V. Metals Analysis

I. Purpose

    a. To learn the basic theory and operation of the atomic absorbance spectrometer (AAS).

    b. To determine the amount of zinc and iron collected on membrane filters using NIOSH methods.

    c. To discuss comparable analyses using x-ray fluorescence (XRF), inductively coupled plasma atomic emission spectroscopy (ICP/AES) and inductively coupled plasma mass spectrometry (ICP/MS).

II. Readings   Quantitative Chemical Analysis, 6th Edition, by Harris, D.C., chapter 21 (pgs 494-516)

      NIOSH Procedure 7030 (Zn) & 7702 (Pb by portable XRF)

III. Outline

This experiment has 3 parts:

Part 1: Preparation of samples and standard calibration solutions.
Part 2: Development of calibration curve and analysis of samples by AAS.
Part 3: Determine effect of interferences by standard addition technique.

You should plan your time as follows:

Day 1:
1. Preparation for AAS analysis
    First, Clean all glassware.
      a. Spike filters with known amounts of zinc and iron.
      b. Digest blank, unknown sample and spiked filters (will take up to two hours depending on filters and matrix).
      c. Bring to known volume and retain for later analysis.
      d. Prepare iron and zinc working standards by dilution of stock solution.

Day 2:   Continue with AAS analysis:

      a. Demonstration and familiarization with AAS instrument
      b. Run your calibration standards for each metal and obtain calibration curves
      c. Measure metal concentrations in the samples, blanks and spikes
      d. Prepare the standard additions for each metal to determine any interferences.
      e. Measure metal concentrations in the standard addition samples.

If the portable XRF instrument is available, there will be a short demonstration of the instrument and a discussion of XRF spectroscopy.

IV. Cautions

    1. WEAR SAFETY GLASSES, PROTECTIVE GLOVES AND LAB COATS WHENEVER YOU HANDLE ACIDS!

    2. Be careful with acid vapors, use the laboratory hood. Be careful with the liquid acid. Pour the estimated daily volume needed from the large gallon jug to a smaller labeled container. (Do not pour unused acid back into the original container). Unused acid is neutralized with sodium bicarbonate.

    3. **All used solutions are to be treated as hazardous wastes. Labeled bottles are supplied for the correct disposal protocol. (Separate disposal of concentrated acids and dilute solutions. Metal containing wastes are transferred to a separate waste container).** Unused acid is neutralized with sodium bicarbonate

V.   Supplies for Laboratory

        GLASSWARE (Laboratory supplied)
        100 ml volumetric flask
        50 ml volumetric flask
        25 ml volumetric flasks for samples
        10 ml volumetric flask for standard additions
        50 ml beakers for sample digestions
        1 Liter volumetric flask for 1% Nitric Acid
        watch glasses
        PIPETTES (Laboratory supplied)
        1-5 ml
        0.1 - 1.0 ml
        10-100 μl micropipette, 3 pipetters and many tips
        METAL STANDARD SOLUTION (made in 1% HNO_3)
        Zn 1000 μ**g/ml or** ppm standard
        Fe 1000 μ**g/ml or** ppm standard
        Please try to use less than 10 ml of each standard.

        CHEMICALS
        Concentrated HNO_3
        Distilled water

        OTHER
        Filters (blanks, to use for spiking, and include those from mock sampling)
        Cassettes
        Tweezers
        Tape
        Labeling tape and pen

Analysis of Metals by X-ray Fluorescence.

In addition to the field sampling followed by laboratory-based analytical procedures for metals, the industrial hygienist often times needs the capability to directly and in real time determine the metals present. A recently developed tool of the x-ray fluorescence spectrophotometer in the form of a hand-held portable instrument has been perfected to not only directly analyze paint and surfaces in situ, but can measure the elements on thin films such as filters, and in soil or sediment samples.

The advantages of the technique are that it is non-destructive, multi-element, instant readout, sensitive, pre-calibrated and very portable. The disadvantages are that the initial cost is high and that a license for handling a radioactive source is required.

Principle of Operation

X-ray fluorescence is the interaction of x-radiation with the inner electrons of the atoms. The electrons are ejected to higher energy states and subsequently radiation is emitted as electrons drop into the vacancies. The emitted radiation is energetic enough to be in the form of x-rays that are very characteristic of each specific atom. The phenomenon can conveniently be used to detect all elements larger than sodium and will identify non-metals as well as metals. The results can be quantitative because quantity of emitted x-rays is proportional to the amount of the element that is present.

