs following the procedures described in Section 5.3.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. The resultant combined sample is referred to as Fraction 1. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. Measure and record the combined volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50 ml aliquot and label as Fraction 1B. Label the remaining 250 ml portion as Fraction 1A. Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front half mercury.

5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 50 ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as Fraction 2A. The Fraction 2B aliquot should be prepared and analyzed as described in Section 5.4.3. Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid to lower Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in Sections 5.3.4.1 and 5.3.4.2, below.

5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent hydrogen peroxide and heat for 10 more minutes. Add 50 ml of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water.

5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent nitric acid and heat for 6 minutes in intervals of 1 to 2 minutes at 600 Watts. Allow the sample to cool. Add 10 ml of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 ml of hot water and heat for an additional 5 minutes.



Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

5.3.5 Container No. 5 (Impingers 4 & 5). Measure and record the total volume of this sample to within 0.5 ml. This sample is referred to as Fraction 3. Follow the analysis procedures described in Section 5.4.3.

5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

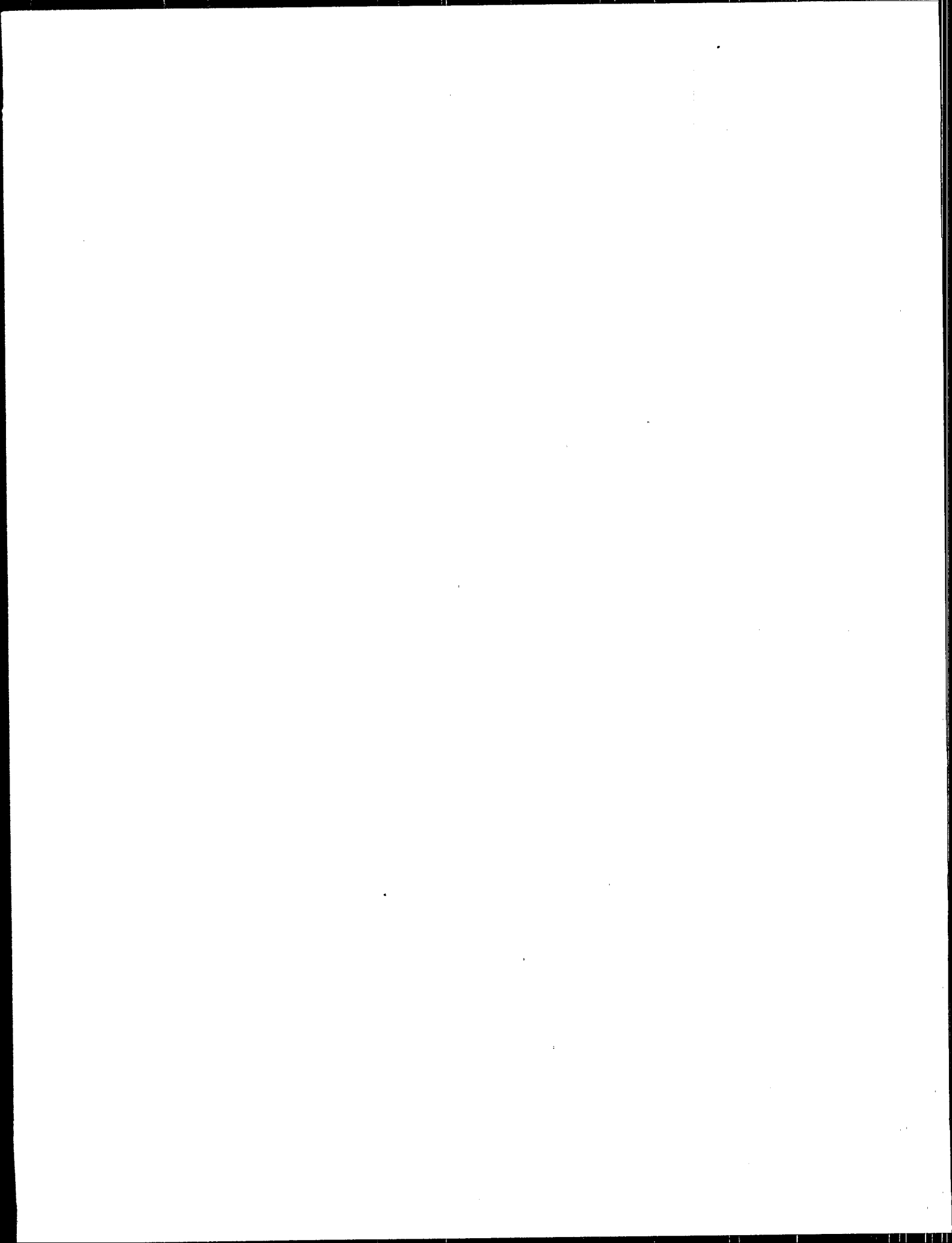
5.4 Sample Analysis. For each sampling train, five individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure A-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICAP or AAS analysis as described in Sections 5.4.1 and/or 5.4.2. Fraction 1B is for determination of front half mercury as described in Section 5.4.3.

The back half of the train was used to prepare the third through fifth samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the H<sub>2</sub>O and HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury.

The fifth sample, labeled Fraction 3, consists of the impinger contents and rinses from the permanganate Impingers 4 and 5. This sample is analyzed for mercury as described in Section 5.4.3. The total back half mercury catch is determined from the sum of Fraction 2B and Fraction 3.

5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using EPA Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 200.7. The quality control procedures described in Section 7.3.1 of this method shall be followed. Recommended wavelengths for use in the analysis are listed below.

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Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

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The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Initially, analyze all samples for the target metals plus iron and aluminum. If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic and lead.

Note: When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used; since all front half samples will contain hydrofluoric acid, use an alumina torch.

5.4.2 AAS by Direct Aspiration and/or Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired, Table A-2 should be used to determine which techniques and methods should be applied for each target metal. Table A-2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to Section 6.3 and follow the quality control procedures specified in Section 7.3.2.

5.4.3 Cold Vapor AAS Mercury Analysis. Fraction 1B, Fraction 2B, and Fraction 3 should be analyzed for mercury using cold vapor atomic absorption spectroscopy following the method outlined in EPA Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up

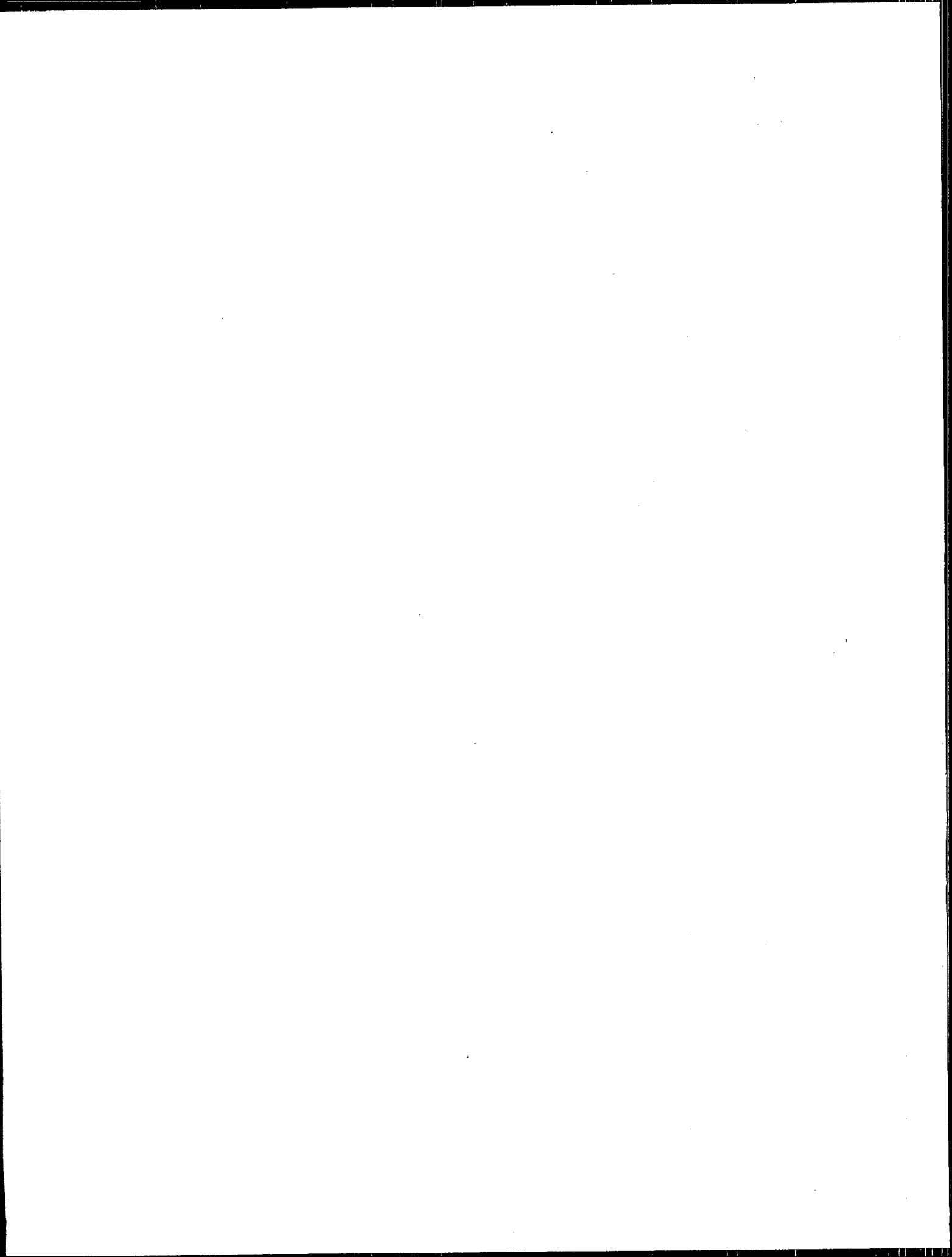




TABLE A-2. APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/ml Pb Ni, Cu, or acid	Use secondary wavelength of 231.1 nm. Match sample & standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic volatility - Aluminum	Spiked samples & add nickel nitrate solution to digestates prior to analyses Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium Barium ionization	High hollow cathode current & narrow band set 2 mL of KCl per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al High Mg & Si	Add 0.1% fluoride Use method of standard additions
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects
Cd	Aspiration	7130	228.8	Absorption & light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips
Cr	Aspiration	7190	357.9	Alkali metal Absorption & scatt	KCl ionization suppressant in sample & stand Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	All calcium nitrate for a known constant effect and to eliminate effect of phosphate

(continued)

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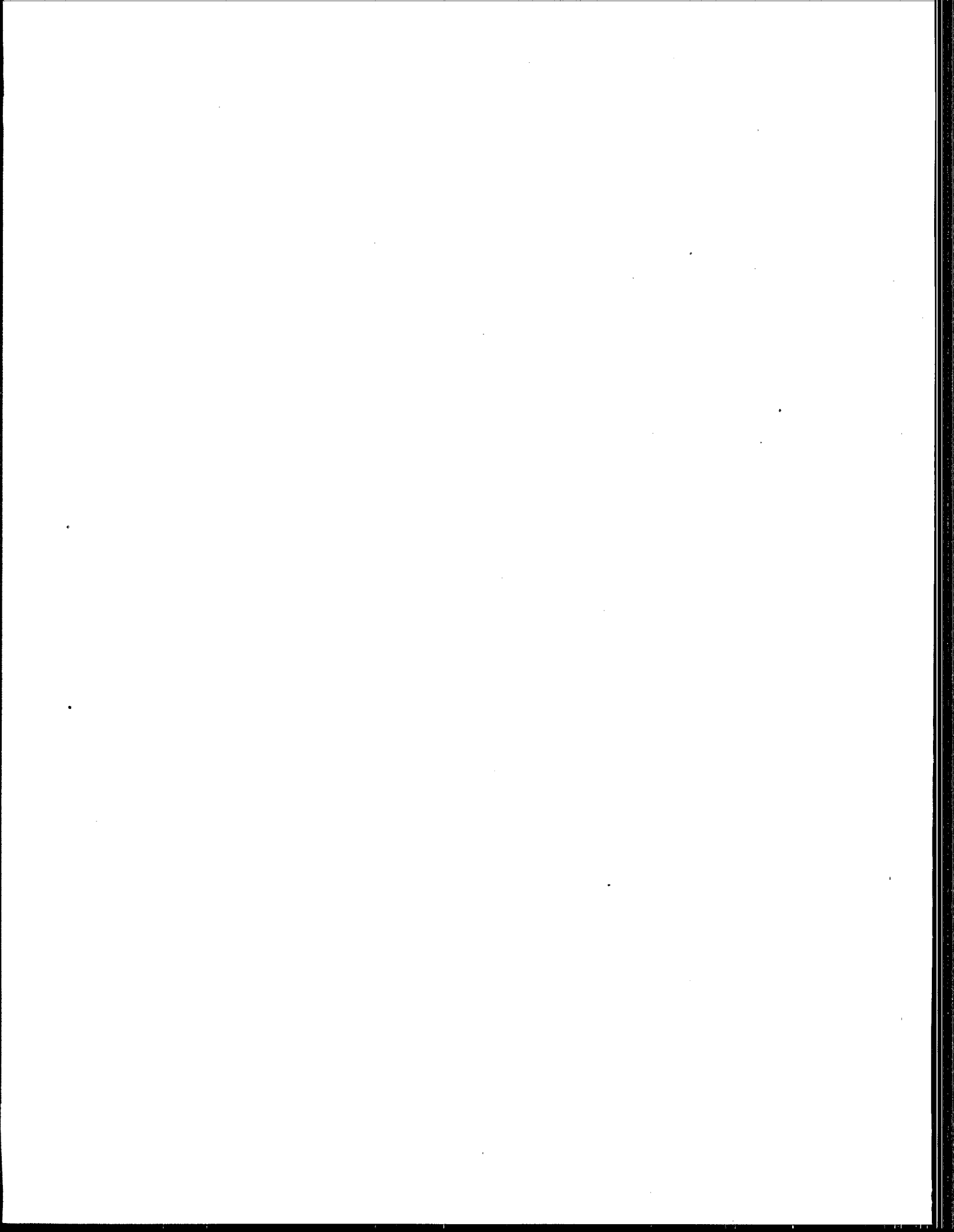
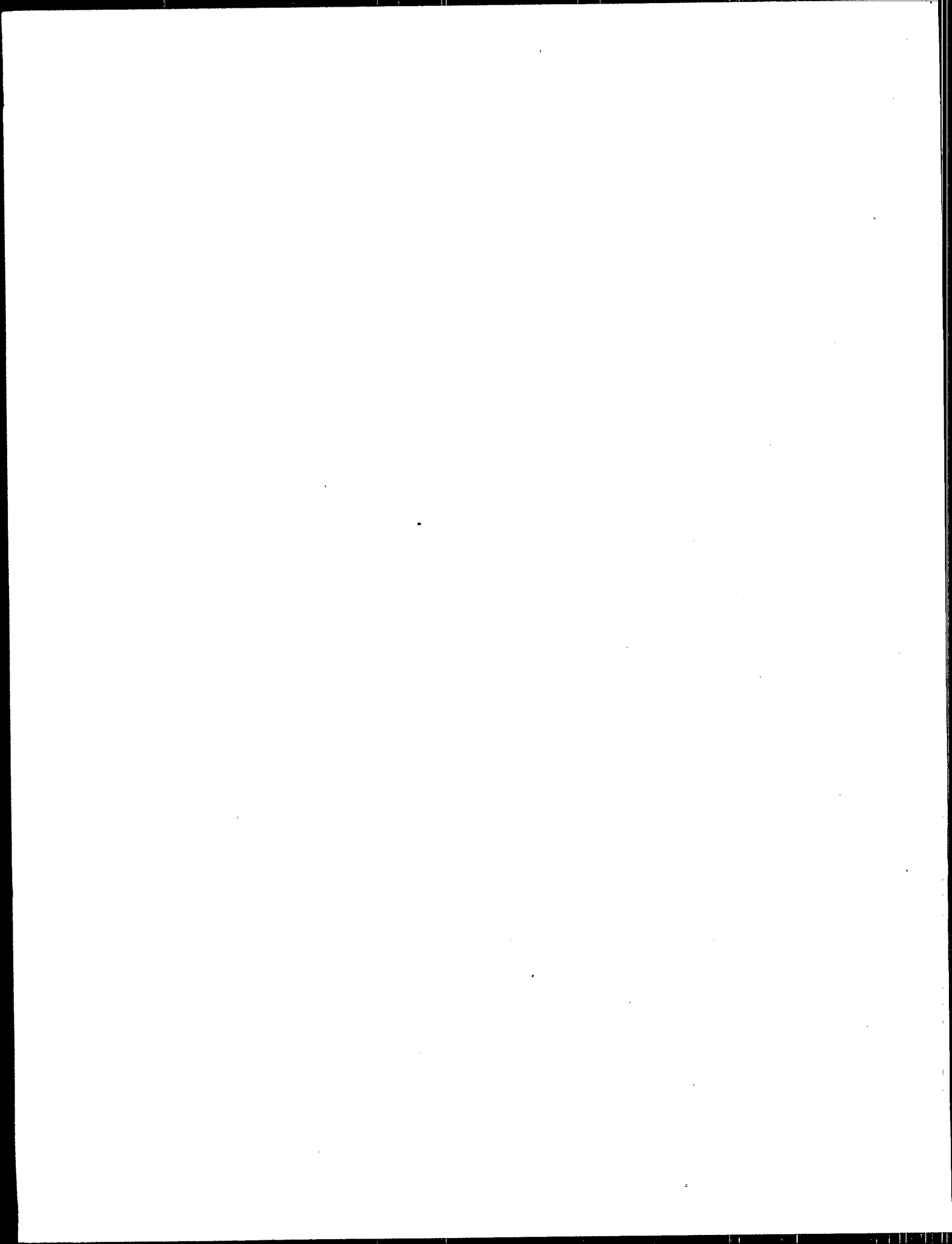


TABLE A-2 (CONTINUED)

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Cu	Aspiration	7210	324.7	Absorpt & scatter	Consult manufacturer's manual
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternat	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 uL of phosphorus acid to 1-mL of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternat	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternat Fe, Co, & Cr	Background correction required Matrix matching or a nitrous-oxide/acetylene flame
Se	Furnace	7740	196.0	Nonlinear responses Volatility	Sample dilution or use 352.4 nm line Spike samples & reference materials & add nickel nitrate to minimize volatilization
				Adsorpt & scatter	Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorpt & scatter AgCl insoluble	Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex
Tl	Aspiration	7840	276.8	Viscosity	Sample & standards monitored for aspiration rate
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Hydrochloric acid should not be used
Zn	Aspiration	7950	213.9	High Si, Cu & P Contamination	Background correction is required Verify that losses are not occurring for volatilization by spiked samples or standard add Palladium is a suitable matrix modifier Strontium removes Cu and phosphate Care should be taken to avoid contamination



the calibration curve as described in Section 7.3 of Method 303F. Add approximately 5 ml of each sample to BOD bottles. Record the amount of sample added. The amount used is dependent upon the expected levels of mercury. Dilute to approximately 120 ml with mercury-free water. Add approximately 15 ml of 5 percent potassium permanganate solution to the Fraction 2B and Fraction 3 samples. Add 5 percent potassium permanganate solution to the Fraction 1B sample as needed to produce a purple solution lasting at least 15 minutes. A minimum of 25 ml is suggested. Add 5 ml of 50 percent nitric acid, 5 ml of concentrated sulfuric acid, and 9 ml of 5 percent potassium persulfate to each sample and each standard. Digest the solution in the capped BOD bottle at 95°C (205°F) in a convection oven or water bath for 2 hours. Cool. Add 5 ml of hydroxylamine hydrochloride solution and mix the sample. Then add 7 ml of stannous chloride to each sample and analyze immediately.

## 6. Calibration

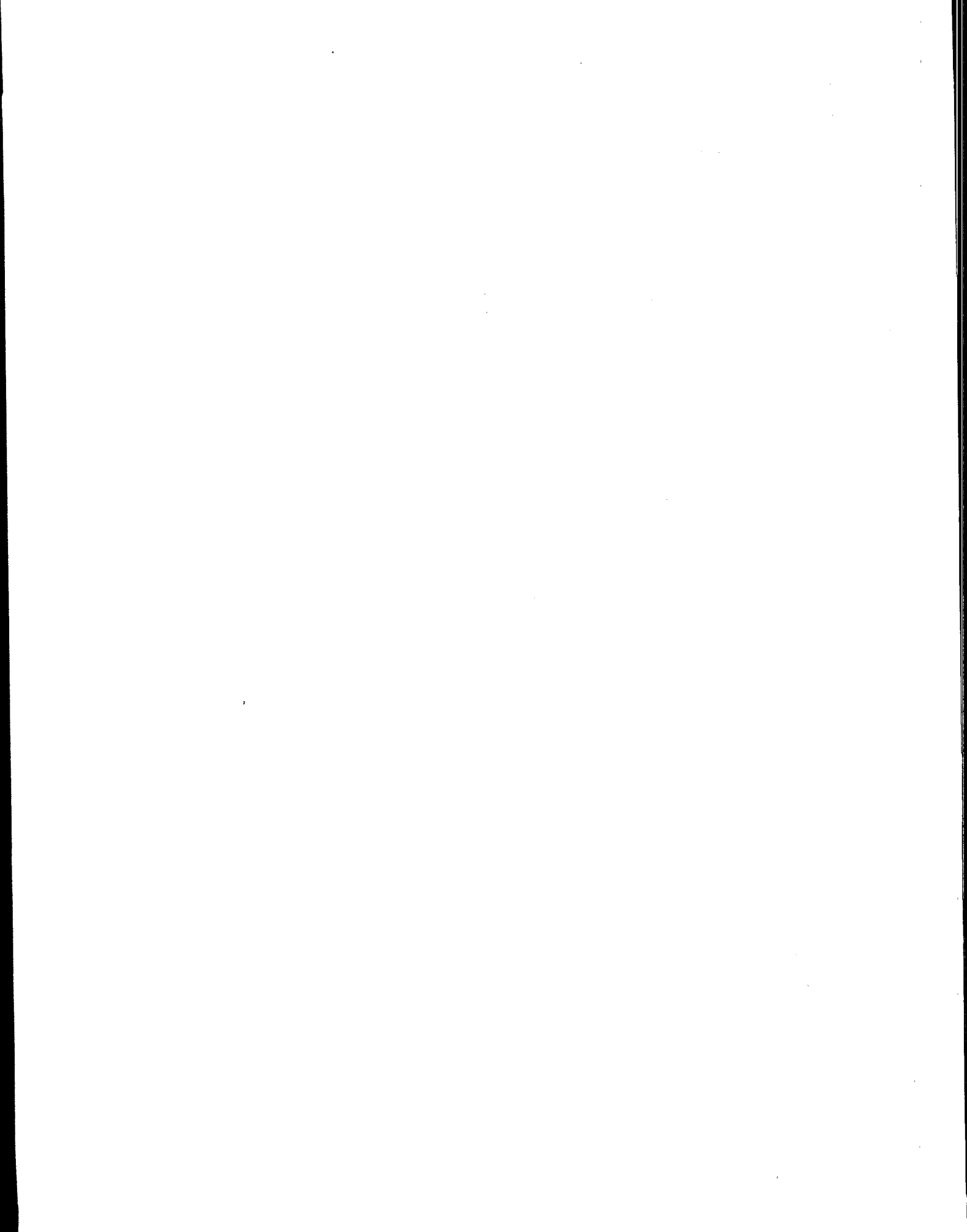
Maintain a laboratory log of all calibrations.

