SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 12.1

DETERMINATION OF INORGANIC LEAD EMISSIONS FROM STATIONARY SOURCES USING A WET IMPINGEMENT TRAIN

OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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1. Overview

    1.1   Principle

        Particulate and gaseous lead emissions are
withdrawn isokinetically from the source and
collected in a wet impingement train containing
diluted nitric acid and a backup filter. The
collected samples are digested in acid solution
and analyzed by atomic absorption spectrometry
using an air/acetylene flame.

    1.2 Applicability

        This method applies to the determination of
inorganic lead (Pb) emissions from specified
stationary sources only.

1.2.1 Alternative Test Method for Inorganic Lead

An EPA Method 5 setup or an in-stack filter (with 0.1N HNO_3 impinger solution instead of water) may be used if the filter and impinger catch are treated and analyzed for Pb as described in Section 3 of this method.

1.3 Range

For a minimum analytical accuracy of $\pm$ 10 percent, the lower limit of the range is 100 μg. The upper limit can be considerably extended by dilution.

1.4 Analytical Sensitivity

Typical sensitivities for a 1 percent change in absorption (0.0044 absorbance units) are 0.2 and 0.5 μg Pb/ml for the 217.0 and 283.3 nm lines respectively.

1.5   Interferences

Sample matrix effects may interfere with the
analysis for Pb by flame atomic absorption.   If
suspected, these matrix effects may be confirmed
and possibly eliminated by using the Method of
Standard Additions.   High concentrations of
copper may interfere with the analysis of Pb at
217.0 nm.   This interference can be avoided by
analyzing the sample at 283.3 nm.

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2. Field Procedure

2.1 Sampling Apparatus

2.1.1 Sampling Train

A schematic of the sampling train is shown in Figure 12.1-1. It consists of the following components:

a. Probe nozzle, probe liner, Pitot tube, differential pressure gauge, temperature sensor, filter holder, metering system, barometer, and gas density determination equipment. Same as Method 5.1.

b. Impingers

Four impingers connected in series
with leak-free ground glass fittings
or any similar leak-free
noncontaminating fittings. For the
first and second impingers, use the
Greenburg-Smith design with the
standard tip. For the third and
fourth impingers, use the Greenburg-
Smith design, modified by replacing
the tip with a 1.3 cm (0.5 in.) ID
glass tube extending to about 1.3 cm
(0.5 in.) from the bottom of the
flask.

The first and second impingers contain
100 ml of 0.1N HNO_3 solution, the
third is empty, and the fourth
contains a known weight of silica gel
or equivalent desiccant. Instead of
using silica gel, determine the
moisture leaving the third impinger by
measuring the temperature and pressure
at the exit of the impinger train and

applying Dalton's law of partial
pressures.

2.2   Reagents

2.2.1   Sampling Train

NOTE: Mention of trade names or specific
products does not constitute an
endorsement by the South Coast Air Quality
Management District.

a.   Filter

Gelman Spectro Grade, Reeve Angel 934
AH MSA 1106 BH, all with lot assay for
Pb, or other high purity glass filter,
without organic binder, exhibiting at
least 99.95 percent efficiency (<0.05
percent penetration) on 0.3 micron
dioctyl phthalate smoke particles.

Conduct the filter efficiency test
using ASTM Standard Method 2986-71 or
use test data from the supplier's
quality control program.

b. Silica Gel

Indicating-type, 6 to 16 mesh, dried at 175°C (350°F). Silica gel may be used as received.

c. Crushed Ice or Dry Ice

d. Stopcock Grease

Acetone insoluble, heat-stable silicone grease.

e. Water

Deionized, distilled, to conform to ASTM Specification D1193-77, Type 3.

If high concentrations of organic matter are not expected to be present, the analyst may delete the potassium permanganate test for oxidizable organic matter. Reference to water throughout the method implies deionized, distilled water.

f. Nitric Acid, 0.1N

Dilute 6.5 ml of concentrated HNO_3 to
1 liter with water.

2.3   Procedure

2.3.1 Sampling

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

2.3.2 Pretest Preparation

Follow the procedure outlined in Method
5.1, except the filter need not be
weighed.

2.3.3 Preliminary Determinations

Follow the procedure outlined in Method
5.1.

2.3.4   Preparation of Collection Train

Follow the procedure outlined in Method
5.1, except place 100 ml of 0.1N HNO_3 in
each of the first two impingers, leave the
third impinger empty, and transfer
approximately 200 to 300 g of preweighed
silica gel from its container to the
fourth impinger. Set up the train as
shown in Figure 12.1-1.