Experiment and Demonstration

The purpose of this part of the Metals Experiment of ENVH 555, will be to demonstrate the use of a field portable x-ray fluorescence spectrometer, and to employ the Niton Instrument to measure metals on filter samples.

Instrumentation

The Niton is a small hand held instrument that contains a radioactive source to provide the incident x-ray beam. The beam is focused on the sample. The spectrophotometric portion of the Niton receives the emitted radiation, selects the most characteristic x-ray lines from each element, determines their intensity, and then converts the signal into microgram results for each element.

Reference: NIOSH, NMAM, Method 7702, "Lead by Field Portable XRF",1998.

Metals analysis by AAS

Part 1a: Preparation of Samples and filter blanks

In this experiment you will use the AAS to quantitatively analyze the zinc and iron content **on your filters and in <u>liquid samples supplied by the instructors.</u>**

1. Clean all glassware as prescribed in the NIOSH methods.

2. **Use 1% HNO3 solution in preparing standards and in making dilutions.**

3. You will be spiking blank filters with known amounts of Zn and Iron as a QC procedure to evaluate the effectiveness of the digestion procedure. Determine the amount of Zn & Fe you need to spike on a filter (You want it to be within the instrument's range). Record this data in your notebook and spike the filter. **For this part only, concentrated solutions will be used for spiking.**

4. Digestion of samples:
   You will be digesting the filters you collected in expt 2. In addition you will digest appropriate spiked filters and filter blanks. MCE filters should be digested with conc. HNO_3. All other filters should be digested with 5N HNO_3, which will solubilize the aerosol samples but will not dissolve the filter.

   a. Carefully add 2 mL of HNO_3; digest the samples, spikes and blank filters on the hot plate in the hood:

   b. Before digesting your samples and blanks, practice the entire digestion and dilution process with unused filters. Do not have hot plate at too high temperature.

   c. Details of the digestion method are described in the NIOSH method.

5. Dilute each solution to volume with 1% HNO_3 in a 25 mL volumetric flask.

Part 1b: Preparation of Calibration Standards

1. Prepare 50 mL of each standard by dilution of the respective 1000 µg/ml **(or** ppm) <u>stock solutions.</u> Prepare 5 standards with concentrations of 0.1 – 5 µg/ml.

   Four of the five standard solutions can be prepared with both metals included, but at least one standard solution for each should contain only one metal. Why?

Part 2: Calibration Curves and Sample Analysis

1. An instructor will show you how to load your samples into the AAS.

2. The appropriate standards and sample solutions are aspirated directly into the AAS.

3. Record the absorbance for each standard and sample solution. Replicate readings will indicate precision. Prepare a graph of the standards: concentration vs absorbance.

4. Concentration of sample in µg/ml is read from a plot of absorbance versus µg/ml of the standards.

5. Contaminants in air (assuming all samples were collected from air).

$$\frac{\text{mg contaminant}}{\text{m}^3} = \frac{\text{[Observed concentration, } \mu\text{g/ml] X [final solution volume, mL] x [dilutions]}}{\text{[air volume sampled, in liters]}}$$

Part 3: Standard Additions

In this part, you will use the technique of standard additions to determine the zinc content of your previously digested and diluted samples.

1. Choose a filter sample concentration that is low, but in the usable calibration range. From this prepare three sample aliquots in 5 or 10 mL flasks by adding known amounts of zinc to two of the three flasks: (1) original solution, (2) original + added zinc, and (3) original + more added. **In this case the added zinc will be <100 μl of a prepared zinc standard.** The **final concentrations** of the three solutions should approximately cover the calibration range for the AAS (within the range of your standard curve).

2. Measure and plot the response ratio readings vs. the μg of zinc added/mL and back extrapolate until the curve reaches a zero response ratio (refer to example plot below). The negative value at the X-intercept should be the number of μg of Zn/ml in the original sample solution.