6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

6.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 4.4. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. The instrument calibration should be checked once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed.

6.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses. Prepare the standards as outlined in Section 4.4. Calibrate the spectrometer using these prepared standards. Calibration procedures are also outlined in the EPA methods referred to in Table A-2 and in Standard Methods for Water and Wastewater, 15th Edition, Method 303F (for mercury). Each standard curve should be run in duplicate and the mean values used to calculate the calibration line. The instrument should be recalibrated approximately once every 10 to 12 samples.

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## 7. Quality Control

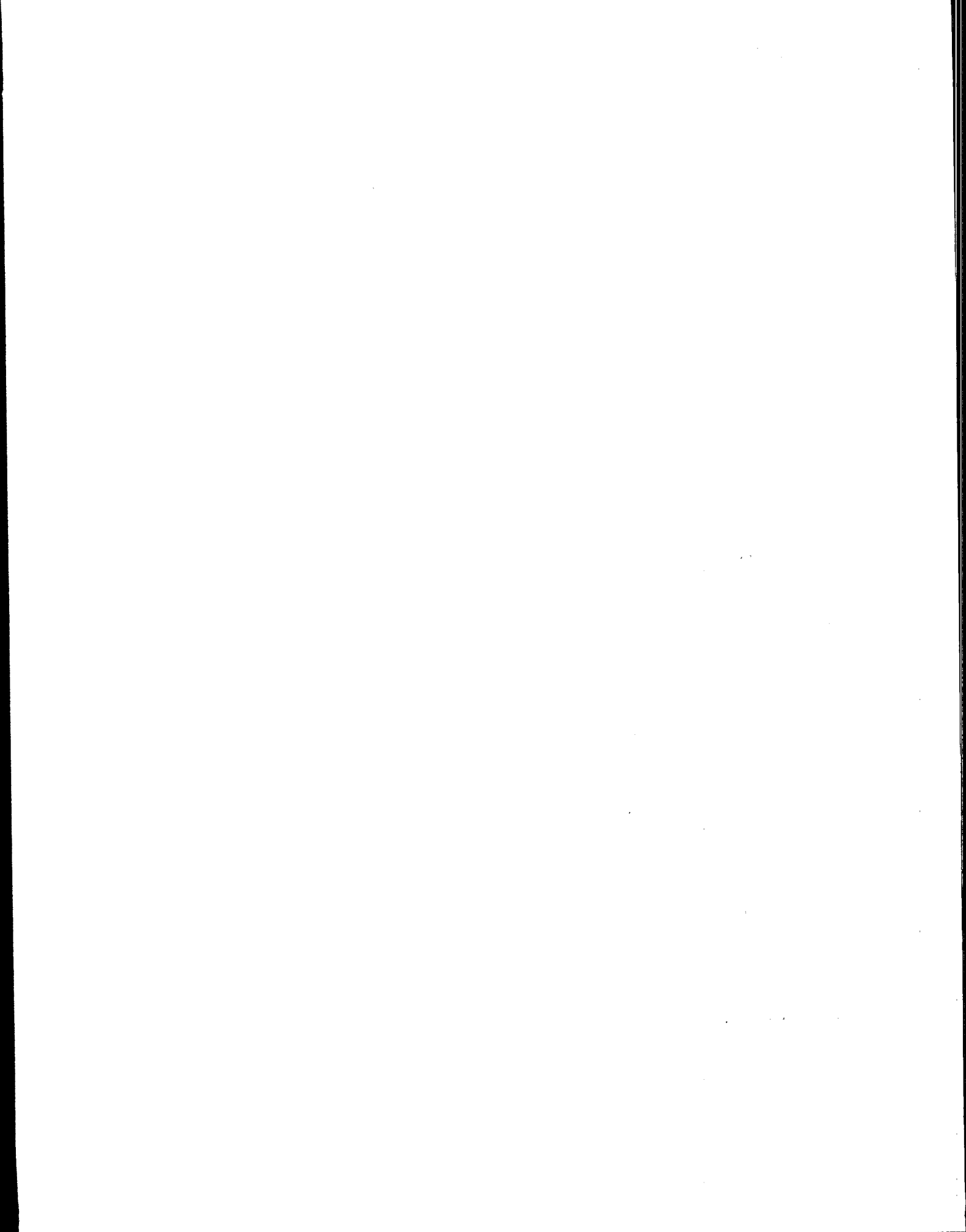
7.1 Sampling. Field Reagent Blanks. The blank samples in Container Numbers 7 through 12 produced previously in Sections 5.2.7 through 5.2.11, respectively, shall be processed, digested, and analyzed as follows. Digest and process Container No. 12 contents per Section 5.3.1, Container No. 7 per Section 5.3.2, and half of Container No. 8 per Section 5.3.3. This produces Fraction Blank 1A and Fraction Blank 1B from Fraction Blank 1. Combine the remaining half of Container No. 8 with the contents of Container No. 9 and digest and process the resultant volume per Section 5.3.4. This produces Fraction Blank 2A and Fraction Blank 2B from Fraction Blank 2. Container No. 10 and Container No. 11 contents are Fraction Blank 3. Analyze Fraction Blank 1A and Fraction Blank 2A per Section 5.4.1 and/or 5.4.2. Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blank 3 per Section 5.4.3. The analysis of Fraction Blank 1A produces the front half reagent blank correction values for the metals except mercury; the analysis of Fraction Blank 1B produces the front half reagent blank correct value for mercury. The analysis of Fraction Blank 2A produces the back half reagent blank correction values for the metals except mercury, while separate analysis of Fraction Blanks 2B and 3 produce the back half reagent blank correction value for mercury.

7.2 An attempt may be made to determine if the laboratory reagents used in Section 5.3 caused contamination. They should be analyzed by the procedures in Section 5.4. The Administrator will determine whether or not the laboratory blank reagent values can be used in the calculation of the stationary source test results.

7.3 Quality Control Samples. The following quality control samples should be analyzed.

7.3.1 ICAP Analysis. Follow the quality control shown in Section 8 of Method 6010. For the purposes of a three run test series, these requirements have been modified to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by standard addition), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 5% of average or repeat all analysis).

7.3.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Antimony, Arsenic, Barium, Beryllium, Cadmium, Copper, Chromium, Lead, Nickel, Manganese,





Mercury, Phosphorus, Selenium, Silver, Thallium, and Zinc. All samples should be analyzed in duplicate. Perform a matrix spike on one front half sample and one back half sample or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of additions. A quality control sample should be analyzed to check the accuracy of the calibration standards. The results must be within 10% or the calibration repeated.

7.3.3 Cold Vapor AAS Analysis for Mercury. All samples should be analyzed in duplicate. A quality control sample should be analyzed to check the accuracy of the calibration standards (within 10% or repeat calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA Method 7470 or in Standard Methods for Water and Wastewater, 15th Edition, Method 303F.

## 8. Calculations

8.1 Dry Gas Volume. Using the data from this test, calculate  $V_{g(std)}$ , the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

8.2 Volume of Water Vapor and Moisture Content. Using the data obtained from this test, calculate the volume of water vapor  $V_{w(std)}$  and the moisture content  $B_w$  of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

8.3 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

8.4 Metals (Except Mercury) in Source Sample.

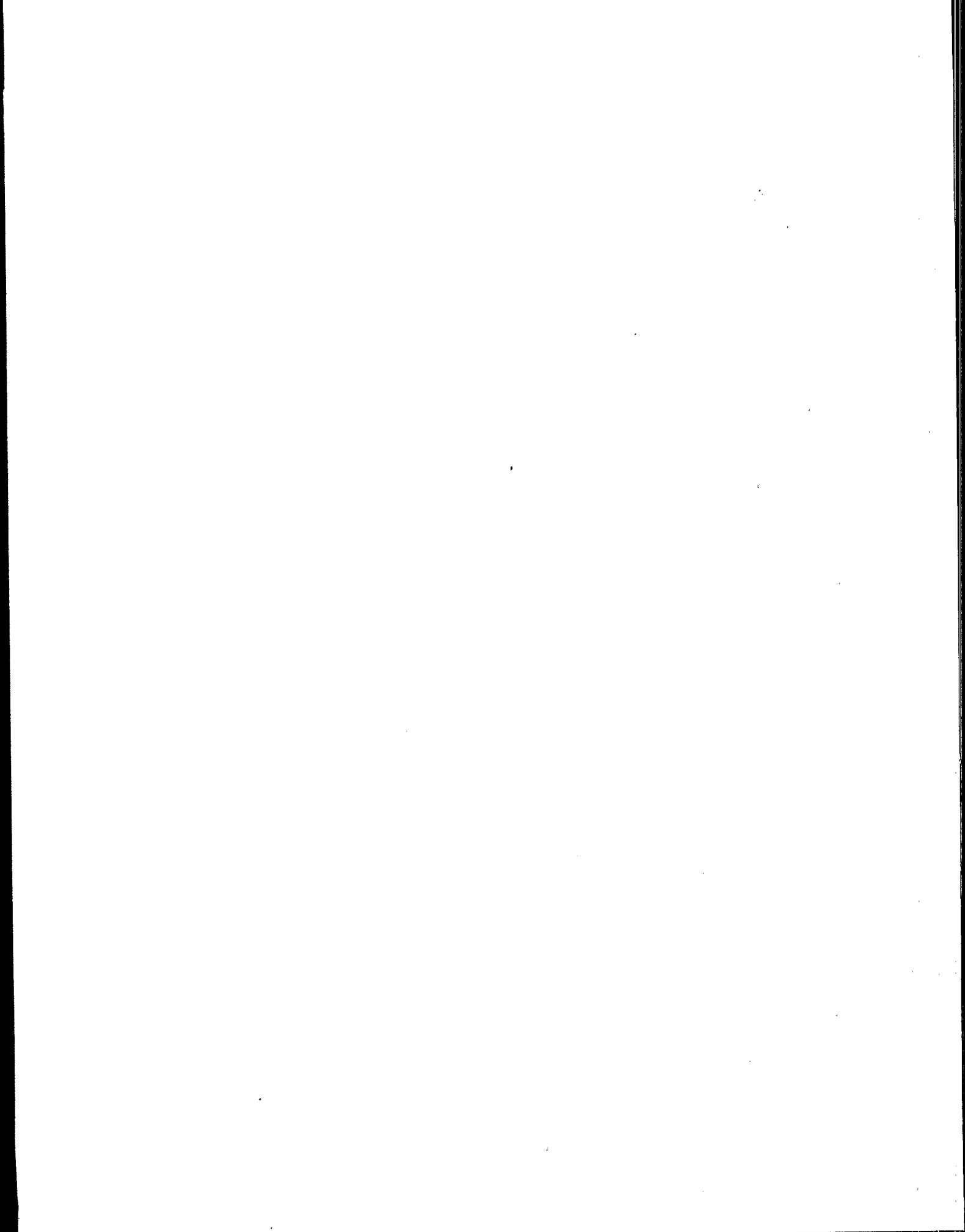
8.4.1 Fraction 1A, Front Half, Metals (except Hg). Calculate the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{rh} = C_a F_d V_{soln,1}$$

Eq. 1\*

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\*If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.



where:

$M_{fh}$  = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1), ug.

$C_a$  = concentration of metal in sample Fraction 1A as read from the standard curve (ug/ml).

$F_d$  = dilution factor ( $F_d$  = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading  $C_a$ . For example, when the dilution of Fraction 1A is from 2 to 10 ml,  $F_d = 5$ ).

$V_{soln.1}$  = total volume of digested sample solution (Fraction 1), ml.

8.4.2 Fraction 2A, Back Half, Metals (except Hg). Calculate the amount of each metal collected in Fraction 2 of the sampling train using the following equation.

$$M_{bh} = C_a F_a V_a \quad \text{Eq. 2*}$$

where:

$M_{bh}$  = total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2), ug.

$C_a$  = concentration of metal in sample Fraction 2A, as read from the standard curve (ug/ml).

$F_a$  = aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A.

$V_a$  = volume of digested sample analyzed (concentrated Fraction 2A), ml.

8.4.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \quad \text{Eq. 3*}$$

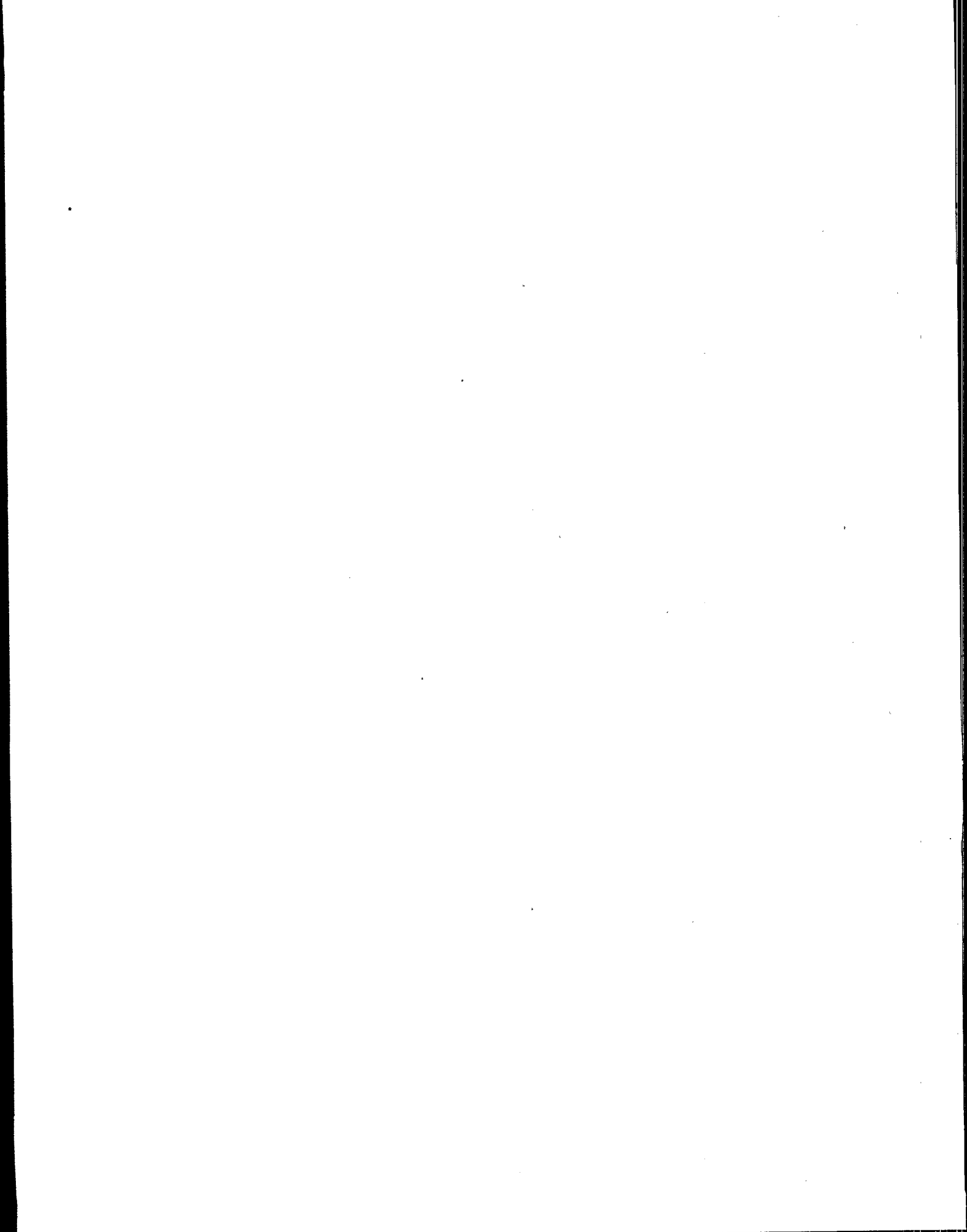
where:

$M_t$  = total mass of each metal (separately stated for each metal) collected in the sampling train, ug.

$M_{fhb}$  = blank correction value for mass of metal detected in front half field reagent blank, ug.

$M_{bhb}$  = blank correction value for mass of metal detected in back half field reagent blank, ug.

\*If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.



Note: If the measured blank value for the front half ( $m_{rnb}$ ) is in the range 0.0 to A ug [where A ug equals the value determined by multiplying 1.4 ug per square inch ( $1.4 \text{ ug/in.}^2$ ) times the actual area in square inches ( $\text{in.}^2$ ) of the filter used in the emission sample],  $m_{rnb}$  may be used to correct the emission sample value ( $m_{rh}$ ); if  $m_{rnb}$  exceeds A ug, the greater of the two following values (either I. or II.) may be used:

I. A ug, or

II. the lesser of (a)  $m_{rnb}$ , or (b) 5 percent of  $m_{rh}$ .

If the measured blank value for the back half ( $m_{bnb}$ ) is in the range 0.0 to 1 ug,  $m_{bnb}$  may be used to correct the emission sample value ( $m_{bh}$ ); if  $m_{bnb}$  exceeds 1 ug, the greater of the two following values may be used: 1 ug or 5 percent of  $m_{bh}$ .

#### 8.5 Mercury in Source Sample.

8.5.1 Fraction 1B, Front Half, Hg. Calculate the amount of mercury collected in the front half, Fraction 1, of the sampling train using the following equation:

$$Hg_{rh} = \frac{Q_{rh}}{V_{f1B}} \times V_{soln,1} \quad \text{Eq. 4}$$

where:

$Hg_{rh}$  = total mass of mercury collected in the front half of the sampling train (Fraction 1), ug.

$Q_{rh}$  = quantity of mercury in analyzed sample, ug.

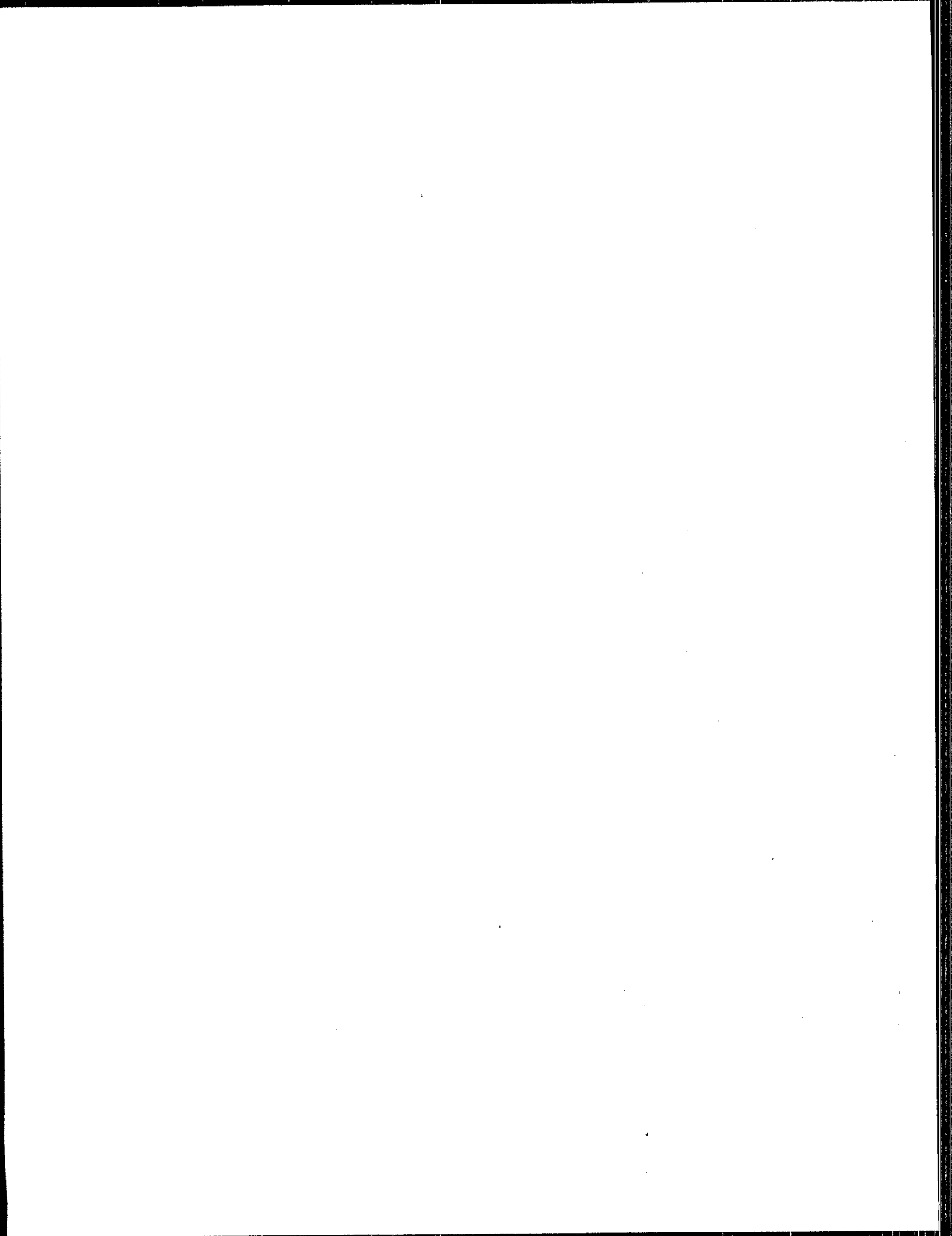
$V_{soln,1}$  = total volume of digested sample solution (Fraction 1), ml.

$V_{f1B}$  = volume of Fraction 1B analyzed, ml. See the following Note.

Note:  $V_{f1B}$  is the actual amount of Fraction 1B analyzed. For example, if 1 ml of Fraction 1B were diluted to 100 ml to bring it into the proper analytical range, and 1 ml of the 100 ml dilution was analyzed,  $V_{f1B}$  would be 0.01.

8.5.2 Fraction 2B and Fraction 3, Back Half, Hg. Calculate the amount of mercury collected in Fractions 2 and 3 using Equations 5 and 6, respectively. Calculate the total amount of mercury collected in the back half of the sampling train using Equation 7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f1B}} \times V_{soln,2} \quad \text{Eq. 5}$$



where:

$Hg_{bh2}$  = total mass of mercury collected in Fraction 2, ug.  
 $Q_{bh2}$  = quantity of mercury in analyzed sample, ug.  
 $V_{f2B}$  = volume of Fraction 2B analyzed, ml (see Note in Section 8.5.1).  
 $V_{soln,2}$  = total volume of Fraction 2, ml.

$$Hg_{bh3} = \frac{Q_{bh3}}{V_{f2B}} \times V_{soln,3} \quad \text{Eq. 6}$$

where:

$Hg_{bh3}$  = total mass of mercury collected in Fraction 3, ug.  
 $Q_{bh3}$  = quantity of mercury in analyzed sample, ug.  
 $V_{f3}$  = volume of Fraction 3 analyzed, ml (see Note in Section 8.5.1).  
 $V_{soln,3}$  = total volume of Fraction 3, ml.