2.3.5   Leak Check Procedures

Follow the leak check procedures outlined
in Method 5.1.

2.3.6   Sampling Train Operation

Follow the procedure outlined in Method
5.1. Record the data on a form. See
Figure 12.1-2.

2.3.7   Calculation of Percent Isokinetic

Same as Method 5.1.

2.3.8 Sampling Train Calibration

Calibrate the sampling train components as
in Method 5.1.

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3. Laboratory Procedures

3.1 Apparatus

3.1.1 Sampling Train

A schematic of the sampling train is shown in Figure 12.1-1. See description in Section 2.1.

3.1.2 Sample Recovery

a. Brushes

Brushes must have nylon bristles and stainless steel, Teflon or other non-contaminating handles. The brushes must be properly sized and shaped to brush out the probe liner and nozzle.

b.   Wash Bottles

Glass or polyethylene.

c.   Sample Storage Containers

Chemically resistant, borosilicate glass bottles, for 0.1 nitric acid (HNO_3) impinger and probe solutions and washes, 1000 ml. Use screw cap liners that are either rubber backed Teflon or leak free and resistant to chemical attack by 0.1N HNO_3. (Narrow mouth glass bottles have been found to be less prone to leakage.) Polyethylene bottles also may be used.

d.   Graduated Cylinder

To measure condensed water to within 2 ml. Use a graduated cylinder that has a minimum capacity of 500 ml, and subdivisions no greater than 5 ml.

e.   Balance (Optional)

To measure condensed water in the train. Balance must weigh to 0.5 g or less.

f.   Funnel

Glass, to aid in sample recovery.

3.1.3 Analysis

a.   Atomic Absorption Spectrophotometer

With lead hollow cathode lamp and burner for air/acetylene flame.

b.   Hot Plate

c.   Erlenmeyer Flasks

125 ml, 24/40, standard taper, ground glass joints.

d. Membrane Filters

   Millipore SCWPO 4700 or equivalent.

e. Filtration Apparatus

   Millipore vacuum filtration unit or
   equivalent, for use with membrane
   filters.

f. Volumetric Flasks

   100 ml, 250 ml, and 1000 ml.

3.2 Reagents

3.2.1 Sampling Train

   See Section 2.2.

a. Water

   See Section 2.2.1 e.

3.2.2 Pretest Preparation

6N HNO_3 is needed. Dilute 390 ml of
concentrated low trace metal HNO_3 to 1
liter with water.

3.2.3 Sample Recovery

0.1N HNO_3 (see Section 2.2.1.f) is needed
for sample recovery.

3.2.4 Analysis

Use ACS reagent grade chemicals or
equivalent, unless otherwise specified.

a. Water

See Section 2.2.1.e.

b. Nitric Acid, HNO_3

Concentrated, low trace metal.

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

Dilute 500 ml of concentrated low trace metal HNO_3 to 1 liter with water.

d. Stock Lead Standard Solution, 1000 µg Pb/ml

Dissolve 0.1598 g of lead nitrate $[Pb(NO_3)_2]$ in about 60 ml of water, add 2 ml concentrated HNO_3, and dilute to 100 ml with water.

e. Working Lead Standards

Using pipet transfer 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of stock lead standard solution into 250 ml volumetric flasks. Add 5 ml of concentrated HNO_3 to each flask and dilute to volume with water. These working standards contain 0.0, 4.0, 8.0, 12.0, 16.0, and 20.0 µg Pb/ml respectively. As needed, prepare

additional standards at other
concentrations in a similar manner.

 f. Air

  Suitable quality for atomic absorption
  analysis.

 g. Acetylene

  Suitable quality for atomic absorption
  analysis.

 h. Hydrogen Peroxide, 3 Percent (V/V)

  Dilute 10 ml of 30 percent H_2O_2 to 100
  ml with water.

3.3 Pretest Preparation

Soak all surfaces that may come in contact with
the sample (except metal parts) for at least 2
hours in 1:1 low trace metal HNO_3. Rinse with
water, and dry. Parts that must be soaked
include: impingers, filtration apparatus, plastic
sample and blank bottles, Erlenmeyer flasks, and
beakers. Metal parts may be rinsed with 1:1

HNO_3, rinsed with water, and dried before use.

3.4   Sample Train Preparation

During preparation and assembly of the sampling train, keep all opening covered until just prior to assembly or sampling.

Assemble the impinger as shown in Figure 12.1-1. Load each of the first two impingers with exactly 100 ml of 0.1N HNO_3. Leave the third impinger empty. Place approximately 200 to 300 g of silica gel in the fourth impinger and record its weight to the nearest 0.5 g.