Illustration of Standard Additions
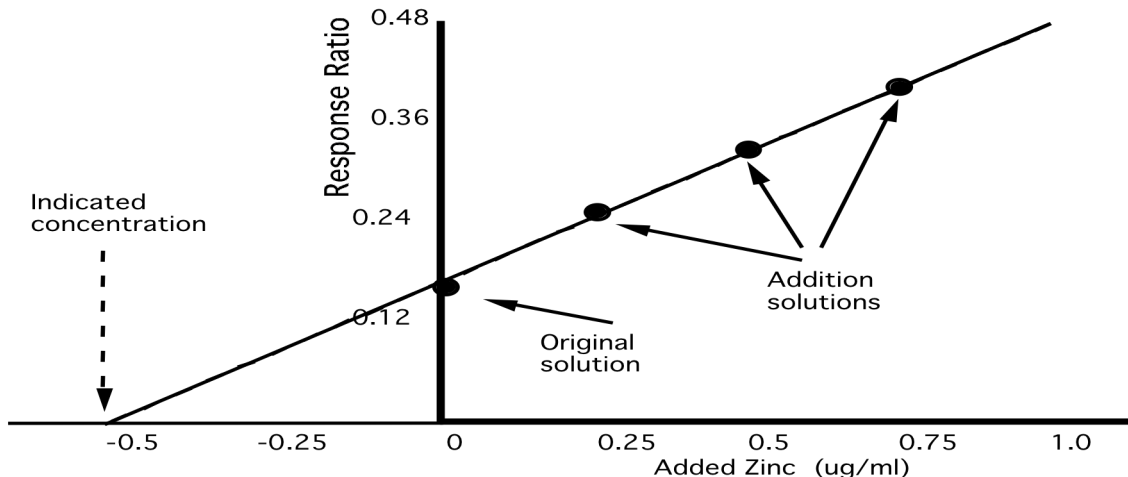
Write-up

 In addition to the provisions of the general description of the lab report, the following is expected:

1.   Description & calculation/tabulation of preparation of calibration standards.

2.   Description and calculations of preparation of 'spiked' samples

3.   A table showing the prepared calibration standards, with their absorbance values, average absorbance, standard deviation of replicate runs and of replicate samples and %CV. (all can be included in one table).

4.   Linear regression values (utilizing the internal standard) and graphs for the zinc and iron standards.

5.   Table of sample results including sample number, sample location, air volume, AAS response, μg/filter and air concentration (in mg/m^3). **Compare the relative quantities of each metal with the relative quantities of total weight pick-up on the filters. Does this relationship represent a constant fraction of each metal in the aerosol?**

6.   Data and graph showing standard addition method. State the calculated value for the sample as calculated from the standards additions and compare it to the original regression value.

7.   What could your data say about a chromium exposure if the zinc levels you measured where in the chemical form chromate ($ZnCrO_4$) instead of Zinc Oxide? Hint: convert the amount of zinc to that of $ZnCrO_4$. Would this hazard be greater or not?

8.   What sample preparation would be required for the XRF analysis of filters. How does XRF and AAS analysis compare for metals (compare useable concentration range, detection limits, specificity vs. interference and ease of analysis for multiple metals)?

*Remember to include a worked example for each type of calculation you undertake in the analysis

V. Additional Questions.

1. Why should all standards be prepared with 1% nitric acid solution?

2. If a sample gives an AAS response that is off scale (either beyond range of calibrants, or detector is saturated), how can valid results be obtained? If dilution is warranted, how much should it be diluted?

3. When you made up your calibrants, why was it important that at least one solution for each metal contained only one metal?