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3} \quad \text{Eq. 7}$$

where:

$Hg_{bh}$  = total mass of mercury collected in the back half of the sampling train, ug.

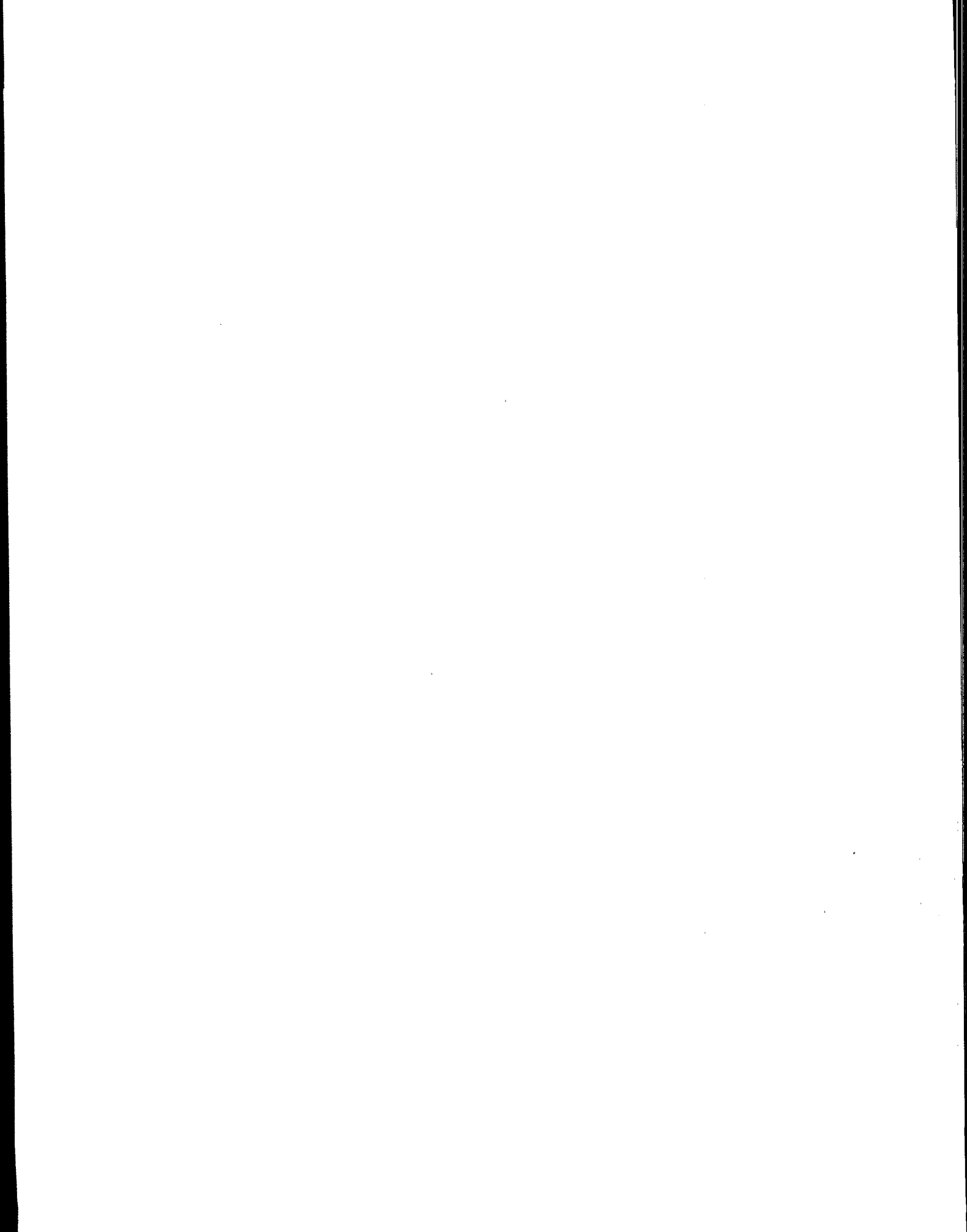
8.5.3 Total Train Mercury Catch. Calculate the total amount of mercury collected in the sampling train using Equation 8.

$$M_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \quad \text{Eq. 8}$$

where:

$M_t$  = total mass of mercury collected in the sampling train, ug.  
 $Hg_{fhb}$  = blank correction value for mass of mercury detected in front half field reagent blank, ug.  
 $Hg_{bhb}$  = blank correction value for mass of mercury detected in back half field reagent blank, ug.

Note: If the total of the measured blank values ( $Hg_{fhb} + Hg_{bhb}$ ) is in the range of 0 to 3 ug, then the total may be used to correct the emission sample value ( $Hg_{fh} + Hg_{bh}$ ); if it exceeds 3 ug, the greater of the following two values may be used: 3 ug or 5 percent of the emission sample value ( $Hg_{fh} + Hg_{bh}$ ).





8.6 Metal Concentration of Stack Gas. Calculate the cadmium, total chromium, arsenic, nickel, manganese, beryllium, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_d (M_t / V_{n(std)}) \quad \text{Eq.9}$$

where:

$C_s$  = concentration of each metal in the stack gas, mg/dscm.

$K_d$  =  $10^{-3}$  mg/ug.

$M_t$  = total mass of each metal collected in the sampling train, ug.

$V_{n(std)}$  = volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

8.7 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively.

## 9. Bibliography

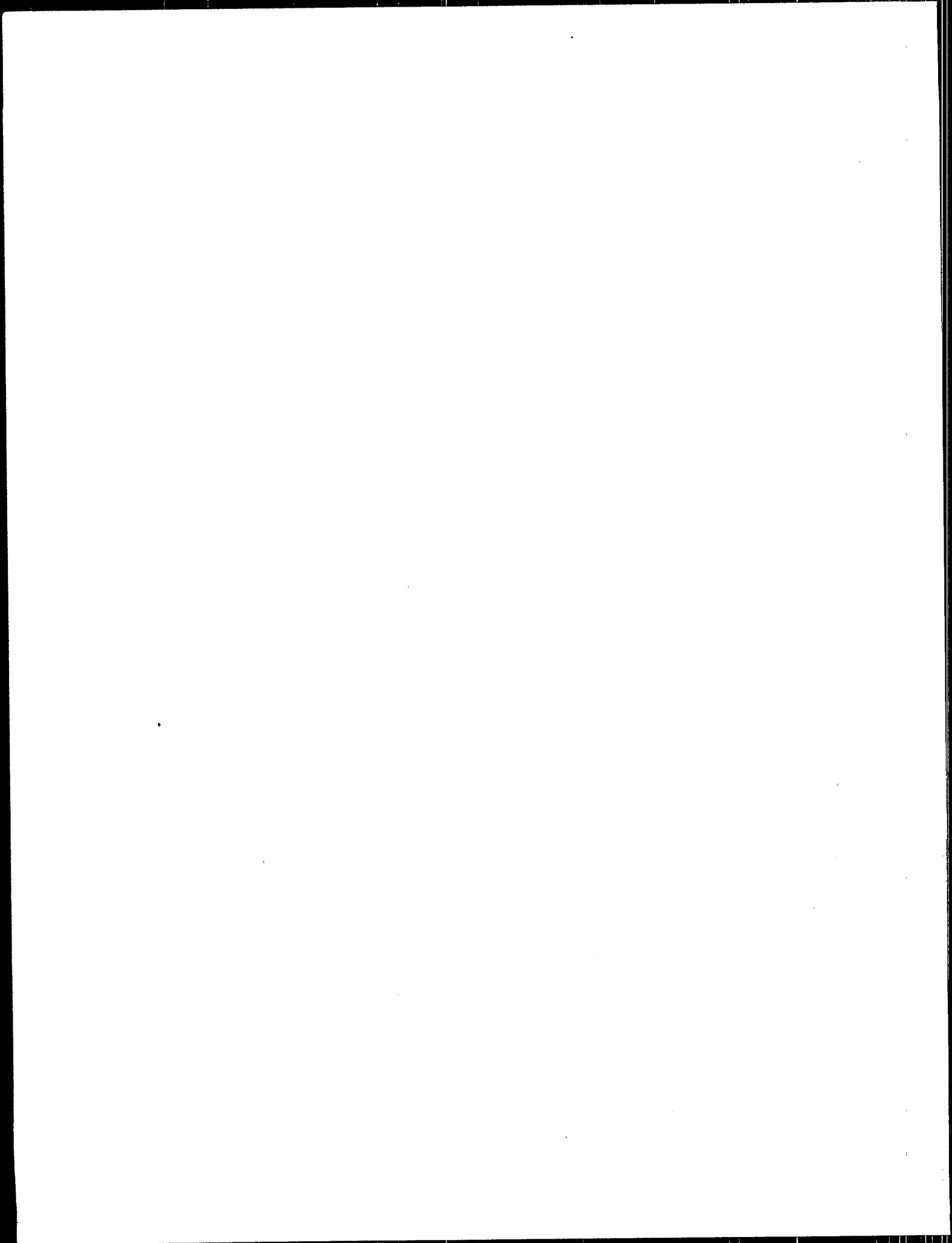
9.1 Method 303F in Standard Methods for the Examination of Water Wastewater, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

9.2 EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, D.C. 20460.

9.3 EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

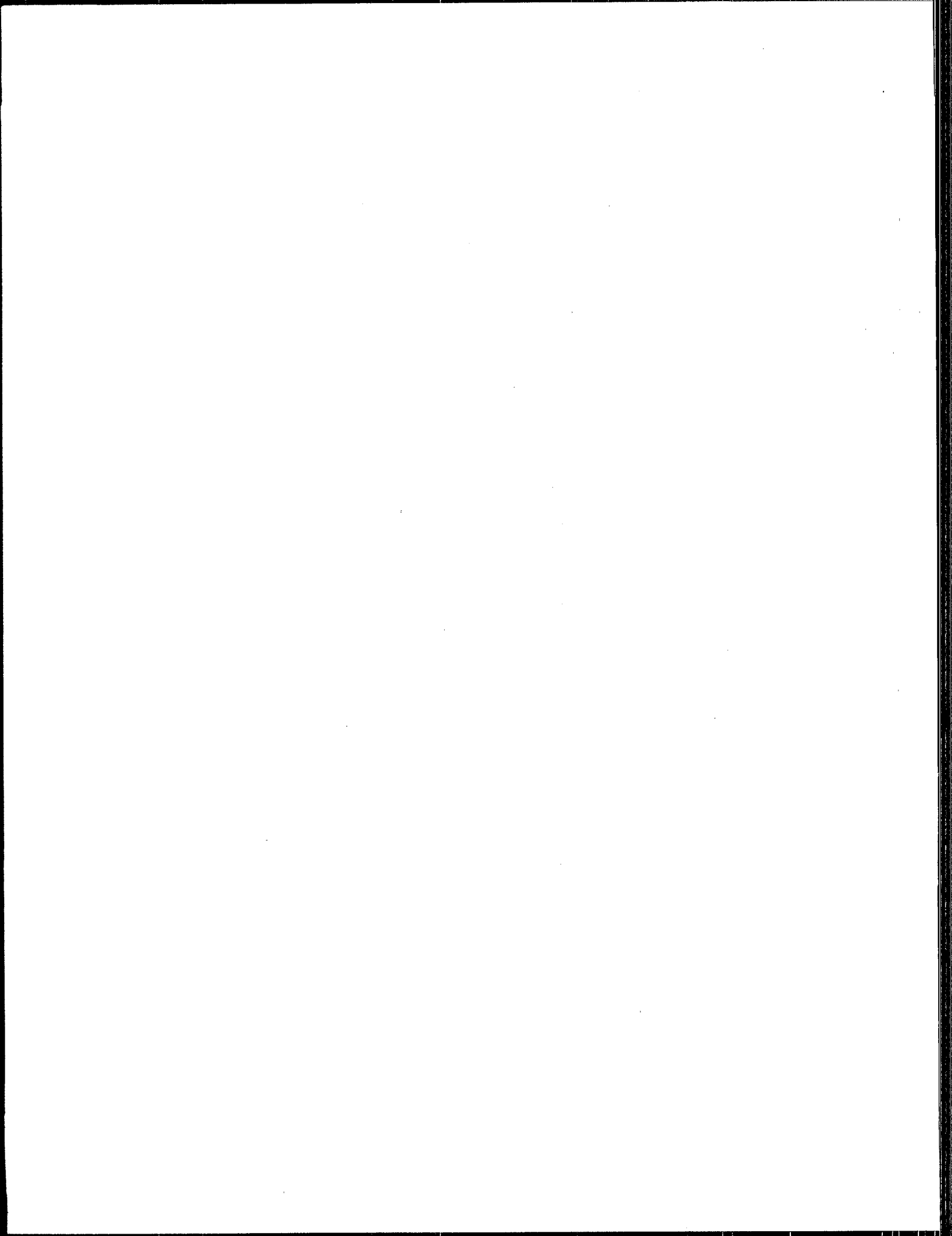
9.4 EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1987.

This document is a preliminary draft  
\* has not been formally released by EPA  
and should not at this stage be construed  
to represent Agency policy. It is being  
circulated for comment on its technical  
accuracy and policy implications



## APPENDIX B

### MEASUREMENT OF TOTAL HYDROCARBONS IN STACK GASES



**METHOD 25A—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER**

**1. Applicability and Principle**

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a flame ionization analyzer (FIA). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

**2. Definitions**

2.1 Measurement System. The total equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of the system that is used for one or more of the following: sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

2.1.2 Organic Analyzer. That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

2.2 Span Value. The upper limit of a gas concentration measurement range that is

specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

2.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.

2.4 Zero Drift. The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.5 Calibration Drift. The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair or adjustment took place.

2.6 Response Time. The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

2.7 Calibration Error. The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

**3. Apparatus**

A schematic of an acceptable measurement system is shown in Figure 25A-1. The essential components of the measurement system are described below:

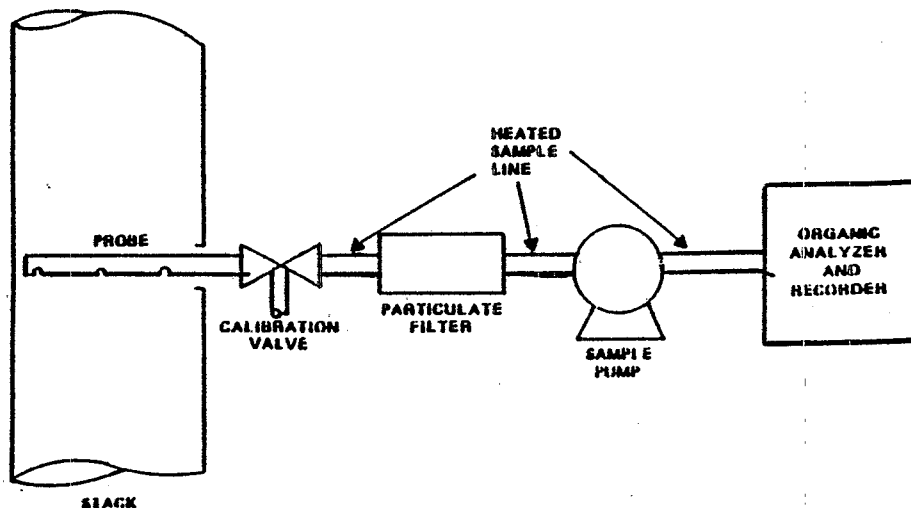
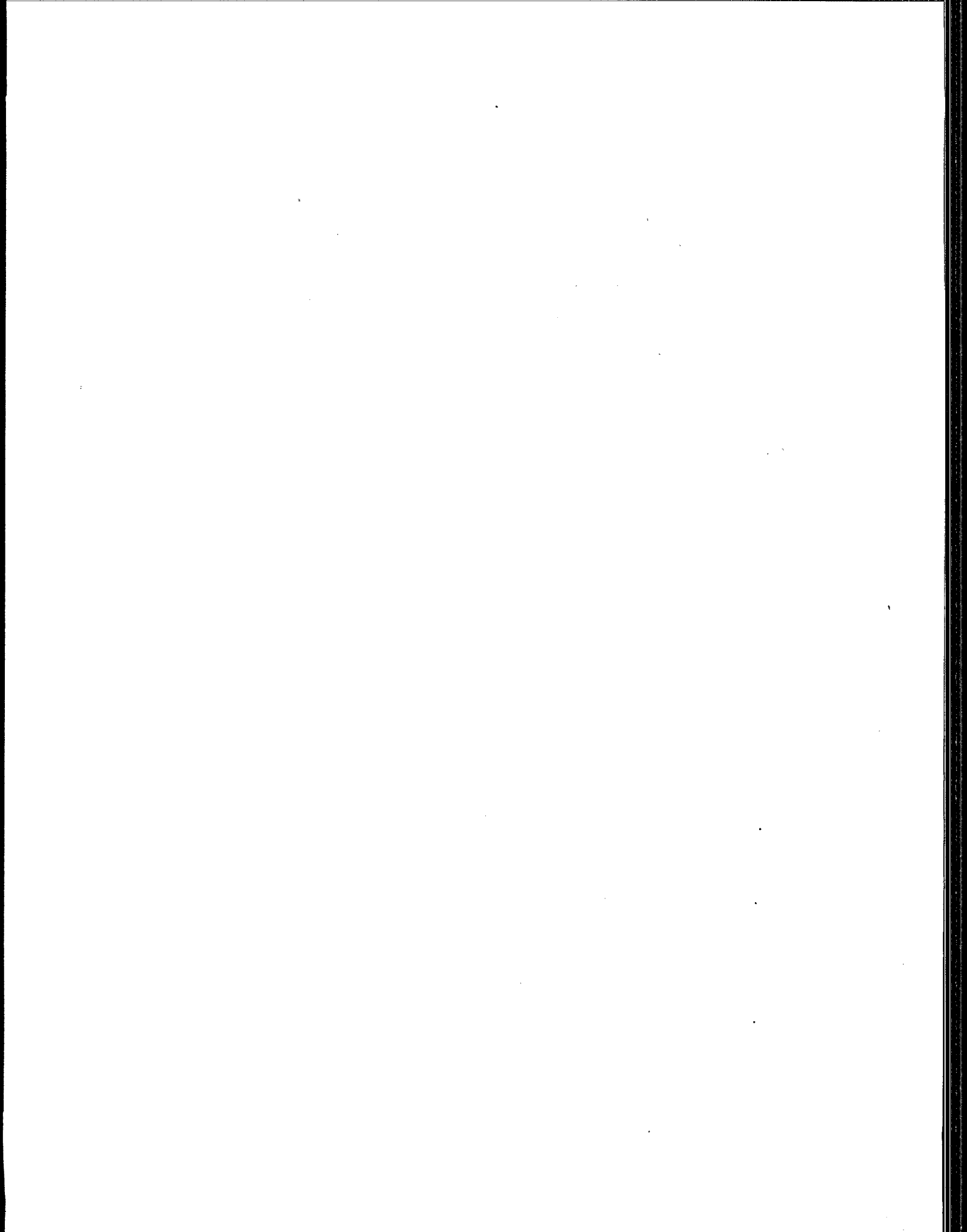


Figure 25A-1. Organic Concentration Measurement System.



3.1 Organic Concentration Analyzer. A flame ionization analyzer (FIA) capable of meeting or exceeding the specifications in this method.

3.2 Sample Probe. Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross-section.

3.3 Sample Line. Stainless steel or Teflon\* tubing to transport the sample gas to the analyzer. The sample line should be heated, if necessary, to prevent condensation in the line.

3.4 Calibration Valve Assembly. A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

3.5 Particulate Filter. An in-stack or an out-of-stack glass fiber filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter should be heated to prevent any condensation.

3.6 Recorder. A strip-chart recorder, analog computer, or digital recorder for recording measurement data. The minimum data recording requirement is one measurement value per minute. Note: This method is often applied in highly explosive areas. Caution and care should be exercised in choice of equipment and installation.

#### 4. Calibration and Other Gases

Gases used for calibrations, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1, listed in Reference 9.2. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than  $\pm 2$  percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems, may be used with prior approval of the Administrator.

Calibration gases usually consist of propane in air or nitrogen and are determined in terms of the span value. Organic compounds other than propane can be used following the above guidelines and making the appropriate corrections for response factor.

\* Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

4.1 Fuel. A 40 percent  $H_2$ /60 percent  $He$  or 40 percent  $H_2$ /60 percent  $N_2$  gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 Zero Gas. High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

4.3 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

4.4 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 High-level Calibration Gas. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

#### 5. Measurement System Performance Specifications

5.1 Zero Drift. Less than  $\pm 3$  percent of the span value.

5.2 Calibration Drift. Less than  $\pm 3$  percent of span value.

5.3 Calibration Error. Less than  $\pm 5$  percent of the calibration gas value.

#### 6. Pretest Preparations

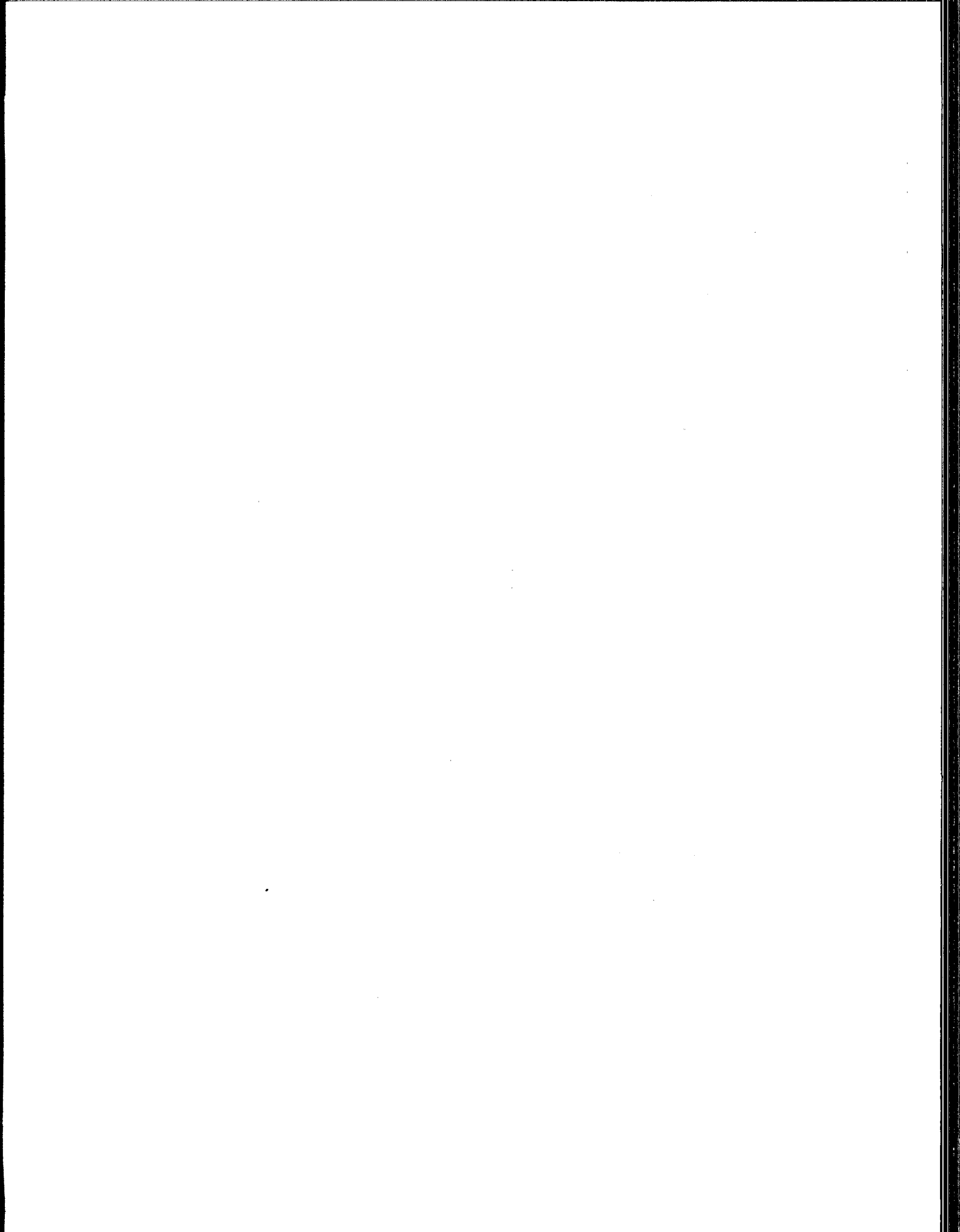
6.1 Selection of Sampling Site. The location of the sampling site is generally specified by the applicable regulation or purpose of the test; i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 meters or 2 equivalent diameters upstream of the gas discharge to the atmosphere.