If moisture content is to be determined gravimetrically, weigh each impinger plus its contents to the nearest 0.5 g and record the weights.

Place a filter in the filter holder. Be sure to properly center the filter, and properly place the gasket to prevent the sample gas stream from circumventing the filter.

Connect the impingers and filter holder as shown in Figure 12.1-1. Seal the train or its components for transport to the sampling site. Reserve 200 ml of 0.1N HNO_3 as a blank.

3.5   Sample Train Leak Check

Leak check the sample collection train using procedures found in the Section 2.3.5.

3.6   Sample Recovery

Inspect the train for general condition prior to and during disassembly. Note if the silica gel is expended and if the train or its components are sealed. Note any abnormal conditions, such as torn filters and cloudy impinger liquid. Recover the sample in an area that is clean and protected from the wind.

3.6.1 Filter

Carefully remove the filter from the filter holder and place it in its identified Petri dish container. If it is necessary to fold the filter, fold the sample-exposed side to the inside.

Carefully transfer to the Petri dish all
visible sample matter and filter fibers
that adhere to the filter holder gasket by
using a dry Nylon bristle brush and/or a
sharp blade. Seal the container.

Reserve a filter from the batch used for
sampling and place in a plastic Petri
dish. Seal the container and label it to
clearly identify the contents.

3.6.2 Probe, Nozzle and Impingers

Taking care that dust on the outside of
the probe or other exterior surfaces does
not get into the sample, quantitatively
recover sample matter or any condensate
from the probe nozzle, probe fitting, and
probe liner, by washing these components
with 0.1N HNO_3 and placing the wash into
a glass sample storage container. Measure
and record (to the nearest 2 ml) the total
amount of 0.1N HNO_3 used for this and the
following rinses. It may be more
convenient to use a predetermined amount
of 0.1N HNO_3 (e.g. 300 ml) to rinse the

sampling equipment. Perform the 0.1N HNO_3 rinses as follows:

Carefully remove the probe nozzle and rinse the inside surfaces with 0.1N HNO_3 from a wash bottle while brushing with a stainless steel, Nylon bristle brush. Brush until the 0.1N HNO_3 rinse shows no visible particles, and make a final rinse of the inside surface. Brush and rinse with 0.1N HNO_3 the inside parts of the Swagelok fitting in a similar way until no visible particles remain.

Rinse the probe liner with 0.1N HNO_3 and add it to the above rinsings. While rotating the probe so that all inside surfaces will be rinsed with 0.1N HNO_3, tilt the probe and squirt 0.1N HNO_3 into its upper end. Let the 0.1N HNO_3 drain from the lower end into the sample container. A glass funnel may be used for transferring liquid washes to the container.

Follow the rinse with a probe brush. Hold the probe in an inclined position and

squirt 0.1N HNO_3 into the upper end of the
probe as the probe brush is being pushed
with a twisting action through the probe.
Hold the sample container beneath the
lower end of the probe and catch any 0.1N
HNO_3 and sample matter brushed from the
probe. Run the brush through the probe
three times or more until no visible
sample matter is carried out with the 0.1N
HNO_3 and none is visible on the probe
liner.

With stainless steel or other metal
probes, run the brush through in the
above-prescribed manner at least six
times, since metal probes have small
crevices in which sample matter can be
entrapped. Rinse the brush with 0.1N HNO_3
and quantitatively collect the washings in
the sample container. After the brushing
make a final rinse of the probe as
described above.

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

and record each impinger plus contents to the nearest 0.5 g. Alternatively, change in the impinger content volume may be measured with a graduated cylinder.

Disassemble and degrease the first three impingers. Add their contents to the probe and nozzle washings. Rinse each impinger three times with 0.1N HNO_3, using a brush if necessary to dislodge any particulate matter. Add the washings to the sample.

In a similar manner, rinse the impinger connectors and the front half of the filter holder three times with 0.1N HNO_3, using a brush if necessary to dislodge particulate matter. Add the washings to the sample.

Note: Continue recording the amount of 0.1N HNO_3 used if you are not using a predetermined amount.

If the sample is to be transported to the laboratory, mark the level of the liquid on the sample container. Tighten the cap

securely and label the container to
clearly identify its contents.

Add the same amount of 0.1N HNO_3 as used
for rinsing to the 200 ml reagent blank
reserved from the train preparation. Mark
the liquid level, tighten the cap
securely, and label the container to
clearly identify its contents.