4. Can metal particle results be reported in parts per million of air?
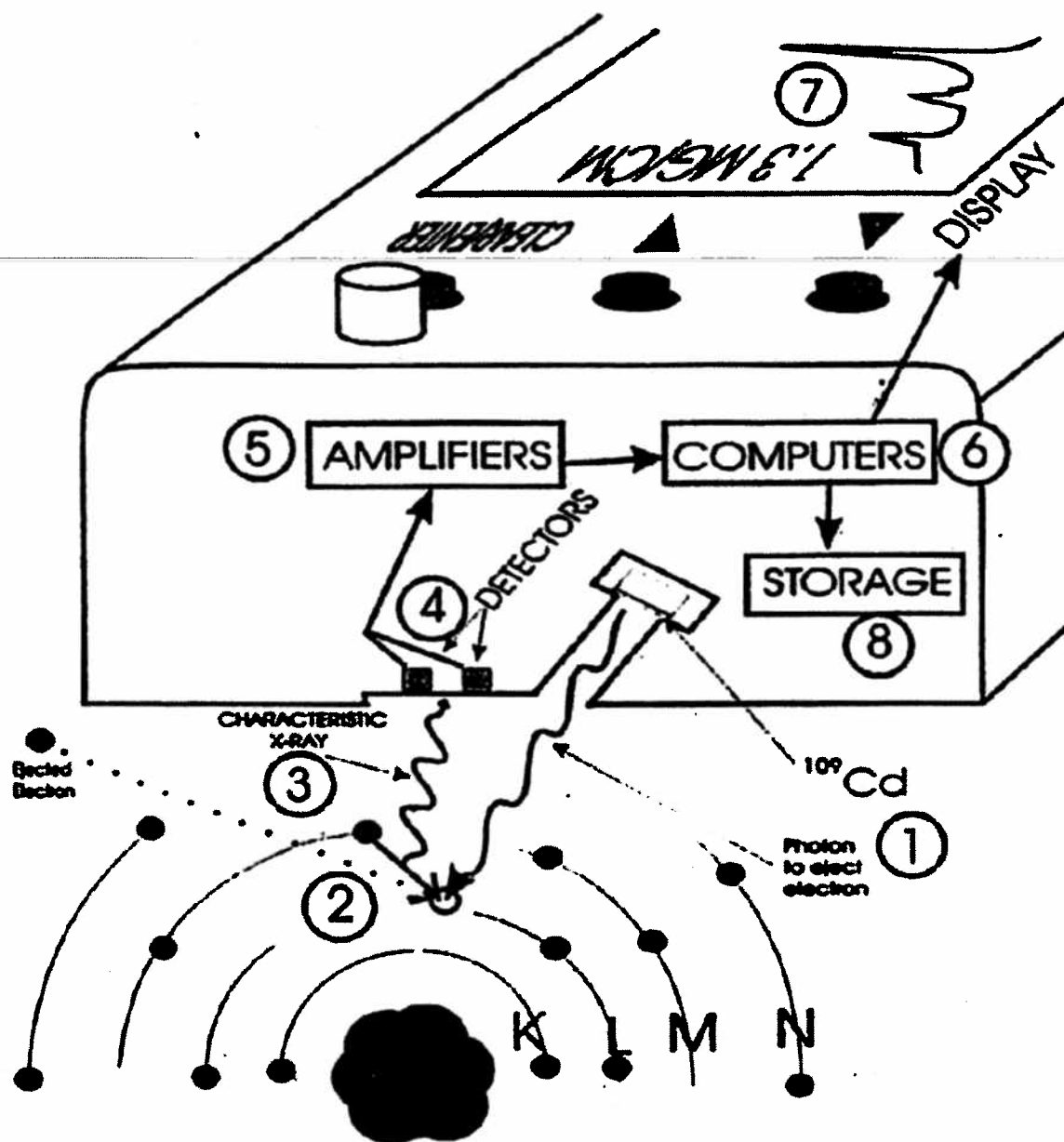
NITON XL-309

NITON 700 Series

X-Ray Fluorescence Instruments

NITON® XL-700 Series High Resolution Instruments

Elemental Limits of Detection in Soils, mg/kg (ppm)

XRF limits of detection (LOD's) are dependent upon: (1) testing time, (2) soil matrix, and (3) level of statistical confidence. NITON specifies detection limits following the EPA protocol of 99.7% confidence level, for the testing times shown. Individual LOD's improve as a function of the square root of the testing time.

Some instrument manufacturers may ONLY specify LOD's for optimal matrices such as SiO_2 (sand). These matrices are not representative of typical soil types, and therefore do not represent "real world" testing conditions. NITON specifies LOD data for typical soil matrices, represented by NIST Standard Reference Materials (SRM), as well as an optimal SiO_2 matrix.

LOD's will be higher in an SRM-type soil, especially for Cr and Mn, because of typically high levels of iron (2-3%).