6.2 Location of Sample Probe. Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

FIA equipment can be calibrated for almost any range of total organics concentrations. For high concentrations of organics ( $>1.0$  percent by volume as propane) modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

6.4 Calibration Error Test. Immediately prior to the test series, (within 2 hours of the start of the test) introduce zero gas and





high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

6.5 Response Time Test. Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

#### 7. Emission Measurement Test Procedure

7.1 Organic Measurement. Begin sampling at the start of the test period, recording time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 Drift Determination. Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

#### 8. Organic Concentration Calculations

Determine the average organic concentration in terms of ppmv as propane or other

calibration gas. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

If results are required in terms of ppmv as carbon, adjust measured concentrations using Equation 25A-1.

$$C_c = K C_{\text{meas}} \quad \text{Eq. 25A-1}$$

Where:

$C_c$  = Organic concentration as carbon, ppmv.

$C_{\text{meas}}$  = Organic concentration as measured, ppmv.

$K$  = Carbon equivalent correction factor,

$K=2$  for ethane.

$K=3$  for propane.

$K=4$  for butane.

$K$  = Appropriate response factor for other organic calibration gases.

#### 9. Bibliography

9.1 Measurement of Volatile Organic Compounds—Guideline Series. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-450/2-78-041. June 1978. p. 46-54.

9.2 Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Research Triangle Park, NC. June 1978.

9.3 Gasoline Vapor Emission Laboratory Evaluation—Part 2. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC. EMB Report No. 75-GAS-6. August 1975.

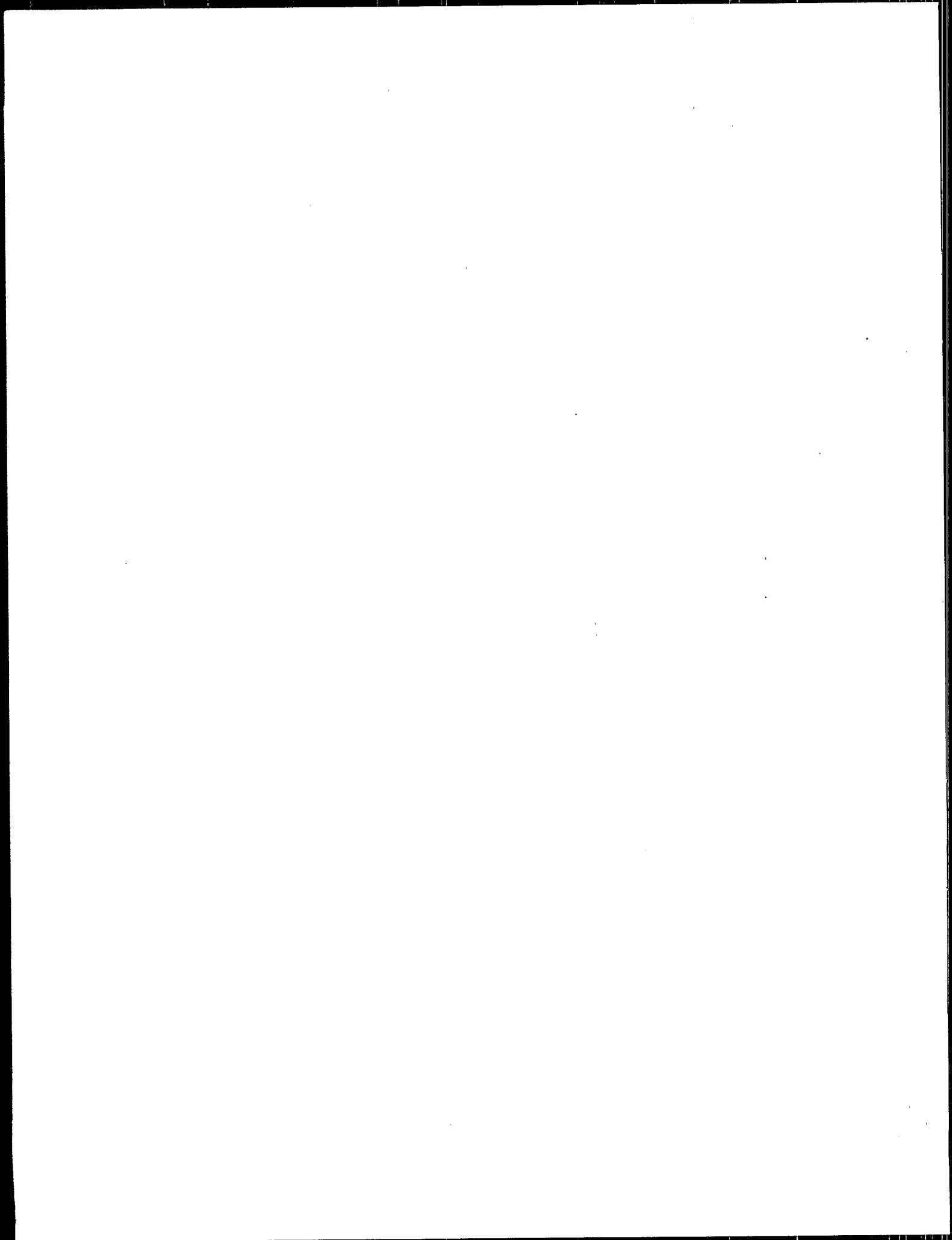
#### METHOD 25B—DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A NONDISPERSIVE INFRARED ANALYZER

##### 1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes. (Other organic materials may be measured using the general procedure in this method, the appropriate calibration gas, and an analyzer set to the appropriate absorption band.) The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.

1.2 Principle. A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a nondispersive infrared analyzer (NDIR). Results are reported as volume concentration equivalents of the calibration gas or as carbon equivalents.

##### 2. Definitions



The terms and definitions are the same as for Method 25A.

### 3. Apparatus

The apparatus is the same as for Method 25A with the exception of the following:

3.1 Organic Concentration Analyzer. A nondispersive infrared analyzer designed to measure alkane organics and capable of meeting or exceeding the specifications in this method.

### 4. Calibration Gases

The calibration gases are the same as required for Method 25A, Section 4. No fuel gas is required for an NDIR.

### 5. Measurement System Performance Specifications

5.1 Zero Drift. Less than  $\pm 3$  percent of the span value.

5.2 Calibration Drift. Less than  $\pm 3$  percent of the span value.

5.3 Calibration Error. Less than  $\pm 5$  percent of the calibration gas value.

### 6. Pretest Preparations

6.1 Selection of Sampling Site. Same as in Method 25A, Section 6.1.

6.2 Location of Sample Probe. Same as in Method 25A, Section 6.2.

6.3 Measurement System Preparation. Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

6.4 Calibration Error Test. Same as in Method 25A, Section 6.4.

6.5 Response Time Test Procedure. Same as in Method 25A, Section 6.5.

### 7. Emission Measurement Test Procedure

Proceed with the emission measurement immediately upon satisfactory completion of the calibration.

7.1 Organic Measurement. Same as in Method 25A, Section 7.1.

7.2 Drift Determination. Same as in Method 25A, Section 7.2.

### 8. Organic Concentration Calculations

The calculations are the same as in Method 25A, Section 8.

### 9. Bibliography

The bibliography is the same as in Method 25A, Section 9.

## METHOD 27—DETERMINATION OF VAPOR TIGHTNESS OF GASOLINE DELIVERY TANK USING PRESSURE-VACUUM TEST

### 1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of vapor tightness of a gasoline delivery tank which is equipped with vapor collection equipment.

1.2 Principle. Pressure and vacuum are applied alternately to the compartments of

a gasoline delivery tank and the change in pressure or vacuum is recorded after a specified period of time.

### 2. Definitions and Nomenclature

2.1 Gasoline. Any petroleum distillate or petroleum distillate/alcohol blend having a Reid vapor pressure of 27.6 kilopascals or greater which is used as a fuel for internal combustion engines.

2.2 Delivery Tank. Any container, including associated pipes and fittings, that is attached to or forms a part of any truck, trailer, or railcar used for the transport of gasoline.

2.3 Compartment. A liquid-tight division of a delivery tank.

2.4 Delivery Tank Vapor Collection Equipment. Any piping, hoses, and devices on the delivery tank used to collect and route gasoline vapors either from the tank to a bulk terminal vapor control system or from a bulk plant or service station into the tank.

2.5 Time Period of the Pressure or Vacuum Test ( $t$ ). The time period of the test, as specified in the appropriate regulation, during which the change in pressure or vacuum is monitored, in minutes.

2.6 Initial Pressure ( $P_i$ ). The pressure applied to the delivery tank at the beginning of the static pressure test, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.7 Initial Vacuum ( $V_i$ ). The vacuum applied to the delivery tank at the beginning of the static vacuum test, as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.8 Allowable Pressure Change ( $\Delta p$ ). The allowable amount of decrease in pressure during the static pressure test, within the time period  $t$ , as specified in the appropriate regulation, in mm H<sub>2</sub>O.

2.9 Allowable Vacuum Change ( $\Delta v$ ). The allowable amount of decrease in vacuum during the static vacuum test, within the time period  $t$ , as specified in the appropriate regulation, in mm H<sub>2</sub>O.

### 3. Apparatus

3.1 Pressure Source. Pump or compressed gas cylinder of air or inert gas sufficient to pressurize the delivery tank to 500 mm H<sub>2</sub>O above atmospheric pressure.

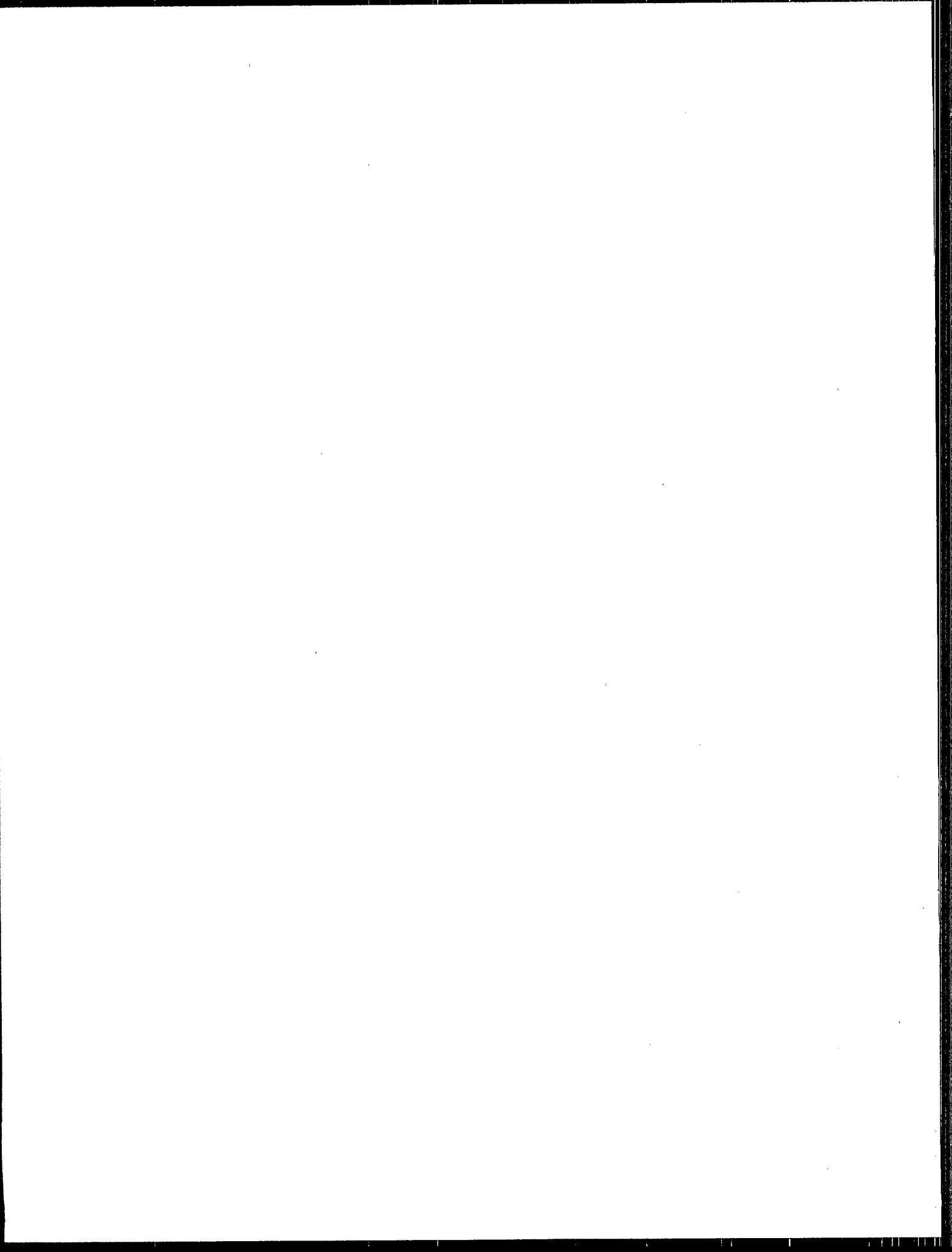
3.2 Regulator. Low pressure regulator for controlling pressurization of the delivery tank.

3.3 Vacuum Source. Vacuum pump capable of evacuating the delivery tank to 250 mm H<sub>2</sub>O below atmospheric pressure.

3.4 Pressure-Vacuum Supply Hose.

3.5 Manometer. Liquid manometer, or equivalent instrument, capable of measuring up to 500 mm H<sub>2</sub>O gauge pressure with  $\pm 2.5$  mm H<sub>2</sub>O precision.

3.6 Pressure-Vacuum Relief Valves. The test apparatus shall be equipped with an inline pressure-vacuum relief valve set to acti-

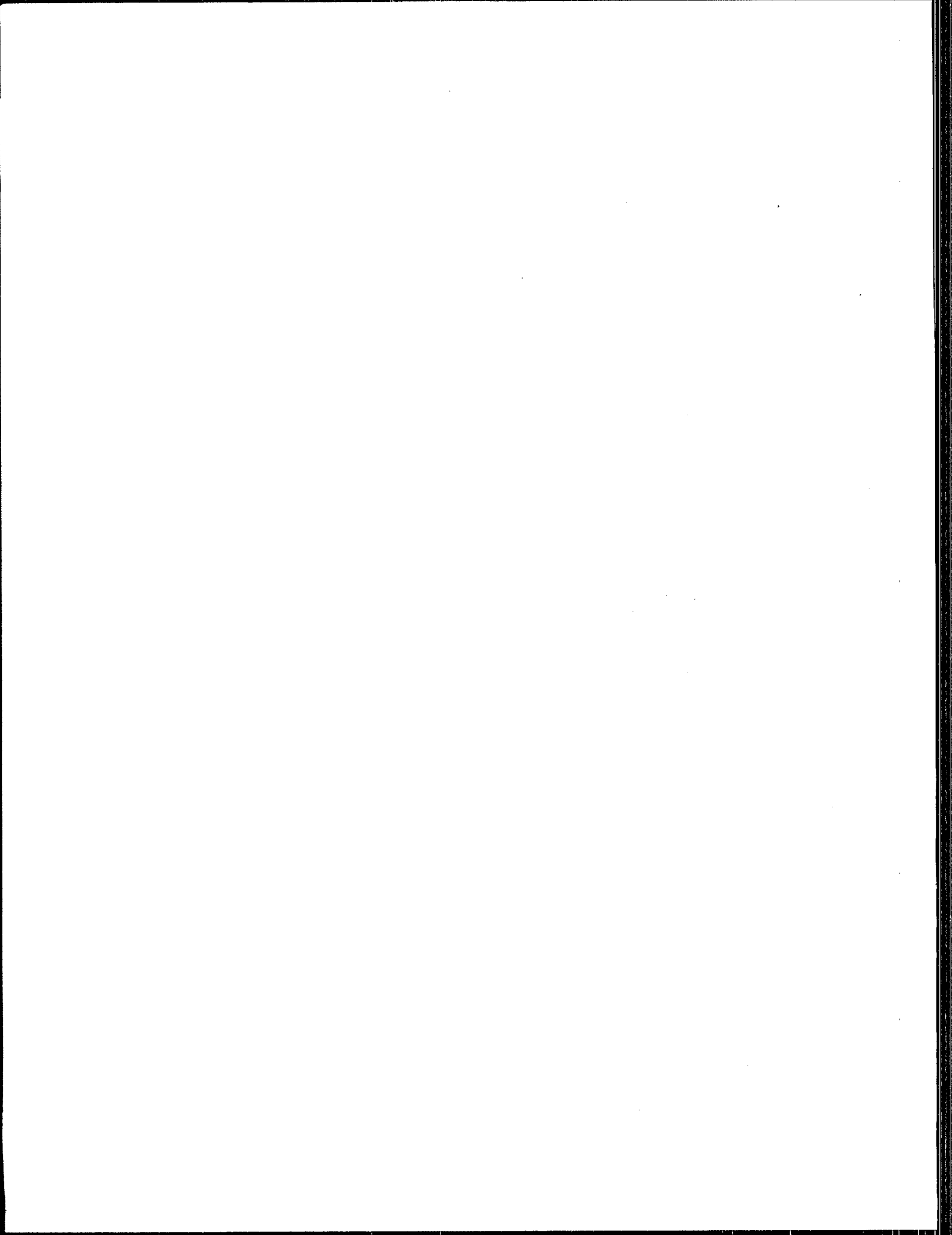


## APPENDIX C

### DRAFT METHOD FOR DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS FROM STATIONARY SOURCES<sup>a</sup>

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<sup>a</sup>This method is a preliminary draft that has not been formally released by EPA.



DRAFT - 08/13/90

METHOD  $\text{Cr}^{+6}$  - DETERMINATION OF HEXAVALENT CHROMIUM EMISSIONS  
FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of hexavalent chromium ( $\text{Cr}^{+6}$ ) emissions from hazardous waste incinerators, municipal waste combustors, and sewage sludge incinerators. With the approval of the Administrator, this method may also be used to measure total chromium. The sampling train, constructed of Teflon components, has only been evaluated at temperatures less than 300°F. Trains constructed of other materials, for testing at higher temperatures, are currently being evaluated.

1.2 Principle. For incinerators and combustors, the  $\text{Cr}^{+6}$  emissions are collected isokinetically from the source. To eliminate the possibility of  $\text{Cr}^{+6}$  reduction between the nozzle and impinger, the emission samples are collected with a recirculatory train where the impinger reagent is continuously recirculated to the nozzle. Recovery procedures include a post-sampling purge and filtration. The impinger train samples are analyzed for  $\text{Cr}^{+6}$  by an ion chromatograph equipped with a post-column reactor and a visible wavelength detector. The IC/PCR separates the  $\text{Cr}^{+6}$  as chromate ( $\text{CrO}_4^{2-}$ ) from other components in the sample matrices that may interfere with the  $\text{Cr}^{+6}$ -specific diphenylcarbazide reaction that occurs in the post-column reactor. To increase sensitivity for trace levels of chromium, a preconcentration system is also used in conjunction with the IC/PCR.

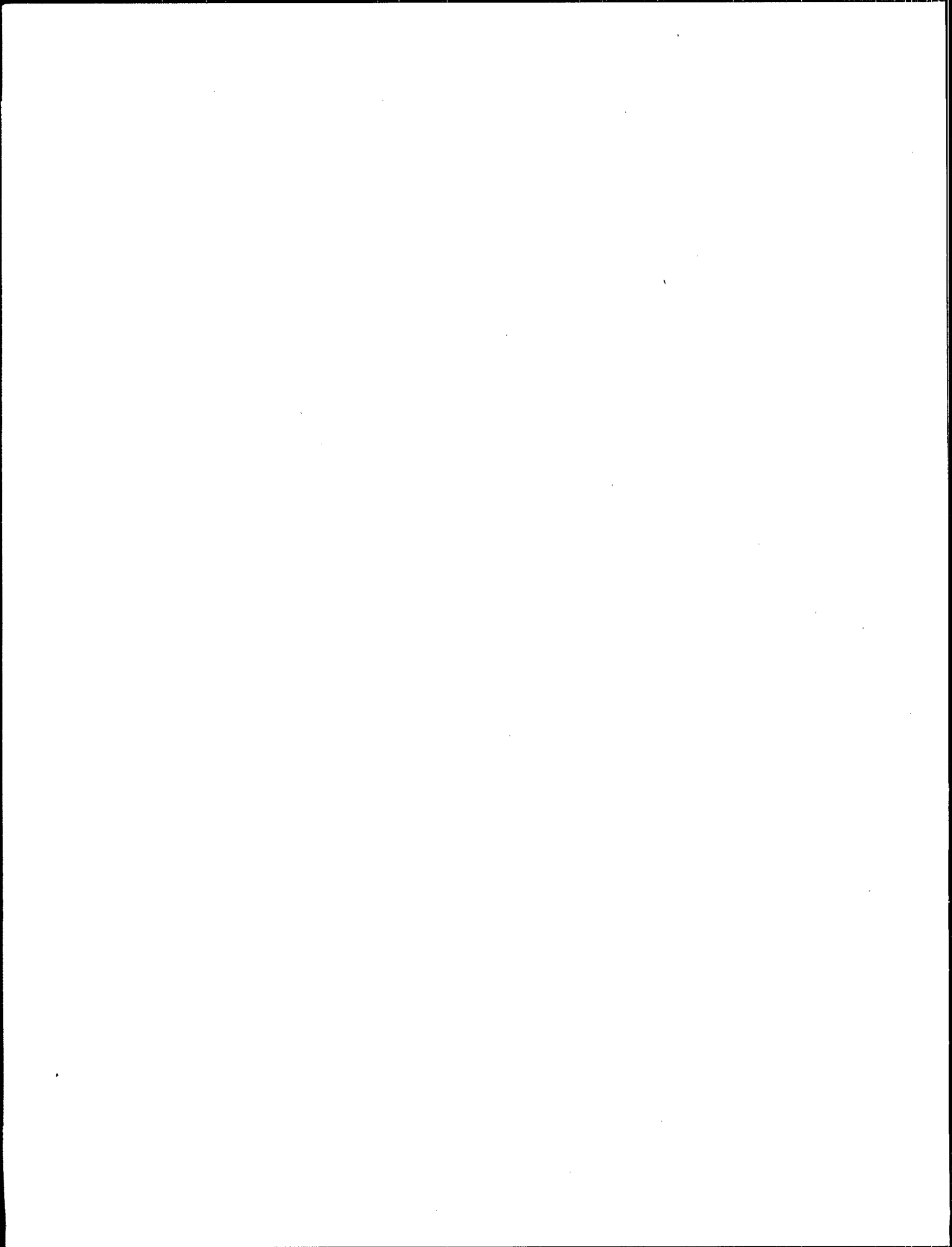
2. Range, Sensitivity, Precision, and Interference

2.1 Range. Employing a preconcentration procedure, the lower limit of the detection range can be extended to 16 nanograms per dry standard cubic meter (ng/dscm) with a 3 dscm gas sample (0.1 ppb in solution). With sample dilution, there is no upper limit.