3.7   Sample Preparation and Analysis

3.7.1 Filter

Using clean stainless steel or plastic
scissors, cut the filter into strips and
transfer the strips and all loose
particulate matter into a 125 ml
Erlenmeyer flask. Rinse the Petri dish
with 10 ml of 50 percent HNO_3 to ensure a
quantitative transfer and add to the
flask. Cover the flask until it is used
later. (If the total volume required in
the following section is expected to
exceed 80 ml, use a 250 ml Erlenmeyer

flask in place of the 125 ml flask.)
Process the blank filter in the same way.

3.7.2 Container Recovery

If the sample has been transported from
the field, check the liquid level to
determine if leakage has occurred. Record
observations on the analysis sheet. If a
noticeable amount of leakage had occurred,
either void the sample or take steps to
adjust the final results, subject to the
approval of the Executive Officer.

Wipe off the cap area, unseal the
container, and transfer the sample to a
clean beaker. Rinse the container and cap
into the beaker, using a brush if
necessary to dislodge particulate matter.
Transfer the blank to another beaker using
the same procedure. Heat the sample
slowly to near dryness on a hot plate,
transfer to a steam bath, and bring to
dryness.

3.7.3   Sample Extraction for Lead

Based on the approximate stack gas particulate concentration and the total volume of stack gas sampled, estimate the total weight of particulate sample collected. Transfer the sample residue to the 125 ml Erlenmeyer flask that contains the filter, using a rubber policeman and 10 ml of 50 percent HNO_3 for every 100 mg of sample collected in the train, or a minimum of 30 ml of 50 percent HNO_3, whichever is larger. Treat the blank beaker and filter in the same manner.

Place the Erlenmeyer flask on a hot plate and heat with periodic stirring for 30 minutes at a temperature just below boiling. If the sample volume falls below 15 ml, add more 50 percent HNO_3. Add 10 ml of 3 percent H_2O_2 and continue heating for 10 minutes. Add 50 ml of hot (80°C) water and heat for 20 minutes. Remove the flask from the hot plate and allow to cool. Filter the sample through a Millipore membrane filter or equivalent

and transfer the filtrate to a 250 ml
volumetric flask. Dilute to volume with
water.

3.7.4   Lead Determination

Calibrate the spectrophotometer as
described in Section 3.9 and determine the
absorbance for each source sample, the
combined filter blank, and the 0.1N HNO_3
blank. Analyze each sample three times in
this manner. As required, make dilutions
to bring all sample Pb concentrations into
the linear absorbance range of the
spectrophotometer.

If the Pb concentration of a sample is at
the low end of the calibration curve and
high accuracy is required, take the sample
to dryness on a hot plate and dissolve the
residue in the appropriate volume of water
to bring it into the optimum range of the
calibration curve. Analyze the prepared
reagent blank using the same procedure.

3.7.5 Matrix Effects

The analysis for Pb by atomic absorption
is sensitive to the chemical composition
and physical properties of the sample
(e.g. pH, viscosity). These are called
matrix effects. Since the Pb procedure
described here will be applied to many
different sources, many sample matrices
will be encountered. Thus, at least one
sample from each source must be checked
using the following method to ascertain
that the chemical composition and physical
properties of the sample did not cause
erroneous analytical results.

Add or spike an equal volume of standard
solution to an aliquot of the sample
solution, then measure the absorbance of
the resulting solution and the absorbance
of the unspiked sample. Calculate the Pb
concentration using:

$$C_s = C_a \frac{A_s}{A_t - A_s}$$

where:

C_s = Concentration of the sample, μg/ml

C_a = Concentration of the standard

A_s = Absorbance of the sample

A_t = Absorbance of the spiked sample solution

Method of additions procedures are described in the section entitled "General Information" of the Perkin Elmer Corporation Manual. If the results of the method of additions procedure on the source sample do not agree to within 5 percent of the value obtained by the conventional atomic absorption analysis, reanalyze all samples from the source using a method of additions procedure.

3.8   Calculations and Reporting

For each source sample, correct the average absorbance for the contribution of the filter blank and the 0.1N HNO_3 blank. Use the calibration curve and this corrected absorbance to determine the μg Pb concentration in the

sample aspirated into the spectrophotometer. Calculate the total Pb content $C^O{}_{Pb}$ (in µg) in the original source sample; correct for all the dilutions that were made to bring the Pb concentration of the sample into the linear range of the spectrophotometer.

3.9   Calibration

3.9.1   Spectrophotometer

Measure the absorbance of the standard solutions using the instrument settings recommended by the spectrophotometer manufacturer. Repeat until good agreement ($\pm$ 3 percent) is obtained between two consecutive readings.