Element	60 Second Testing Times		120 Second Testing Times	
	Sand Matrix	SRM Matrix	Sand Matrix	SRM Matrix
[109]Cd Isotope				
Cr	220	420	150	300
Mn	220	700	150	500
Fe	280	560	200	400
Co	120	380	80	270
Ni	100	210	70	150
Cu	70	100	50	60
Zn	40	70	25	50
As[1]	20	25	10	15
Pb	20	30	10	20
Hg	25	40	15	25
Rb	10	15	7	10
Sr	8	12	5	8
Zr	8	12	5	8
Mo	12	15	8	10
[241]Am Isotope				
Cd	35	50	25	35
Ag[2]	190	190	130	130
Ba	35	45	25	30
Sn[2]	140	150	100	100
Sb	65	75	45	50
[55]Fe Isotope				
V	120	NA	90	NA
Ti	350	NA	250	NA
Ca	0.15%	NA	0.10%	NA
K	0.35%	NA	0.25%	NA

[1] Data for As (arsenic) is representative of low levels of Pb (lead). High Pb levels will tend to increase As LOD's.

[2] LOD levels for Ag (silver) and Sn (tin) are artificially high due to a tin and silver detector collimator used in the instrument. Future hardware modifications will improve these numbers. Consult a NITON representative for details.

NITON®

The Leader in Portable XRF Technology

ZINC and compounds, as Zn 7030

Zn MW: 65.37 (Zn); CAS: 7440-66-6 (Zn), RTECS: ZG8600000 (Zn)
83.17 (ZnO) 1314-13-2 (ZnO) ZH4810000 (ZnO)

| METHOD: 7030, Issue 2 | EVALUATION: PARTIAL | Issue 1: 15 February 1984 |
| | | Issue 2: 15 August 1994 |

OSHA : 5 mg/m^3 (ZnO fume & resp. fraction);
10 mg/m^3 (ZnO dust)
NIOSH: 5 mg/m^3 (ZnO); 15 mg/m^3/15 min (ZnO dust); STEL
10 mg/m^3 (ZnO Fume)
ACGIH: 5 mg/m^3, STEL 10 mg/m^3 (ZnO fume)
10 mg/m^3 (ZnO dust)

PROPERTIES: metal; valence 2; MP 419 °C (Zn)

SYNONYMS: vary depending upon the compound.

SAMPLING	MEASUREMENT
SAMPLER: FILTER (0.8-µm cellulose ester membrane)	**TECHNIQUE:** ATOMIC ABSORPTION, FLAME
FLOW RATE: 1 to 3 L/min	**ANALYTE:** zinc
VOL-MIN: 2 L @ 5 mg/m^3 **-MAX:** 400 L	**ASHING:** conc. HNO_3, 6 mL; 140 °C
	FINAL SOLUTION: 1% HNO_3, 100 mL
SHIPMENT: routine	**FLAME:** air-acetylene, oxidizing
SAMPLE STABILITY: stable	**WAVELENGTH:** 213.9 nm
BLANKS: 2 to 10 field blanks per set	**BACKGROUND CORRECTION:** D_2 or H_2 lamp, if needed
	CALIBRATION: Zn^{2+} in 10% HNO_3
ACCURACY	**RANGE:** 10 to 100 µg per sample [1]
RANGE STUDIED: not studied	**ESTIMATED LOD:** 3 µg per sample [2]
BIAS: not measured	**PRECISION ($\bar{S}_r$):** 0.03 [1]
OVERALL PRECISION ($\hat{S}_{rT}$): not measured	
ACCURACY: not determined	

APPLICABILITY: The working range is 1 to 10 mg/m^3 for a 10-L sample. This is an elemental analysis, not compound specific. Aliquots of the samples can be analyzed separately for many additional metals.

INTERFERENCES: None known.

OTHER METHODS: This method is a revision and replacement of P&CAM 173 for Zinc [1,3]. Method 7300 (plasma emission) is an alternate analytical method. Method 7502 (X-ray diffraction) is specific for ZnO.

REAGENTS:

1. Nitric acid, conc.
2. Nitric acid, 1% (v/v). Add 10 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Calibration stock solution, 1000 µg/mL Zn. Commercial standard or dissolve 1.00 g Zn metal in minimum volume of (1+1) HCl; dilute to 1 L with 1% (v/v) HNO_3.
4. Air, filtered.
5. Acetylene.
6. Distilled or deionized water.

   *   See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with air-acetylene burner head and zinc hollow cathode lamp or electrodeless discharge lamp.
4. Regulators, 2-stage, for air and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, With watchglass covers.*
6. Volumetric flasks, 100-mL.*
7. Micropipets, 1 to 100 µL.*
8. Hotplate, surface temperature 140 °C.