2.2 Sensitivity. A minimum detection limit of 8 ng/dscm with a 3 dscm gas sample can be achieved by preconcentration (0.05 ppb in solution).

2.3 Precision. The precision of the IC/PCR with sample preconcentration is 5 to 10 percent. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of  $\text{Cr}^{+6}$  and 3.5 ug/dscm of total chromium is 25% and 9% for  $\text{Cr}^{+6}$  and total chromium, respectively.

2.4 Interference. Components in the sample matrix may cause  $\text{Cr}^{+6}$  to convert to trivalent chromium ( $\text{Cr}^{+3}$ ) or cause  $\text{Cr}^{+3}$  to convert to  $\text{Cr}^{+6}$ . A post-sampling nitrogen purge and sample filtration are included to eliminate many of these interferences. The chromatographic separation of  $\text{Cr}^{+6}$  using ion chromatography reduces the potential for other metals to interfere with the post-column reaction. For the IC/PCR analysis, only compounds that coelute





with Cr<sup>6</sup> and affect the diphenylcarbazide reaction will cause interference. Periodic analysis of deionized (DI) water blanks is used to demonstrate that the analytical system is essentially free from contamination. Sample cross-contamination that can occur when high-level and low-level samples or standards are analyzed alternately is eliminated by thorough purging of the sample loop. Purging can easily be obtained by increasing the injection volume of the samples to ten times the size of the sample loop.

### 3. Apparatus

3.1 Sampling Train. Schematics of the recirculatory sampling trains employed in this method are shown in Figures Cr<sup>6</sup>-1 and Cr<sup>6</sup>-2. The recirculatory train is readily assembled from commercially available components. All portions of the train in contact with the sample are either glass, quartz, Tygon, or Teflon, and are to be cleaned as per subsection 5.1.1.

The metering system is identical to that specified by Method 5 (see section 3.8.1); the sampling train consists of the following components:

3.1.1 Probe Nozzle. Glass or Teflon with a sharp, tapered leading edge. The angle of taper shall be  $\leq 30^\circ$  and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator.

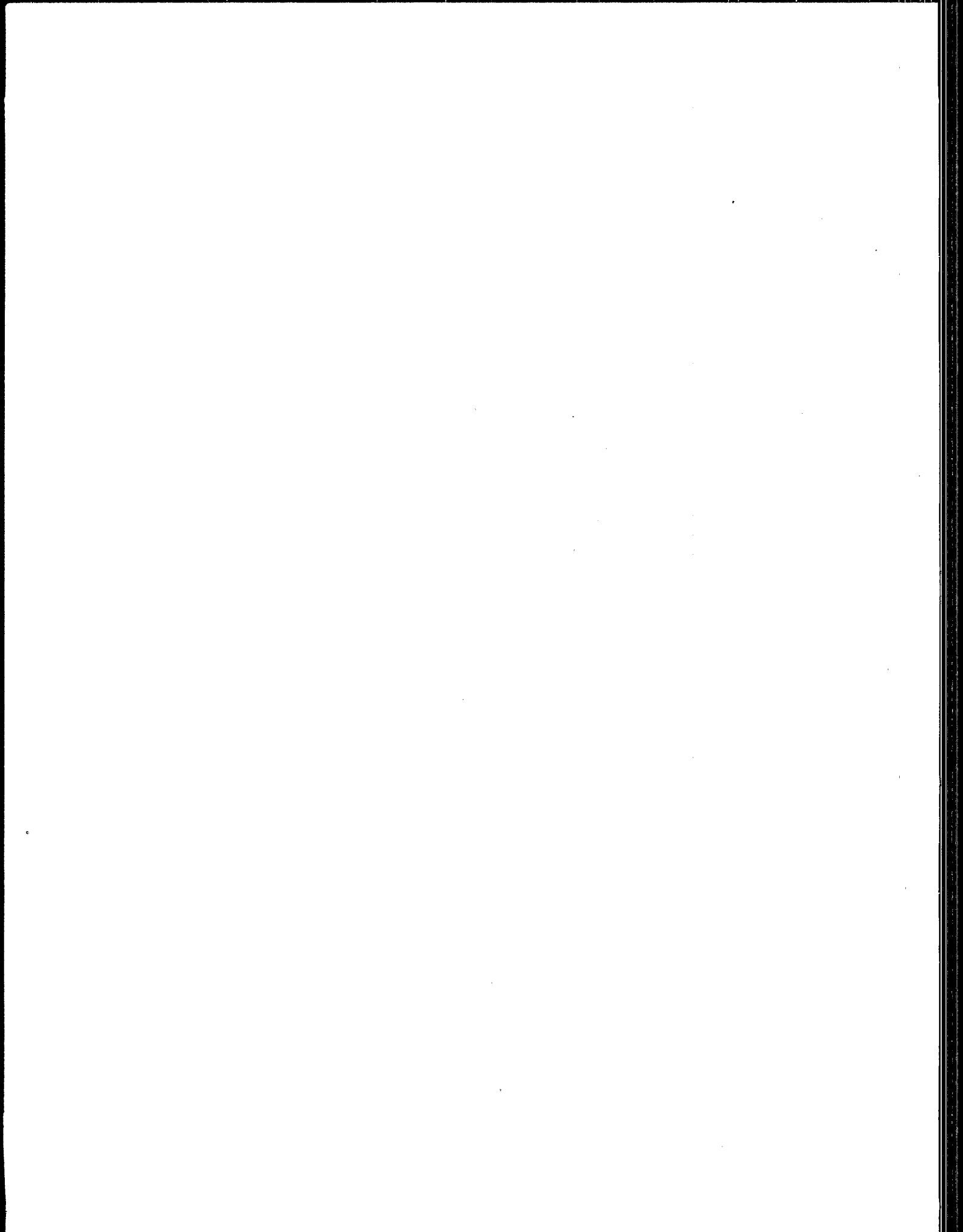
A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) -- or larger if higher volume sample trains are used -- inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 6.

3.1.2 Teflon Aspirator or Pump/Sprayer Assembly. Teflon aspirator capable of recirculating absorbing reagent at 50 ml/min while operating at 0.75 cfm. Alternatively, a pump/sprayer assembly may be used instead of the Teflon aspirator. A Teflon union-T is connected behind the nozzle to provide the absorbing reagent/sample gas mix; a peristaltic pump is used to recirculate the absorbing reagent at a flow rate of at least 50 ml/min. Teflon fittings, Teflon ferrules, and Teflon nuts are used to connect a glass or Teflon nozzle, recirculation line, and sample line to the Teflon aspirator or union-T. Tygon, C-flex\* or other suitable inert tubing for use with peristaltic pump.

3.1.3 Teflon Sample Line. Teflon, 3/8" outside diameter (OD) and 1/4" inside diameter (ID), or 1/2" OD x 3/8" ID, of suitable length to connect aspirator (or T-union) to first Teflon impinger.

3.1.4 Teflon Recirculation Line. Teflon, 1/4" O.D. and 1/8" I.D., of suitable length to connect first impinger to aspirator (or T-union).

\*NOTE: Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.



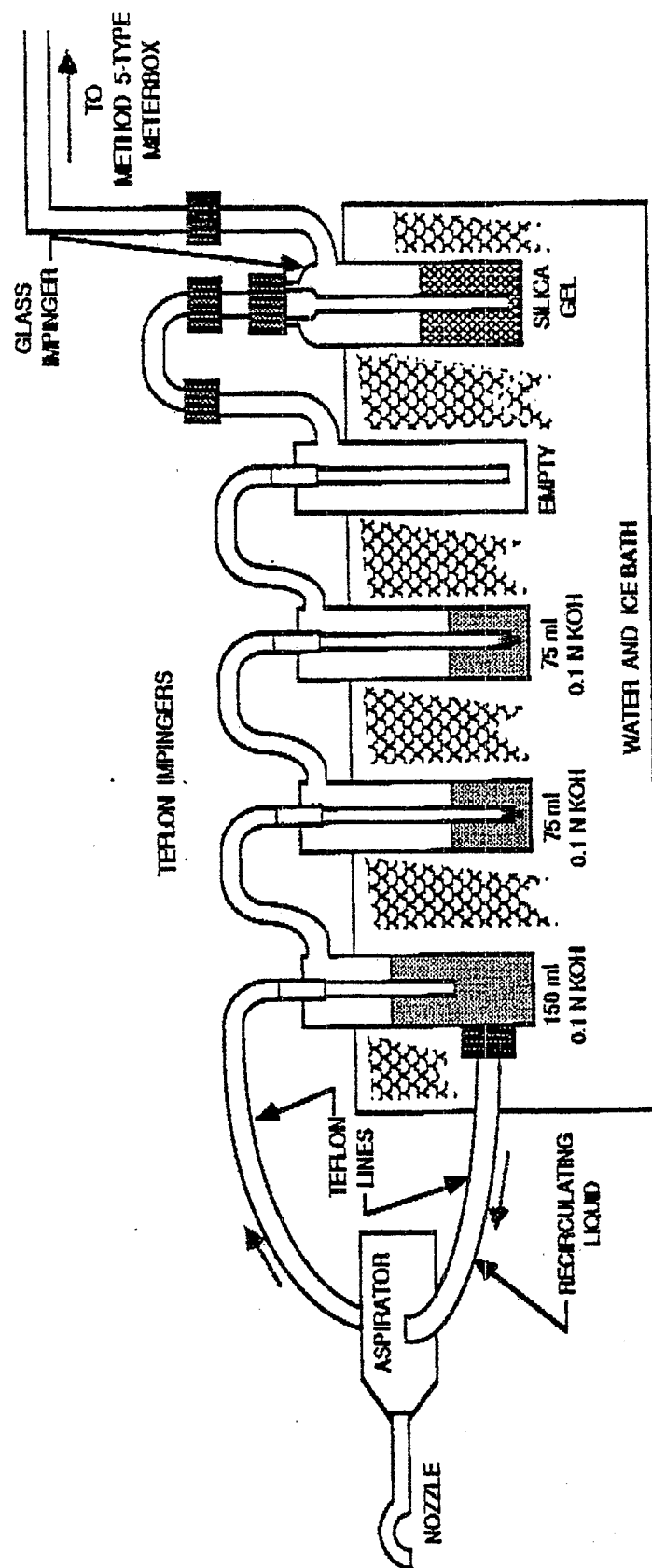
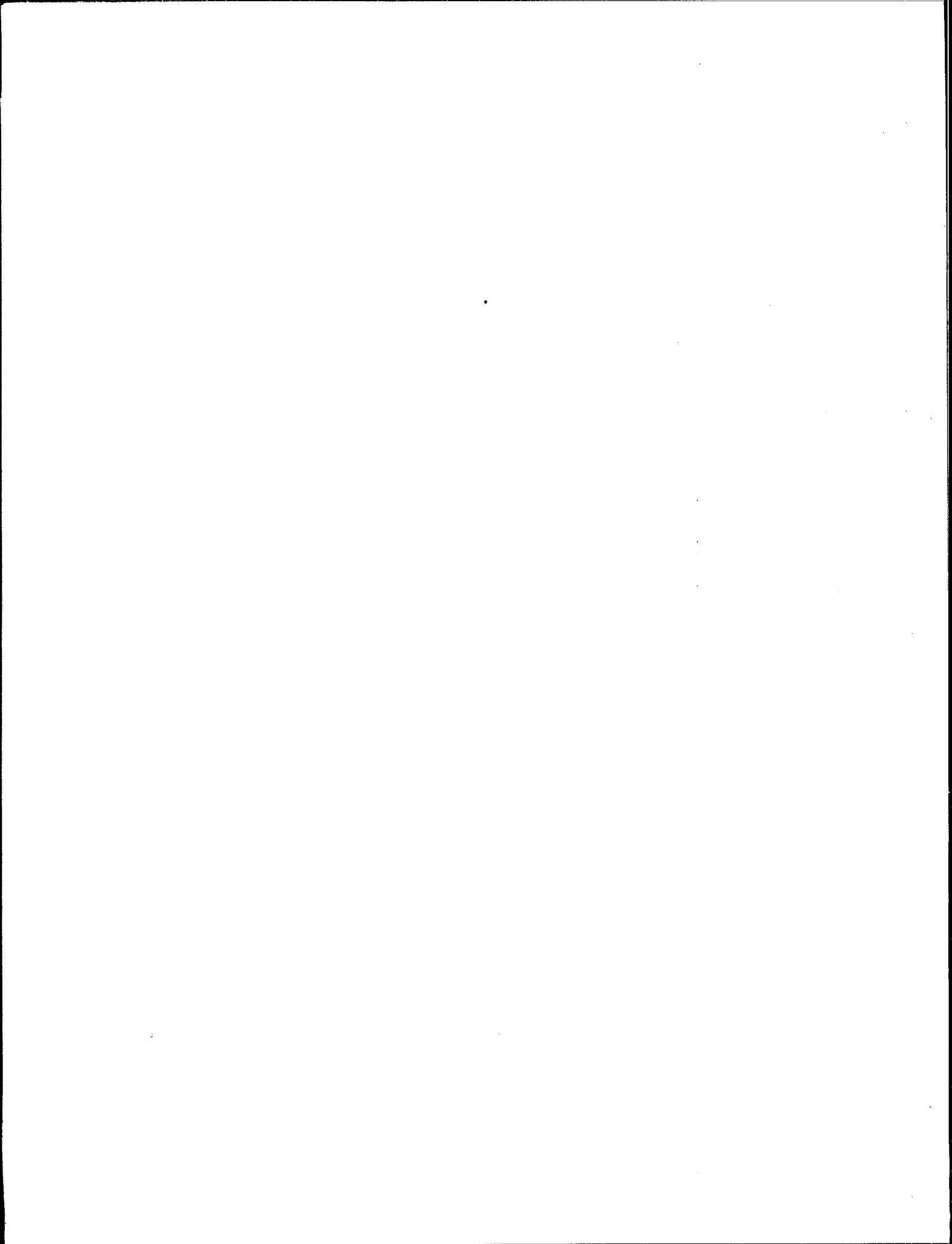


Figure Cr-6 -1. Schematic of recirculatory impinger train with aspirator assembly.



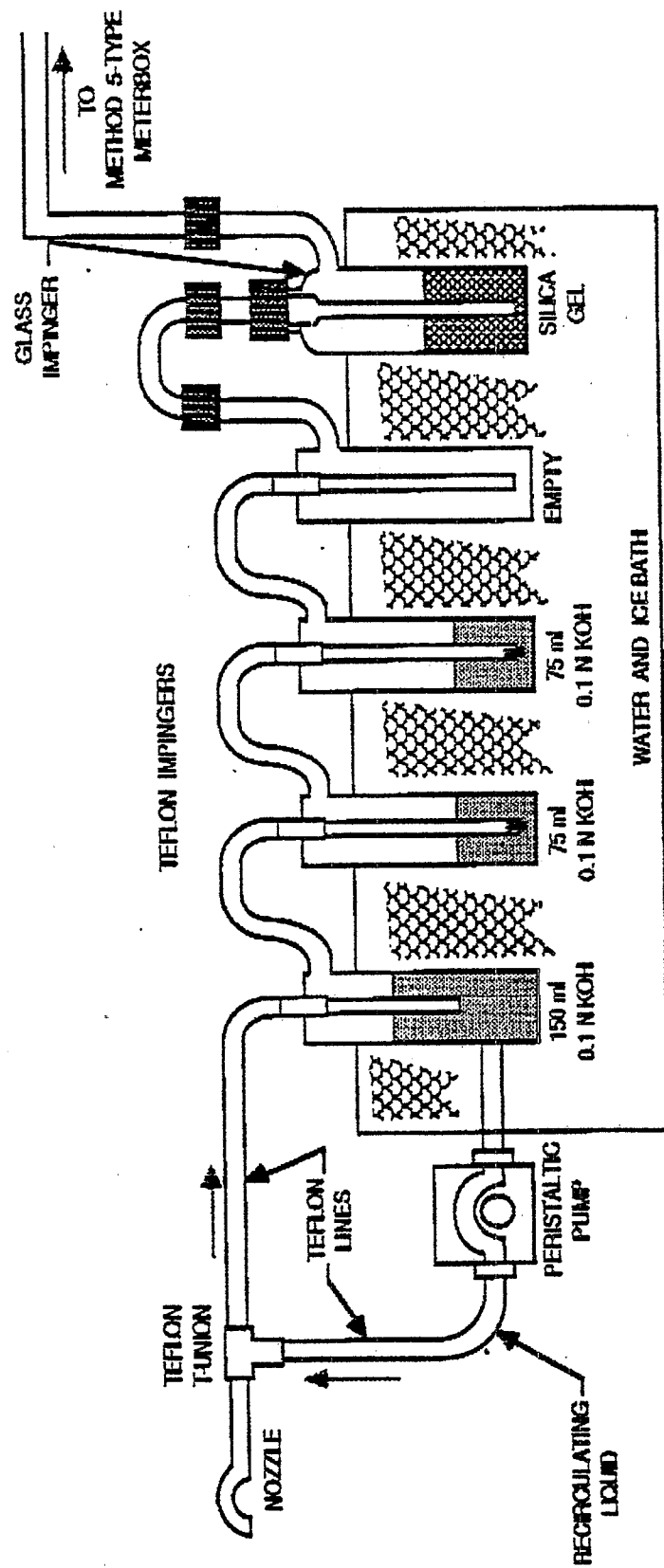
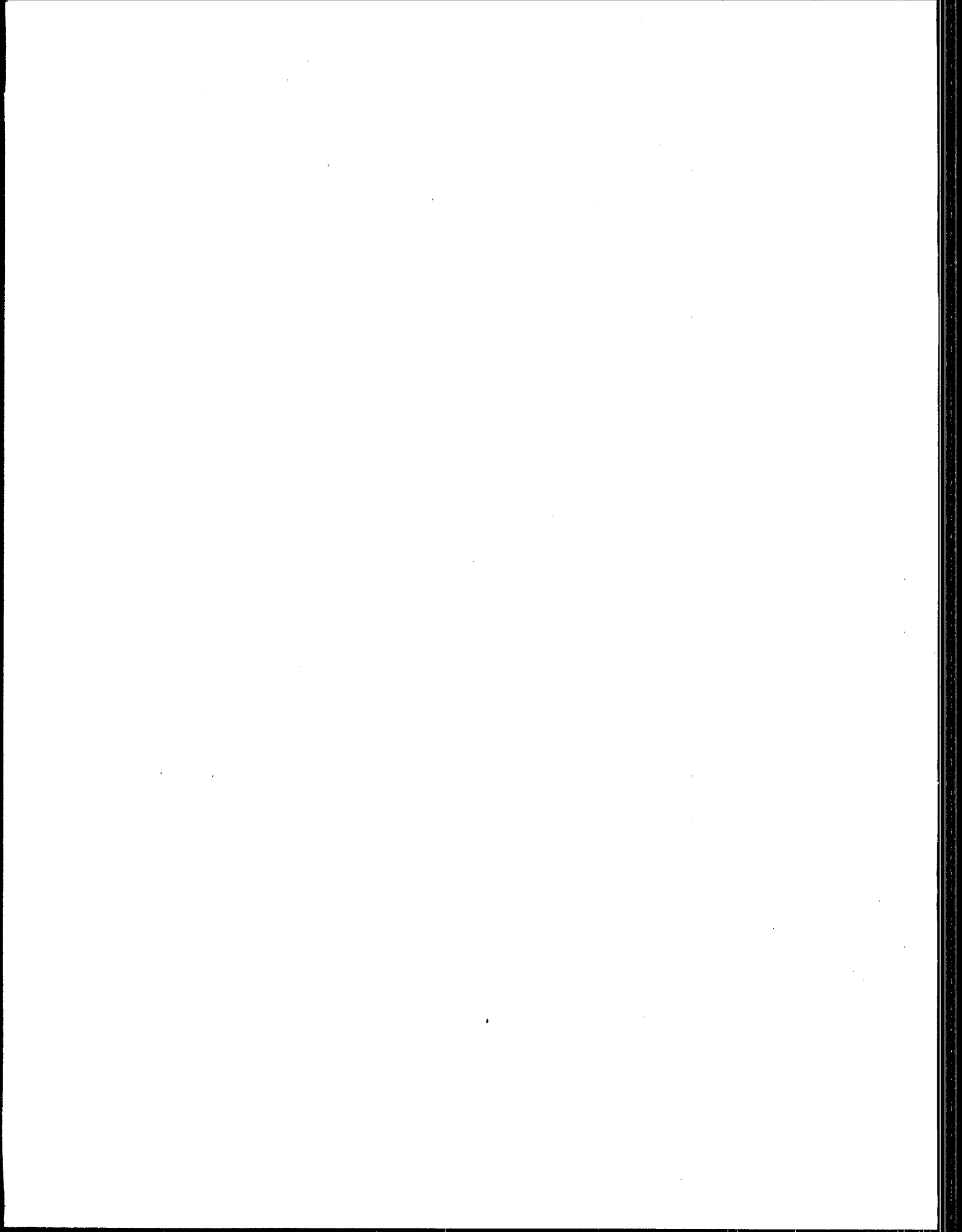


Figure Cr-6 -2. Schematic of recirculatory impinger train with pump/sprayer assembly.