Plot the absorbance (y-axis) versus concentration in µg Pb/ml (x-axis). Draw or compute a straight line through the linear portion of the curve. Do not force the calibration curve through zero, but if the curve does not pass through the origin or at least lie closer to the origin than $\pm$ 0.003 absorbance units, check for

incorrectly prepared standards and for curvature in the calibration curve.

To determine stability of the calibration curve, run a blank and a standard after every five samples and recalibrate, as necessary.

3.10 Quality Control

3.10.1 Gravimetric

At each step, redetermine one weight in ten, or one per set, whichever occurs first. If the impinger weights do not agree within $\pm$ 0.5 g, check the balance calibration and reweigh the entire set.

3.10.2 Analytical

Analyze a midpoint standard, obtained independently from the calibration standards, with each set of samples. If the measured value is not within $\pm$ 10 percent of expected, void the analysis, recalibrate the instrument, and reanalyze the samples.

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4.   **Engineering Calculations and Reporting**

4.1   Dry Gas Volume

Using the data from this test, calculate $V_{m(std)}$,
the total volume of dry gas metered corrected to
standard conditions (60^OF and 29.92 mm Hg). If
necessary, adjust for leakages as outlined in
Method 5.1.

4.2   Volume of Water Vapor and Moisture Content

Using data obtained in this test and equations of
Method 5.1, calculate the volume of water vapor,
$V_{w(std)}$, and the moisture content, B_{ws}, of the
stack gas.

4.3   Lead Concentration

Calculate the stack gas Pb concentration as
follows:

$$C_{Pb} = \frac{K \ C^O_{Pb}}{V_{m(std)}}$$

where:

C_{Pb} =   Stack gas Pb concentration, mg/dscm

K   =   0.001 mg/μg
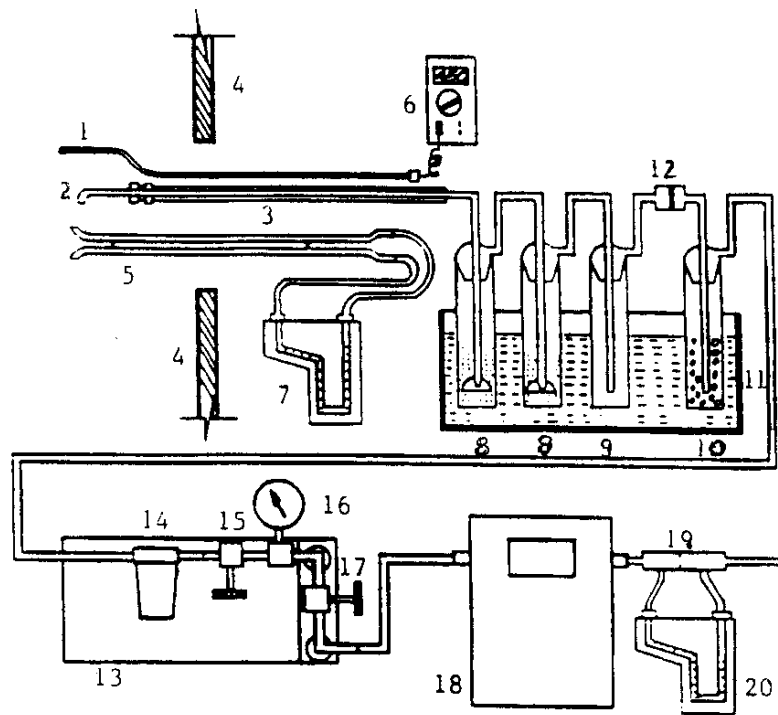
= 2.205×10^{-9} lb/μg

C^O_{Pb} =   Total Pb content in source sample, μg

(from Section 3.8)

$V_{m(std)}$ =   Total volume of dry gas metered,

corrected to standard condition

(60^OF and 29.92 mm Hg)

4.4   Isokinetic Variation and Acceptable Results

Same as Method 5.1.

1. Temperature Sensor	11. Ice Bath
2. Nozzle	12. Filter
3. Glass Lined Stainless Steel Probe	13. Sealed Pump (Leak Free)
4. S-type Pitot Tube	14. Filter for Pump
5. Stack Wall	15. Metering Valve
6. Temperature Sensor Meter	16. Vacuum Gauge
7. Pitot Tube Inclined Manometer	17. By-pass Valve
8. Impinger with 100 ml 0.1N HNO_3	18. Temperature Compensated
9. Empty Bubbler	Dry Gas Meter
10. Bubbler with Silica Gel	19. Orifice
	20. Orifice Inclined Manometer

Figure 12.1-1

Lead Sampling Train Setup-Wet Impingement Method