   *   Clean with conc. HNO_3 and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 2 to 400 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD). Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 6 mL conc. HNO_3 and cover with a watchglass. Start reagent blanks at this point.
5. Heat on hotplate (140 °C) until sample dissolves and a slightly yellow solution is produced. Add additional acid as needed to completely destroy organic material.
6. When the sample solution is clear, remove watchglass and rinse into the beaker with 1% HNO_3.
7. Place the beakers on the hotplate and allow to go to near dryness (ca. 0.5 mL liquid remaining).
8. Rinse walls of beaker with 10 mL 10% HNO_3. Reheat 5 min to dissolve the residue, then allow to air cool.
9. Transfer the solution quantitatively to a 100-mL volumetric flask and dilute to volume with distilled or deionized water.
   NOTE: Dilute to a smaller volume, e.g., 10 mL, if required for sensitivity of analysis for other metals in the sample.

CALIBRATION AND QUALITY CONTROL:

10.   Add known amounts, covering the range 0 to 100 µg Zn per sample, of calibration stock solution to 100-mL volumetric flasks and dilute to volume with 1% HNO_3.
11.   Analyze the working standards together with the samples and blanks (steps 16 and 17).
12.   Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
13.   Aspirate a standard for every 10 samples to check instrument drift.
14.   Check recoveries with at least one spiked media blank per 10 samples.
15.   Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

16.   Set spectrophotometer according to manufacturer's recommendations and to conditions on page 7030-1.
       NOTE: Non-atomic absorption may require the use of D_2 or H_2 continuum background correction in some samples.
17.   Aspirate standards and samples. Record absorbance readings.
       NOTE: If the absorbance values for the samples are outside of the range of the standards, dilute the solutions with 1% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

18.   Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of zinc in the sample, C_s, and average media blank, C_b, from the calibration graph.
19.   Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of zinc in the volume of air sampled, V (L):

$$C = \frac{(C_s V_s - C_b V_b)}{V}, \ mg/m^3.$$

EVALUATION OF METHOD:

Estimated LOD was 3 µg Zn per sample [2]. Since only the analytical procedure was studied, bias, overall precision, and accuracy were not determined.

REFERENCES:

[1]   NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
[2]   User check, UBTL, NIOSH Seq.# 3990-P (unpublished, November 29, 1983).
[3]   Criteria for a Recommended Standard...Occupational Exposure to Zinc Oxide, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-104 (1976).

METHOD WRITTEN BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS.

LEAD BY FIELD PORTABLE XRF 7702

Pb MW: 207.19 (Pb) CAS: 7439-92-1 (Pb) RTECS: OF7525000 (Pb)
223.19 (PbO) 1317-3608 (PbO) OG1750000 (PbO)

METHOD: 7702, Issue 1   **EVALUATION: FULL**   **Issue 1: 15 January 1998**

OSHA: 0.05 mg/m^3
NIOSH: <0.1 mg/m^3; blood lead ≤ 60 µg/100 g
ACGIH: 0.05 mg/m^3; BEI blood 30 µg/ 100 mL

PROPERTIES: soft metal; d 11.3 g/mL @ 20 °C; MP 327.5°C; BP 1740°C; valences +2, +4 in salts

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SYNONYMS: elemental lead and lead compounds except alkyl lead

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SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.8-µm, 37-mm, mixed cellulose ester membrane)	**TECHNIQUE:**	X-RAY FLUORESCENCE (XRF), PORTABLE, L-SHELL EXCITATION (e.g., ^{109}Cd source)
FLOW RATE: 1 to 4 L/min			NOTE: Performance parameters are based upon research conducted with the NITON® 700 XRF [1].
VOL-MIN: -MAX:	570 L @ 30.0 µg/m^3 [1] 1900 L @ 9.0 µg/m^3		
SHIPMENT:	routine	**ANALYTE:**	lead
SAMPLE STABILITY:	stable	**CALIBRATION:**	lead thin-film standards (Micromatter Co., or equivalent); internal instrument calibration
BLANKS:	2 to 10 field blanks per set	**RANGE:**	17 to 1500 µg of Pb per sample [1]
ACCURACY		**ESTIMATED LOD:**	6 µg of Pb per sample [1]
RANGE STUDIED:	0.1 to 1514.6 µg/m^3 (as Pb) (based upon lead mass loadings)		
BIAS:	0.069 [1]		
PRECISION ($\bar{S}_{rT}$):	0.054 @ 10.3 to 612 µg Pb per sample		
ACCURACY:	±16.4%		