3.1.5 Teflon Impingers. Four Teflon impingers; Teflon tubes and fittings, such as made by Savillex, can be used to construct impingers 2" diameter by 12" long, with vacuum-tight 3/8" O.D. Teflon compression fittings. Alternatively, standard glass impingers that have been Teflon-lined, with Teflon stems and U-tubes, may be used. Inlet fittings on impinger top to be bored through to accept 3/8" O.D. tubing as impinger stem. The second and third 3/8" OD Teflon stem has a 1/4" OD Teflon tube, 2" long, inserted at its end to duplicate the effects of the Greenburg-Smith impinger stem. The first impinger stem should extend to 2" from impinger bottom, high enough in the impinger reagent to prevent air from entering recirculating line; the second and third impinger stems should extend to 1/2" from impinger bottom. The first impinger should include a 1/4" O.D. Teflon compression fitting for recirculation line. The fourth impinger serves as a knockout impinger.

3.1.6 Glass Impinger. Silica gel impinger. Vacuum-tight impingers, capable of containing 400 g. of silica gel, with compatible fittings. The silica gel impinger will have a modified stem (1/2" ID at tip of stem).

3.1.7 Thermometer, (identical to that specified by Method 5) at the outlet of the silica gel impinger, to monitor the exit temperature of the gas.

3.1.8 Metering System, Barometer, and Gas Density Determinations Equipment. Same as Method 5, Section 2.1.8 through 2.1.10, respectively.

3.2 Sample Recovery. Clean all items for sample handling or storage with 10% nitric acid solution by soaking, where possible, and rinse thoroughly with DI water before use.

3.2.1 Nitrogen Purge Line. Inert tubing and fittings capable of delivering 0 to 1 scf/min (continuously adjustable) of nitrogen gas to the impinger train from a standard gas cylinder (See Figure Cr-6-3). Standard 3/8-inch Teflon tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve may be used.

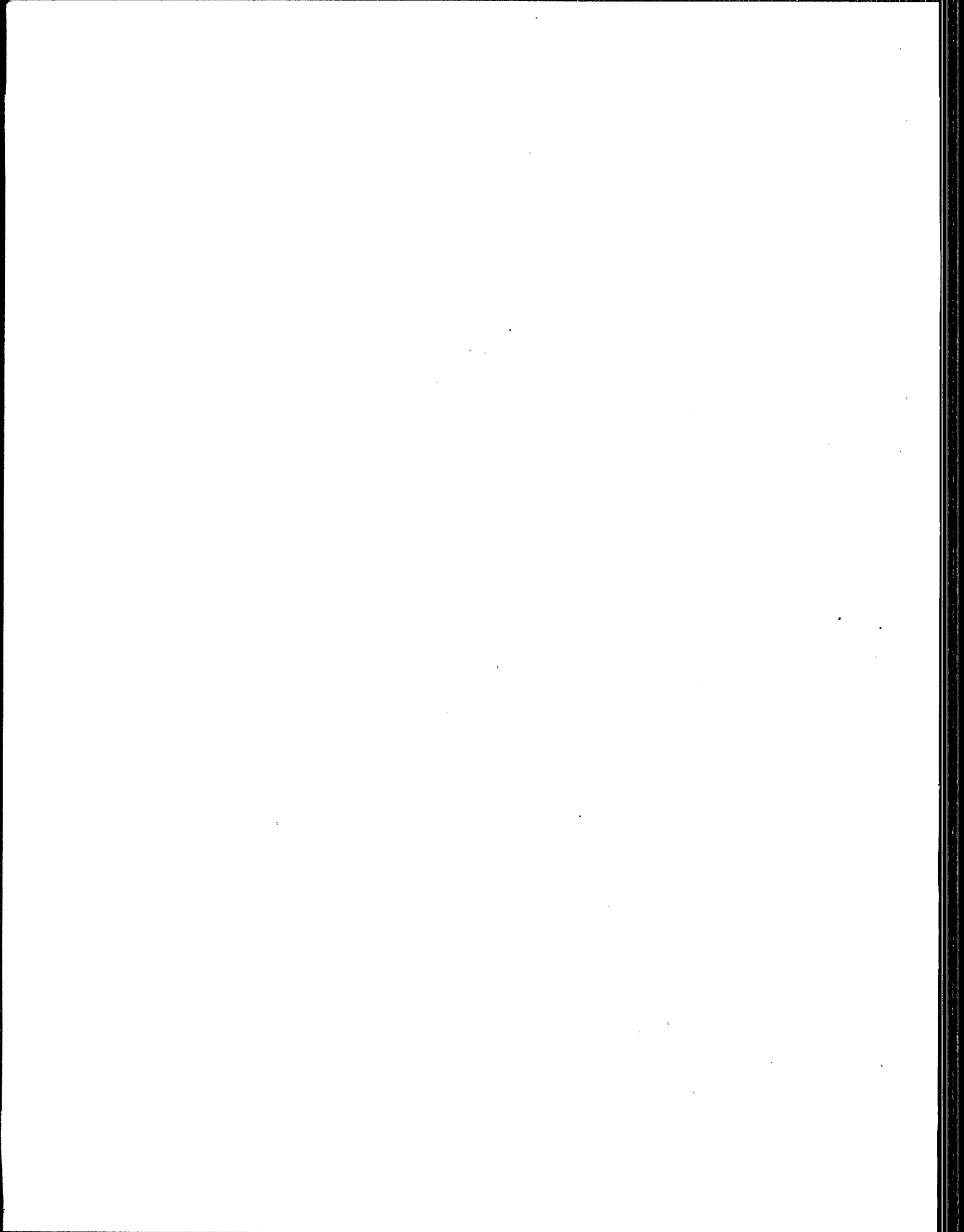
3.2.2 Wash Bottles. Two polyethylene wash bottles, for DI water and nitric rinse solution.

3.2.3 Sample Storage Containers. Polyethylene, with leak-free screw cap, 500-ml or 1000-ml.

3.2.4 1000-ml Graduated Cylinder and Balance.

3.2.5 Plastic Storage Containers. Air tight containers to store silica gel.

3.2.6 Funnel and Rubber Policeman. To aid in transfer of silica gel from impinger to storage container; not necessary if silica gel is weighed directly in the impinger.





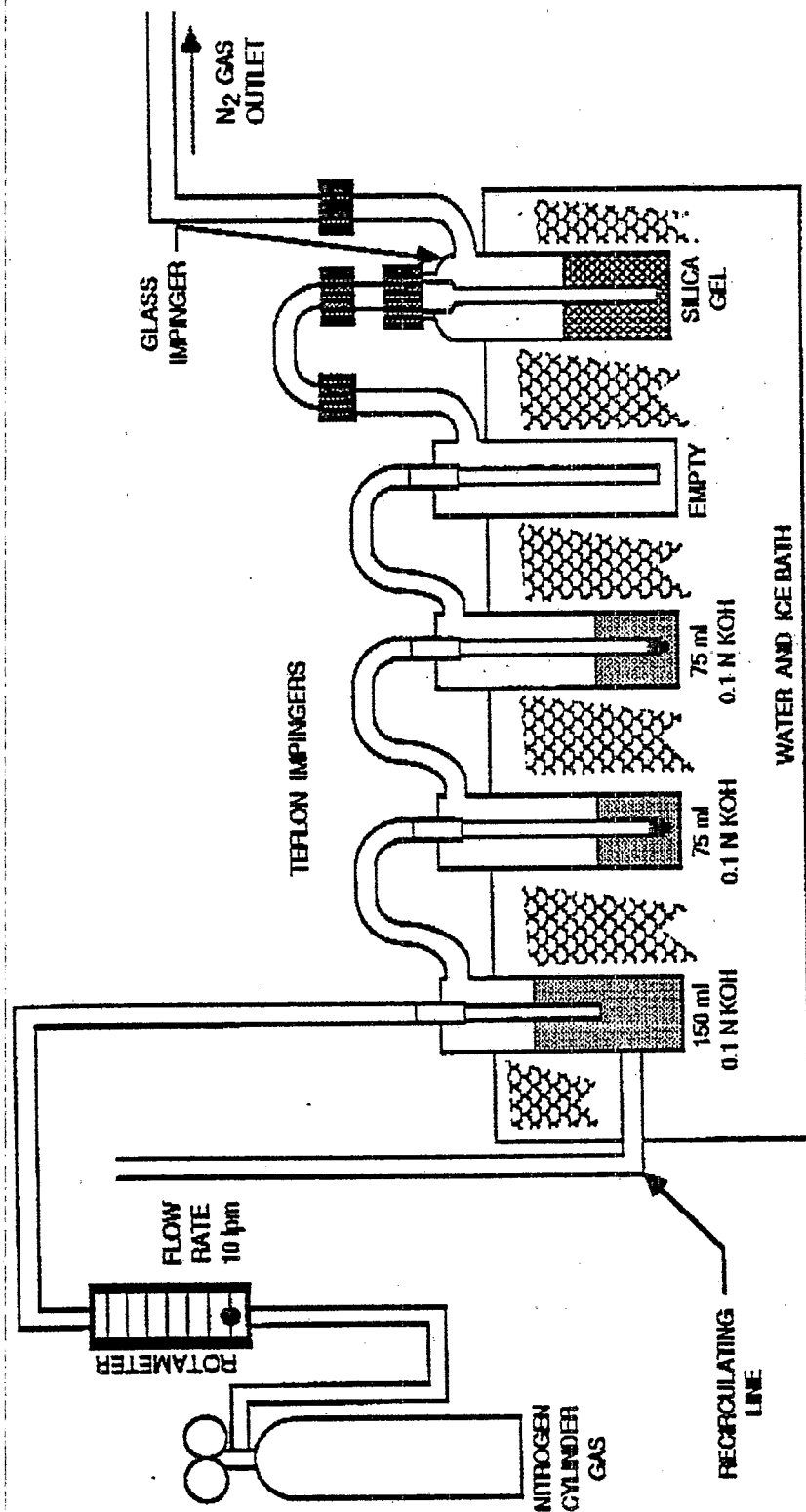
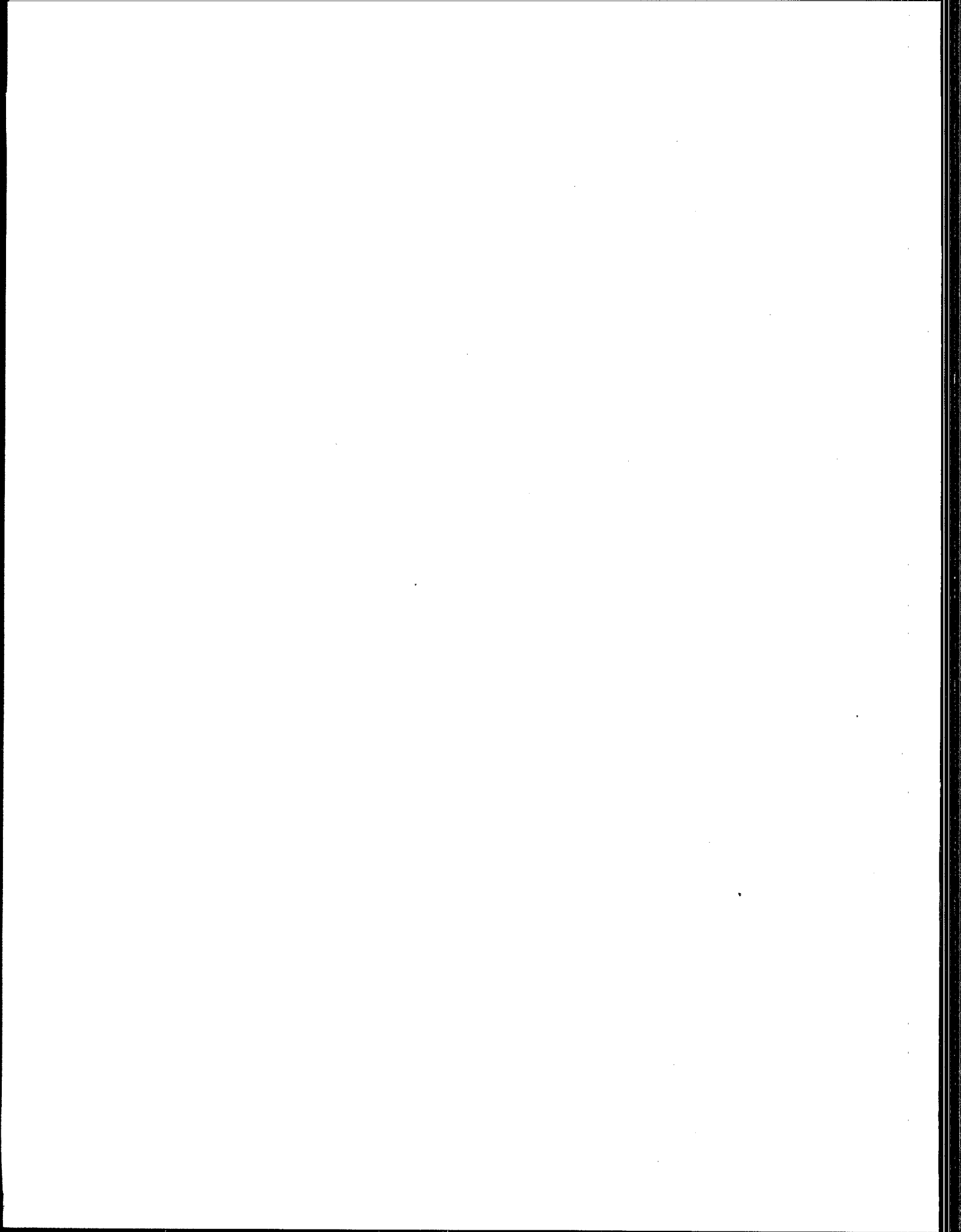


Figure C1-6 -3. Schematic of post test nitrogen purge system.



3.3 Sample Preparation for Analysis. Sample preparation prior to analysis includes purging the sample train immediately following the sample run, and filtering the recovered sample to remove particulate matter immediately following recovery.

3.3.1 Beakers, Funnel, Volumetric Flasks, Volumetric Pipets, and Graduated Cylinders. Assorted sizes, Teflon or glass, for preparation of samples, sample dilution, and preparation of calibration standards. Prepare initially following procedure described in Section 5.1.3 and rinse between use with 0.1 N  $\text{HNO}_3$  and DI water.

3.3.2 Filtration Apparatus. Teflon, or equivalent, for filtering samples, and Teflon filter holder. Teflon impinger components have been found to be satisfactory as a sample reservoir for pressure filtration using nitrogen.

### 3.4 Analysis.

3.4.1 IC/PCR System. High performance liquid chromatograph pump, sample injection valve, post-column reagent delivery and mixing system, and a visible detector, capable of operating at 520 nm, all with a non-metallic (or inert) flow path. An electronic recording integrator operating in the peak area mode is recommended, but other recording devices and integration techniques are acceptable provided the repeatability criteria and the linearity criteria for the calibration curve described in Section 5.5 can be satisfied. A sample loading system will be required if preconcentration is employed.

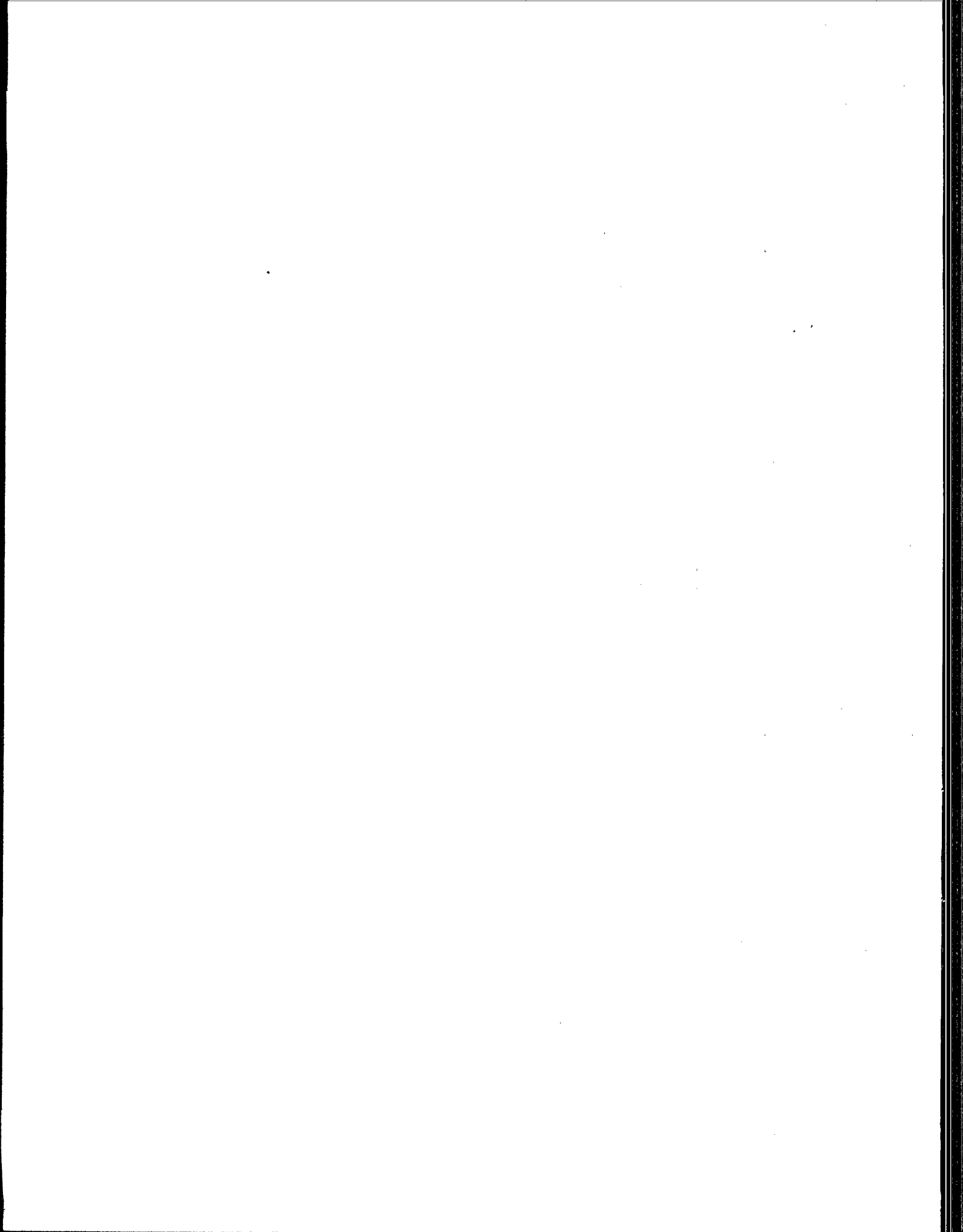
3.4.2 Analytical Column. A high performance ion chromatograph (HPIC) non-metallic column with anion separation characteristics and a high loading capacity designed for separation of metal chelating compounds to prevent metal interference. Resolution described in Section 5.4 must be obtained. A non-metallic guard column with the same ion-exchange material is recommended.

3.4.3 Preconcentration Column. An HPIC non-metallic column with acceptable anion retention characteristics and sample loading rates as described in Section 5.5.

3.4.4 0.45  $\mu\text{m}$  filter cartridge. For the removal of insoluble material. To be used just prior to sample injection/analysis.

## 4. Reagents

All reagents should, at a minimum, conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. All prepared reagents should be checked by IC/PCR analysis for  $\text{Cr}^{+6}$  to assure that contamination is below the analytical detection limit for direct injection or, if selected, preconcentration. If total chromium is also to be determined, the reagents should also be checked by the analytical technique selected to assure that contamination is below the analytical detection limit.



#### 4.1 Sampling.

4.1.1 Water. Deionized water. It is recommended that water blanks be checked prior to preparing sampling reagents to ensure that the  $\text{Cr}^{+6}$  content is less than the analytical detection limit.

4.1.2 Potassium Hydroxide, 0.1 N. Add 5.6 gm of KOH(s) to approximately 900 ml of DI water and let dissolve. Dilute to 1000 ml with DI water.

4.1.3 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.

4.2 Sample Recovery. The reagents used in sample recovery are as follows:

4.2.1 Water. Same as subsection 4.1.1.

4.2.2 Nitric Acid, 0.1 N. Add 6.3 ml of concentrated  $\text{HNO}_3$  (70 percent) to a graduated cylinder containing approximately 900 ml of DI water. Dilute to 1000 ml with DI water, and mix well.

#### 4.3 Sample Preparation

4.3.1 Water. Same as subsection 4.1.1.

4.3.2 Nitric Acid, 0.1 N. Same as subsection 4.2.2.

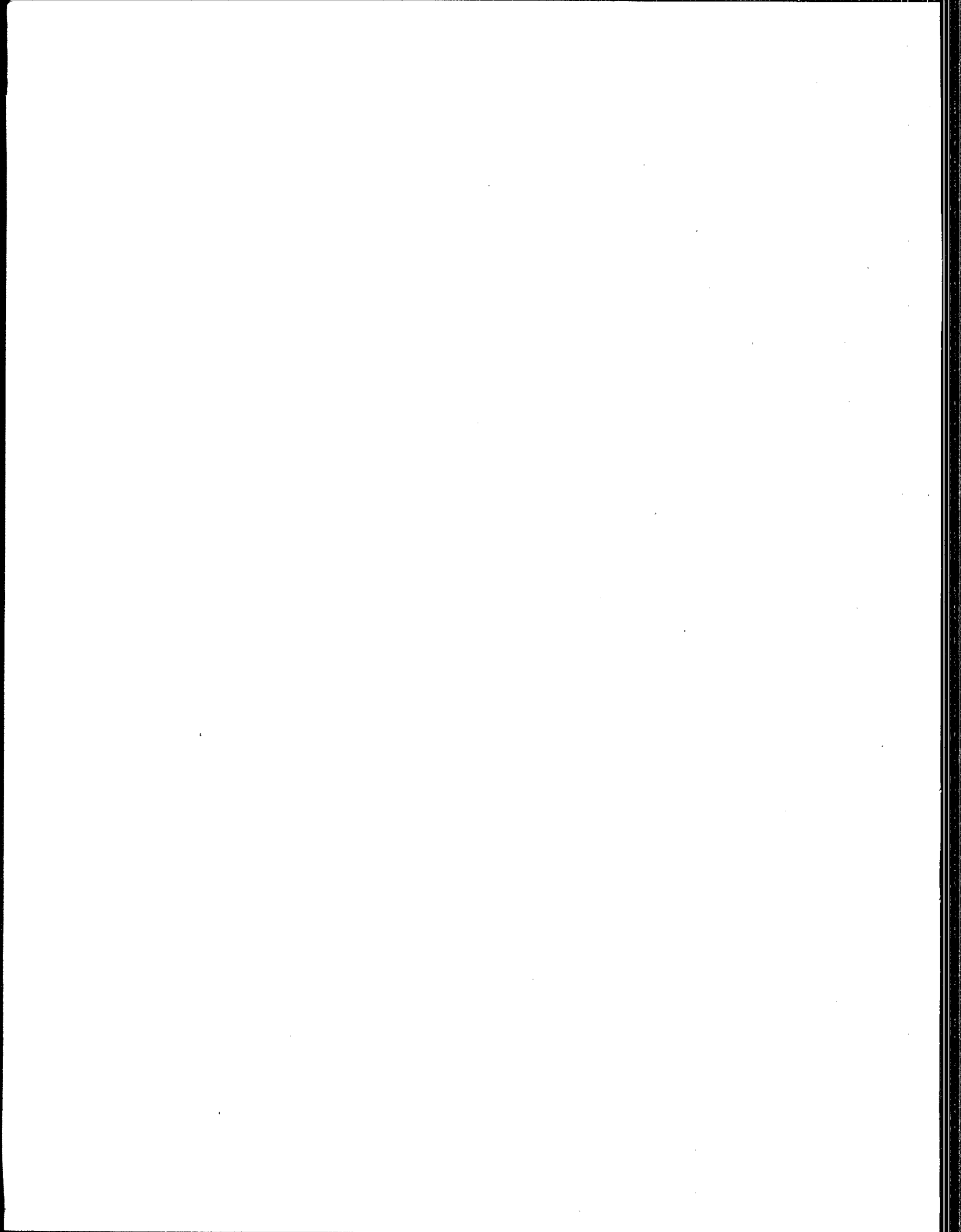
4.3.3 Filters. Acetate membrane, or equivalent, filters with 0.45 micrometer or smaller pore size to remove insoluble material.

#### 4.4 Analysis.

4.4.1 Chromatographic Eluent. The eluent used in the analytical system is ammonium sulfate based. It is prepared by adding 6.5 ml of 29% ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and 33 grams of ammonium sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ] to 500 ml of DI water. The mixture should then be diluted to 1 liter with DI water and mixed well. Other combinations of eluents and/or columns may be employed provided peak resolution, as described in Section 5.4, repeatability and linearity, as described in Section 6.2, and analytical sensitivity are acceptable.

4.4.2 Post-column Reagent. An effective post-column reagent for use with the chromatographic eluent described in Section 4.4.1 is a diphenylcarbazide (DPC) based system. Dissolve 0.5 g of 1,5-diphenylcarbazide (DPC) in 100 ml of ACS grade methanol. Add to 500 ml of degassed containing 50 ml of 96% spectrophotometric grade sulfuric acid. Dilute to 1 liter with degassed DI water.

4.4.4  $\text{Cr}^{+6}$  Calibration Standard. Prepare  $\text{Cr}^{+6}$  standards from potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ , FW 294.19). To prepare a 1000 ug/ml  $\text{Cr}^{+6}$  stock solution, dissolve 2.829 g of dry  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1 liter of DI water. To prepare working standards, dilute the stock solution to the chosen standard concentrations for instrument calibration with 0.05 N KOH to achieve a matrix similar to the actual field samples.



4.4.5 Performance Audit Sample. A performance audit sample shall be obtained from the Quality Assurance Division of EPA and analyzed with the field samples. The mailing address to request audit samples is:

U. S. Environmental Protection Agency  
Atmospheric Research And Exposure Assessment Laboratory  
Quality Assurance Division  
Source Branch, Mail Drop 77-A  
Research Triangle Park, North Carolina 27711

The audit sample should be prepared in a suitable sample matrix at a concentration similar to the actual field samples.

## 5. Procedure

5.1 Sampling. The complexity of this method is such that to obtain reliable results, testers should be trained and experienced with test procedures.

5.1.1 Pretest Preparation. All components shall be maintained and calibrated according to the procedures described in APTD-0576, unless otherwise specified herein.

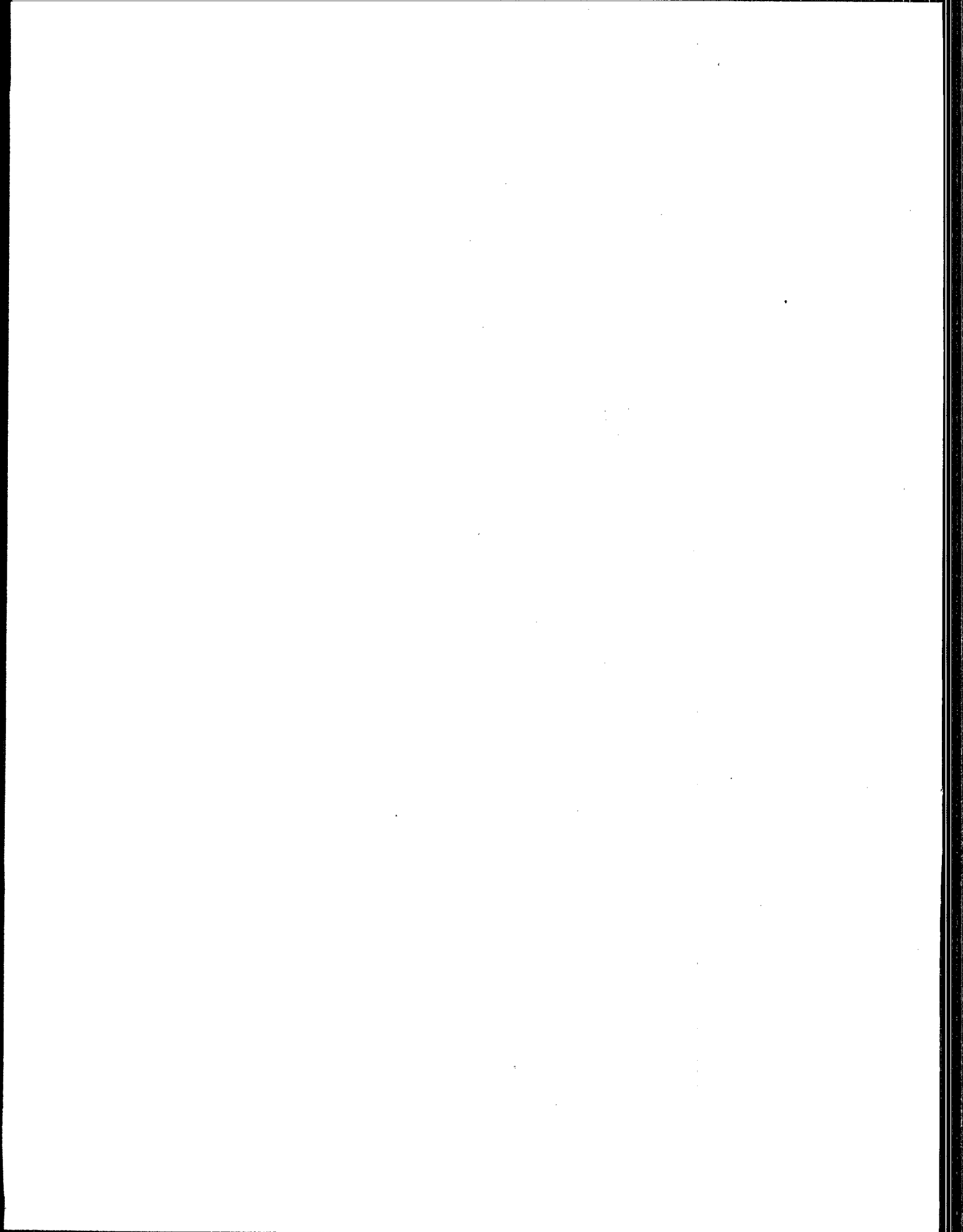
Rinse all sample train components from the glass nozzle up to the silica gel impinger and sample containers with hot tap water followed by washing with hot soapy water. Next, rinse the train components and sample containers three times with tap water followed by three rinses with DI water. All the components and containers should then be soaked overnight, or a minimum of 4 hours, in a 10 % (v/v) nitric acid solution, then rinsed three times with DI water. Allow the components to air dry prior to covering all openings with Parafilm, or equivalent.

5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

5.1.3 Preparation of Sampling Train. Measure 300 ml of 0.1 N KOH into a graduated cylinder (or tare-weighed precleaned polyethylene container). Place approximately 150 ml of the 0.1 N KOH reagent in the first Teflon impinger. Split the rest of the 0.1 N KOH between the second and third Teflon impingers. The next Teflon impinger is left dry. Place a preweighed 200-to 400-g portion of indicating silica gel in the final glass impinger. (For sampling periods in excess of two hours, or for high moisture sites, 400-g of silica gel is recommended.)

Retain reagent blanks of the 0.1 N KOH equal to the volumes used with the field samples.

5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).





5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. The sampling train should be iced down with water and ice to insure heat transfer with the Teflon impingers.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

5.2 Post-test Nitrogen Purge. The nitrogen purge is used as a safeguard against the conversion of hexavalent chromium to the trivalent oxidation state. The purge is effective in the removal of  $\text{SO}_2$  from the impinger contents.

Attach the nitrogen purge line to the input of the impinger train. Check to insure the output of the impinger train is open, and that the recirculating line is capped off. Open the nitrogen gas flow slowly and adjust the delivery rate to 10 L/min. Check the recirculating line to insure that the pressure is not forcing the impinger reagent out through this line. Continue the purge under these conditions for one-half hour periodically checking the flow rate.

5.3 Sample Recovery. Begin cleanup procedures as soon as the train assembly has been purged at the end of the sampling run. The probe assembly does may be disconnected from the sample train prior to sample purging.

The probe assembly should be allowed to cool prior to sample recovery. Disconnect the umbilical cord from the sample train. When the probe assembly can be safely handled, wipe off all external particulate matter near the tip of the nozzle, and cap the nozzle prior to transporting the sample train to a clean up area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

5.3.1 Container No. 1 (Impingers 1 through 3). Disconnect the first impinger from the second impinger and disconnect the recirculation line from the aspirator or peristaltic pump. Drain the Teflon impingers into a precleaned graduated cylinder or tare-weighed precleaned polyethylene sample container and measure the volume of the liquid to within 1 ml or 1 gm. Record the volume of liquid present as this information is required to calculate the moisture content of the flue gas sample. If necessary, transfer the sample from the graduated cylinder to a precleaned polyethylene sample container. With DI water, rinse four times the insides of the glass nozzle, the aspirator, the sample and recirculation lines, the impingers, and the connecting tubing, and combine the rinses with the impinger solution in the sample container.

5.3.2 Container No. 2 ( $\text{HNO}_3$  rinse optional for total chromium). With 0.1 N  $\text{HNO}_3$ , rinse three times the entire train assembly, from the nozzle to the fourth impinger, and combine the rinses into a separate precleaned polyethylene sample container for possible total chromium analysis. Repeat the rinse procedure a final time with DI water, and discard the water rinses. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.



5.3.3 Container No. 3 (Silica Gel). Note the color of the indicating silica gel to determine if it has been completely spent. Quantitatively transfer the silica gel from its impinger to the original container, and seal the container. A funnel and a rubber policeman may be used to aid in the transfer. The small amount of particulate that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or the silica gel plus impinger) to the nearest 0.5 g.

5.3.4 Container No. 4 (0.1 N KOH Blank). Once during each field test, place a volume of reagent equal to the volume placed in the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

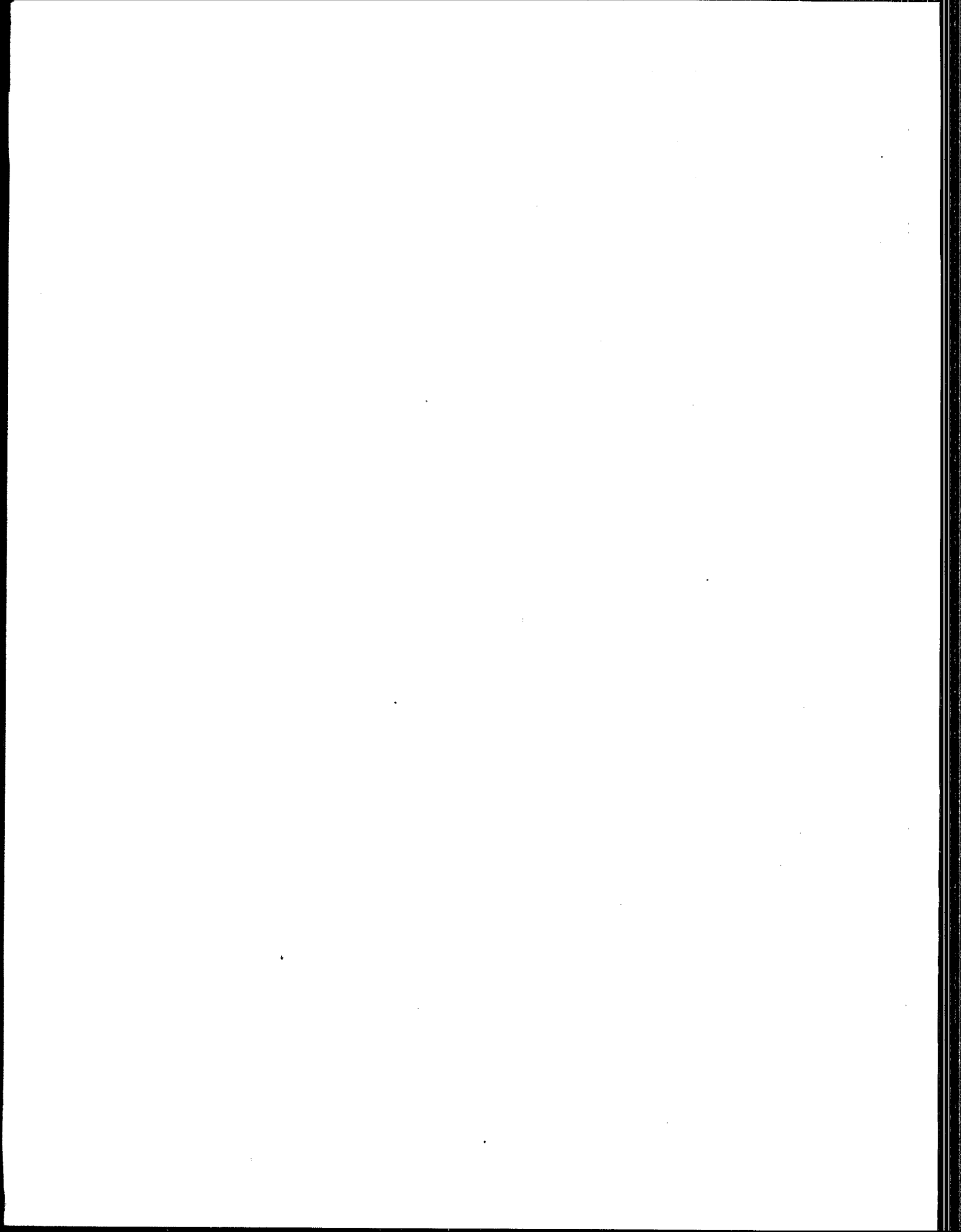
5.3.5 Container No. 5 (DI water Blank). Once during each field test, place a volume of DI water equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

5.3.6 Container No. 6 (0.1 N HNO<sub>3</sub> Blank). Once during each field test if total chromium is to be determined, place a volume of 0.1 N HNO<sub>3</sub> reagent equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

5.4 Sample Preparation. For determination of Cr<sup>6+</sup>, the sample should be filtered immediately following recovery to remove any insoluble matter. Nitrogen gas may be used as a pressure assist to the filtration process (see Figure Cr<sup>6+</sup>-4).

Filter the entire impinger sample through a 0.45 micrometer Teflon filter (or equivalent), and collect the filtrate in a 1000-ml graduated cylinder. Rinse the sample container with DI water three separate times and pass these rinses through the filter, and add the rinses to the sample filtrate. Rinse the Teflon reservoir with DI water three separate times and pass these rinses through the filter, and add the rinses to the sample. Determine the final volume of the filtrate and rinses and return them to the rinsed polyethylene sample container. Label the container clearly to identify its contents. Rinse the Teflon reservoir once with 0.1 N HNO<sub>3</sub> and once with DI water and discard these rinses.

If total chromium is to be determined, quantitatively recover the filter and residue and place them in a vial. (The acetate filter may be digested with 5 ml of 70% nitric acid; this digestion solution may then be diluted with DI water for total chromium analysis.)



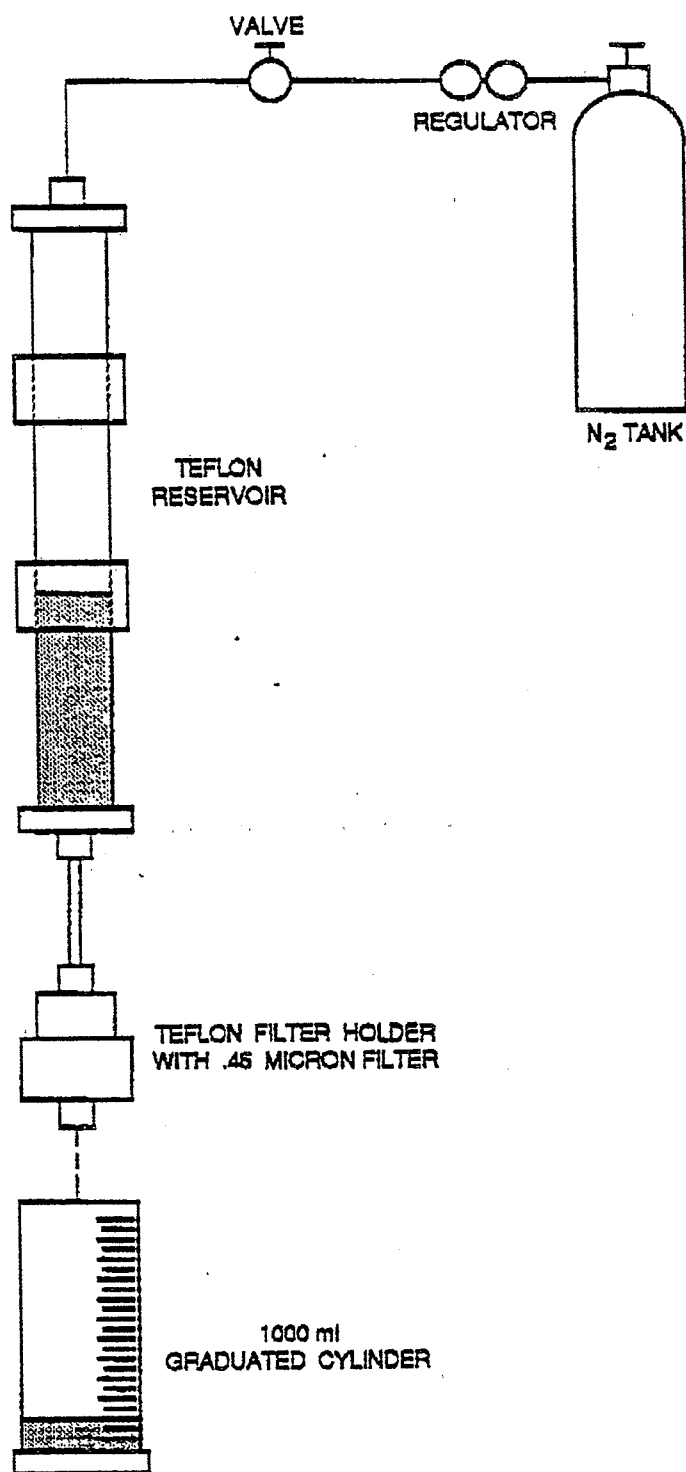
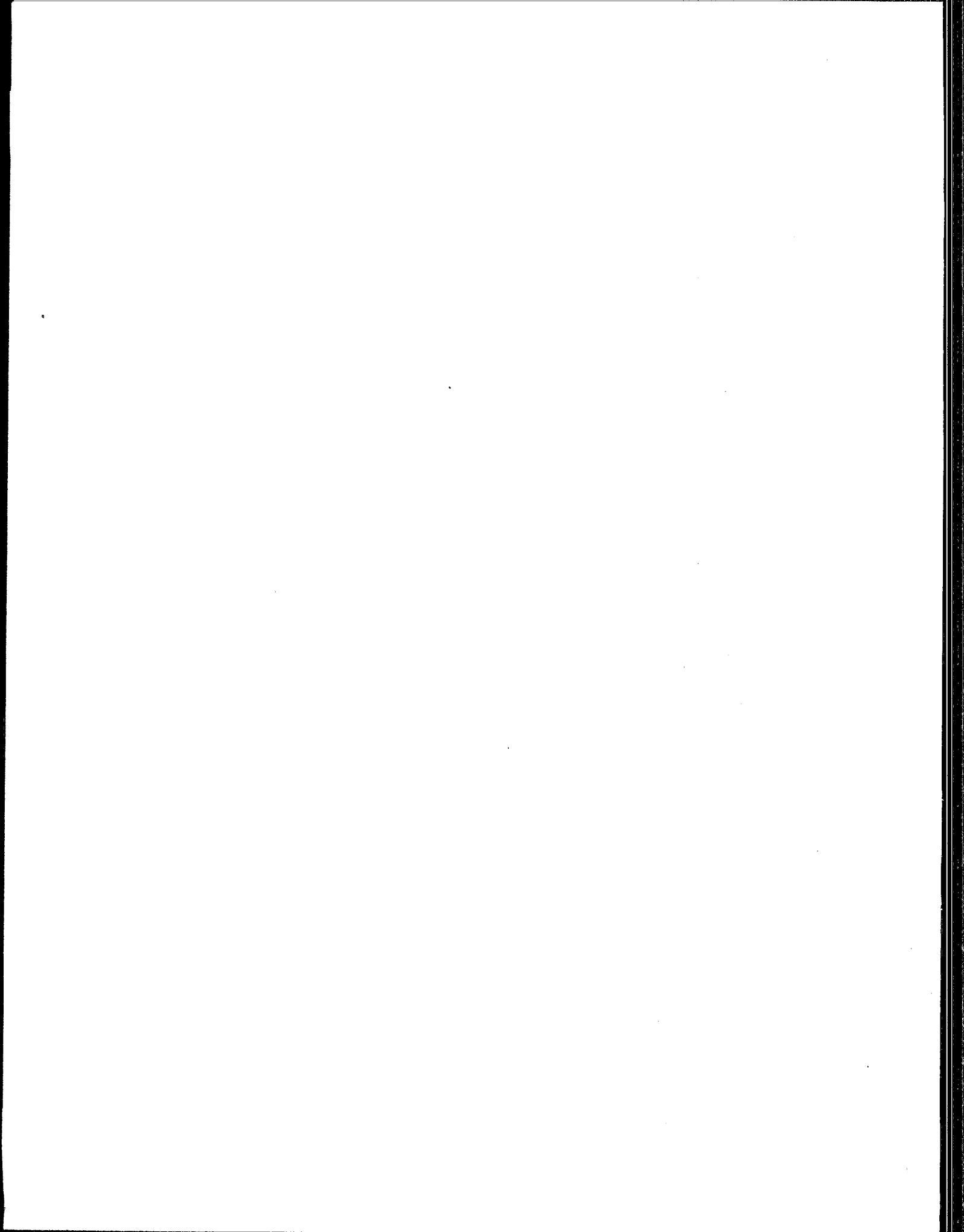


Figure Cr<sup>+6</sup>-4. Schematic of sample filter system.



5.4.1 Container 2 ( $\text{HNO}_3$  rinse, optional for total chromium). This sample shall be analyzed in accordance with the selected procedure for total chromium analysis. At a minimum, the sample should be subjected to a digestion procedure sufficient to solubilize all chromium present.

5.4.2 Container 3 (Silica Gel). Weigh the spent silica gel to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

5.5 Sample Analysis. The  $\text{Cr}^{+6}$  content of the sample filtrate is determined by ion chromatography coupled with a post column reactor (IC/PCR). To increase sensitivity for trace levels of chromium a preconcentration system is also used in conjunction with the IC/PCR.