APPLICABILITY: This method was evaluated for air samples on filters only. The working range of this method is 0.017 mg/m^3 to 1.5 mg/m^3. This is a field portable analytical method, particularly useful for the analysis of initial exposure assessment samples, or for applications where laboratory analysis is impractical. Additionally, the method is non-destructive; samples analyzed in the field can later be analyzed in a laboratory. The method is applicable to all elemental lead forms, including lead fume, and all other aerosols containing lead.

INTERFERENCES: The presence of bromine will cause XRF readings for lead to be elevated, resulting in a positive bias error. Other interferences may exist in other XRF instruments.

OTHER METHODS: Laboratory-based methods include atomic spectrophotometric methods following hot plate acid digestion: NIOSH methods 7082 (flame atomic absorption spectrophotometry) [2], 7105 (graphite furnace atomic absorption spectrophotometry) [3], and 7300 (inductively coupled plasma atomic emission spectrophotometry) [4]. A field-portable analytical method for lead air filter samples using ultrasound/ASV has been developed, NIOSH Method 7701[5]. A field-portable screening method by spot test kit has been developed, NIOSH Method 7700 [6].

REAGENTS:

1. None

EQUIPMENT:

1. Sampler: Mixed cellulose ester filter, 0.8-μm pore size, 37-mm diameter, with cellulose back-up pad, in a closed-faced cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Field portable, L-shell X-Ray Fluorescence (XRF) instrument with a Cadmium-109 source.
4. Filter sleeve: thin cardboard with 37-mm dia. cut out, and covered with a light adhesive between two pieces of acetate (Mylar™) (NITON, Bedford, MA, or equivalent).
   NOTE: Material must be transparent to X-ray.
5. Filter test platform to hold the filter (specific to instrument).
6. Forceps
7. Thin film standard reference materials from 15 $\mu g/cm^2$ to 150 $\mu g/cm^2$ (Micromatter Co., Deer Harbor, WA), or equivalent [7,8].

SPECIAL PRECAUTIONS: None

SAMPLING:

1. Calibrate each sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate (1 to 4 L/min) for a total sample size of approximately 1000 L. Do not exceed a filter loading of 2 mg total dust.

SAMPLE PREPARATION:

3. With forceps, transfer the MCE filter without the backup pad to a filter sleeve. The sleeve material must be transparent to X-rays (see EQUIPMENT, Item 4).
   NOTE: Take special care when removing the filter from the backup pad to avoid loss of lead-containing dust.
4. Place the filter into 37-mm opening and seal with Mylar™ film to prevent losses and allow undisturbed analysis of the filter.
5. Place the sealed filter onto the filter test platform of the instrument for analysis.
   NOTE: The NITON® 700 Series XRF has a filter test platform that allows for three readings with no substrate effect.

CALIBRATION AND QUALITY CONTROL:

6. Start XRF and allow a 30-minute warm-up period. The instrument will conduct an internal self-calibration.
7. Using thin film standards [8], verify the internal calibration to within ± 5% of the calibration standard. Use a minimum of three standards at concentrations of 15 $\mu g/cm^2$, 150 $\mu g/cm^2$, and one standard concentration between these two values.
8. Restart the instrument as needed to assure instrument accuracy prior to sample analysis.
   NOTE: When the thin film standard measurements are not within the specified parameters, the instrument may need to be recalibrated at the factory.
9. Analyze one thin film standard every 2 hours to check for instrument drift.
10. Repeat step 7 when all analyses are completed as a post-calibration check.

MEASUREMENT:

11. Set instrument parameters and analyze filter samples as specified by the manufacturer. The following measurement technique is based upon the NITON® 700 XRF.
    a. Analyze the middle of the sample filter first (see Figure 1, M).
    b. Allow the instrument to take a one source-minute reading (This may take longer than one real-time minute, depending upon the source strength). A one source-minute reading will assure the accurate L-shell reading necessary for the analysis of lead air filter samples.
    c. Analyze the filter sample at the top of the filter for one source minute (see Figure 1, T).
    d. Analyze the filter sample at the bottom of the filter for one source minute (see Figure 1, B).
    e. The instrument software uses an algorithm that converts the three readings in $\mu g/cm^2$ into an analytical result in μg of lead per sample. This result will be displayed following the third filter reading [1].
    f. Analyze one standard every 2 hours (step 8).
    g. Repeat three-reading calibration check following completion of analyses (step 8).