Prior to preconcentration and/or analysis, all field samples will be filtered through a 0.45  $\mu\text{m}$  filter. This filtration should be conducted just prior to sample injection/analysis.

The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent (as described in 3.4.3), followed by removal of the analyte from the absorbent. The sample is injected into a sample loop of the desired size (repeated loadings or larger size loop for greater sensitivity) and the  $\text{Cr}^{+6}$  is collected on the resin bed of the column. When the injection valve is switched, the eluent displaces the concentrated  $\text{Cr}^{+6}$  sample moving it off the preconcentration column and onto the IC anion separation column. After separation from other sample components,  $\text{Cr}^{+6}$  forms a specific complex in the post-column reactor with a diphenylcarbazide reaction solution, and the complex is then detected by visible absorbance at a wavelength of 520 nm. The amount of absorbance measured is proportional to the concentration of the  $\text{Cr}^{+6}$  complex formed. The IC retention time and absorbance of the  $\text{Cr}^{+6}$  complex is compared with known  $\text{Cr}^{+6}$  standards analyzed under identical conditions to provide both qualitative and quantitative analyses.

Prior to sample analysis establish a stable baseline with the detector set at the required attenuation by setting the eluent flowrate at approximately 1 ml/min and post column reagent flow rate at approximately 0.5 ml/min. (Note: As long as the ratio of eluent flowrate to PCR flowrate remains constant, the standard curve should remain linear.) Inject a sample of DI water to insure that no  $\text{Cr}^{+6}$  appears in the water blank.

First, inject the calibration standards prepared, as described in Section 4.4.4, to cover the appropriate concentration range, starting with the lowest standard first. Next, inject, in duplicate, the performance audit sample, followed by the 0.1 N KOH field blank and the field samples. Finally, repeat the injection of the calibration standards to allow for compensation of instrument drift. Measure areas or heights of the  $\text{Cr}^{+6}$ /DPC complex chromatogram peak. The response for replicate, consecutive injections of samples must be within 5 percent of the average response, or the injection should be repeated until the 5 percent criteria can be met. Use the average response (peak areas or heights) from the duplicate injections of calibration standards to generate a linear calibration curve. From the calibration curve, determine the concentration of the field samples employing the average response from the duplicate injections.

The results for the analysis of the performance audit sample must be within 10 percent of the reference value for the field sample analysis to be valid.





6. Calibration. Maintain a written log of all calibration activities.

6.1 Sample Train Calibration. Calibrate the sample train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

6.2 Calibration Curve for the IC/PCR. Prepare working standards from the stock solution described in Section 4.4.4. by dilution with a DI water solution to approximate the field sample matrix. Prepare at least four standards to cover one order of magnitude that bracket the field sample concentrations. Run the standards with the field samples as described in Section 5.5. For each standard, determine the peak areas (recommended) or the peak heights, calculate the average response from the duplicate injections, and plot the average response against the  $\text{Cr}^{+6}$  concentration in  $\mu\text{g/l}$ . The individual responses for each calibration standard determined before and after field sample analysis must be within 5 percent of the average response for the analysis to be valid. If the 5 percent criteria is exceeded, excessive drift and/or instrument degradation may have occurred, and must be corrected before further analyses are performed.

Employing linear regression, calculate a predicted value for each calibration standard with the average response for the duplicate injections. Each predicted value must be within 7 percent of the actual value for the calibration curve to be considered acceptable. Remake and/or rerun the calibration standards. If the calibration curve is still unacceptable, reduce the range of the curve.

7. Calculations

7.1 Dry Gas Volume. Using the data from the test, calculate  $V_{m(\text{std})}$ , the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

7.2 Volume of Water Vapor and Moisture Content. Using the data from the test, calculate  $V_{w(\text{std})}$  and  $B_{ws}$ , the volume of water vapor and the moisture content of the stack gas, respectively, using Equations 5-2 and 5-3 of Method 5.

7.3 Stack Gas Velocity. Using the data from the test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

7.4 Total  $\mu\text{g Cr}^{+6}$  Per Sample. Calculate as described below:

$$m = (S-B) \times V_{1s} \times d$$

Where:

m = Mass of  $\text{Cr}^{+6}$  in the sample,  $\mu\text{g}$ ,

S = Analysis of sample,  $\mu\text{g Cr}^{+6}/\text{ml}$ ,

B = Analysis of blank,  $\mu\text{g Cr}^{+6}/\text{ml}$ ,

$V_{1s}$  = Volume of sample after filtration, ml, and,

d = Dilution factor (1 if not diluted).



## APPENDIX D

### EXAMPLE CALCULATION FOR DETERMINING THE ALLOWABLE SLUDGE FEED RATE



The following calculations demonstrate the determination of the maximum sludge feed rate allowed within the proposed rules for the disposal of sewage sludge published in the *Federal Register* on February 6, 1989. The formulas used are provided in the proposed rule.

These example calculations show the steps involved in calculating the maximum allowable sludge feed rate based upon:

- the average concentration of each toxic metal in sludge feed (obtained via long term monitoring);
- the control efficiency of the incineration system for each toxic metal (obtained from stack sampling); and
- the dispersion factor (obtained from dispersion modeling).

The calculation is demonstrated in this case for two metals. Facility "X" collected the following information involving two of the regulated metals.

- Chromium--50 mg/kg of sludge
- Lead--180 mg/kg of sludge
- 96% control of chromium by the incinerator and air pollution control device
- 85% control of lead by the incinerator and air pollution control device
- A calculated dispersion factor of 7.52  $\mu\text{g}/\text{m}^3/\text{g}/\text{sec}$
- An average sludge feed rate of 7 metric tons/hr (dry weight basis)

#### CALCULATION FOR CHROMIUM

From the proposed rule, the formula is

$$C = \frac{\text{RSC} \times 86,400}{\text{DF} \times (1 - \text{CE}) \times \text{SF}}$$

Where:

C=Maximum allowable concentration of arsenic, cadmium, chromium, or nickel in sewage sludge, in milligrams per kilogram (dry weight basis).

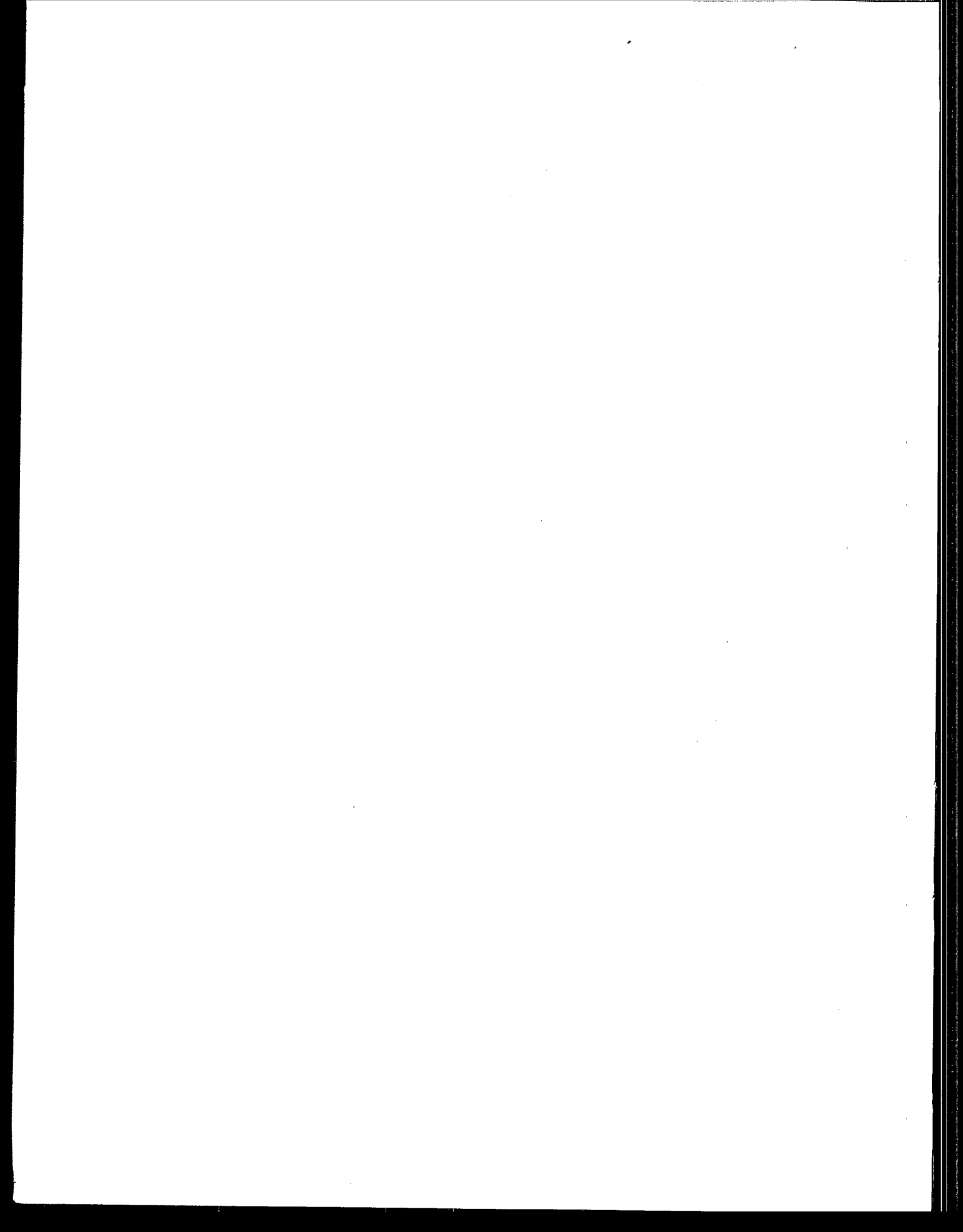
CE=Sewage sludge incinerator control efficiency.

DF=Dispersion factor, in micrograms per cubic meter, per gram, per second.

RSC=Risk specific concentration, in micrograms per cubic meter.

86,400=Number of seconds in a day.

SF=Sewage sludge feed rate, in metric tons per day (dry weight basis).



Solve for SF and make substitutions:

$$SF = \frac{RSC \times 86,400}{DF \times (1-CE) \times C}$$

$$RSC = 0.085 \text{ } \mu\text{g/m}^3$$

$$SF = \frac{0.085 \times 86,400}{7.52 \times (1-.96) \times 50}$$

$$SF = 488 \text{ metric tons/day (dry basis)}$$

$$= 20 \text{ metric tons/hr (dry basis)}$$

Conclusion: The allowable feed rate of sludge based on chromium content is higher than the average sludge feed rate of 7 metric tons per hour (dry basis).

#### CALCULATION FOR LEAD

$$C = \frac{.25 (\text{NAAQS}) \times 86,400}{DF \times (1-CE) \times SF}$$

Where:

C=Maximum allowable concentration of lead in sewage sludge, in milligrams per kilogram (dry weight basis).

NAAQS=National Ambient Air Quality Standard for lead (1.5 micrograms per cubic meter maximum arithmetic mean averaged over a calendar quarter).

86,400=Number of seconds in a day.

DF=Dispersion factor, in micrograms per cubic meter, per gram, per second.

CE=Sewage sludge incinerator control efficiency.

SF=Sewage sludge feed rate, in metric tons per day (dry weight basis).

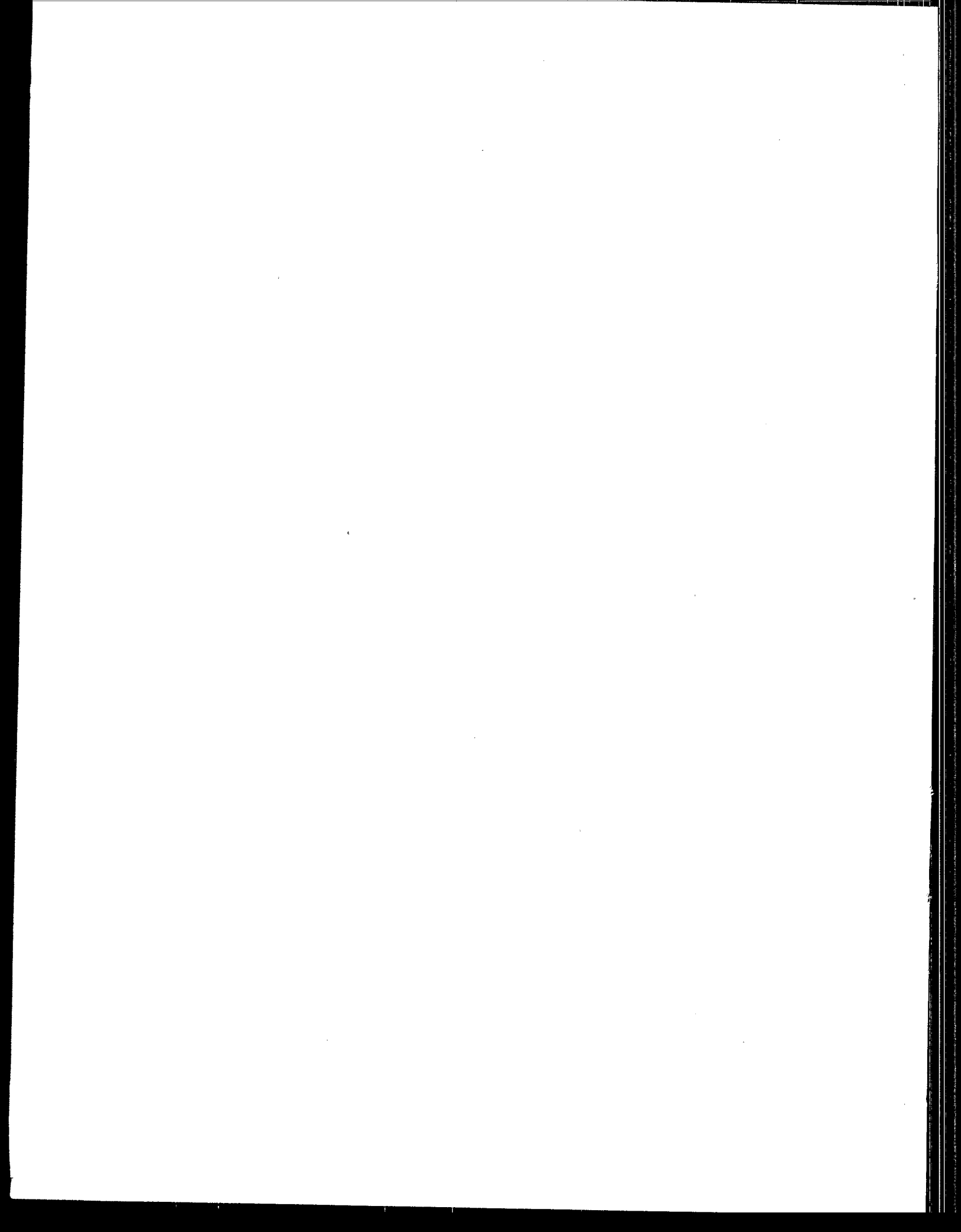
Solve for SF and make substitutions:

$$SF = \frac{.25 (\text{NAAQS}) \times 86,400}{DF \times (1-CE) \times C}$$

$$= \frac{.25 (1.5) (86,400)}{7.52 (1-.85) \times 180}$$

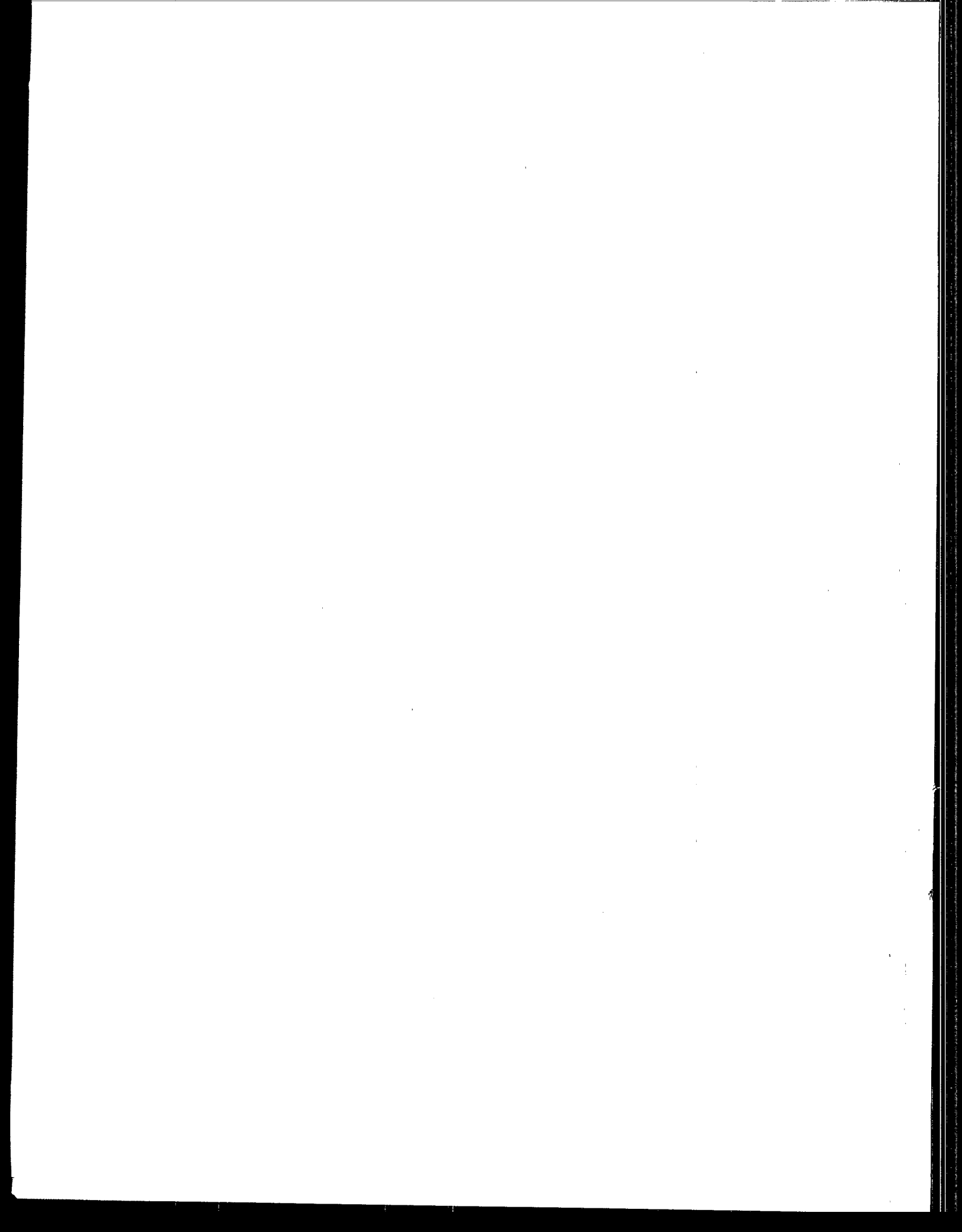
$$= 160 \text{ metric tons/day (dry basis)}$$

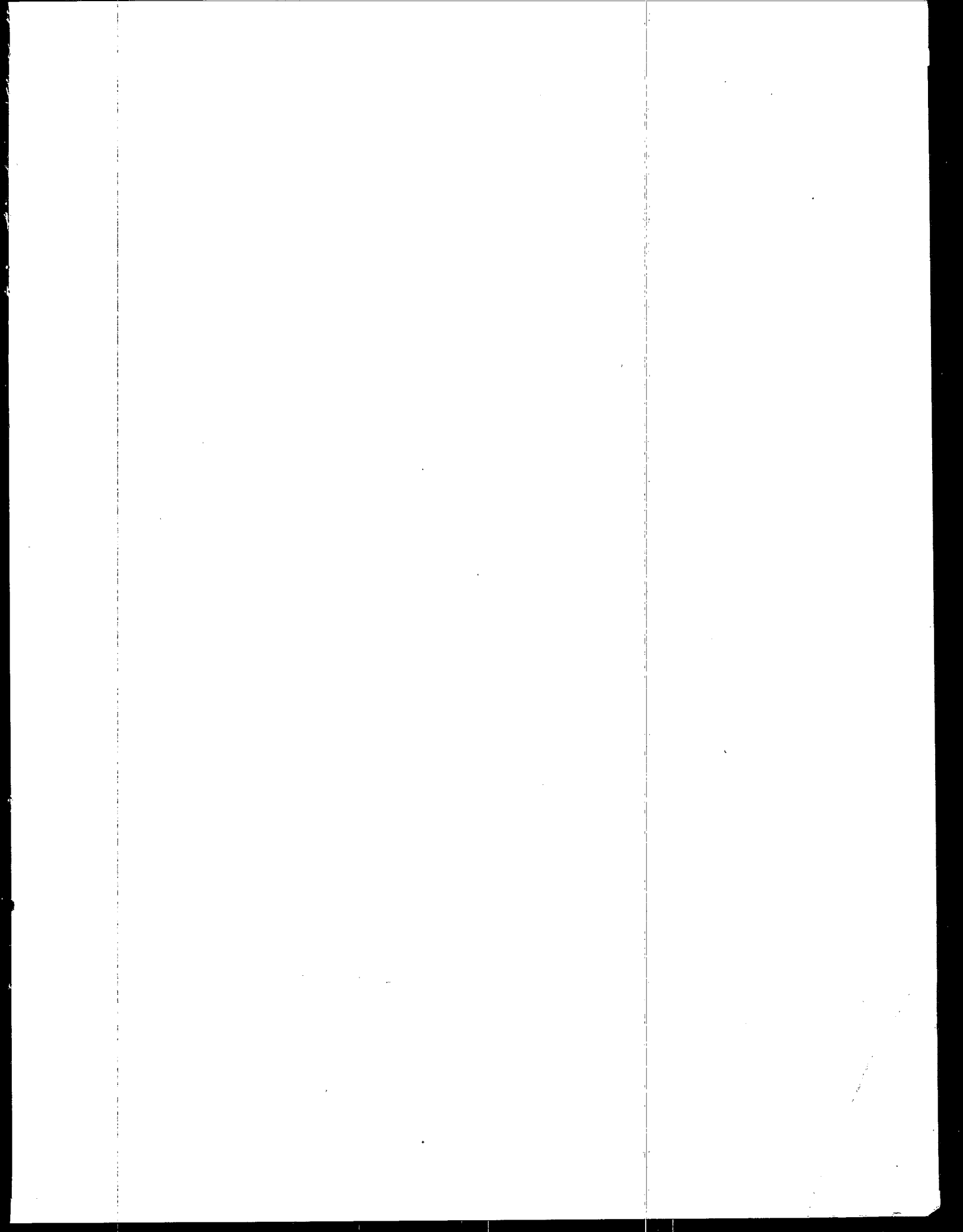
$$= 6.6 \text{ metric tons/hr (dry basis)}$$





Conclusion: Based upon the lead content of the sludge feed, the maximum allowable feed rate is less the average feed rate of 7 metric tons per hour (dry basis). This facility would need to operate at less than the average feed rate unless improvements can be demonstrated in the control efficiency of lead emissions.





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