CALCULATIONS:

12. Using the measured lead concentration, W (μg), calculate the concentration, C (mg/m^3) of lead in the air volume sampled, V (L):

$$C = \frac{W}{V}, \ mg/m^3$$

   NOTE: $\mu g/L \equiv mg/m^3$

EVALUATION OF METHOD:

This method was validated on field samples [1] by collecting lead particulate samples from bridge lead abatement projects. Airborne concentrations of lead within the containment of a sand blasting bridge lead abatement project ranged from 1 to 10 mg/m^3. Area samples were collected for periods of time ranging from 15 seconds to 2 hours. This sampling protocol yielded 61 filter samples with lead loadings ranging between 0.1 to 1514.6 μg of lead per sample. Four personal samples were collected from a hand-scraping bridge lead abatement project for a total sample size of 65. The samples were first analyzed using a non-destructive, field portable XRF method. Samples subsequently were subjected to confirmatory analysis by the laboratory based NIOSH method 7105, Lead by GFAAS [3]. The method was statistically evaluated according to the NIOSH Guidelines for Air Sampling and Analytical Method Development and Evaluation [9]. The overall precision ($\hat{S}_{rT}$) of the XRF method was calculated at 0.054 with a 95% confidence interval (CI) of 0.035 to 0.073, and the bias was 0.069 with a 95% CI of 0.006 to 1.515. The XRF method accuracy was determined to be ± 16%; however, at the upper 90% CI, the accuracy is ± 27%. Since the confidence interval includes the ± 25%, meeting the NIOSH accuracy criteria of ± 25% is inconclusive. However, the samples used to evaluate this method were field samples. Laboratory prepared aerosol samples would be expected to give better precision. Additionally, the XRF method is non-destructive; samples analyzed in the field can subsequently be analyzed in a laboratory using a method with greater accuracy, as needed. The filter sleeve used with the NITON® 700 Series XRF used a Mylar film to cover and seal the 37-mm filter. The lead particulate on the surface of the filter came into contact with the Mylar™ film. Both the Mylar™ film and the filter were digested with nitric acid and hydrogen peroxide as is specified in NIOSH Method 7105 [3].

REFERENCES:

[1]   Morley JC [1997]. Evaluation of a portable x-ray fluorescence instrument for the determination of lead in workplace air samples [Thesis]. Cincinnati, OH: University of Cincinnati, Department of Environmental Health, College of Medicine.
[2]   NIOSH [1994]. Lead by FAAS: Method 7082. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and

Health, DHHS (NIOSH) Publication No. 94-113.

[3]   NIOSH [1994]. Lead by GFAAS: Method 7105. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[4]   NIOSH [1994]. Elements: Method 7300. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[5]   NIOSH [1994]. Lead by ultrasound/ASV: Method 7701 (supplement issued 1/15/98). In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 98-119.

[6]   NIOSH [1994]. Lead in air by chemical spot test: Method 7700 (supplement issued 5/15/96). In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 96-135.

[7]   National Institute of Standards and Technology, Standard Reference Material Program, Standard Reference Material 2579, Lead paint film on Mylar sheet for portable X-ray fluorescence analyzers, Gaithersburg, MD 20899.

[8]   Micromatter Co., XRF Calibration Standards, P.O. Box 123, Deer Harbor, Washington, 98243, Phone (360) 3 76-4007.

[9]   NIOSH [1995]. Kennedy, E.R., Fishbach, T.J., Song, R., Eller, P.M., Shulman, S.S.. Guidelines for Air Sampling and Analytical Method Development and Evaluation. Cincinnati, Ohio: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117.
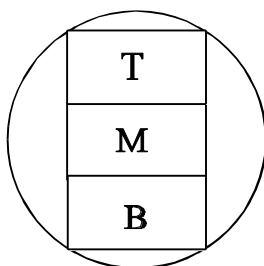
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Figure 1: Analysis of a 37-mm filter   using XRF
   (XRF windows identified as M, T,   and B are 2 cm x 1 cm)